

The role of thermochemical sulfate reduction in the origin of Mississippi Valley-type deposits. I. Experimental results

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ABSTRACT

The kinetics of thermochemical sulfate reduction (TSR) were studied in experiments at 205–250°C, with determination of both sulfate and sulfide at intervals during the runs of up to 430 h. Analysis of the data indicates the reaction to have first-order kinetics, and extrapolating these data, plus data from the literature, to 150°C gives a range of possible rate constants from 10⁰ to 10⁻⁴ year⁻¹. Although the rate law has not been well established, a reasonable estimate allows calculation of the amount of sulfide ore formed as a function of flow conditions and time. It is here concluded that TSR could happen during the formation of Mississippi Valley-type ore deposits, subject to several caveats.

Key words: kinetics, MVT, sulfate reduction, TSR

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INTRODUCTION

Mississippi Valley-type (MVT) ore deposits (so-named because several classic MVT districts are located within the drainage basin of the Mississippi River) are epigenetic stratabound carbonate-hosted sulfide bodies composed predominantly of sphalerite and galena. A great deal of fluid inclusion evidence shows that the fluids responsible for their formation are highly saline brines having temperatures usually above 90°C but less than 200°C. They are similar in composition to brines found at depth in many large sedimentary basins, differing only in having significant concentrations of zinc and lead. On the basis of hydrologic modeling (e.g. Garven *et al.* 1993), these brines are typically concluded to have been expelled to the basin margins, where the sulfide ore deposits form. There has been much controversy over the reasons for the precipitation of the sulfides. A commonly held theory is that zinc and lead are transported in low-H₂S brines as chloride complexes, and are precipitated when the metal-bearing solution encounters a previously formed accumulation of H₂S (the ‘mixing hypothesis’). Such accumulations of H₂S are known to be derived by

reduction of seawater sulfate, usually in the form of gypsum or anhydrite, either by bacterial action at temperatures below 80°C, or by an abiological reaction above this temperature, called thermochemical sulfate reduction (TSR). The possibility that bacteria capable of reducing sulfate at high temperatures might have a role in MVT formation has long intrigued geologists. The study of such high-temperature organisms (hyperthermophiles) is now an active area of research (e.g. Stetter 2006). The presently known upper temperature limit of growth for hyperthermophiles (about 113°C) is well below the formation temperature of many, but not all, MVT deposits. We assume in this communication that hyperthermophiles are not involved in MVT formation.

Another puzzling feature of MVT deposits is the fact that carbonates appear to be both dissolved and precipitated during the formation of the deposits. This is one of the subjects of the companion paper (Anderson and Thom, *in press*).

There is a considerable amount of information about TSR in the petroleum literature. According to petroleum geologists, high H₂S-concentration natural gas accumulations (‘sour gas’ fields) are formed when evaporate-derived

sulfate is reduced by petroleum (mostly methane and the *n*-alkanes) at depths usually greater than 3000 m, where temperatures significantly exceed 100°C. A particularly well-studied example is the gas reservoirs in the Permo-Triassic Khuff formation, Abu Dhabi (Worden *et al.* 2000). The problem with associating such natural gas deposits with MVT ore formation is (i) there is no obvious spatial relationship; (ii) MVT deposits are interpreted to form at much shallower depths; and (iii) in most cases there are no local evaporites.

The kinetics of the TSR reaction is just one of several controls on the rate of H₂S formation in sour gas fields, as shown by Worden *et al.* (2000). However, it is known to be an extremely slow reaction, and it is widely concluded that because of this, TSR cannot generate enough H₂S to make an ore body during the relatively short period of ore formation (10⁴–10⁶ years: Lavery and Barnes 1971; Garven *et al.* 1993; Lewchuk & Symons 1995; Rowan & Goldhaber 1995), and so sulfate reduction must take place before ore formation (e.g. Goldhaber & Orr 1995). This could be at some remote (unknown) location, or it could take place at the site of ore deposition, with H₂S trapped at the site of later ore deposition in either case. The MVT situation is a bit simpler than the sour gas petroleum case, in that the source of the sulfate is probably not tied to local evaporites, but may be the aqueous sulfate found in all basinal brines, whatever their ultimate origin. MVT deposits commonly contain bitumen which is sometimes suspected to be the reductant for sulfate. An alternative idea is that heating of kerogen in the host carbonates generates reducing gases such as methane and hydrogen, which reduces the aqueous sulfate in the brines, either before or during ore formation (Anderson 1991).

Thermochemical sulfate reduction has been carried out experimentally at temperatures as low as 175°C (Orr 1982), but most experiments have been at 250°C or higher because reaction rates are slow (Kiyosu 1980; Kiyosu & Krouse 1990, 1993; Cross *et al.* 2004). Many of these studies are summarized and discussed in Goldstein & Aizenshtat (1994), Goldhaber & Orr (1995), and Nöth (1997).

In this report, new data on the rate of TSR are presented. In addition, we discuss some important issues which have not received much attention in the TSR literature, including: (i) the reason for the pH effect; (ii) the significance of the fact that H₂S is an autocatalyst (i.e. its presence enhances reduction even though it is a reaction product, not a reactant); and (iii) more generally, why the TSR reaction is so slow. Finally, although the rate law for TSR has not been definitively established, we use a plausible estimate to show that, contrary to conventional wisdom, TSR can be fast enough to generate H₂S during ore formation.

EXPERIMENTAL

Experimental procedure

Thermochemical sulfate reduction experiments were carried out in a 500 ml Tem-Pres HRA-550 titanium pressure vessel containing Na₂SO₄, H₂SO₄, Na₂S·9H₂O, C₇H₈ (toluene), and H₂O. The composition and pH of the solutions were controlled by mixing various proportions of these reagents. The total sulfur content (ΣS) ranged from 0.2 to 0.4 M and initial pH varied from 1.00 to 6.05 at 25°C (Tables 1 and 2). These compositions and pH values were chosen to investigate trends and observations seen in prior investigations of sulfate reduction, particularly the effect of

Table 1 Experimental results of successful sulfate reduction by toluene.

Run no.	Temperature (°C)	Pressure (bar)	Time (h)	Sulfate (M)*	Sulfide (M)	Missing S (M)†	pH‡
TSR-5-0	25	1	–	0.167	0.063	0.000	1.27
TSR-5-1	250	64	0	0.190	0.038	0.002	
TSR-5-2	250	64	33	0.428	0.052	–0.250	
TSR-5-3	250	62	99	0.078	0.071	0.081	
TSR-5-4	250	64	125	0.053	0.064	0.113	
TSR-5-5	250	64	151	0.074	0.076	0.080	
TSR-5-6	250	60	287	0.061	0.088	0.081	
TSR-5-7	250	60	360	0.069	0.080	0.081	
TSR-7-0	25	1	–	0.296	0.112	0.000	1.39
TSR-7-1	250	67	0	0.326	0.082	–0.001	
TSR-7-2	250	68	27	0.292	0.131	–0.016	
TSR-7-3	250	68	59	0.268	0.165	–0.025	
TSR-7-4	250	68	94	0.230	0.136	0.041	
TSR-8-0	25	1	–	0.299	0.118	0.000	1.33
TSR-8-1	225	45	0	0.320	0.059	0.037	
TSR-8-2	225	45	46	0.269	0.081	0.067	
TSR-8-3	225	45	71	0.256	0.079	0.081	
TSR-8-4	225	45	99	0.256	0.097	0.064	
TSR-8-5	225	47	147	0.300	0.101	0.016	
TSR-8-6	225	48	196	0.262	0.095	0.060	
TSR-11-0	25	1	–	0.300	0.118	0.000	1.44
TSR-11-1	208	33	0	0.429	0.068	–0.080	
TSR-11-2	205	34	78	0.325	0.050	0.042	
TSR-11-3	205	34	117	0.419	0.042	–0.044	
TSR-11-4	205	34	170	0.417	0.050	–0.049	
TSR-11-5	205	33	266	0.308	0.044	0.065	
TSR-11-6	205	33	332	0.295	0.046	0.076	
TSR-11-7	205	33	433	0.280	0.045	0.092	
TSR-12-0	25	1	–	0.295	0.112	0.000	1.15
TSR-12-1	248	61	0	0.399	0.043	–0.035	
TSR-12-2	252	68	23	0.239	0.121	0.047	
TSR-12-3	252	72	77	0.219	0.141	0.048	
TSR-12-4	252	71	103	0.230	0.154	0.024	
TSR-12-5	252	69	151	0.174	0.188	0.045	

*Bold face values are sulfate analyses where the calcium electrode experienced interference by other ions (Cl[–] and some hydrothermal product of NH₄⁺).

†Negative values mean that the total sulfide and sulfate concentration is greater than the total sulfur originally put into the reaction vessel. The usual reason appears to be that values for the sulfate concentrations are too high.

‡pH calculated by speciation at 25°C.

Run no.	Temperature (°C)	Pressure (bar)	Time (h)	Sulfate (M)*	Sulfide (M)	Missing S (M)†	pH‡
TSR-9-0	25	1	–	0.296	0.117	0.000	6.05
TSR-9-1	244	62	0	0.261	0.057	0.094	
TSR-9-2	244	61	33	0.272	0.066	0.074	
TSR-9-3	243	61	71	0.287	0.073	0.053	
TSR-9-4	243	61	118	0.281	0.075	0.056	
TSR-10-0	25	1	–	0.565	0.107	0.000	1.00
TSR-10-1	250	44	0	0.615	0.058	–0.001	
TSR-10-2	250	43	49	0.495	0.023	0.154	
TSR-10-3	252	42	75	0.713	0.061	–0.103	
TSR-10-4	249	45	166	0.798	0.054	–0.180	
TSR-10-5	249	45	244	0.868	0.054	–0.250	
TSR-10-6	249	44	290	1.559	0.060	–0.946	

*Bold face values are sulfate analyses where the calcium electrode experienced interference by other ions (Cl^- and some hydrothermal product of NH_4^+).

†Negative values mean that the total sulfide and sulfate concentration is greater than the total sulfur originally put into the reaction vessel. The usual reason appears to be that values for the sulfate concentrations are too high.

‡pH See Table 1 for footnotes.

Table 2 Experimental results of failed sulfate reduction by toluene.

pH. The vessel initially contained 350–425 ml of solution to allow room for the expansion of water with increasing temperature. Toluene was generally 30–40 g, thus in great excess. K-type thermocouples were inserted within the walls of the reaction vessel to record temperature. Pressure was measured with an Omegadyne pressure transducer capable of reading pressures from 0 to 30000 psi. The titanium reaction vessel was placed in a Thermcraft single winding, split tube, proportional control electric furnace, and heated to temperatures in the range of 200–250°C. At run conditions, all pressure and temperature measurements were handled by Labview® which showed that pressure readings gave a precision of ± 5 psi and the temperature readings about $\pm 1^\circ\text{C}$. The temperature gradient measured between the top and bottom thermocouples was never more than 4°C and usually around 2°C and the temperatures given in all experiments is the average of the two readings. All experiments occurred at saturation vapor pressures for the temperature of each experiment and contained three phases: a gas phase, an organic liquid phase, and an aqueous phase.

Analytical methods

Throughout the duration of each experiment, samples were taken intermittently to analyze for sulfate and sulfide concentrations. To take samples, the closure of the titanium pressure vessel was fitted with a hollow titanium sampling tube which extended three-quarters of the way down the vessel, allowing samples to be taken as the liquid volume decreased. When analyzing for sulfide and sulfate, three separate aliquots were taken from the vessel, totaling about 8–15 g of solution. The first aliquot sampled was taken as a disposable sample so that the tubing between the reaction

chamber and the sampling spout would be clear of any previous sample residue. The disposable sample was injected into a 2 M NaOH solution so that the $\text{H}_2\text{S}(\text{aq})$ would not volatilize. The following aliquot was injected into a sulfide anti-oxidant buffer [a solution of 2 M NaOH, 0.2 M ethylenediaminetetraacetic acid (EDTA), and 0.2 M ascorbic acid] and then titrated with a standardized solution of $\text{Pb}(\text{NO}_3)_2$ to determine the sulfide concentration. A Man-Tech® automatic titration module connected to a silver–silver sulfide electrode carried out the titration.

The third sample was injected into a 2 M NaOH solution in order to transport the sample volume from the reaction vessel to a fume hood. A 6 M HCl and a 0.05 M BaCl_2 solution were then added, precipitating barium sulfate (BaSO_4). The solution was then buffered to a pH of 10 with an ammonium chloride/ammonium hydroxide solution and titrated with EDTA. Sulfate concentration was then calculated from the amount of EDTA used during this back titration. To carry out the titration, the Man-Tech automatic titration module was equipped with a calcium electrode, which is also sensitive to barium.

Interference from other solution components is often a problem with single ion electrode measurements. In the case of the calcium and sulfide electrodes, the calcium electrode had more interference problems than the sulfide electrode. The biggest interference problem was from the Cl^- ion, which was added as 6 M HCl to acidify the sulfate sample solution before precipitation of BaSO_4 . As the amount of Cl^- increased the inflection point on the sulfate titration curve broadened, increasing the uncertainty of the analysis. To avoid this, a minimal amount of HCl was added to the solution. Another problem with sulfate concentration determination was the possibility of sulfide oxidation during quenching and measuring phases. This possible oxidation

was avoided to some extent by adding ascorbic acid to the NaOH transportation solution, which was selectively oxidized if oxygen began to dissolve in the solution during quenching and analyzing phases. As a result of these inherent analytical problems, a combination of accuracy and precision given to all sulfate and sulfide concentrations reported is ± 0.025 and ± 0.01 M, respectively.

RESULTS

Successful sulfate reduction experiments are reported in Table 1. As the various irreversible reactions (sulfate reduction and organic decomposition/oxidation) proceeded in the vessel, decreases in sulfate and increases in sulfide concentrations were observed in the temperature range of 250–200°C.

No attempt was made to eliminate oxygen in the water or from the vapor phase at the start of the experiments, so there was a noticeable adjustment of the initial sulfide/sulfate ratio at the beginning of each run due to this oxygen. The H₂S vapor pressure was calculated from the concentration of sulfide analyzed in solution and by using the data of Suleimenov & Krupp (1994) on the solubility of H₂S in pure water at saturation vapor pressures and temperatures. The moles of H₂S in the gas necessary to create this H₂S pressure was calculated from their experimental data at reaction temperatures (200–250°C) given the known volumes of the gas phase and the concentration of H₂S in the solution, and taking into account the change in the volumes of vapor and aqueous phases due to sampling. The calculated moles of sulfide in the liquid phase was nearly always less than that determined by analytical measurement of sulfide in solution and is attributed to the fact that an unknown amount of sulfur is organically bound, and that some sulfur has an intermediate valence state that the titration method does not recognize. The occasional result showing the total analyzed sulfate plus sulfide greater than the total sulfur put in the vessel at the start of the experiment is attributed to problems with the sulfate analysis. These differences are reported in Tables 1 and 2 as ‘missing sulfur’.

As some experiments proceeded, there was a significant change in reduction rates. That is, the change in sulfate concentration as a function of time initially showed a steep negative slope, and then as the reaction time increased the negative slope in sulfate concentration flattened to zero. For example, sulfate reduction in TSR-5 appeared to stop or dramatically slow down 40–50 h after the beginning of the run (Fig. 1). Although this must be partly due to the decreasing concentration of sulfate, it is very likely also a pH effect, discussed in more detail below.

The dependence of reaction rates on pH has been noted in several studies, but has not been quantified. Ohmoto & Lasaga (1982) attributed this rate control to the formation

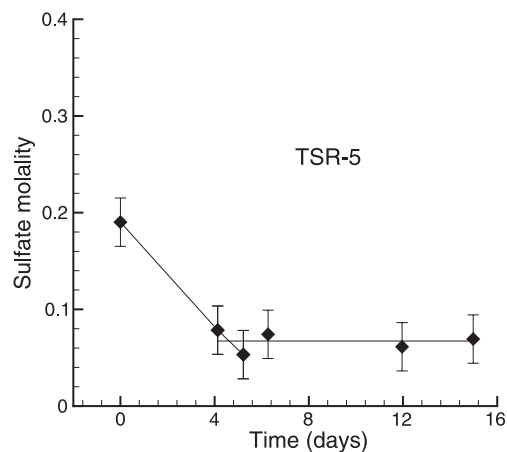


Fig. 1. Sulfate concentration as a function of time in experiment TSR-5. The change in slope is interpreted as the result of the evolving pH of the solution, which is becoming more basic with time. Error bars on sulfate concentrations are ± 0.025 M.

of thiosulfate as a rate-determining step. Other authors (e.g. Kiyosu 1980; Goldhaber & Orr 1995) have noted this effect, but have not speculated on its cause. In our experiments, the initial pH values were controlled by varying the amount of H₂SO₄ relative to Na₂SO₄. With initial pH ranging from 1 to 4, the rate constants do tend to be greater at lower initial pH values (Table 3), but there are not sufficient data to quantify this effect. A major difficulty in quantifying the effect of pH on the reaction is knowing the pH during the experiment at run conditions. Numerous speciation calculations were performed, both on our experiments and those in the literature, decoupling C⁴⁻ and C⁴⁺, and adding data for many known organic reactions. These calculations show that the pH during the run is much more basic than the starting pH, which is not unexpected, but also, that it can change by 2–3 pH units, becoming more basic during the run. The problem with this sort of calculation is that it depends on what chemical species are present, and this has never been completely determined for any TSR reaction. The reason for the pH effect is discussed below.

To identify the effect of temperature on the rate of TSR, three experiments were performed with similar

Table 3 Rate constants for TSR by toluene in the presence of H₂S.

Experiment	Temp (°C)	Initial pH (TSR-X-1)	Total S (M)	Rate (k) (year ⁻¹)	Analyses included
TSR-5	252	1.86	0.230	1.57 ± 0.04	1,3,4
TSR-6	275	5.46	0.294	0.68 ± 0.03	6,7,9,10
TSR-7	250	3.84	0.407	1.14 ± 0.03	1,2,3,4
TSR-8	225	3.70	0.416	0.5 ± 0.3	1,4,5,6
TSR-11	208	3.29	0.419	0.20 ± 0.05	2,5,6,7
TSR-12	251	1.35	0.407	1.92	1,2

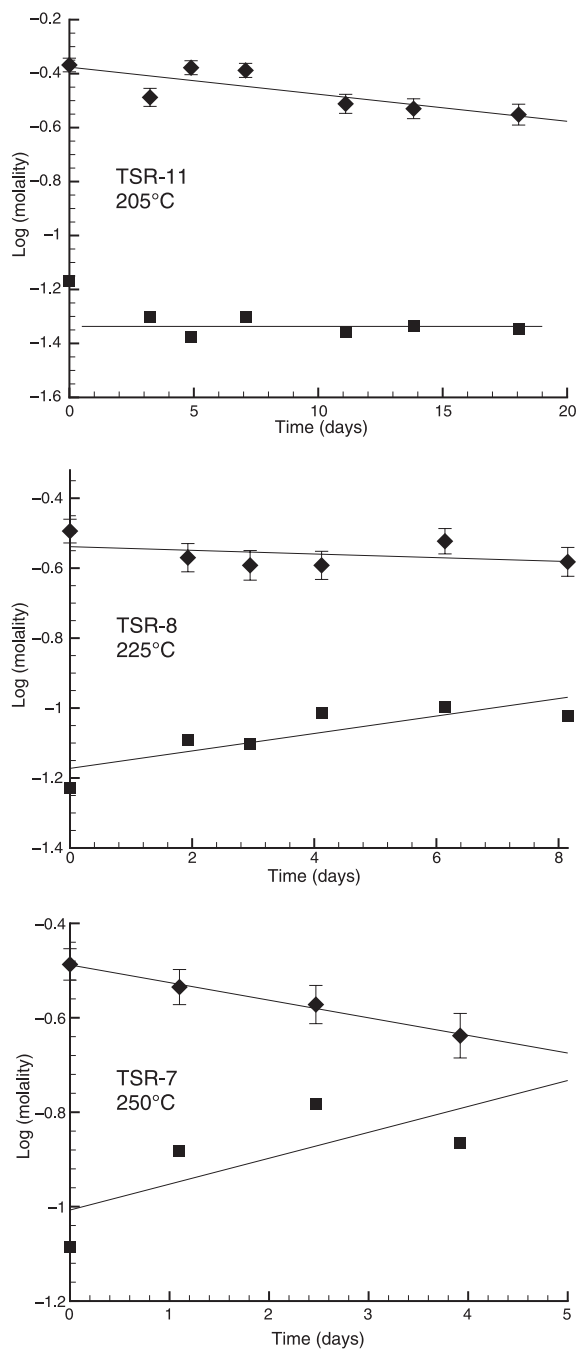


Fig. 2. Sulfate and sulfide results for TSR-7, TSR-8, and TSR-11. Squares denote sulfide as H_2S . Circles denote sulfate. The slopes of the lines give the rate constants. Error propagation of 0.025 M on the initial measured concentration gives an error of about ± 0.04 . Scatter in the data for TSR-8 is attributed to interference with the calcium electrode.

concentrations and pH values at 25°C but held at three different temperatures 205, 225, and 250°C (Fig. 2). Concentrations of initial sulfate and sulfide at 25°C were 0.298 and 0.116, respectively, and the pH at 25°C was 1.34. For each experiment, the log of the sulfate concen-

tration was observed to decrease linearly with time. The slopes of these linear relationships gave the rate constants, which were observed to decrease with decreasing temperature (Table 3). Of these three experiments, TSR-7 and TSR-8 (reaction temperatures 250 and 225°C, respectively) were observed to have an increase in sulfide concentrations with the concomitant reduction of sulfate. TSR-11 (205°C), on the other hand, showed an initial slight decrease in sulfide concentration, followed by no change. This decrease in sulfate with no increase in sulfide has also been observed by Kiyosu & Krouse (1990) and by Kaiser (1988), but in those cases longer run times eventually produced sulfide. TSR-11 was perhaps not long enough to show this. This effect may be due to the slow build-up of intermediate-valence species which are required for reduction to occur (see below).

The scatter seen in TSR-8 data is attributed to Cl^- interference on the calcium electrode. It was after this experiment that it was realized how much interference chloride causes and experimental methods were changed so as to decrease the amount of HCl added to the solution being analyzed. Included in Table 3 is a column indicating which analyses were included to determine the rate constants of each successful experiment. There were two requirements for an analysis to make it into the rate determining values: (i) that the sulfate concentrations did not take a huge excursion between readings, presumably due to interference from the electrode and (ii) the values were contained in a single decreasing concentration set and did not incorporate values from an obvious change in reduction rates.

Unsuccessful sulfate reduction experiments are reported in Table 2. In TSR-9, the reason for unsuccessful reduction appears to be the high initial pH. In TSR-10, the reactivity of the nitrogen redox couple was tested to investigate the possibility that it participates in the reduction of sulfate when present, as in the experiments of Toland *et al.* (1958) and Orr (1982). Nitrogen in ammonium has a valence state of -3 and should theoretically oxidize to $\text{N}_2(\text{g})$ (oxidation state 0) in the presence of sulfate. In TSR-10 (250°C), no toluene was present and sulfate was added in the forms of H_2SO_4 , Na_2SO_4 , and $(\text{NH}_4)_2\text{SO}_4$. As a result of the unsuccessful reduction of sulfate to sulfide, shown by the constant H_2S concentrations over the duration of the experiment (Table 2), it was concluded that the presence of ammonium does not affect the rate of sulfate reduction, and can be ignored as a redox reagent under our experimental conditions.

Interpretation

Figure 3 shows most of the rate data determined for TSR as an Arrhenius plot, extrapolated to a typical MVT

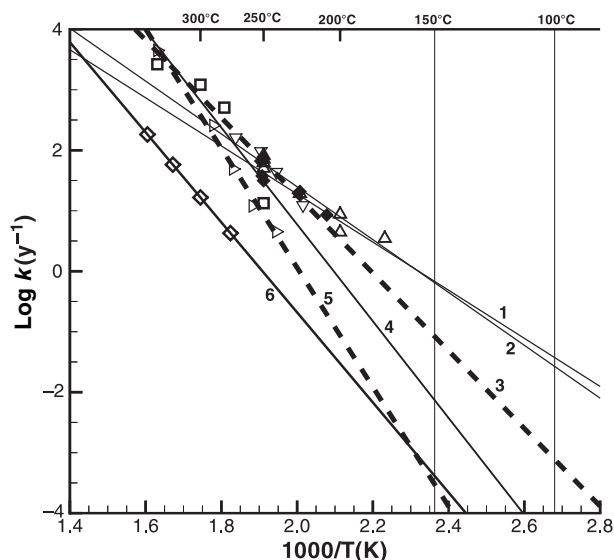


Fig. 3. Arrhenius plot of most available rate constant data (in year⁻¹ units) for TSR. Legend: 1. Present study; 2. Orr (1982); Goldhaber & Orr (1995); 3. Kiyosu & Krouse (1993); 4. Kiyosu (1980); 5. Kiyosu & Krouse (1990); 6. Cross *et al.* (2004). Data from Bannikova (1998) and Nikolaeva *et al.* (1982) are omitted, but do not change the general conclusions.

temperature of 150°C (data from Kiyosu 1980; Orr 1982; Kiyosu and Krouse 1990, 1993; Cross *et al.* 2004). At this temperature, the rate constant values range from about $\log k = 0$ to $\log k = -4$. This range is probably due to the various reductants, pH, and other experimental conditions used.

Hydrogen sulphide as autocatalyst

It has frequently been reported that the combination of aqueous sulfate and organic matter does not result in TSR, unless some H₂S is present to start with. Because H₂S is a reaction product, not a reactant, the reaction can be referred to as autocatalytic. The reason for this is that to transform sulfate, in which sulfur has a +6 valence state, to sulfide, in which it has a -2 state, eight electron per sulfur atom must be transferred, whether by electron transfer between species, or by bond-breaking and transfer of atoms or groups of atoms between species. Combined with the fact that only one, or at most two electrons can be transferred in any single reaction (Basolo & Pearson 1967; Schoonen & Strongin 2005), this probably means that there must be sulfur species having all of the intermediate valence states present in the solution to effect the transfer. These species are the intermediate-valence sulfur species (thiosulfate, sulfite, polythionates, etc.), which act as a bridge for electrons between sulfate and sulfide. The activities of intermediate sulfur species are maximized when SO₄²⁻ (or HSO₄⁻) and H₂S have equal activities, and fall off rapidly as redox conditions move away from this

condition. Most successful TSR experiments, both those reported here and those in the literature, have taken place with substantial concentrations of both sulfate and H₂S, which places them close to the equal activity sulfate/sulfide boundary. If no H₂S is present, then no intermediate sulfur species are present, so no electron transfer and no sulfate reduction can take place. A final point is that under these sulfide-sulfate equilibrium conditions, the intermediate sulfur species are not metastable or unstable, but stable equilibrium species. The fact that the intermediate sulfur species have very low concentrations (Fig. 4A-C) helps to explain the slow rate of TSR.

Intermediate-valence sulfur species also apparently facilitate electron transfer between carbon species as well. Seewald (1997) and McCollom *et al.* (2001) report that the presence of partially oxidized sulfur species greatly enhances the rates of reactions between hydrocarbons, methane, and CO₂. It is also possible that electron transfer is through the conducting band of coexisting sulfides (see e.g. Xu and Schoonen 1995) or the metallic walls of the pressure vessel, if species with different valence states are adsorbed. Both Seewald (1997) and McCollom *et al.* (2001) showed that coexisting minerals play an important role in the kinetics of the various reactions between organic compounds, and the role of mineral surfaces in sulfate reduction is a major unknown factor (Schoonen & Strongin 2005).

It is often stated that organic matter will only reduce sulfate if H₂S is present initially. This is not strictly true, because as Toland (1960) showed, any sulfur species with a valence less than 6+ will initiate sulfate reduction by organic matter, because they will disproportionate to other intermediate-valence sulfur species and H₂S. It is possible that the pH effect on TSR, i.e. the fact that increasing acidity increases the reaction rate, is due not to the H⁺ ion itself, but because of the effect it has on the concentration of other species involved in the reaction, namely the intermediate-valence species. Many of these species actually decrease in concentration with increasing acidity along the HSO₄⁻/H₂S boundary (Fig. 4A-C), which would not be effective in promoting the TSR reaction. Those that decrease are the polysulfides, S₂O₃²⁻, S₂O₄²⁻, and SO₃²⁻. The species which increase in concentration with increasing acidity along the HSO₄⁻/H₂S boundary are SO₂, HS₂O₃⁻, HSO₃⁻, H₂SO₃, and S_nO₆²⁻ (*n* = 2-6). There are no data for aqueous S⁰ other than a brief note by Boulegue (1978) reporting the solubility of sulfur at 25°C, but it must also increase with increasing acidity, parallel to the saturation index, which is shown in Fig. 4D.

Sulfur is the only intermediate-valence sulfur species which is known to react with organic compounds to form H₂S and other species (Toland *et al.* 1958, and earlier references therein). It has therefore often been

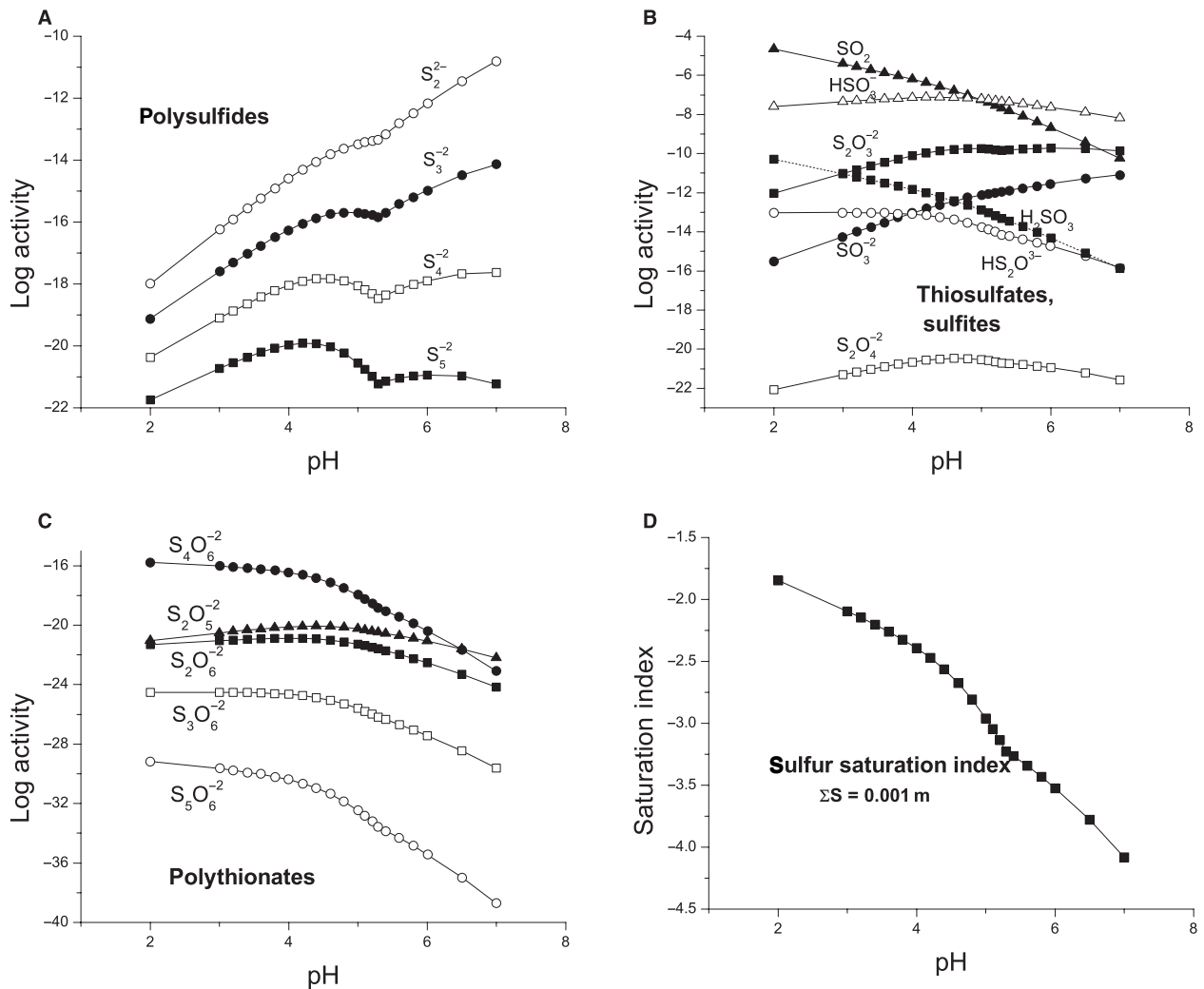


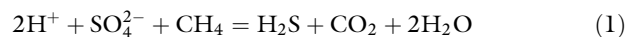
Fig. 4. (A–C). Concentrations of intermediate valence sulfur species along the HSO_4^-/H_2S and SO_4^{2-}/H_2S boundaries at 250°C. Inflection points occur at the HSO_4^-/SO_4^{2-} boundary. (D) Sulfur saturation index at 250°C. Calculated using data in Shock *et al.* (1997).

suggested (Orr 1974; Goldhaber & Orr 1995) that the reaction of sulfate and H_2S to form sulfur is the important intermediate step in the reduction of sulfate by organics, and that therefore the presence of H_2S is required. We suggest that this is essentially correct, but that (i) the reaction of sulfate and H_2S to form sulfur is not a rate-determining step, but that the sulfate–sulfide equilibrium establishes equilibrium concentrations of all the intermediate sulfur species, including $S^0(aq)$ and that it is this that reacts with organics, not necessarily liquid sulfur; (ii) the concentration of $S^0(aq)$ is strongly dependent on pH; and (iii) the presence of all the other intermediate sulfur species is required to effect electron transfer. The kinetics of the various elementary reactions involved are not known, but the most important factor in the kinetics of the overall reaction, such as reported here, may simply be the very low concentrations of

all the intermediate species, including and especially $S^0(aq)$.

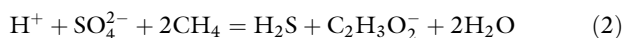
The rate law

Only fragmentary data for the TSR rate law are known. For example Orr (1982) determined the effect of varying H_2S concentration on the rate constant, but many other factors are involved, including pH, reductant concentration, the nature of the reductant, and sulfate concentration. The usual way of writing this reaction,

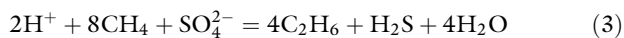


is an overall reaction, giving no clue as to the mechanism. However, it may not even accurately represent the overall reaction. It assumes that all the C^{4-} in methane is oxidized

to C^{4+} in CO_2 which may not be the case. A wide variety of organic compounds are possible intermediates in the oxidation of methane to CO_2 . For example oxidation to acetate is written



Oxidation to ethane is written as



and there are many other possibilities, as shown by Toland (1960) for other reductants. Of course, all such partially oxidized organic species are also possible reducing agents for sulfate, and given the thermodynamic equilibrium, all such reactions will eventually result in complete conversion of any and all of them to CO_2 . The question is whether any of the experimental results summarized here achieved such complete transfer of C^{4-} to C^{4+} , or whether during the reaction some metastable product assemblage prevailed, such as the combination of acetate and CO_2 . There is considerable evidence for such metastable relationships in basinal brines (Helgeson *et al.* 1993; Shock 1994). It is very likely that at least some CO_2 is produced, at least in nature, because in studies of TSR in petroleum reservoirs, calcite is interpreted to be a reaction product (e.g. Worden *et al.* 2000). The point is that we neither know exactly what this reaction is in any specific case, nor how quickly possible metastable intermediate carbon species evolve into CO_2 . Such considerations are more important in the dynamic MVT situation than in the static sour gas petroleum situation.

CH_4 is used here in a general sense as referring to any organic compound, such as toluene in our case, though several studies show that methane and related alkanes are in fact the reducing agents responsible for TSR in petroleum fields (Krouse *et al.* 1988; Worden & Smalley 1996; Worden *et al.* 2000; Cai *et al.* 2001, 2003, 2004, 2005). There are few published experimental studies of TSR using methane as reductant, although Toland (1960) listed one experiment using methane, $(NH_4)_2SO_4$, and H_2S at 325–350°C for 70 min with major products CO and CO_2 . The study on reduction of sulfate by hydrocarbons by Yue *et al.* (2006) did not contain water, and so is not comparable to the TSR reactions considered here.

The reducing agent in experimental studies is usually in excess, as in our case, meaning its activity is constant during the reaction, and so it need not appear in the rate equation for experimental data. This would not necessarily be the case in natural applications. All experimental work so far shows the reaction to be first order, as shown by the fact that log (concentration) versus time plots are linear, some to almost 90% reaction. In other words, it appears that the rate law (assuming a constant reductant activity) may be as simple as

$$\text{rate} = k(SO_4)^n \quad (4)$$

where (SO_4) is sulfate concentration, k the rate constant, and $n = 1$. That the rate law is first order in sulfate concentration was also suggested by Cross *et al.* (2004). The possible errors involved in using linear plots to determine reaction order are well illustrated by Rimstidt & Newcomb (1993). Nevertheless, given the available data there is little choice, and this is the rate law used in the following calculations.

Relevance to ore deposition

If it is assumed that the rate constant for TSR at 150°C is in the range of 10^0 to 10^{-4} year $^{-1}$ (Fig. 3), and that the rate law is given by equation (4), then the quantity of H_2S generated for various flow conditions, times, rate constants, and sulfate concentrations can be calculated. Assuming that all this H_2S precipitates ZnS then gives an estimate of how much ore would be formed, and whether this might happen during ore formation.

To do this, consider the flow of Zn and H_2S in and out of a box, representing a vein system at 150°C, as shown in Fig. 5. The accumulation of ZnS in the vein is equal to the difference between the amount of Zn entering and leaving the vein. In the box, H_2S is generated by TSR, precipitating ZnS . Assuming that the ore is not zinc-limited, i.e. all H_2S generated precipitates ZnS , the amount of ZnS precipitated equals the amount of H_2S generated and the amount of sulfate reduced. Therefore, the difference between $Zn(\text{in})$ and $Zn(\text{out})$ of the box is the same as the sulfate(in) and sulfate(out) of the box. One could also assume that the H_2S is generated not in the vein but else-

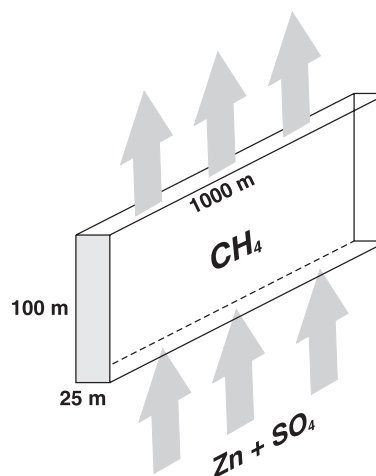


Fig. 5. The flow model. The volume of the box was determined by calculating the volume of 1×10^6 tons of Zn metal as ZnS (2×10^7 tons of 5% Zn ore), multiplied by 10. The inlet fluid has a composition of 3 M $NaCl$, 0.01 M Zn , and 0.025 M SO_4^{2-} (Table 4).

where, and enters the vein during the fluid flow. This raises additional problems, but this is handled here by assuming however and wherever the H_2S is generated, it appears in the vein at our calculated rates.

The equations governing this situation are those for the 'Constant Stirring Tank Reactor' or CSTR model, discussed in many Chemical Engineering texts, for example Schmidt (2005, Chapter 3). Mass balance considerations for a first-order reaction lead to the equation

$$(SO_4)_{in} - (SO_4)_{out} = (SO_4)_{in} - \frac{(SO_4)_{in}}{1 - t \times k} \quad (5)$$

where (SO_4) is the sulfate concentration in molality, t the residence time in years, and k the rate constant in $year^{-1}$ units. The residence time is the time an element of solution spends in the box, and is defined as V/r , where V is the volume of fluid in the box in m^3 , and r the volumetric flow rate in $m^3 year^{-1}$. The volume of fluid in the box is the total volume times the porosity, and the volumetric flow rate is defined as FA , where F is the specific discharge or Darcy flow rate ($m^3 m^{-2} year^{-1}$) and A the inlet area (m^2), or the area over which the solution flows into the box.

This results in the moles of sulfate reduced, hence the moles of ZnS precipitated, per kilogram of solution per year. Multiplying by the number of kilograms of fluid per year and the number of years, and converting moles of Zn to kilograms, gives the mass of Zn precipitated in a given number of years. The results of these calculations for the box shown in Fig. 5 and other parameters shown in Table 4 are shown in Figs 6 and 7. Clearly, a $\log k$ of -1 (or of course $\log k = 0$, not shown) will easily produce an ore deposit in geologically reasonable times (10^4 to 10^6 years; Lavery and Barnes 1997; Garven *et al.* 1993; Lewchuk & Symons 1995; Rowan & Goldhaber 1995), while a $\log k$ of -4 will not. Intermediate k values obviously produce intermediate values.

Caveats

The parameters employed, such as the dimensions of the box, the fluid composition and the flow rates, are fairly arbitrary, and might be changed within certain limits. But many such changes would not change the main conclu-

Table 4 Parameters used in the calculation.

Box volume	$2.5 \times 10^6 m^3$
Inlet area	$25000 m^2$
Fluid volume in box	$5.0 \times 10^5 m^3$
Porosity	0.2
Sulfate molality	0.025
Zn molality	0.01
Temperature	$150^\circ C$

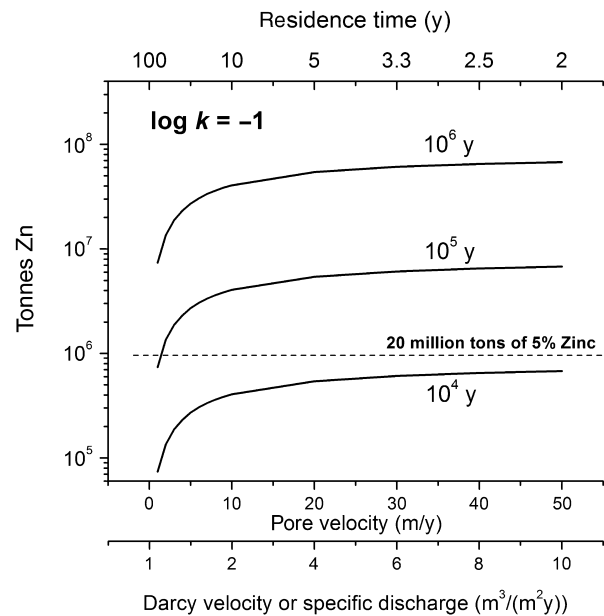


Fig. 6. Tons of Zn precipitated as a function of time and fluid flow at a rate constant of 10^{-1} . The position of an ore deposit of 20 million tons of 5% Zn is shown as a reference.

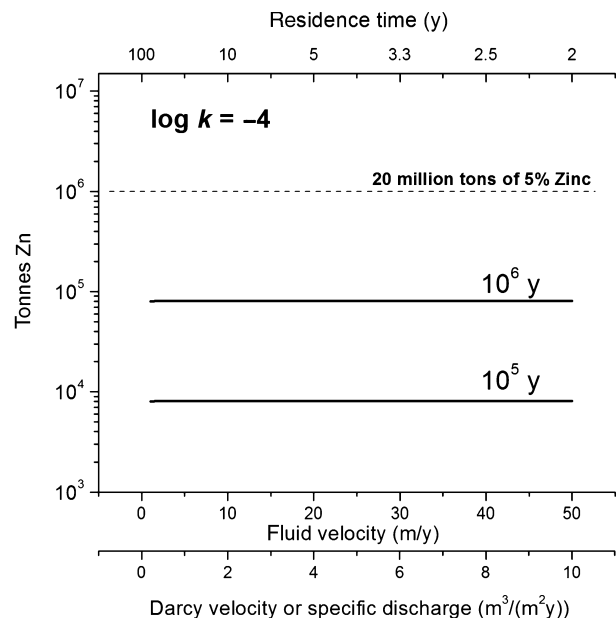


Fig. 7. Tons of Zn precipitated as a function of time and fluid flow at a rate constant of 10^{-4} . The position of an ore deposit of 20 million tons of 5% Zn is shown as a reference.

sions. Figure 6 shows that the calculated tonnages could be too great by a factor of 10 or even 100, without changing the conclusion that rate constants in the upper part of the possible range are still fast enough to produce ore during deposition.

However, it is by no means clear that experimental results are directly applicable to natural situations. As mentioned, the reductant in nature appears to be methane and related alkanes, but no experimental work has used these reductants, which may well be less reactive than the reductants which have been used, such as toluene and acetic acid. As also mentioned, no concerted attempt at determining the rate law has been made. The one used here may be inadequate. It does seem that TSR is faster at low pH values, although Cross *et al.* (2004) found that pH did not affect the rate in the range 6–7. This is important, because TSR takes place in carbonate environments and may be carbonate-buffered (acid-generating sulfide precipitation in the MVT environment complicates this possibility). A completely unknown factor is the catalytic effect of mineral surfaces. Finally, as emphasized by Kaiser (1988), it is also by no means certain that using the Arrhenius plot to extrapolate from high experimental temperatures to lower natural temperatures is justified. Using this equation assumes that the reaction mechanism remains the same over the temperature interval. Only a detailed knowledge of the specific reaction mechanism will allow evaluation of this problem.

All these factors mean that TSR rates in nature may be different than those found experimentally, and that our calculated ore tonnages show only what is possible in our present state of knowledge.

SUMMARY AND CONCLUSIONS

- Experiments are reported in which aqueous sulfate was reduced by toluene at temperatures from 205 to 250°C, with determination of both sulfate and sulfide concentrations during the runs.
- The rate constants determined are for a first-order reaction, and are similar to those found by Orr (1982) and Kiyosu & Krouse (1993).
- Experimentally-derived TSR rate constants, when extrapolated to a typical MVT temperature of 150°C have a range of $k = 10^0 \text{ year}^{-1}$ to $k = 10^{-4} \text{ year}^{-1}$.
- Using a plausible rate law, rate constants in the upper part of the extrapolated range and reasonable values for flow parameters, it is shown here that, contrary to common assumptions, TSR is fast enough to occur during ore deposition.
- The rate law appears to be first order in sulfate concentration, but other factors such as pH and reductant activity may be involved.
- TSR is invoked in a great many studies of MVT deposits, but our knowledge of both the reaction mechanism and what factors control the rate at which it proceeds are still weak. Having such knowledge would help greatly in interpreting the origins of MVT deposits.

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