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High H_2S contents and other effects of thermochemical sulfate reduction in deeply buried carbonate reservoirs: a review

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Abstract The accumulation of high H_2S concentrations in oil and gas fields is usually associated with deeply buried high-temperature carbonate reservoirs and is attributed to the abiological oxidation of hydrocarbons by sulfate – thermochemical sulfate reduction (TSR). This review aims at providing an overview of the literature and assessing existing uncertainties in the current understanding of TSR processes and their geological significance. Reaction pathways, various reaction products, the autocatalytic nature of TSR, and reaction kinetics are discussed. Furthermore, various criteria for recognizing TSR effects, such as petrographic/diagenetic alterations and stable isotope geochemistry of the inorganic as well as the organic reactants, are summarized and evaluated. There is overwhelming geological evidence of TSR taking place at a minimum temperature of 110–140 °C, but the temperature discrepancy between experimental data and nature still exists. However, the exact nature and mechanisms of catalysts which influence TSR are not known. Local H_2S variations may reflect steady-state conditions dominated by H_2S buildups and flux out of the system. The latter is controlled by lithological and geological factors.

Key words Thermochemical sulfate reduction (TSR) · Sour gas · Hydrogen sulfide · Carbonate reservoirs · Bitumen · Sulfur · Mississippi Valley-type ore deposit

Introduction

Numerous gas and oil fields contain H_2S as free gas or dissolved in reservoir fluids. Worldwide variation of H_2S concentrations of up to 90% in gas phase are known (Krouse et al. 1988, and citations therein; Amurskiy et al. 1980; Orr 1977). H_2S contents in natural gases higher than 10% generally increase handling costs substantially. However most "sour gases" contain 1–5% H_2S, and gases with more than 10% H_2S are typically found in sour gas provinces. Some of the best known sour gas provinces are the Middle and Upper Devonian carbonates of South–Central Alberta, with the Leduc and Bearerhill formations. Further examples are the Jurassic evaporitic limestones and quartzose clastics of the southeastern United States (Smackover and Norphlet formations). Sour gas is also known from the Permian Zechstein formation of Northwestern Germany and the Cretaceous and Upper Jurassic reservoirs in the Lacq Field of southern France. All of these reservoirs are associated with carbonate deposits adjacent to or interbedded with evaporites and high reservoir temperatures of 70–120 °C or higher (Orr 1977; Worden et al. 1995).

At reservoir temperatures below 80 °C biochemically controlled reactions dominate, e.g., anaerobic microorganisms utilize sulfate as an oxidant in metabolic processes to oxidize organic matter. Stetter et al. (1987), Elsgaard et al. (1994), and Jørgensen et al. (1992) describe hyperthermophilic sulfate-reducing bacteria at temperatures of 110 °C. Biological sulfate reduction (BSR) generally leads to low levels of H_2S ($<3\%$) and can be represented by the following simplified net reaction:

$$2CH_3O + SO_4^{2-} \Rightarrow 2HCO_3^- + H_2S$$

The amount of H_2S formed by thermal cracking (maturation) depends on the organic sulfur content of the original crude oil. It normally amounts to 2–3 H_2S vol% of the reservoir gas (Orr 1974, 1977).

The process of non-biological thermochemical sulfate reduction (TSR) was first suggested by Barton (1967) in relation to ore deposits. Various authors describe sulfur-rich degraded solid organic matter, sulfate and metal sulfides in Mississippi Valley-type ore

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deposits (Powell and Macqueen 1984; Marikos 1986). Orr (1974, 1977) proposed thermochemical reduction of sulfate by hydrocarbons in oil-field sediments to be the major process to form much higher H_2S concentrations (>10%) in highly mature carbonate reservoirs (100–150 °C; $R_0 = 1–1.5\%$). The reaction temperatures in such geological settings are intermediate between the temperature regime of BSR and the much higher temperatures (175–375 °C) of experimental thermochemical sulfate reduction (Toland 1960; Drean 1978; Kiyosu 1980; Nikolayeva et al. 1982; Trudinger et al. 1985; Kiyosu and Krouse 1990; Ohmoto and Lasaga 1982). The net-reaction scheme is the same as for microbial sulfate reduction, except that the ratio of H_2S and CO_2 varies with the state of oxidation of the organic substrate utilized (Orr 1977).

Thermochemical sulfate reduction can be represented by the following simplified net reaction (Orr 1974; Machel 1987; Machel et al. 1995):

$$\text{hydrocarbons} + SO_4^{2-} \Rightarrow \text{altered hydrocarbons} + \text{solid bitumen} + HCO_3^-(CO_2) + H_2S(HS^{--}) + (\text{heat})$$

The main prerequisites for TSR are temperatures >100 °C, the presence of reactive organic material, and sulfate in the host rocks. Since carbonate host rocks usually contain low amounts of iron, H_2S concentrations can build up without concomitant removal as FeS_2 minerals.

In summary, during TSR organic matter is oxidized and dissolved sulfate (SO_4^{2-}), i.e., reservoir anthydrite, is reduced to form hydrogen sulfide, bicarbonate ions and carbon dioxide, as well as numerous organic sulfur compounds. In the presence of alkali earth metals carbonate cements and/or replacements of the dissolved sulfates can occur. If transition or base metals are available, iron sulfides, galena, and spharlerite can precipitate. The reaction is initialized by small amounts of H_2S produced by thermal cracking of organic compounds. The H_2S reacts with aqueous sulfate (reservoir sulfate) forming native sulfur, polysulfides, and thiosulphate, which then oxidize and dehydrogenate organic matter. However, sulfate alone will not react unless lower-oxidation-state sulfur is present (Goldstein and Aizenshtat 1994). As a result of TSR, the H_2S content in petroleum reservoirs increases with progressing temperature/maturity and the sulfur isotopic composition of both reduced organic and inorganic sulfur changes towards that of reservoir sulfate (Orr 1974). This implies that little or no isotopic fractionation takes place during the addition of abiogenic sulfide produced from sulfate (see Fig. 1).

Thermochemical sulfate reduction is a self-catalyzing process, because rising temperatures, high H_2S partial pressure, and an increasing amount of reactants force the reaction to proceed faster (e.g., Orr 1974, 1977; Machel et al. 1995).

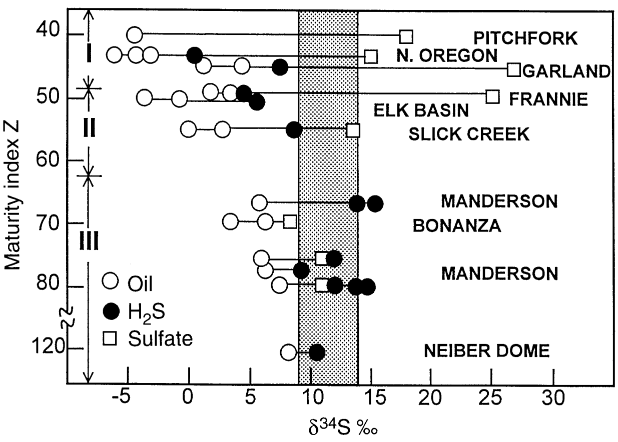

Fig. 1 The $\delta^{34}S$ (CDT) of H_2S and organic sulfur in Palaeozoic oils of the Big Horn basin (USA) as a function of oil maturity (Z increases with increasing values). The sulfur-isotope ratios of oils, hydrogen sulfide, and dissolved sulfate increase with increasing maturity and change toward the sulfur-isotope ratio of the reservoir sulfate. The *shaded area* indicates the Permian sulfate range. Similar effects were observed in the Lacq gas field (France), in the Permian-Triassic of Abu Dhabi (Worden and Smalley 1993; Worden et al. 1995). (From Orr 1974)

There is considerable controversy on chemical and physical changes that occur during TSR such as changes in pH and carbonate alkalinity, the specific dissolved sulfate species, such as HSO_4^-, $NaSO_4^-$, and SO_4^{--}, the concentration of the sulfate and that of the reducing agents, the role of catalysts and reaction pathways, and the precise threshold temperature (Toland 1960; Kiyosu et al. 1990; Nicolayeva et al. 1982; Nicholson and Goldhaber 1991). The main objective of this paper is an evaluation and review of the different aspects of TSR scattered in the current literature.

Reaction pathways and reaction products

Thermochemical sulfate reduction can be described by two successive generalized reactions for the chemical reduction of sulfate by organic matter where hydrogen sulfide acts as a catalyst as well as a reaction product. A series of unspecified steps are involved. Orr (1974) used methylene groups ($-CH_2-$) to propose the following mechanisms:

Sulfate–hydrogen sulfide reaction

$$SO_4^{2-} + 3H_2S \underset{k-1}{\overset{k1}{\Leftrightarrow}} 4S^0 + 2H_2O + 2OH^-$$

Oxidation (dehydrogenation) of hydrocarbons by S^0

$$4S^0 + 1.33(-CH_2-) + 2.66H_2O \overset{k2}{\Rightarrow} 4H_2S + 1.33CO_2$$

Polysulfides/elemental sulfur

Reaction (1) was postulated as the rate (k1) determining step provided that adequate amounts of oxidizable organic matter are present. The symbol "S^0" is not necessarily elemental sulfur (S_8^0), but represents reactive intermediate species, probably catenated polysulfides (HS_x^0 or HS_x^-) which rapidly react with organic molecules by hydrogen abstraction (ORR 1974, 1982, 1990; LaLonde 1990). Probable intermediates in this reaction are thiosulfate species $H_2S_2O_3$, $HS_2O_3^-$, $S_2O_3^{2-}$ (Ohmoto and Lasaga 1982).

One widely discussed problem in the literature is the type of reactive sulfur species involved. In a very thorough review Goldstein and Aizenshtat (1994) conclude that both elemental sulfur and polysulfides are the most reactive species for TSR, and not thiosulfates, as suggested by Ohmoto and Lasaga (1982). For the reduction of S^{6+} to S^{2-} Goldstein and Aizenshtat (1994) stipulate a multi-step mechanism producing sulfur with redox states intermediate between sulfate and sulfide. Low-activation energies are required for further transformations between these sulfur compounds hereby mainly forming thiyl radicals from polysulfides, which in turn oxidate hydrocarbons at lower activation energies than thiyl radicals derived from disulfides or thiols.

Hydrogen abstraction by elemental sulfur is known to take place at minimal reaction temperatures of about 175 °C (see Pryor 1962). Chen and Morris (1972) showed experimentally that elemental sulfur and excess sulfide form polysulfides abiologically. Polysulfides may then react with bicarbonate to form elemental sulfur (Davis and Kirkland 1970). Elemental sulfur (oxidation of S^{2-} to S^0), however, can be formed via the reaction between dissolved sulfate and hydrogen sulfide (see Dinur et al. 1980; Orr 1982; Machel 1992; Machel et al. 1995) with respect to the H_2S pressure and a low pH as follows:

$$3H_2S + SO_4^{2-} + 2H^+ \Rightarrow 4S^0 + 4H_2O + OH^-$$

According to experiments by Davis et al. (1970) and Hussain and Krouse (1978) abiological sulfide oxidation at low pH with excess dissolved sulfate is only possible at higher temperatures, i.e., during TSR. Machel (1992) and Machel et al. (1995) descsribe sulfur formation at temperatures over 100 °C during the reaction of H_2S with saturated hydrocarbons if catalysts (silica gel, clays) are present (see also Altered hydrocarbons and solid bitumen).

Sulfur accumulation can only take place if no further reactions with hydrocarbons occur, because elemental sulfur is an active oxidizing agent for many organic compounds (mainly resins and asphaltenes) at higher temperatures. Laboratory experiments by Orr (1982) show that sulfur does not accumulate in the presence of toluene, but is formed in large amounts at a temperature of 250 °C, if toluene is absent.

The reverse reaction of Reaction (1) is negligible (as the constant k − 1 is very small) if the reaction rate in Reaction (2) is high enough to keep the reactive sulfur concentration low. At low concentrations of oxidizable organic matter, however, the hydrolysis of S^0(k − 1) may compete with Reaction 2 (Orr 1982, 1990).

Significant H_2S formation with concomitant oxidation of organic matter has been observed only under acidic conditions (Trudinger et al. 1985). Thermal cracking of crude oil (maturation) resulting in H_2S formation and/or the aqueous dissociation products HS^- and S^{2-} probably initiate Reaction (1) and may act as a catalyst (Machel 1989). Orr (1982) measured sulfate reduction rates at 175–250 °C in pressure vessels containing $(NH_4)_2SO_4$, H_2S, H_2O, N_2, and toluene over reaction times of 92–620 h. His experiments show that reduction rates increase with increasing amounts of H_2S up to approximately 3.5 bar load pressure and more slowly at higher pressures (3.5–14 bar).

Sulfur deposits in reservoirs

In sour gas reservoirs elemental sulfur can occur in three different forms which are controlled by temperature, pressure, and composition of the gas phase (Hyne et al. 1991; Woll 1983, Woll 1983, Machel 1992):

1. Sulfur can occur as a free phase, i.e., either as a liquid or as a solid. Its freezing point of 116–119 °C can be decreased to 90 °C in the presence of H_2S under pressure, which is an advantage during reservoir handling, because liquid sulfur causes fewer plugging problems (Woll 1983; Hyne et al. 1991).
2. Physically dissolved sulfur is mostly found in the gas phase and in small amounts in the aqueous phase.
3. Chemically dissolved sulfur as hydrogen polysulfides occurs in the gas phase as well as in liquid sulfur.

Physical dissolution is common in reservoirs with $H_2S < 50\%$, whereas polysulfide solution takes place only when greater H_2S concentrations are present (Hyne 1986). Increasing H_2S concentrations enable more elemental sulfur to be incorporated as polysulfides, thus increasing the "sulfur carrying power" (Hyne and Derdall 1989; Hyne 1991). During production or exhumation (e.g., uplift) of sour gas reservoirs temperature and pressure are lowered, resulting in the precipitation of elemental sulfur, which is the result of hydrogen polysuifide disproportionation and concomitant decrease in physical solubility. The deposited elemental sulfur can occur as a solid, as liquid droplets, or as solid suspended particles of colloidal size (Hyne et al. 1991; Machel 1992).

Organic compounds

Various experiments at temperatures higher than 200 °C by Toland (1960), Kiyosu (1980), and Trundinger et al. (1985) show that the following hydrocarbons react abiologically with aqueous sulfate: n-paraffins, low molecular weight n-alkanes (methane, ethane), low molecular weight n-alkenes, n-octadecane, carbohydrates, and alkylated aromatic compounds (see review by Machel 1987; Machel et al. 1995). Dehydrogenation reactions are known to be selective and depend on the hydrocarbon structure (Kiyosu et al. 1990). According to Orr (1990) benzylic C–H bonds (i.e., Ar–CH_2–) are the most reactive and aromatic hydrogens are the least reactive. Toland (1960) demonstrated the oxidation of various organic compounds with aqueous sulfate to organic acids at temperatures of 315–350 °C in the presence of H_2S. He observed that no reaction took place with sulfate alone as an oxidant. His experiments showed that methane was partly converted (0.1%) to CO, CO_2, and H_2O, but alkenes or methyl-substituted aromatics were preferentially oxidized.

Condensate liquids analyzed by Claypool and Mancini (1989) indicate that during TSR in the Jurassic Smackover formation (U.S. Gulf Coast) the saturate fractions were removed, i.e., they were the most reactive hydrocarbons.

The reactivity of normal and branched alkanes has not yet been studied in much detail, but CH_4 very probably is the least reactive alkane, because high H_2S concentrations are often associated with methane-rich gases (Orr 1982; W.L. Orr, pers. commun.). This is in good agreement with the carbon isotopic data indicating sulfate reduction by light hydrocarbon gases in Devonian/Carboniferous reservoirs of western Canada (Krouse et al. 1988). The authors describe greater shifts in ^{13}C-values for ethane and propane than for methane, thus showing that the latter was not oxidized to the same extent. Experiments by Kiyosu et al. (1990) on oxidation of light hydrocarbons give further evidence in this direction. The carbon isotope variations observed, indicate that the reaction rate constants are in the order $k_{propane} > k_{ethane} > k_{methane}$, thus implying that ethane and propane are more reactive than methane. Orr (1990), therefore, concluded that gases become progressively dryer during TSR, i.e., enriched in methane as all other alkanes are destroyed. This is in accordance with the thermodynamic stability of methane at higher temperatures when comparaed with higher-weight alkanes (see review by Machel et al. 1995). Thus, the often-cited simplified overall reaction scheme summarized below (Worden and Smalley 1993; Worden et al 1995, Siebert 1985; Heydari and Moore 1989), showing H_2S and calcite formation at the expense of methane, is only possible if methane is the only carbon source. The absence of solid bitumen combined with low ^{13}C-values in carbonates indicate biogenic methane to be the organic reactant (Machel et al. 1995).

$$CaSO_4 + CH_4 \rightarrow CaCO_3 + H_2O + H_2S.$$

The net reaction, i.e., the reduction of sulfate to hydrogen sulfide and the oxidation of organic matter, represented by the methylene group (–CH_2–), to carbon dioxide via carboxylic acids, can be written as follows, if all the sulfur generated is used up by reactive organic matter (Orr 1974):

$$SO_4^{2-} + 1.33(\text{–}CH_2\text{–}) + 0.66H_2O \rightarrow H_2S$$
$$+ 1.33CO_2 + 2OH^-$$

The intermediate carboxylic acids which can decarboxylate to CO_2 could cause solution of minerals and ion transport (Orr 1982). Also, depending on the cations present at the TSR reaction site various minerals phases can precipitate, because the net reaction involves production of OH^- ions, thus increasing the pH (see pH dependency).

Altered hydrocarbons and solid bitumen

Further organic reaction products observed during TSR as well as during BSR are solid bitumens formed from polymerization and/or sulphurized bitumens. These latter NSO compounds are generally termed “altered hydrocarbons” (Machel 1987) and can be formed together with elemental sulfur by the reaction of H_2S with saturated hydrocarbons if catalysts such as silica gel or clays are present (shown experimentally by Rudakova and Velikowski 1947) at temperatures above 100 °C. However, if methane is the only organic reactant, all carbon is oxidized to carbonate and some CO_2 and CO, but no bitumen is formed. At lower temperatures this can be the case in a bacteriogenic setting or, at higher temperatures, during thermal maturation of kerogen when mainly methane is generated (Machel et al. 1995).

The following net reaction scheme is given by Machel (1992):

$$H_2S + \text{hydrocarbons} \rightarrow S^0 + \text{altered hydrocarbons}.$$

The elemental sulfur formed in this way as well as some NSO compounds can be physically mixed with solid organic precipitates, i.e., with bitumen (Palacas Love 1972; Orr 1974; Sassen 1988; Sassen and Chinn 1989). Most of the sulfur, however, cannot survive as a free phase, because polysulfides are formed.

Leventhal (1990) demonstrated how TSR altered organic matter in a Mississippi Valley-type ore deposit (Viburnum Trend, Southeast Missouri). This change is documented as a loss of hydrogen (lower H/C ratio), the near absence of n-alkanes, the predominance of aromatic molecules, and a higher sulfur content of organic matter in contact with ore.

Evidence of bitumen being formed in TSR reactions is given by Powell and Macqueen (1994) who analyzed sulfur isotopes of solid bitumen in a carbonate hosted

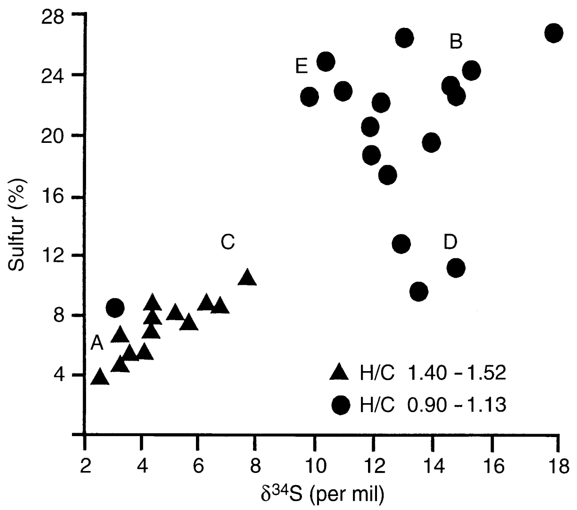

Fig. 2 Thermochemical sulfate reduction (TSR) also occurs in carbonate-hosted lead–zinc and iron sulfide ore deposits which are often associated with bitumen and heavy oil. Powell and Macqueen's (1984) data (letters *A–D* refer to samples) from Pine Point, Northwest Territories, Canada, show that δ^{34}S-values in bitumens increase with increasing sulfur content, indicating that isotopically heavy sulfur is incorporated during TSR. Altered bitumens have a mean sulfur content of 22% (unaltered: 7.8%) and δ^{34}S-values of approximately + 12.4‰ (unaltered: + 4.6‰)

ore deposit at Pine Point, Northwest Territories, Canada (Fig. 2). Their data indicate that the incorporation of isotopically heavy sulfur during thermal alteration of solid bitumen can be related to thermochemical sulfate reduction and production of H_2S with the following reaction:

$$10C_{30}H_{45}SO + 98S^0$$

$$\rightarrow (C_{30}H_{30}S_4)_{10}O_3 + 7H_2O + 68H_2S$$

Another comparable situation is the alteration of organic matter by ascending oxidizing brines in the organic-rich Permian Kupferschiefer in Southwest Poland (Püttmann et al. 1987). Their study shows a significant alteration in the extractable bitumen in the lower part of the section, i.e., aliphatic hydrocarbons as well as aliphatic side chains of aromatic compounds have been removed. Similar alterations in bitumens could possibly occur by oxidation due to TSR.

Kiyosu (1980) and Kiyosu and Krouse (1990) carried out isotope exchange experiments by heating dextrose with mixtures of equimolar solutions of dilute sulfuric acid and sodium sulfate. At 280 °C approximately 40% of the sulfate was converted and elemental sulfur and "black precipitates" containing some hydrolyzable sulfur as well as organically bonded sulfur were observed. According to Kaiser (1988) the oxidation of dextrose and other sugars is thermodynamically favored at 250 °C with $\Delta G = 3200$ kj/mol according to the simplified reaction:

$$C_6H_{12}O_6 + HSO_4 + 3H^+ \rightarrow 3\,H_2S + 6\,CO_2 + 6\,H_2O$$

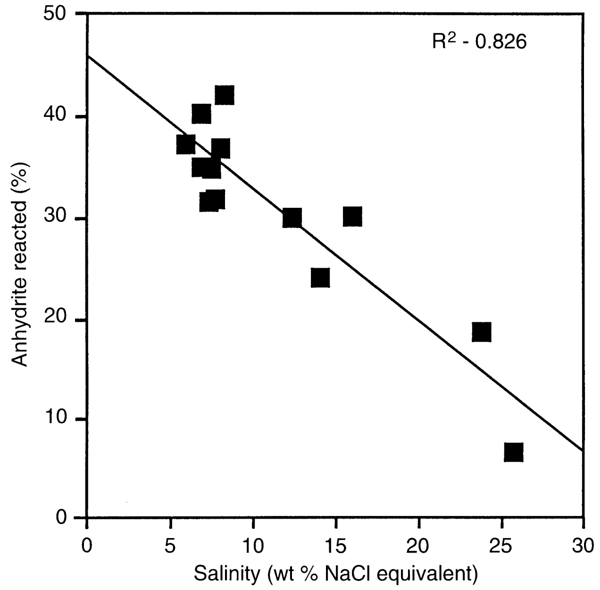

Fig. 3 Worden and Smalley's (1993) data document decreasing formation water salinity in fluid inclusions in calcite as the extent of anhydrite alteration to calcite increases with progressive TSR

Kaiser (1988) experimentally showed that 50% of the reduced sulfur is incorporated in "organic char" (or residual polymer; see Goldstein and Aizenshtat 1994) containing 14% sulfur. Similar products described as "viscous black tar" and "dark viscous gum" containing up to 11% organically bound sulfur are reported by Douglas and Mair (1965). Goldstein and Aizenshtat (1994) are very critical when extrapolating the results of experimental studies involving the oxidation of sugars to TSR in the geosphere, because of the complex reactions sugars and sugar derivates often undergo with acids at temperatures higher than 200 °C.

Water

In analogy to BSR, thermochemical sulfate reduction reactions in diagenetic environments are only possible in the presence of dissolved sulfate (Machel 1987; Machel et al. 1995, and citations therein; Orr 1974, 1990).

Worden and Smalley's (1993) fluid inclusion data of calcite replacing anhydrite in a dolomitic reservoir rock indicate that formation water salinity of fluid inclusions in calcite decreases as the extent of anhydrite alteration to calcite increases with progressive TSR (Fig. 3). Mass balance calculations show that the original saline formation water has been diluted between 5 to 6 times by fresh TSR water.

Reaction conditions and reaction rates

According to experiments by Toland (1960), Kiyosu (1980), and Nikolayeva et al. (1982) the rate of abiogenic sulfate reduction depends on the specific dissolved sulfate species such as HSO_4^-, $NaSO_4^-$, and SO_4^{2-}, the concentration of the sulfate and that of the reducing agents, temperature, and pH.

pH dependency

The equilibrium distribution of the different ionic species for sulfate (H_2SO_4, HSO_4^-, SO_4^{2-}) and hydrogen sulfate (H_2S, HS^-, S^{2-}) depends mainly on pH (Ohmoto and Lasaga 1982). These authors expect the rate of sulfate reduction to increase at low-pH conditions, because the speciation of thiosulfate compounds with intermediate valency state sulfur depends on pH. Igumnov (1976), however, showed that the rate constants of the sulfide with sulfate reaction are dependent on temperature and complexly dependent on pH. At 200–400 °C the sulfur exchange rate decreased with increase in pH up to pH = 4, was almost constant at pH = 4–7, and decreased at higher pH. The activation energies also depend on pH. Experiments by Kiyosu (1980) indicate that the rates of sulfate reduction to H_2S by dextrose within a temperature range of 250–340 °C decreased with increasing pH. At pH = 4 and a low sulfate concentration Drean (1978) did not observe reduction of sulfate by methane or xylene after 30 days at 325 °C.

Thermochemical sulfate reduction leads to carbonate precipitation because it involves a net increase in pH, an increase in carbonate alkalinity due to released HCO_3^-, and an increased calcium ion content (dissolution of calcium sulfate). Dolomite cements or replacements can form if magnesium is available. Anderson and Garven (1987) and Anderson (1983) predict carbonate dissolution if sulfides precipitate, e.g., in sediments containing iron oxides, unless, for example, sulfate reduction consumes the released acids.

Based on the reactions discussed above, the reaction products, as well as pH changes, forward modelling software packages permit prediction of possible porosity increases and porosity redistribution in reservoirs (e.g., the SOLVEQ/CHILLER software package used by Nicholson and Goldhaber 1991) to model reaction paths of TSR in the Whitney Canyon–Carter Creek Field, Wyoming).

Reaction kinetics and temperature ranges

Temperature

The most important aspect when discussing sulfate-reduction redox reactions is temperature. The upper temperature limit for BSR lies between 60 and 80 °C (see Introduction). The cited threshold reaction temperatures for TSR in the current literature vary in the range of 80–200 °C (see citations in Worden et al. 1995).

In a very critical review Trudinger et al. (1985) state that "there has been no unequivocal demonstration of net sulfide formation from sulfate" at temperatures below 200 °C. In laboratory experiments TSR has not been demonstrated below 175–250 °C (Toland 1960; Kiyosu 1980; Trudinger et al. 1985), whereas thermodynamic calculations indicate temperatures as low as 140–175 °C (Orr 1982; Anisimov 1978; see also review by Goldstein and Aizenshtat 1995, and citations therein). Various studies on TSR in geological environments are cited and compiled by Worden et al. (1995). The lowest postulated onset temperatures are 100–110 °C (Orr 1982; Krouse et al. 1988; Wade et al. 1989; Viau et al. 1989). Based on fluid inclusion data Machel (1987) concluded a threshold temperature between 120 and 145 °C. Thermochemical sulfate reduction in the Jurassic Smackover formation (U.S. Gulf Coast) occurred at 120–150 °C (Heydari and Moore 1989; Nunn and Sassen 1986). In a very conclusive study of the Permian-Triassic Khuff formation of Abu Dhabi Worden et al. (1995) show that gas souring as well as the extent of anhydrite reaction (conversion to calcite) occurs only at depths greater than 4300 m, i.e., at a temperature greater than 140 °C (Fig. 4). They further confirmed this threshold temperature with fluid inclusion data. Their assessed temperature, based on three independent methods, is in good accordance with published temperatures from other studies. They further state that the great temperature discrepancies in the literature very probably result from the following considerations: (a) gas chemistry vs temperature studies indicate lower temperatures, because soured gas can have migrated from deeper hotter formations; and (b) experimental studies must usually be time limited. The high temperature conditions are then extrapolated to long-term

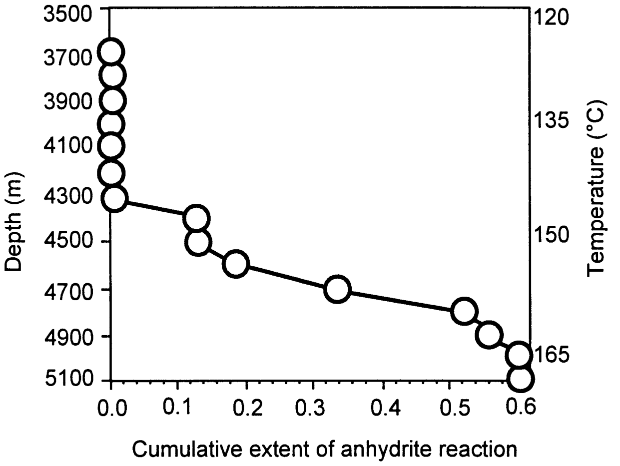

Fig. 4 Worden et al. (1995) used the extent of anhydrite alteration to calcite to assess the degree of TSR in Permian-Triassic sediments of the Khuff formation of Abu Dhabi. The degree of alteration is plotted vs depth and temperature. Anhydrite replacement by calcite commenced in samples deeper than 4300 m and temperatures higher than 140 °C

lower-temperature diagenetic environments. Also, difficulties in measuring small amounts of reaction products because of slow reaction kinetics and incomplete equilibration must be taken into account.

Other factors controlling reaction rates

Decreasing salinities can effect reaction kinetics of TSR, because CH_4 solubility in water increases under these conditions (Duan et al. 1992). Therefore, even at a constant temperature, the rate of TSR increases, making a greater volume of progressively less saline water available to mediate the reaction. Therefore, TSR is considered to be an autocatalytic reaction which is accelerated by the production of water (Worden and Smalley 1993). This would also explain the sudden increase in H_2S content of natural gas reservoirs with temperatures higher than 140 °C (see Fig. 4; Worden et al. 1995). A kinetically controlled reaction would result in a gradual increase.

Thermochemical sulfate reduction has been demonstrated to be an autocatalytic reaction because sulfide increases the rate and is formed with increasing conversion (Orr 1974, 1977, 1982). However, since an increase in pH also occurs with increasing conversion, the reaction rate decreases. Thus, the net effect of increasing both H_2S and pH with conversion is not certain (W.L. Orr, pers. commun.).

According to Machel (1987) the temperature discrepancy discussed above between laboratory experiments and geological observations can be partly attributed to the lack of appropriate catalysts in laboratory experiments.

Effects of TSR

Isotopic evidence

Sulfur

In laboratory experiments Kiyosu and Krouse (1990) demonstrated that during abiogenic sulfate reduction the sulfate becomes progressively enriched in ^{34}S with decreasing sulfate concentration and increasing temperatures. This indicates that the sulfate with the lighter isotope is easily reduced due to the kinetic isotope effect, which occurs when the sulfur–oxygen bonds in the sulfate break (Harrison and Thode 1957). The kinetic sulfur-isotope fractionation decreases with increasing temperature (see review by Machel et al. 1995, and citations therein). Furthermore, the kinetic isotope effect is independent of reducing agents such as organic matter and may depend on the atomic hydrogen produced during the decomposition of the reducing agents (Kiyosu and Krouse 1990).

In addition to increasing H_2S contents of natural gases attributed to TSR in the temperature range of 70–120 °C Orr (1974, 1977, 1982) noted characteristic changes in the ratio of sulfur isotopes ($^{34}S/^{32}S$) of H_2S and organic sulfur in oils. He documented that the $\delta^{34}S$ (CDT) of H_2S and organic sulfur in Palaeozoic oils of the Big Horn basin (USA) changes towards that of reservoir sulfate as the hydrocarbons become mature, implying that only a negligible isotopic fractionation takes place during anhydrite reaction with hydrocarbons. The H_2S thus formed reacts with organic matter to form organic sulfur compounds with the same $\delta^{34}S$-values as the H_2S (Fig. 1). Uniform sulfur isotope values of H_2S, native sulfur, and anhydrite are also documented by Worden and Smalley (1993) for Permian reservoir rocks. Also, sulfur-isotope data of Heydari and Moore (1989; Jurassic Smackover formation, USA) suggest that sulfate in late diagenetic anhydrite was recycled from Jurassic depositional anhydrite ($\delta^{34}S$ for Jurassic depositional sulfate: + 16 to 19%; Claypool et al. 1980) and $\delta^{34}S$ for late diagenetic anhydrite of the Smackover formation: + 18.6‰). The $\delta^{34}S$-values for elemental sulfur are similar to the values for reservoir sulfates.

During microbiological sulfate reduction (BSR), however, a kinetic isotope fractionation of − 15 to − 65‰ are documented (e.g., Kaplan et al. 1963; Ohmoto and Rye 1979), resulting in depleted $\delta^{34}S$-ratios of H_2S or metal sulfides relative to the source sulfate. However, this depletion is only indicative of a biogenic origin of H_2S and not of the elemental sulfur (see review by Machel 1992).

In an extensive review dealing with the isotope signatures in various TSR and BSR products, Machel et al. (1995) attribute the often observed "apparent zero ‰ fractionation between sour gas, elemental sulfur and metal sulfides" during TSR in diagenetic environments to the fact that no kinetic isotope fractionation is preserved, because the system is no longer open or reactions are completed or nearly completed. This can be the case if TSR reactions run out of dissolved sulfate, e.g., if sulfate dissolution is slower than TSR. Thus, in summary, these authors further state that sulfur isotopic data of inorganic sulfur compounds alone cannot be used to distinguish between BSR and TSR.

The sulfur isotope composition of H_2S formed by thermal maturation is related to the source kerogen/NSO compounds (variations of ca. 6‰ in the different sulfur compounds; Krouse et al. 1987) and thus has heavier $\delta^{34}S$-values than bacteriogenic H_2S. The thermally formed H_2S can have a very similar isotopic signature to H_2S formed by TSR if no fractionation takes place (Machel et al. 1995). According to Orr (1977) bacterial sulfate reduction and thermal maturation in most crude oils results in $\delta^{34}S$-values 15 ± 5‰ lower than those for the associated sulfate.

A further line of evidence for TSR is the incorporation of isotopically heavy sulfur during thermal alteration of solid bitumen and the production of H_2S. This was examined by Powell and Macqueen (1984; Fig. 2) in a carbonate-hosted ore deposit, Pine Point, Canada. The altered bitumens have a higher mean sulfur content of 22% (unaltered: 7.8%) and the $\delta^{34}S$-values are approximately $+12.4‰$ (unaltered: $+4.6‰$). High-temperature ($>130\,°C$) gas condensates (Jurassic Smackover formation, southwestern Alabama) enriched in heavy sulfur with $\delta^{34}S$-values as high as 24‰ and high sulfur contents (1–1.4%) are described by Claypool and Mancini (1989).

Solid bitumens formed by thermal polymerization/gas deasphalting can be differentiated from TSR-derived bitumens, because the former have $\delta^{34}S$-values related to the organic material that polymerizes (see Machel et al. 1995), i.e., either depleted or identical to the parent crude oil.

Sulfur-isotope distributions reflect the early diagenetic changes in the sulfur cycle which are important when interpreting later events. According to Goldstein and Aizenshtat (1994) multistep changes in the oxidation state of sulfur during TSR could influence the isotopic distribution, and thus, also the final $\delta^{34}S$-values. Furthermore, the authors suggest that it is the formation of polythionates that enables isotope exchange and not thiosulfate formation as suggested by Ohmoto and Lasaga (1982).

Carbon isotope ratios of gases and organic matter

Another line of evidence often used to evaluate TSR is the carbon isotopic composition of the organic compounds involved in the reaction. When considering actual geological settings, the effects of TSR on the carbon-isotope distribution, however, are very complex and poorly understood, since there a great variety of processes resulting in the release of CO_2 from organic compounds (see also discussion by Machel et al. 1995).

Krouse et al. (1988) consider the carbon isotopic composition of light hydrocarbon gases from the Upper Devonian of southwestern Alberta, Canada, as compelling evidence for TSR. They show that particularly the $\delta^{13}C$ (PDB) values for ethane and propane in deep sour gas are approximately 10‰ higher (= heavier) than in other shallower Devonian gases (Kiyosu et al. 1990). C_2H_6 and C_3H_8 become more enriched in ^{13}C during TSR, whereas CO_2 becomes more depleted, indicating that ^{12}C reacted preferentially. Thus, ^{13}C-depleted product CO_2 was added to the original CO_2 and unreacted hydrocarbon gases become more enriched in ^{13}C (Viau et al. 1989).

Claypool and Mancini (1989) also noticed a depth-related trend of increasing ^{13}C-content with increasing burial depth in carbon-isotope ratios of the C_{15+} hydrocarbons of the Jurassic Smackover formation. The methane formed by thermal cracking of the larger petroleum molecules is depleted in ^{13}C with $\delta^{13}C$-values of -45 to $-38‰$.

Additional examples for TSR by oxidation of organic compounds are given by Sassen (1988) for the Jurassic Smackover formation. The $\delta^{13}C$-values of extractable organic matter (EOM) indicate participation of TSR in the formation of late solid bitumen, pyrobitumen, and elemental sulfur during crude oil destruction (Fig. 5). The incorporation of reactive isotopically light alkanes into solid bitumen formed during TSR can result in -5 to $-7‰$ depleted $\delta^{13}C$-values (Sassen 1990).

The carbon-isotope signature of solid bitumens depends on maturity and parent crude oil as well as on the different formation processes (Curiale 1986). Nevertheless, Machel et al. (1995) note that solid bitumen formed by TSR seems to be the only type depleted in ^{13}C.

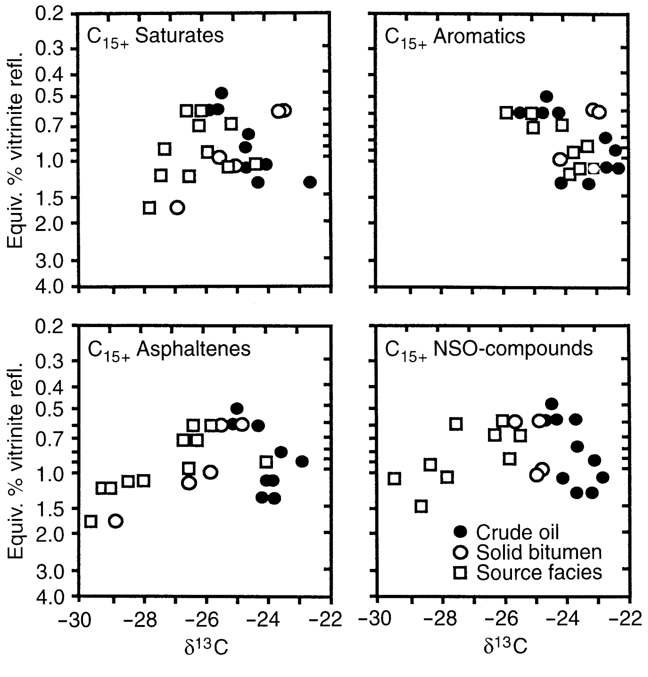

Fig. 5 Sassen's (1988) data for the Jurassic Smackover formation show that the carbon isotopic composition of all C_{15+} components, i.e., in saturates, aromatics, NSO, and asphaltenes in crude oil (*filled circles*), become progressively heavier during maturation, whereas the isotopic composition in late-forming extractable organic matter (EOM) of saturates, asphaltenes, and NSO components and bitumen show the reverse trend. In EOM and crude oils the $\delta^{13}C$-values of aromatics become heavier, however, suggesting preferential loss of isotopically light carbon. The lighter carbon-isotope signature found for EOM at the same maturation level as for the associated oils as well as the observed H_2S contents, elemental sulfur associated with pyrobitumen, and anhydrite prompted Sassen (1988) to suggest that isotopically light crude oil components (e.g., aromatic hydrocarbons) were incorporated into the late C_{15+}-EOM/bitumen by reactions involving TSR

Carbon- and oxygen-isotope ratios of calcite and dolomite

The carbon isotopic composition of carbonates can be used to recognize the occurrence of TSR, because TSR involves the replacement of anhydrite by calcite, e.g., the precipitation of calcite and very often the growth of saddle dolomite (Machel 1987; Heydari and Moore 1989). Machel et al. (1995) compiled the following organic carbon δ^{13}C-values from the literature: -50 to -70‰ (PDB) for biogenic methane; -20 to -30‰ (PDB) for crude oil; and -20 to -45‰ (PDB) for gas condensates. Most carbonate isotopic ratios, however, result from the mixing of the above-mentioned organic carbon with dissolved inorganic carbon. Anhydrite replacement by calcite during low-temperature bacterial sulfate reduction usually has a very light isotopic carbon composition ranging from -5 to -40‰ PDB (e.g., Davis and Kirkland 1970; Pierre and Rouch 1988).

Calcite in deeply buried Smackover samples containing isotopically light carbon (-1.7 to -12.4% PDB) indicates an origin from hydrocarbon oxidation due to TSR (Sassen et al. 1987). The carbon-isotope ratios for calcite shown by Krouse et al. (1988) imply that light hydrocarbon gases with δ^{13}C-values lower than -29‰ served as reducing agents in Devonian reservoirs (Canada).

Heydari and Moore (1989) also interpreted certain carbon-isotope trends in calcite cements of the Smackover formation as resulting from TSR. Calcite cement formed at temperatures less than 100 °C has δ^{13}C-values ranging from $+3.5$ to $+6.0$‰ (PDB), whereas δ^{13}C-values for replacing calcite range between -2.0 to $+4.2$‰ (PDB). Late diagenetic calcites, which precipitated after bitumen formation, range from -1.6 to -16.3‰ (PDB) indicating that the incorporated carbon was partly derived from thermal oxidation of hydrocarbon gases.

Carbon-isotope ratios in dolomites of the Devonian Nisku reef trend in Alberta, Canada, examined by Machel (1987) show that organically derived carbon, e.g., isotopically light carbon that was released during TSR was incorporated in saddle dolomites from near former oil/water contacts (δ^{13}C: -12‰ PDB).

Machel et al. (1995) give a very conclusive review over the possible oxygen-isotope ratios in carbonates precipitating from TSR reactions. The temperature increase due to TSR and the incorporation of oxygen liberated from the sulfate groups (due to TSR and BSR) are the main causes for depleted δ^{18}O-values relative to the host-rock carbonates. However, significant depletions can only be measured if sulfate reduction occurred in a closed system.

Petrographic evidence

Based on scanning electron microscopy and EDX analysis and observations on petrographic thin sections of samples of the deeply buried Smackover reservoirs, Sassen (1988) and Heydari and Moore (1989) showed the effects of the TSR reactions by documenting the formation of late solid bitumen and pyrobitumen (Thompson-Rizer 1987), a high-temperature replacement of solid sulfate by calcite, the reprecipitation of calcite (or dolomite) cement with Ca from dissolved calcium sulfate, as well as by finding anhydrite and elemental sulfur on stylolite surfaces. Sulfate reduction in carbonate reservoirs of the deep Smackover trend also resulted in formation of metal sulfides such as pyrite, galena, and sphalerite (Moore and Druckmann 1981), since transition or base metals were present.

If sufficient magnesium is available, dolomite can be formed, as is the case in partially dissolved dolomitized rocks. Precipitation of ankerite, siderite, witherite, and strontianite is possible if the respective metals are available.

Krouse et al. (1988) and Machel (1989) also document calcite replacing anhydrite nodules in Devonian reservoirs in Canada. Often the degree of replacement decreases away from the edge of the nodule (Worden and Smalley 1993; Worden et al. 1995), indicating that replacement (microdissolution–reprecipitation) took place in a fluid film progressing along cleavage planes, and resulting in poikilotopic anhydrite inclusions. Sulfur inclusions in replacing calcite can be found (Heydari and Moore 1989).

“Altered hydrocarbons,” a TSR by-product, can polymerize and precipitate as solid bitumen in pores. Cracks in bitumen or pyrobitumen can later be healed by calcite cement with typical light carbon-isotope signatures (Heydari and Moore 1989). These solid bitumens are usually sulfurized (see Fig. 2; Powell and Macqueen 1984). On the other hand, elemental sulfur may also be present, as observed by Sassen et al. (1987) and Sassen and Moore (1988). The significance of this elemental sulfur in solid bitumen is not known at the moment. Bitumens are not formed when methane is the main reactive hydrocarbon (Machel 1989; Machel et al. 1995).

Carbonates can be dissolved during the acid-generating reactions, e.g., by precipitation of metal sulfides (e.g., Anderson and Garven 1989), thus creating significant *secondary porosity*. Porosity increase is also possible by replacement of anhydrite by calcite (21-vol. % decrease during replacement). However, increased porosity can be occluded by calcite precipitation (Worden and Smalley 1993).

Viau et al. (1989) and Nicholson and Goldhaber (1991) used mass transfer geochemical modelling packages (SOLMNEQ and EQ3/6) to calculate porosity modifications by TSR. Their results show that the formation of metal sulfides increases the dissolution efficiency of H_2S by 5–8 times. Thus, small amounts of sulfide could increase porosity by 2–4%. Formation of elemental sulfur, however, promotes precipitation of dolomite which leads to a 0.5% porosity decrease.

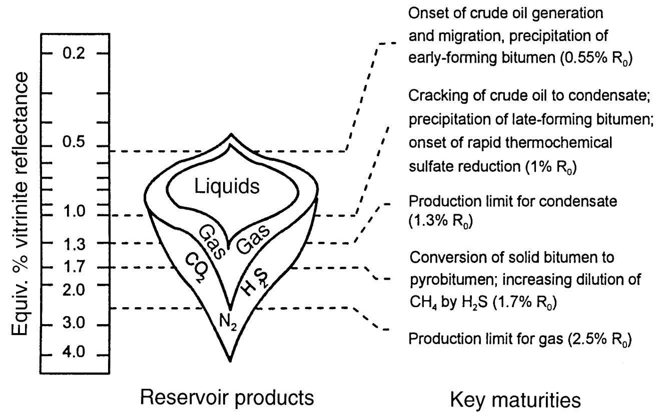

Fig. 6 Generalized relationship between thermal maturity, stages of hydrocarbon generation and destruction, and TSR in the Smackover Trend (compiled from Sassen 1988 and Sassen et al. 1987)

Accumulation of non-hydrocarbon gases

The origin of non-hydrocarbon gases as a result of TSR can be documented to result from the geothermal history of the Jurassic Smackover formation in the Gulf of Mexico basin (Fig. 6). At a thermal maturity equivalent to 0.55% R_0 vitrinite reflectance crude oil generation and migration was indicated in the Smackover formation (Sassen and Moore 1988). In the very deeply buried parts of the basin and at advanced maturity levels crude oil in Upper Smackover reservoirs was cracked, resulting in formation of gas condensates and solid bitumen residues (Sassen 1988). In the deepest and highest matured Smackover reservoirs ($>1.3\%$ R_0) hydrocarbon gases were gradually destroyed by thermochemical sulfate reduction leading to an enrichment of the non-hydrocarbon components in reservoirs below 6 km depth. The non-hydrocarbon reservoir gas in the Black Creek field (Smackover formation at a depth of ca. 6100 m) at a temperature of approximately 200 °C is composed of 77.8% H_2S, 20.2% CO_2, and 0.3% N_2 (Sassen 1990).

Thermochemical sulfate reduction is documented in the Smackover formation by a high-temperature replacement of solid sulfate by calcite (Heydari and Moore 1989). The CO_2 for the reaction was derived from decomposition of carbonate host rock or from kerogen decarboxylation (Siebert 1985). Thermochemical sulfate reduction also explains the destruction of methane in deep Smackover reservoirs (Sassen and Moore 1988).

Removal and solubility of H_2S

The local variation in H_2S abundance is not only determined by its generation, but also by the various mechanisms that can remove H_2S from gas reservoirs. The main removal mechanisms comprise the following (Orr 1977):

1. Formation of sulfide minerals, mainly pyrite. Iron removes all free H_2S by pyrite formation and therefore the accumulation of hydrogen sulfide without concomitant removal as FeS_2 minerals is only possible in iron-poor sedimentary rocks, such as in carbonates.
2. Removal by water. H_2S gas and CO_2 are much more soluble in water than hydrocarbon gases and N_2. Saturation solubilities for H_2S in water are a function of pressure and temperature (Sellieck et al. 1952). Orr (1977) states that most oil and gas reservoirs would be free of H_2S if an adequate water contact were given, because solubility under reservoir conditions is so high. In natural environments permeability controls flow pathways and oil–water and gas–water contacts. Water in contact with high H_2S pressures would become saturated, but the hydrodynamic flow would continuously remove the dissolved H_2S from the hydrocarbon fluids. During up-dip migration coupled with temperature and pressure decrease most of the dissolved sulfide is usually removed by formation of sulfides such as pyrite. Thus, an H_2S gas phase may never be released.

The H_2S concentrations in reservoirs very probably reflect "local steady-state conditions" which are dominated by the generation of H_2S by TSR reactions as well as by the export flux of H_2S. This equilibrium is controlled by porosity, tortuosity, thickness of carbonates, as well as the type of pore-filling phase, e.g., oil, gas, or water formation. Besides the formation of sulfides, which effectively removes H_2S from the system, Wade et al. (1989) postulate a removal mechanism strongly related to dispersion of H_2S resulting from advective mixing of formation fluids. They demonstrated for the Smackover formation (Gulf Coast) how porosity and thickness affect H_2S concentrations. A thin, porous interval leads to a low H_2S content at the top of the formation, whereas a thick, low-porosity interval is responsible for a high H_2S content in the reservoir. For a given H_2S-rich gas field (Chatom field) with a unidirectional fluid flow rate of 3×10^{-15} m/s the calculated flux of 1.5×10^{-11} mol m^{-2} s^{-1} results in H_2S removal of 6000 mol/year. According to the authors this value is 4–5 orders of magnitude higher than removal by molecular dispersion. Furthermore, the presence of microfractures within sections of low porosity enhances convective fluid flow.

Summary and conclusions

This review aims at providing an overview of the existing literature and the current understanding of TSR processes and their geological significance. This concerns especially the often-debated problem of assessing correct reaction kinetics and reaction products, as well as the autocatalytic nature of the reactions. Also, criteria for recognition of the effects of TSR are summarized. The latter are based on petrographic examinations as well as on stable-isotope geochemistry of inorganic as well as organic reactants. In this context Machel et al. (1995) compiled and discussed numerous criteria for distinguishing between reaction products of TSR and BSR.

Reaction rates and catalysts

In a very critical review Trudinger et al. (1985) do not exclude the possibility that abiological sulfate reduction below 200 °C may be geochemically significant in natural environments. The reaction rates measured in the laboratory usually cannot be directly compared to estimated reaction rates in nature. For example, in an aqueous media only some functional groups are oxidized by sulfur or polysulfides and methyl compounds are converted into organic acids (Pryor 1962). This means that in a natural environment only a small fraction of the organic compounds are available for TSR. However, if methane is the main source, it can be completely oxidized by sulfate at a temperature of at least 300 °C as demonstrated by Toland (1960). Thus, in natural environments the question of mass balancing the amount and type of reacting organic matter could be important. This would mainly comprise characterizing and assessing the amount of initial organic matter that is able to participate in TSR reactions as well as the altered organic matter resulting from TSR.

Besides a low pH, which markedly stimulates the reaction, another important factor which must be taken into account is high sulfate and H_2S concentrations. In Orr's (1982) experiments a reaction could only be observed at a sulfate concentration greater than eight times that of seawater.

There are a number of studies that give geological, theoretical, and circumstantial evidence for TSR occurring in natural environments at temperatures as low as 135–140 °C. Machel (1987; H.G. Machel, pers. commun.) states that the discrepancy between laboratory experiments and the findings in nature is mainly caused by the still relatively unknown role played by catalysts in natural environments. Trudinger et al. (1985) tested mixtures containing various types of organic carbon as well as a number of possible catalysts, e.g., clay, pyrite, transition metals, and prophyrins. However, none of these materials catalyzed TSR.

Older experimental data by Dhannoun and Fyfe (1972) demonstrate the catalyzing effect of montmorillonite with respect to the reduction of $CaSO_4$ with trimethylpentane. A maximum reduction rate of 0.006% in 85 h at 380 °C could be shown. Also Kartsev et al. (1959) assume that salts of organic acids can catalyze TSR in an unknown fashion.

Obviously, the exact nature and mechanisms of the catalysts which could influence TSR are currently not known.

Oxidation of organic compounds

In laboratory experiments it has been shown that various hydrocarbons react abiologically with aqueous sulfate at temperatures > 200 °C. A certain selectivity has also been demonstrated. Butane shows the highest reactivity (W.L. Orr, pers. commun.) and methane is the most stable during TSR (e.g., Machel et al. 1995). However, very little is currently known about potential reaction mechanisms if the organic phases participating in TSR are hydrocarbon-bearing structures attached to the kerogen. Leventhal (1990) documents kerogen alteration in a Mississippi Valley-type ore deposit, where the main alteration is a loss of hydrogen, absence of n-alkane structures, predominance of aromatic molecules, and a higher sulfur content. W.L. Orr (pres. commun.) also presumes an increase in O- and S-content of the altered organic material due to incorporation of carboxyl acid groups.

The role of bitumen formation during TSR has not been examined in great detail, and as emphasized by Curiale (1986), the origin of solid bitumens is complex. Black precipitates as reaction products of laboratory experiments have been reported by Kiyosu (1980) and Kiyosu and Krouse (1990). They identified this as amorphous carbon by X-ray powder diffraction. Data referring to formation of solid bitumen in natural environments are shown by Sassen (1988) for reservoirs of the Smackover formation and by Powell and Macqueen (1984) related to a carbonate-hosted ore deposit.

In order to fully understand local variations in H_2S concentrations, different key factors controlling these concentrations have to be identified. This implies establishing and delineating (a) the conditions for TSR reactions, e.g., temperature range, availability of sulfate, and reactive organic matter, (b) the lithology and thickness of the source and reservoir rocks, e.g., iron content, and (c) the presence and regional distribution of microfractures, porosity, permeability, faults, etc., which could make convective fluid flow more effective.

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