

Bacterial and thermochemical sulfate reduction in diagenetic settings — old and new insights

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Received 20 November 1998

Abstract

The association of dissolved sulfate and hydrocarbons is thermodynamically unstable in virtually all diagenetic environments. Hence, redox-reactions occur, whereby sulfate is reduced by hydrocarbons either bacterially (bacterial sulfate reduction = BSR) or inorganically (thermochemical sulphate reduction = TSR). Their geologically and economically significant products are similar.

Based on empirical evidence, BSR and TSR occur in two mutually exclusive thermal regimes, i.e. low-temperature and high-temperature diagenetic environments, respectively. BSR is common in diagenetic settings from 0 up to about 60–80°C. Above this temperature range, almost all sulfate-reducing microbes cease to metabolize. Those few types of hyperthermophilic microbes that can form H₂S at higher temperatures appear to be very rare and do not normally occur and/or metabolize in geologic settings that are otherwise conducive to BSR. TSR appears to be common in geologic settings with temperatures of about 100–140°C, but in some settings temperatures of 160–180°C appear to be necessary. TSR does not have a sharply defined, generally valid minimum temperature because the onset and rate of TSR are governed by several factors that vary from place to place, i.e. the composition of the available organic reactants, kinetic inhibitors and/or catalysts, anhydrite dissolution rates, wettability, as well as migration and diffusion rates of the major reactants toward one another.

BSR is geologically instantaneous in most geologic settings. Rates of TSR are much lower, but still geologically significant. TSR may form sour gas reservoirs and/or MVT deposits in several tens of thousands to a few million years in the temperature range of 100–140°C. BSR and TSR may be exothermic or endothermic, depending mainly on the presence or absence of specific organic reactants. However, if the reactions are exothermic, the amount of heat liberated is very small, and this heat usually dissipates quickly. Hence, heat anomalies found in association with TSR settings are normally not generated by TSR.

The main organic reactants for BSR are organic acids and other products of aerobic or fermentative biodegradation. The main organic reactants for TSR are branched and *n*-alkanes, followed by cyclic and mono-aromatic species, in the gasoline range. Sulfate is derived almost invariably from the dissolution of gypsum and/or anhydrite, which may be primary or secondary deposits at or near the redox-reaction site(s).

The products of BSR and TSR are similar, but their relative amounts vary widely and are determined by a number of locally variable factors, including availability of reactants, formation water chemistry, and wettability. The primary inorganic reaction products in both thermal regimes are H₂S(HS[−]) and HCO₃[−] (CO₂). The presence of alkali earth metals often results in the formation of carbonates, particularly calcite and dolomite. Other carbonates, i.e. ankerite, siderite, witherite, strontianite, may form if the respective metal cations are available.

Iron sulfides, galena, and sphalerite form as by-products of hydrogen sulfide generation, if the respective transition or base metals are present or transported to a BSR/TSR reaction site. Elemental sulfur may accumulate as a volumetrically significant

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net reaction product, usually when the system runs out of reactive hydrocarbons. Water may form as a by-product and might result in a local dilution of the formation waters at or near the reaction site. There are case studies of TSR, however, where no dilution of the formation water has occurred, indicating that the amount of water released during TSR was negligible. Porosity may be generated during TSR, but most case studies show that TSR does not usually result in a significant increase in porosity. TSR is likely to take place in fairly narrow reaction zones, where the irreducible water saturation in the hydrocarbon-containing pores is low. In one well known case, the Nisku Formation of Alberta, Canada, this zone is about 10–20 m thick. However, where the irreducible water saturation is high, TSR may take place throughout the entire hydrocarbon-containing pore volume. Solid bitumen may form as a by-product of both BSR and TSR.

The mere presence of any of the above reaction products and by-products does not permit a distinction between BSR and TSR. However, a number of petrographic relationships and geochemical criteria can be used to discriminate these two processes. Specifically, most solid products of BSR and TSR, although similar in gross composition, can be distinguished from one another petrographically, i.e. most BSR (TSR) products form early (late) in the paragenesis and/or have distinctive crystal sizes, shapes, and/or reflectivity. However, there also are cases where BSR products formed relatively late diagenetically, e.g. in uplifted reservoirs after hydrocarbon migration. Gas chromatography, $\delta^{13}\text{C}$ -, $\delta^{34}\text{S}$ -analyses, and/or a combination thereof, offer the best distinguishing geochemical criteria. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diagenetic environments; Bacterial sulfate reduction — BSR; thermochemical sulfate reduction — TSR

1. Introduction

The association of dissolved sulfate and hydrocarbons is thermodynamically unstable in diagenetic environments, which include all geologic settings with temperatures below 200°C and can be divided into near-surface, shallow-, intermediate-, and deep-burial diagenetic settings, hydrocarbon-contaminated plumes, and fractures (Machel, 1999; note: the realm of diagenesis, as used herein, encompasses the realms of diagenesis, catagenesis, and metagenesis of organic geochemistry: Hunt, 1996). Hence, redox-reactions occur, whereby sulfate is reduced by hydrocarbons with concomitant oxidation of the organic compounds, either bacterially (bacterial sulfate reduction = BSR) or inorganically (thermochemical sulphate reduction = TSR). BSR and TSR are here discussed together, because the two processes form similar products and by-products.

BSR has been known for more than 50 years as a common and widespread process in near-surface and shallow burial diagenetic environments (collectively called low-temperature environments/settings further below). Petrographic and geochemical data on BSR are widely scattered in the geologic literature and are derived from dozens of geologic settings that include lakes, marine sediments, salt domes, and shallow burial diagenetic environments with base metal sulfide deposits (Postgate, 1984; Ehrlich, 1990; Brock and Madigan, 1991, and references therein).

TSR has been recognized much more recently as a process of geologic significance (Orr, 1977; Machel, 1987a), and most literature on TSR has been published only during the last decade. A number of case studies and theoretical reviews have shown that TSR is common and widespread in deep burial diagenetic settings (also called high-temperature environments/settings further below). Almost all salient petrographic and geochemical data published on TSR are derived from studies of four locations: (1) the Devonian Nisku Formation in western Canada (Machel, 1986, 1987b; Anderson and Machel, 1988; Machel et al., 1995a; Manzano, 1995; Manzano et al., 1997); (2) Devonian and Mississippian sour gas fields in western Canada (Krouse et al., 1988; Hutcheon et al., 1995); (3) the Jurassic Smackover Formation of the United States (Orr, 1977; Sassen, 1988, 1990; Claypool and Mancini, 1989; Heydari and Moore, 1989; Rooney, 1996; Heydari, 1997); and (4) the Permian Khuff Formation of Abu Dhabi (Worden et al., 1995, 1996). In addition, the published case studies, as well as the experimental and theoretical data, have been summarized during the last decade in several noteworthy, critical reviews. General papers on the reaction mechanisms, natural products, and geochemical characteristics of BSR and TSR are Machel (1987a, 1989, 1992, 1995), Morse et al. (1987), Machel et al. (1995b) and Nöth (1996). Other reviews dealt with more specific aspects of BSR and TSR, such as the organic reactions

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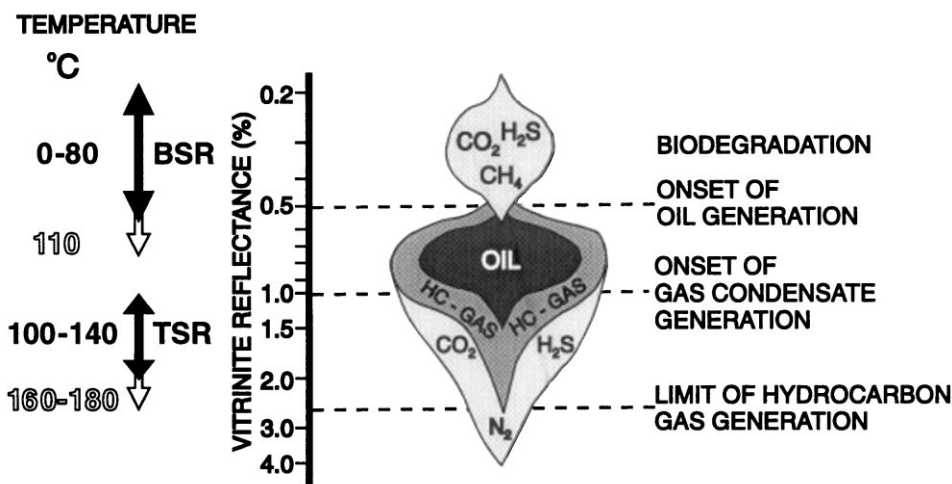


Fig. 1. Generalized relationships between oil and gas generation, temperature, thermal maturity, and bacterial and thermochemical sulfate reduction (assuming normal geothermal gradients of 25–30°C/km) (diagram is updated from Machel et al., 1995b). H_2S in almost all geologic environments is generated by bacterial or thermochemical sulfate reduction in two mutually exclusive thermal regimes that are empirically defined, i.e. BSR: 0–80°C, TSR: 100–140°C (solid arrows). Hollow arrows denote extreme and geologically unusual conditions for BSR and TSR, respectively. Some hyperthermophilic bacteria may perform BSR at temperatures up to 110°C, but these microbes appear to be very rare and geologically insignificant; in some settings that are otherwise conducive to TSR, temperatures of 160–180°C are necessary for TSR to occur (see text for discussion of these two aspects). The upper part of the BSR range overlaps with the lower part of the liquid oil window. Some hydrocarbon gas (mainly $n\text{C}_2$ – $n\text{C}_4$) can be formed abiologically (via ‘thermal’ cracking) at relatively low temperatures that correspond to the liquid oil window or even less (Hunt, 1996; Schaefer et al., 1999). Nitrogen gas is formed mainly from kerogen III at relatively high temperatures that correspond to dry-gas maturity (Littke et al., 1995).

(Goldstein and Aizenshtat 1994), kinetics (Goldhaber and Orr 1995), and the temperature regime of TSR (Worden et al., 1995).

The objective of this paper is to provide a critical synopsis of the presently available data on BSR and TSR, in an attempt to document the state-of-the art of our understanding of these processes. Almost all of the available experimental and theoretical work has been summarized in the review papers cited above and is not repeated here, except for passing references, where appropriate. Emphasis is placed on case studies of geological occurrences, and on those aspects that are insufficiently documented or still controversial, such as the petrographic features that allow discrimination between BSR and TSR, lower and upper temperature limits of TSR in common geologic settings, kinetics of TSR, as well as the amounts of heat and water released during TSR. Taking 1996 as a benchmark, when the last important reviews were published (see above), this paper also contains some

new insights concerning the following aspects: (a) upper temperature limit, metabolic requirements/pathways of, and microbial consortia involved in, BSR; (b) minimum temperature, temperature range, and kinetics of TSR; (c) heat released during TSR; (d) water released during TSR; (e) organic reactants and products of TSR (including solid bitumen); and (f) porosity gain or loss. These considerations are of potential significance to hydrocarbon exploration and/or genetic interpretations of H_2S and base metal sulfide accumulations.

2. Thermal regimes, kinetics, and heat released

Based on empirical evidence, BSR and TSR occur in two mutually exclusive thermal regimes, i.e. low-temperature and high-temperature diagenetic environments, respectively (Orr, 1977; Machel, 1987a). Low-temperature diagenetic environments are here

defined as geologic settings with $0 < T < 60\text{--}80^\circ\text{C}$, which corresponds to vitrinite reflectance values of about 0.2–0.3 (Fig. 1) and depths of less than 2000–2500 m at near normal geothermal gradients. High-temperature diagenetic environments are defined here as geologic settings with $100^\circ\text{C} < T < 150\text{--}200^\circ\text{C}$, which correspond to vitrinite reflectance values of about 1.0–4.0 and fluid pressures that commonly prevail at correlative depths of about 2000–6000 m (Fig. 1). In the present context, it is preferable to consider BSR and TSR relative to absolute temperature rather than relative to thermal maturation. This is because temperature is the single most important factor governing the involved redox-reactions.

2.1. Temperature range for BSR

BSR is known from a multitude of geologic settings that range in temperature from 0 to about 80°C (Postgate, 1984; Ehrlich, 1990). In geologic settings with temperatures above $60\text{--}80^\circ\text{C}$, almost all sulfate-reducing bacteria cease to metabolize, as shown by the almost ubiquitous absence in such settings of their most distinctive metabolic product (H_2S), and by isotopic evidence (Machel and Foght, 2000, and references therein). Some hyperthermophilic sulfate-reducing bacteria can live at temperatures as high as about 110°C (Jørgensen et al., 1992; Stetter et al., 1993; Elsgaard et al., 1994), perhaps even at somewhat higher temperatures. [Currently, 113°C is the highest temperature a microbe, albeit not a sulfate reducing bacterium, is known to be vegetative at (alive, metabolizing, and reproducing); the temperature of 113°C , therefore, currently represents the upper temperature limit of life: Kerr, 1997; Fisk et al., 1998; Stetter, 1999]. Hyperthermophilic sulfate reducers have rarely been found, however, and they appear to be virtually absent, or at least inactive, in common geologic environments that are otherwise conducive to microbial sulfate reduction, such as oil reservoirs with a supply of sulfate. Otherwise, there would not be any sweet (H_2S -devoid) oil reservoirs associated with sulfate at temperatures below about 110°C (Machel and Foght, 2000). Such reservoirs, however, are very common.

A case in point are the Upper Devonian Nisku oil and gas reservoirs in south-central Alberta, Canada (Anderson and Machel, 1988; Machel et al., 1995a). On a structural homocline over a distance of about

200 km, several tens of relatively small reefs, encased in shales and effectively isolated from one another hydrologically, contain up to 20% anhydrite. Updip from a line representing a maximum burial temperature of about $125\text{--}145^\circ\text{C}$, many of these reefs contain paraffinic crude oil that is not biodegraded — yet biodegradable, once inoculated with microbes (experimentally shown: Foght and Machel, unpublished data). In the shallower parts of this reef trend, temperatures are low enough for BSR today, as they have been for at least the last 20 million years, yet all the pooled oils are sweet (Anderson and Machel, 1988; Machel et al., 1995a). Only the gas condensates in the deeper reservoirs are sour, which is the result of TSR (discussed below).

2.2. Temperature range for TSR

Although the lower thermal limit for TSR is somewhat controversial, the available data indicate that as a generalization, there is a *range* of TSR minimum temperatures of about $100\text{--}140^\circ\text{C}$ (Machel, 1998a). Hence, in most geologic settings, TSR takes place as soon as the temperature reaches this range, provided the necessary ‘ingredients’ (sulfate, reactive organics, some sulfur in a reduced form — further discussed below) are present. In some cases, however, higher temperatures of about $160\text{--}180^\circ\text{C}$ are necessary (Fig. 1).

A minimum temperature range for TSR of $100\text{--}140^\circ\text{C}$ has been determined from extrapolation of experimental data (summarized in Goldhaber and Orr, 1995) and from fluid inclusion data from various sour gas fields (Machel, 1987b; Heydari and Moore, 1989; Worden et al., 1995; Simpson et al., 1996). TSR is thermodynamically possible at temperatures as low as 25°C (Dhannoun and Fyfe, 1972; Worden and Smalley, 1996), but reaction rates at temperatures below about $100\text{--}140^\circ\text{C}$ appear to be so low as to be geologically insignificant (further discussed below).

The data of Claypool and Mancini (1989) and Rooney (1996) from the Smackover Formation can be used to define $160\text{--}180^\circ\text{C}$ as the upper temperature range of TSR in common geologic environments, i.e. the upper temperature range that: (i) TSR is known to occur at; and/or (ii) is necessary for TSR in at least some geologic settings. Their data also provide

particularly instructive clues regarding the minimum temperature of TSR. Rooney (1996) reported one questionable case of a Smackover reservoir that may or may not have undergone TSR at 99°C (the gas-chromatographic and isotopic data are ambiguous in this case). However, she provided clear and unambiguous evidence for TSR in Smackover reservoirs at temperatures of 127–180°C. Importantly, some Smackover reservoirs in the upper part of this temperature range did *not* undergo TSR. Claypool and Mancini (1989) found a similar ‘cross-over’, with some TSR-altered gases at lower temperatures than TSR-unaltered gases. In some reservoirs TSR took place at $T > 130^{\circ}\text{C}$, whereas other reservoirs had not undergone TSR at 160°C.

On the other hand, data of the pools in the Devonian Nisku Formation in western Canada define a sharp ‘sour gas line’ or ‘TSR-line’, marking a depth below which all the hydrologically isolated reef pools (encased in shales) underwent TSR, above which none did (an adjacent, elongate reef straddles the TSR-line and was not used to define this line). The maximum burial temperature represented by the TSR line is 125–145°C, based on fluid inclusion data of TSR saddle dolomites, thermal maturation data, and organic geochemical data of the pooled gases (Machel et al., 1995a; Manzano et al., 1997). Similarly, Worden et al. (1995) determined a sharply defined minimum temperature for TSR of 140°C in the Khuff Formation of Abu Dhabi. In both cases the data suggest a well-defined TSR minimum temperature without ‘cross-overs’.

Hence, as a generalization, there is a range of minimum temperatures, and the minimum temperature for TSR may be variable from pool to pool, even within a single sour gas play (as in the Smackover). In some locations there is a specific minimum temperature for TSR, represented by a certain minimum depth (as in the Khuff and the Nisku). The lowest confirmed temperature for TSR to date is 127°C, with questionable evidence pointing to a temperature as low as perhaps 100°C.

There are a number of reasons why TSR should have a range of possible minimum temperatures. The governing factors include the composition of the gases, catalysts, anhydrite availability and dissolution rate, wettability, and migration/diffusion rates of the major reactants toward one another, all of which

may vary from region to region and even from pool to pool. For example, the very fact that TSR involves different types of hydrocarbons with different bonding strengths and activation energies necessitates that there is not just one TSR minimum temperature, but that this temperature is a function of the availability of reactive hydrocarbons (further discussed below). Wettability is another commonly overlooked yet important factor in this context. Just as solid sulfate cannot react at typical TSR reservoir temperatures (Kiyosu et al., 1990), TSR cannot occur in oil-wet (gas-wet) reservoirs because sulfate cannot dissolve. Hence, variations in wettability alone could account for at least some of the observed temperature ‘cross-overs’, such as those in the Smackover trend. Similarly, variations in wettability (and/or in the other factors listed above) can account for variations in TSR phenomena on the smaller scale of individual TSR reaction sites, such as the small-scale variations and trends in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and fluid inclusion data of TSR calcites and TSR dolomites found within individual sour gas pools of various locations (Machel, 1987b; Machel et al., 1995a; Simpson et al., 1996; Worden et al., 1995, 1996). ‘Cross-overs’ on the scale of pools are likely the result of variations of these factors from pool to pool (or, in some cases, of re-migration). Conversely, a well-defined, specific minimum temperature for TSR can be expected only where the reservoir conditions are fairly homogeneous on the scale of a field or a play.

2.3. Kinetics of BSR and TSR

2.3.1. BSR

The onset of BSR is nearly instantaneous and rates are extremely high in most geologic settings, compared to most inorganic geologic processes. This is amply demonstrated by the production of hydrogen sulfide in most sulfate and organic-rich sediments below the depth of oxygen penetration, often only a few mm to m below the depositional surface. In some geologic settings, however, the rate of BSR is limited by the relative paucity and/or slow supply of one of the chief reactants — reactive organic matter or sulfate. In such cases, the overall rate of BSR may be relatively low, i.e. as low as that of the rate-limiting step — commonly the diffusion of sulfate (Berner, 1980).

2.3.2. TSR

The rate of TSR in geologic settings perhaps is one of the least well understood aspects of the overall process. TSR has been performed in the laboratory only at temperatures in excess of 175°C, and geologically significant reaction rates were experimentally measured only above about 250°C (see summaries in Trudinger, 1985; Goldhaber and Orr, 1995). On the other hand, several case studies from Canada, the US, the Middle East, and Russia have shown convincingly that TSR can take place in diagenetic settings with temperatures between about 100 and 140°C (Machel, 1987a, 1998a, and references therein). These findings are consistent with the findings of Orr (1982, 1990) — his experimental data are presented in Goldhaber and Orr, 1995) who experimentally determined the half life of dissolved sulfate to be in the range of 1800 h at 175°C and about 90 h at 250°C at an initial load pressure of 200 psi H₂S, which he converted to a half life of dissolved sulfate of about 700–7000 years in carbonate reservoirs at 100°C. Goldhaber and Orr (1995) recalculated the available kinetic data from their and previous experiments to TSR rates in ‘low H₂S’ and ‘high H₂S’ settings. The latter, with high initial concentrations of H₂S and/or total initial sulfur in solution, yielded rates of about 10^{−9} mol/l/year at 100°C, increasing to 10^{−8} mol/l/year at 120°C and 10^{−6} mol/l/year at 150°C. These rates probably are close to the maximum rates of TSR in geologic settings, considering that ‘high H₂S’ settings, such as carbonate reservoirs with associated anhydrite, are optimum sites for TSR compared to clastic settings or settings of MVT mineralization (Goldhaber and Orr, 1995).

By extension, TSR is very slow or inhibited at temperatures below the inferred minimum temperature of about 100°C, even though the involved reactions are characterized by large negative free energy changes of reaction. High activation energies and/or (hitherto unknown) kinetic inhibitors may be the cause for the sluggishness or absence of TSR below about 100°C. Most experimental studies determined or estimated relatively high activation energies of 33.6–50.0 kcal/mol [140–208 kJ/mol] (Dhannoun and Fyfe, 1972; Kiyosu, 1980; Kiyosu and Krouse, 1990). The large range is probably caused by the use of different hydrocarbon–sulfate mixtures, and one obvious reason for the generally fairly high acti-

vation energies is that the S–O bonds are very strong and hard to break. Two studies, both ‘high H₂S’ sensu Goldhaber and Orr (1995), came up with much lower activation energies, i.e. about 23 kcal/mol [96 kJ/mol] (Orr, 1982, 1990; Goldhaber and Orr, 1995), and about 29 kcal/mol [121 kJ/mol] (data from Kiyosu and Krouse, 1993, recalculated by Goldhaber and Orr, 1995). These relatively low values correlate with the relatively fast TSR rates in ‘high H₂S’ settings (see above).

These considerations imply that: (i) the formation of typical sour gas reservoirs and MVT deposits is feasible via TSR in the temperature range of 100–140°C (Fig. 1); and (ii) various kinetic factors determine at which particular temperature and how fast TSR takes place in a given geologic setting. Typical sour gas reservoirs and MVT deposits may form in a few tens of thousands to hundreds of thousands (x0,000–x00,000) years under the most favorable circumstances, at most in a few million (x,000,000) years (Goldhaber and Orr, 1995). Hence, under favorable circumstances TSR appears to be a geologically relatively fast process, although it is much slower than BSR.

There is no shortage of *potential* kinetic factors that enhance or reduce the rate of TSR in natural environments, and several have been identified experimentally (summarized by Machel, 1987a; Goldhaber and Orr, 1995, and references therein): initial total sulfur concentration in solution (including H₂S pressure); temperature; pH; salts (soaps) of organic acids; organic acids; metal complexes; catalytic action of Ni²⁺ > Co²⁺ > Mn²⁺ > Cu²⁺ > Fe²⁺ > Ca²⁺ = Mg²⁺, and of organic compounds such as phenols, aldehydes, aniline, urea, and vanillin; clay minerals, particularly montmorillonite; and silica gel. The effects of many of these factors are not well understood, but it is clear that increases in temperature and total initial sulfur concentration in solution greatly enhance the overall reaction rate of TSR (Goldhaber and Orr, 1995).

One factor that has been ignored in almost all studies of TSR is wettability. However, the wettability of a reservoir may have a profound influence on the onset temperature and on the rate of TSR, and perhaps also on the subsequent distribution of the reaction products (Machel, 1997). The influence of wettability on TSR is most easily recognized by considering that

HEAT DISTRIBUTION AND DURATION

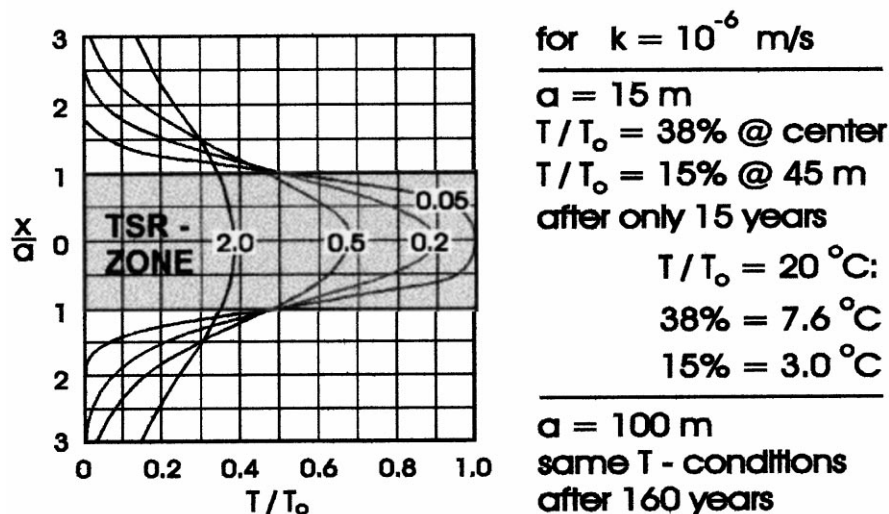


Fig. 2. Temperature distribution across a TSR zone of thickness $2a$ at various times after TSR has ceased. Times are given as curves that designate the dimensionless term kt/a^2 , and temperatures are expressed as fractions of the initial temperature T_0 of the TSR 'hot spot'. x = distance from the center, k = thermal diffusivity. For these calculations, k has been assumed to be $10^{-6} \text{ m}^2/\text{s}$, which is a reasonable mean value for sedimentary rocks. Diagram is modified from Philpotts (1990).

only dissolved sulfate is reactive at diagenetic temperatures, as shown by a number of experimental studies (summarized in Machel, 1987a; Goldhaber and Orr, 1995). It must be concluded that TSR of solid sulfates is not possible in diagenetic environments. Hence, TSR is inhibited in oil-wet systems because solid sulfate is prohibited from dissolving. On the other hand, it is not clear what role wettability plays in reservoirs in which the hydrocarbon fluids are at wet-gas maturity, which appears to be the minimum temperature/maturity range necessary for TSR to occur. It is possible that wettability is not important when there no longer is a liquid hydrocarbon phase coating the mineral surfaces in the reservoir (Machel, 1997). These aspects need further study.

2.4. Heat released

Early studies asserted that BSR and/or TSR are exothermic processes and estimated the heat released as about 30–40 kcal/mol hydrocarbon (Bush, 1970), or 10 kcal/mol calcium sulfate (Dhannoun and Fyfe, 1972). These studies suggested or suspected that 'hot spots' could be generated via reactions between

sulfate and hydrocarbons. Indeed, some sour gas reservoirs are warmer than the surrounding rock units by up to about 10°C (Dunsmore, 1971). In the present author's experience, sour gas reservoirs are rarely, if ever, significantly (more than 10°C) warmer than the surrounding rock units. Moreover, it is now known that the net reaction of TSR can be exothermic or endothermic, depending mainly on the type(s) of organic reactant(s) and/or net reaction stoichiometry (Simpson et al., 1996). The question arises whether observed heat anomalies in association with sour gas reservoirs are the result of TSR or coincidental occurrences.

This question can be approached from the vantage points of reaction kinetics and of heat conduction and convection. As indicated in the previous section, TSR appears to be a relatively fast process. Hence, if a sour gas setting is warmer than the surrounding rock units, TSR may be actively occurring, or the heat liberated earlier during TSR has not yet dissipated. The latter possibility can be quantified with standard methodology from igneous petrology. Temperature anomalies caused by much stronger heat sources, such as igneous intrusions, usually dissipate in geologically short

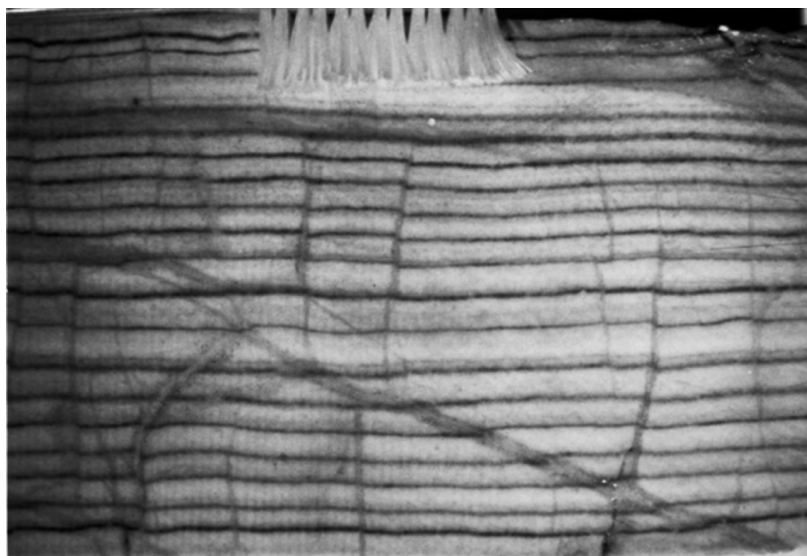


Fig. 3. Hand specimen of primary (sedimentary), laminated/banded anhydrite, Permian Castille Formation, New Mexico. The anhydrite has been partially replaced by calcite through BSR, which is not visible in hand specimen. Tooth brush for scale.

periods of time. The time for heat to dissipate by conduction alone can be calculated using an equation (Philpotts, 1990) that is plotted as Fig. 2. Assuming, e.g. that an intrusion, or a zone that generated heat via TSR, has a thickness of 30 m [which is reasonable for most sour gas pools], the time contour 2.0 (Fig. 2) implies that this 30 m thick zone would cool at its center ($x/a = 0$) to 38% of the initial temperature difference (T/T_0) after only 15 years, whereas 45 m above and below the center of the zone ($x/a = 3$) the temperature would amount to merely 15% of the initial temperature difference after 15 years. In other words, if TSR generated a temperature difference of 20°C [taken here as a possible maximum estimate], this temperature difference would amount to 7.6°C (38%) at the center, and to 3°C (15%) 45 m above and below the center, in 15 years. As a second example, one may consider a TSR zone that is 100 m thick, which could be considered a possible maximum thickness for a TSR zone. In this case, the cooling time to 35 and 15%, respectively, would be about 160 years.

These calculations assume that no more heat is generated after an intrusion or after TSR has ceased. A heat anomaly of perhaps 5–10°C could originate from TSR, if the reactions are exothermic and as long as TSR takes place, but the little heat that

could be generated quickly dissipates. Alternatively, a measured temperature anomaly could be unrelated to TSR but caused by hydrodynamics (hot formation waters flowing upwards relatively rapidly), or by increased heat flow from the basement.

3. Reactants and products of BSR and TSR

The most important redox-reactions involved in BSR and TSR can be represented by a set of simplified mass and charge balance reactions that contain all known and volumetrically significant reactants and products (Machel, 1987a, 1992; Machel et al., 1995b). The most important of these reactions are explained below. All reactions representing inorganic processes are reversible but written only in that direction to which they proceed under the specified conditions. Each microbial reaction proceeds only in the specified direction and involves numerous enzyme-catalyzed steps that are omitted for simplicity. Phenomena at very low and very high pH ($\text{pH} < 4$, $\text{pH} > 9$) are not discussed or are mentioned only in passing, because they are extremely rare and/or very localized in the diagenetic environments of interest here.



Fig. 4. Core specimen of secondary (diagenetic), milky-white anhydrite nodules that formed syndepositionally/early diagenetically, displacively in a semi-lithified mud. Note sub-horizontal compactional elongation of the nodules. Devonian Blue Ridge Member, Alberta, Canada. Scale in cm at stratigraphic top.

3.1. Reactive sulfates

The reactive sulfate for both BSR and TSR is *dissolved* sulfate (SO_4^{2-}) that is derived from seawater, buried seawater, evaporative brines (pore water), and/or from dissolution of solid calcium sulfate (mainly gypsum: $\text{CaSO}_4[2\text{H}_2\text{O}]$, and anhydrite: CaSO_4). Such sulfate rocks can be of various types, e.g. primary-

laminated, early or late diagenetic nodular, corrotopic, or pile-of brick (Figs. 3–8). Some authors have claimed that *solid* anhydrite was reduced during TSR (Heydari and Moore, 1989). However, solid sulfates do not appear to be reactive. Experiments have shown that non-aqueous mixtures of hydrocarbons and solid sulfates remain unreactive even at temperatures as high as 180–315°C (Toland, 1960),

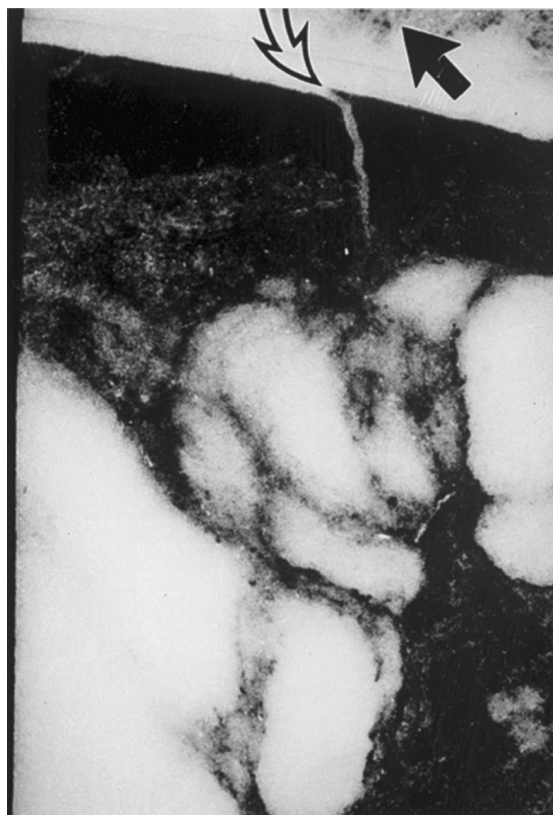


Fig. 5. Core specimen of diagenetic, milky-white anhydrite that formed late diagenetically as cement in sub-horizontal fracture at top, and replacively as nodular masses. Note feeder channel from fracture to nodular mass (hollow arrow), which contains solid bitumen (black arrow) from gas deasphalting or TSR. Devonian Leduc Formation, Alberta, Canada. Width of photograph is about 8 cm.

and gaseous hydrocarbons react only extremely slowly with solid calcium sulfate even at temperatures of several hundred degree centigrade (Kiyosu et al., 1990). Other sources of sulfur, such as volcanic activity, organic compounds, or other sulfate minerals, are negligible in most diagenetic/geologic settings (Orr, 1977).

3.2. Reactive organic compounds

Sources of organic compounds are organic matter such as biopolymers and/or geopolymers in kerogen, crude oil, microbial methane, and thermogenic gas and/or gas condensate. The types of organic compounds that are most reactive in low- and high-



Fig. 6. Thin section photomicrograph, transmitted light — one polarizer, of corrotopic anhydrite, which indicates anhydrite formation from gypsum during burial (Machel, 1986). This is the typical microtexture found in secondary anhydrite masses such as those shown in Figs. 5 and 7. Width of photograph is about 400 μm .

temperature diagenetic settings, respectively, are discussed further below.

3.3. Aerobic biodegradation

Aerobic biodegradation of non-gaseous carbohydrates and hydrocarbons, i.e. biopolymers, geopolymers (kerogen), or crude oil, results in several distinctive changes, including decreases of the abundance of C_2 – C_6 (sometimes C_1) *n*-alkanes, subordnately of aromatics; decreases in the API gravity, gas/oil ratio, and the pour point; as well as increases in the asphaltene and NSO-compounds, sulfur, nitrogen, vanadium, and nickel contents, viscosity, and the $\delta^{13}\text{C}$ values (Volkman et al., 1983). Aerobic biodegradation appears to be a common, albeit not

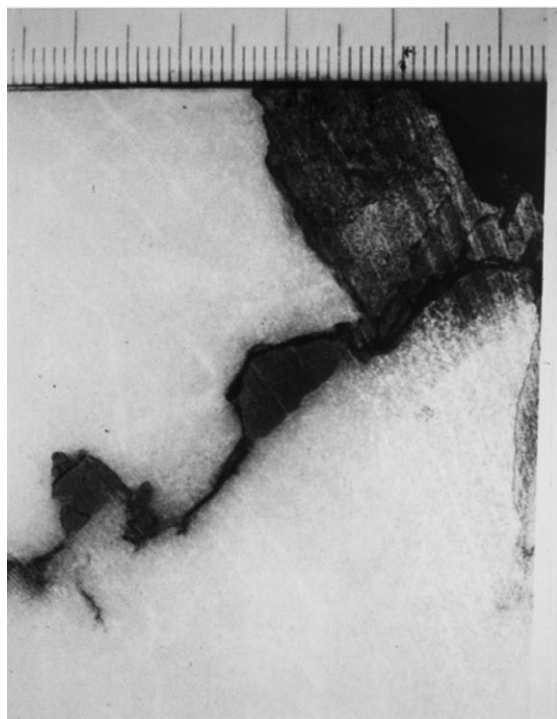


Fig. 7. Core specimen of milky-white anhydrite that formed late diagenetically in sub-horizontal fracture and/or replacively in grey dolostone. Photo is underexposed in order to emphasize the enclosed stylolite with dolomite and clay mineral residues, which indicate that the anhydrite formed after pressure solution and at considerable burial. Devonian Nisku Formation, Alberta, Canada. Scale at stratigraphic top in centimeter with millimeter divisions.

absolute, 'prerequisite' for BSR. This is because almost all known sulfate-reducing bacteria (certainly those of the type *Desulfovibrio*-x) cannot or do not metabolize *n*-alkanes but depend on the metabolic residues of aerobic biodegraders as nutrients, such as organic acids, alcohols, and other compounds (Bailey et al., 1973; Jobson et al., 1979). These types of compounds are generated mainly from the degradation of *n*-alkanes, subordinately aromatics, which are preferred as substrates by aerobic microbes, especially during the early stages of aerobic biodegradation (Volkman et al., 1983). Hence, even a mild to moderate degree of aerobic biodegradation can facilitate extensive bacterial sulfate reduction. Conversely, BSR is absent in many anaerobic geologic environments that contain sulfate and crude oil, which has been interpreted as evidence that here are no microbes

that provide an organic substrate suitable for the sulfate reducers (Bailey et al., 1973; Jobson et al., 1979).

The common prerequisite relationship of aerobic biodegradation to bacterial sulfate reduction does not preclude sulfate reduction in entirely anaerobic geologic settings. Anaerobic fermentative bacteria are known to provide organic substrates suitable for sulfate reducing bacteria. Considering, however, that the organic compounds used by fermentative microbes often are partially oxidized products of aerobic bacterial metabolism (Bernard et al., 1992), aerobic biodegradation remains a common prerequisite for BSR even where fermentative bacteria are present, albeit in an indirect — and spatially possibly remote — way.

There are some geologic settings in which BSR appears to be possible without any direct or remote prerequisite breakdown of complex organic compounds. Firstly, in some geologic settings sulfate-reducing bacteria can live symbiotically with and/or in the vicinity of methanogenic bacteria and utilize methane as a carbon source, as shown by circumstantial and isotopic evidence (Kirkland and Evans, 1976; microbiological evidence for methane utilization by sulfate reducers is inconclusive: Iverson and Jørgensen, 1985). Furthermore, some strains of sulfate-reducing bacteria can metabolize various *n*-alkanes directly (Aeckersberg et al., 1991; Rueter et al., 1994). However, these types of bacteria appear to be extremely rare and/or absent in common diagenetic settings, or they may be present only in a 'dormant' state, e.g. (a) as endospores or (b) their metabolic activity may be inhibited by limited availability of water or nutrients. The evidence for this assertion is the same as that for the absence of hyperthermophilic sulfate reducers in common diagenetic settings. If *n*-alkane oxidizing sulfate reducers were active in common geologic settings, essentially all oil reservoirs that are in contact with sulfate-rich formation waters would be sour. This obviously is not the case. The Nisku reservoirs in Alberta, Canada, have been given as an example above.

3.4. Thermal maturation

Thermal maturation of crude oil and its source kerogen probably is the first important 'reaction' [consisting of several subreactions] involved in TSR.

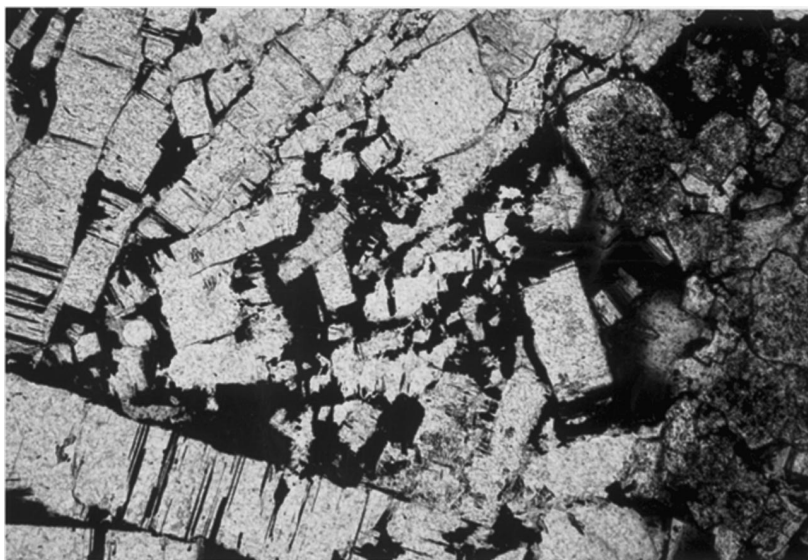
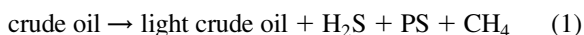


Fig. 8. Thin section photomicrograph, transmitted light — one polarizer, of pile-of-brick anhydrite, which typically forms as a cement at deep burial directly from solution (without a gypsum precursor). Black solid bitumen from gas deasphalting or TSR fills many cleavage planes, cracks, and interstices. Devonian Nisku Formation, Alberta, Canada. Width of photograph is about 2 cm.

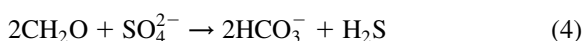
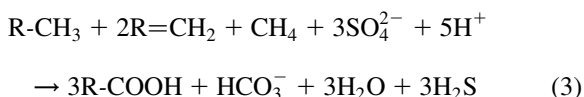
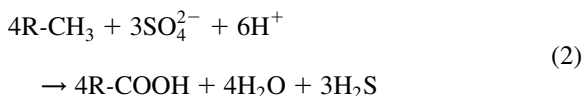
Thermal maturation generates small amounts (generally less than 3%: Orr, 1977) of H_2S , along with HS^- , polysulfides (PS), gas, and gas condensate, as represented by the following schematic reaction (1):



H_2S and polysulfides that are formed during thermal maturation appear to be involved in, and be necessary for, the subsequent reduction of sulfate (Toland, 1960; Orr, 1977, 1990).

3.5. S–O bond rupture

The S–O bond rupture and reduction of S^{6+} to lower valence states is represented by several alternative reactions (2)–(4), depending on the types of reactive organic compounds and pH:



In these reactions, the sulfur is reduced from S^{6+} to S^{2-} , although the initial S–O bond rupture commonly leads to the formation of sulfur with intermediate valence states in the form of S^0 /polysulfides, thiosulfate, and sulfite (Toland 1960; Davis and Kirkland, 1970; Orr, 1974, 1977, 1982, 1990; Chen and Morris, 1972; Krouse, 1977; Morse et al., 1987). These intermediates have been omitted from the reactions above for simplicity because they appear to be unstable and usually are further reduced to sulfide very rapidly (Feely and Kulp, 1957).

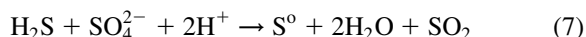
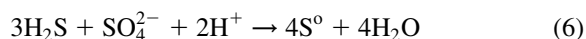
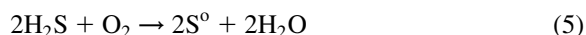
As shown by the alternatives represented by reactions (2)–(4), the reactive organic compounds may be [R-] alkanes including methane, which is valid for both BSR and TSR systems, or alkenes and carbohydrates, which is valid mostly for BSR systems (these compounds are usually absent at advanced levels of thermal maturation). In TSR systems, branched and *n*-alkanes in the gasoline range appear to be the most reactive, followed by cyclic and monoaromatic species in the gasoline range, as shown by isotopic and/or gas-chromatographic data (Krouse et al., 1988; Manzano, 1995; Rooney, 1996; Manzano et al., 1997). Methane is the most stable of all possible reactive organic compounds (Orr, 1990) and would be the last one to go, not the first or the only one, as has

been asserted in some studies (Heydari and Moore, 1989; Worden et al., 1996). There are no case studies where methane has been conclusively demonstrated to be the only or even the major organic reactant (Machel, 1998b).

Important direct, stable reaction products are organic acids, bicarbonate ions and hydrogen sulfide (and/or, depending on pH, their associated and dissociated species: CO_3^{2-} and CO_2 , HS^- , etc.). A possible stable reaction by-product is solid bitumen from polymerization.

3.6. Partial reoxidation to elemental sulfur

Elemental sulfur commonly is formed as an ‘intermediate’ product from partial reoxidation of H_2S , as shown by the following alternatives (reactions (5)–(7)), which are not the only possibilities (see Machel, 1992):

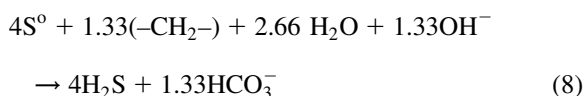


In low-temperature aerobic environments, molecular oxygen (as air or dissolved in groundwater) is a common oxidant (reaction (5)). If the fugacity of oxygen is high enough, S^0 may be further oxidized to SO_4^{2-} to then form sulfuric acid. In high-temperature diagenetic settings, which almost invariably are anaerobic/anoxic, the only common oxidant is excess sulfate. Other reactions between sulfate and hydrogen sulfide yield polysulfides, sulphite, and thiosulfate. Also, H_2S may react abiologically at temperatures above about 100°C with saturated hydrocarbons to produce elemental sulfur and NSO — compounds, if catalysts such as certain clays are present (Orr, 1977; Machel, 1987a, and references therein).

3.7. Reduction of elemental sulfur

Much, if not all, of the elemental sulfur may not survive. As settings of sulfate reduction typically are reducing and/or anoxic, elemental sulfur usually is reduced to sulfide by excess organics. Oxidation of sulfur to sulfuric acid (see above) is only possible in near-surface settings where oxygen and hydrogen

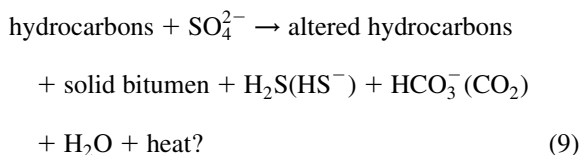
sulfide can diffuse into one another. At temperatures in excess of about 100°C , S^0 is an active oxidizing agent for many hydrocarbons, here symbolized by the functional methylene ($-\text{CH}_2-$) group (reaction (8), after Toland, 1960; Orr, 1990):



In natural environments with crude oil and/or wet gas as the carbon source, this type of redox-reaction also generates naphthenic acids, aromatic compounds, solid bitumen, and numerous inorganic and organic sulfur compounds (polysulfides, mercaptans, thialkenes, thiophenes).

3.8. Net mass balance reaction for BSR and TSR

The above reactions are interdependent because they produce compounds that are partially recycled, i.e. H_2S , S^0 , polysulfides. Hence, these reactions can be combined to a schematic net mass balance reaction (Machel, 1987a):



This net reaction represents the overall process if all the intermediate S^0 (including polysulfides) is used up. The relative proportions of $\text{H}_2\text{S}:\text{HS}^-$ and $\text{HCO}_3^+:\text{CO}_2$ depend on pH, but what changes and controls TSR in situ is not known at present (Orr, 1990; Hutcheon, pers. comm.). Furthermore, it is important to realize that $(\text{H}_2\text{S} + \text{HS}^-)$, $(\text{HCO}_3^- + \text{CO}_2)$, and H_2O are normally not formed in the proportions 1:1:1. These proportions vary as a function of the overall composition of the system. Many H_2S reservoirs have only small percentages of CO_2 , whereby $\text{H}_2\text{S}:\text{CO}_2 > 10$ is not uncommon, and the amount of water formed is often negligible (discussed further below). Furthermore, distinctive NSO-compounds are formed (collectively called ‘altered hydrocarbons’ in reaction (9)), such as benzothiophenes (Manzano et al., 1997). Polysulfides and other compounds with intermediate valence states

of sulfur, although undoubtedly formed as intermediates (see above), are not shown for simplicity.

3.9. Common reaction products and their amounts

The reactions discussed in the previous section have been developed on the basis of reactions and their products found in nature or in laboratory experiments (Machel, 1987a, and references therein; Orr, 1990). Consequently, these reactions permit prediction of the compounds that will form under certain diagenetic conditions. The masses of reactants consumed versus products generated, as well as concomitant pH changes, can be obtained by means of forward modeling with programs as such SOLVEQ, CHILLER, etc. (Nicholson and Goldhaber, 1991; Nicholson, 1992).

3.9.1. Hydrogen sulfide

H₂S is the most conspicuous and abundant product of BSR and TSR. H₂S evolves as a separate gas phase in both BSR and TSR settings once its concentration exceeds its aqueous solubility (initially H₂S forms and is dissolved in the formation water). The amounts of H₂S that can be generated and/or accumulate are constrained by several factors.

The first limit is the availability of organic reactants and sulfate. Obviously, no more H₂S can be formed, once the system runs out of at least one of these two. Typical BSR settings contain up to about 10% H₂S (of the total gas), whereas deep sour gas reservoirs may contain up to about 90% H₂S (Orr, 1977). More specifically, any deep reservoir with more than a few percent H₂S presumably underwent TSR, because thermal cracking of hydrocarbons does generally not provide more than about 1–3% H₂S, limited by the amount of organically bonded sulfur originally present (Orr, 1977).

The second limit is the presence/availability of base and transition metals, such as Fe, Pb, Zn, and Mn. These metals place a limit on H₂S accumulation because the aqueous solubilities of their sulfides are exceedingly low (e.g. the solubility constant of pyrite is $10^{-21.46}$ at 50°C, which is 11 orders of magnitude smaller than that of calcite at the same temperature: Kharaka et al., 1988). Considering further that metal sulfides often form within seconds to minutes after Me²⁺ and S²⁻ come into contact, H₂S is effectively

removed via metal sulfide precipitation almost instantaneously, as soon and as long as base metals are available. This is especially common in BSR settings where Fe is relatively abundant. On the other hand, metal sulfide formation is unimportant in most deeply buried carbonates, which form almost all commercial H₂S reservoirs, because they typically contain negligible amounts of base and transition metals. However, in clastic rocks that contain significant amounts of reduced or reducible base and transition metals, particularly Fe, removal of H₂S is significant (Dixon et al., 1989), and probably is the most important reason for the widespread scarcity or absence of sour clastic reservoirs.

The third limit is specific to BSR settings. H₂S can be generated during BSR as long as sulfate and organic nutrients for the microbes are available, but only as long as the H₂S concentration is below the level that is toxic for bacterial metabolism. It is well known that sulfate-reducing bacteria poison their own environments with H₂S (Reis et al., 1992, and references therein). Hence, if the system is closed and/or the H₂S cannot escape as fast as it is generated, bacterial sulfate reduction will stop as soon as the inhibitory H₂S concentration is reached. Empirically, H₂S concentrations of more than about 5–10% (in the gas phase) require that the gas, if bacterial, was not generated in situ. Such a gas was not formed where it is found, but the H₂S immigrated from a site of sulfate reduction, from whence it escaped before reaching inhibitory or lethal concentration. Hence, for large quantities of H₂S to be formed by BSR, the reaction site must be an open system with continuous inward diffusion of sulfate. Alternatively, H₂S concentrations of more than 5–10% indicate that the gas was formed by TSR (Orr, 1977; Machel, 1987a).

The fourth limit on H₂S concentrations is hydrodynamics, specifically, the solubility of H₂S and hydrodynamic flux. Considering that the aqueous solubility of H₂S is much greater than that of most hydrocarbon gases (Orr, 1977; Barker, 1982), the potential for migration in aqueous solution is greater for H₂S than for sweet gases in regions with strong advection. Hence, the solubility of H₂S probably is not a limiting factor for migration in solution. However, the fluxes of formation waters in deep (3–5 km) reservoirs usually are exceedingly low (Domenico and Schwartz, 1990), which appears to prohibit significant

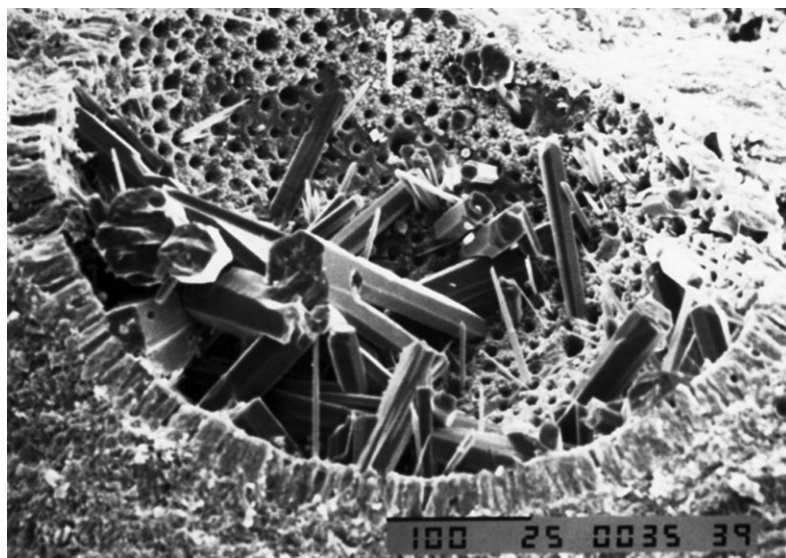


Fig. 9. SEM photomicrograph of columnar/prismatic aragonite cements that formed as a by-product of BSR in a microfossil, Damon Mound salt dome cap rock, Texas. Scale bar = 100 μm . Photo courtesy of Roger Sassen.

removal of H_2S via advection even over geologic times in most locations. This assertion is supported by the relatively common occurrence of deep, highly sour gas reservoirs that apparently formed tens of millions of years ago in the Alberta subsurface and elsewhere. However, arguments have been made that H_2S diffusion out of a system can limit the H_2S concentrations significantly in at least some locations (Wade et al., 1989).

Lastly, oxidation of H_2S is another limiting factor. Oxidation is common in low-temperature diagenetic settings where H_2S diffuses into the overlying oxygenated zones, and where molecular oxygen diffuses or is transported advectively into the BSR zone. Such settings often form elemental sulfur and/or sulfuric acid (Machel, 1992). Oxidation of H_2S is scarce to insignificant in most deep sour gas reservoirs because sufficient amounts of oxidants are not present. In particular, free oxygen, the most powerful and common oxidant in near-surface geologic settings, is essentially absent at depths of more than about 600–1000 m (Andreev et al., 1968).

3.9.2. Carbon dioxide and carbonates

The $\text{H}_2\text{S}:\text{CO}_2$ (HCO_3^-) ratios that are found in natural diagenetic settings of BSR and TSR vary widely. This probably results from two aspects: the

$\text{H}_2\text{S}:\text{CO}_2$ originally formed is variable, and from later processes that selectively remove H_2S and/or CO_2 in variable proportions (Hutcheon and Abercrombie, 1990; Hutcheon et al., 1995).

In systems where pH is controlled by the carbonate system, addition of CO_2 generates porosity via carbonate dissolution. Petrographic observations from many sour gas reservoirs in/with carbonate host rocks in Canada and the US (Machel et al., 1995a; Heydari, 1997, and references cited therein) suggest, however, that porosity gain from TSR is very rare (further discussed below). This, in turn, may suggest that pH in TSR settings is usually not controlled by the carbonate system. In one interesting case study, the siliciclastic Norphlet Formation (Dixon et al., 1989), CO_2 production by TSR has been invoked to prohibit carbonate cementation rather than generating porosity. On the other hand, where pH is buffered by chemical species other than CO_2 , the addition of CO_2 will cause carbonate precipitation, which appears to be rather common. The presence of alkali earth metals results in precipitation of mainly calcite and dolomite, either as cements or as replacements of the dissolving gypsum and/or anhydrite. Other carbonates, i.e. ankerite, siderite, witherite, strontianite, may form if the respective metal cations are available.

The textures of these carbonate can, within limits,

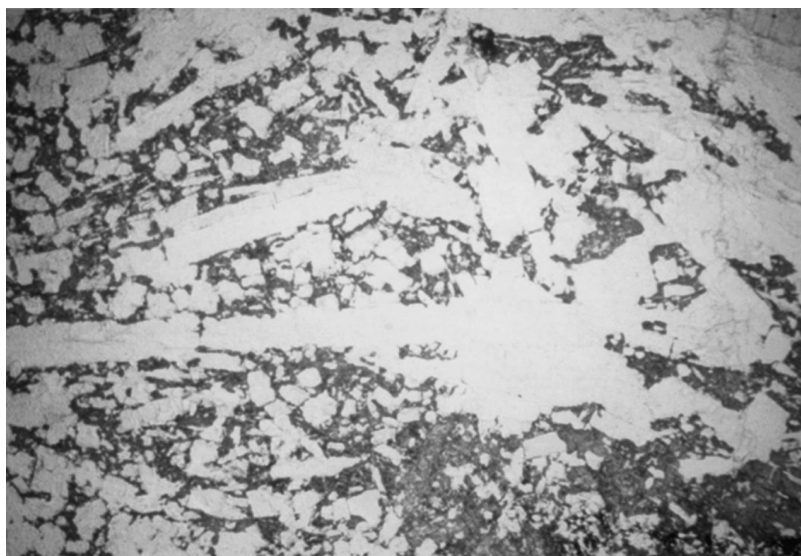


Fig. 10. Thin section photomicrograph, transmitted light — one polarizer, of calcite (stained dark) that partially replaced anhydrite (white/colorless). Typical texture for BSR and TSR. This particular sample is from the Devonian Nisku Formation, Alberta, Canada. Width of photograph is about 5 mm.

be used to distinguish between BSR and TSR. By far the most common carbonate formed as a by-product of BSR is calcite, subordinately aragonite. In settings that have open void spaces, calcium carbonate often begins to form as acicular to columnar aragonite and/

or calcite crystals (Fig. 9) that later coalesce to larger masses. This type of carbonate, however, is volumetrically minor. Much more commonly, calcium carbonate replaces calcium sulfate, such that these two minerals are intimately intergrown with one another

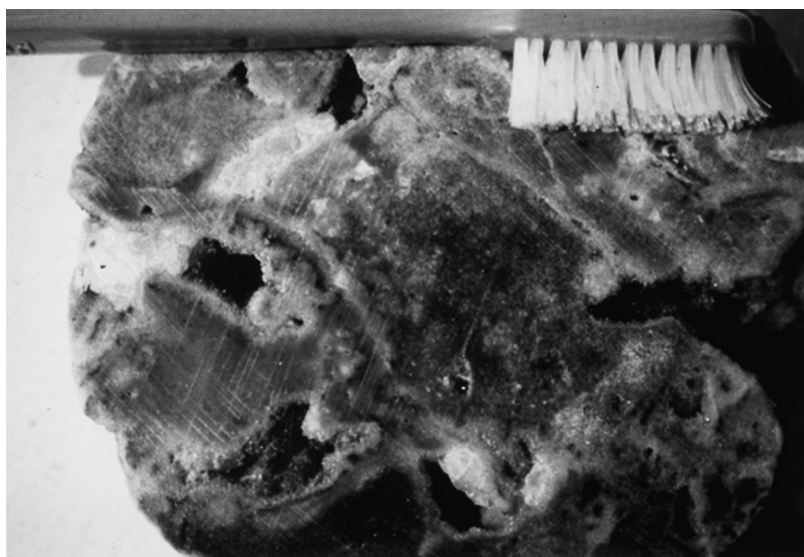


Fig. 11. Core specimen of massive, replacive calcite that formed as a by-product of BSR in Damon Mound salt dome cap rock, Texas. Some vugs (top left, bottom center) contain elemental sulfur as a cement. Tooth brush for scale.



Fig. 12. Outcrop of massive, replace calcite that formed as a by-product of BSR, Damon Mound salt dome cap rock, Texas. People for scale.

(Fig. 10). At advanced stages of BSR, the calcium sulfate may be completely replaced by massive limestones up to the scale of entire outcrops (Figs. 11 and 12), or larger. BSR calcites often have highly depleted $\delta^{13}\text{C}$ -values, caused by a combination of two factors: (1) the highly negative $\delta^{13}\text{C}$ values of the source organic matter (commonly -25 to -30‰ PDB, even lower when the reactant is biogenic methane), which is compounded by (2) negative microbial isotope fractionations (Machel et al., 1995b, and references cited therein).

TSR calcites typically occur as milky white, coarse-crystalline cements (Figs. 13 and 14) and/or as replace masses after anhydrite (Machel, 1989; Machel et al., 1995a; Worden et al., 1996). Such calcites often have depleted $\delta^{13}\text{C}$ -values, albeit not as low as those of BSR calcites, as well as elevated fluid inclusion temperatures (Machel et al., 1995b). Overall the amounts of authigenic TSR carbonates appear to be much smaller than those of BSR calcites, which probably reflects the fact that many BSR settings, especially salt dome cap rocks, are open hydrodynamically, with continuous replenishment of nutrients and/or sulfate via groundwater flow, whereas typical TSR settings are hydrodynamically closed. This is shown by several lines of evidence, including volume data, isotopic compositions of H_2S , calcite, dolomite

and anhydrite, fluid-inclusion and gas chromatographic data, and thermal modeling (Machel et al., 1995a,b; Simpson et al., 1996; and references cited therein).

The second most abundant carbonate formed as a by-product of TSR is dolomite. Furthermore, TSR dolomite is almost exclusively restricted to settings where the host carbonate rock is dolostone. Apparently, the chief source of Mg^{2+} for TSR dolomite is partial dissolution of the dolostone, usually via pressure solution (Machel, 1987b). TSR dolomite typically occurs as a milky white, medium to coarse-crystalline saddle dolomite cement (Figs. 15 and 16), rarely as a replacement.

3.9.3. Metal sulfides

Base and transition metal sulfides often form as by-products of BSR and TSR, if the respective metal cations are present or transported to the reaction site, or if H_2S migrates into an environment containing those metals. The most common minerals are iron sulfides, galena, and sphalerite. As mentioned above, the solubilities of these metal sulfides are exceedingly low, which typically leads to their formation even if the respective metals are present only in trace amounts.

BSR settings typically form iron sulfides, because



Fig. 13. Core specimen of dolostone with late diagenetic, milky-white calcite cement (in fossil mold near top) that formed as a by-product of TSR. Devonian Nisku Formation, Alberta, Canada. Scale at stratigraphic top in centimeter.

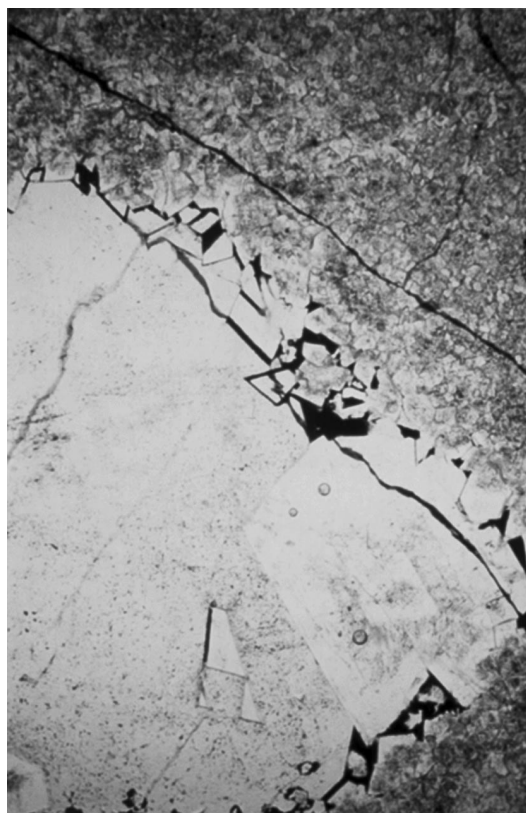


Fig. 14. Thin section photomicrograph, transmitted light — one polarizer, of TSR calcite cement shown in Fig. 13. The margin of this particular moldic pore is rimmed with dolomite cement and some solid bitumen (black) that may have formed as a by-product of thermal cracking or TSR. Width of photograph is about 2 mm.

iron is by far the most abundant and most readily reduced metal in near-surface and shallow burial diagenetic settings. BSR iron sulfide typically forms initially as metastable phases, i.e. iron monosulfides, greigite and mackinawite, which later recrystallize to pyrite, marcasite, and/or pyrrhotite (Rickard et al., 1995). The most common initial textures are scattered clusters of framboids (Fig. 17). Once recrystallized to the more stable forms, BSR iron sulfides typically occur as disseminated, fine- to medium-crystalline clusters of subhedral to anhedral crystals (Fig. 18). Such crystals may display a wide range of sulfur isotope values, which results from, and is indicative of, Rayleigh fractionation during BSR (Riciputi et al., 1996).

By contrast, iron sulfides are rare as by-products of TSR in sour gas reservoirs. This is because most iron

appears to be fixed at very shallow burial during BSR, and because TSR settings typically are deeply buried carbonate rocks that contain very small amounts of Fe to begin with. If Fe is available during TSR, it tends to precipitate as pyrite or marcasite that replaces anhydrite (Fig. 19).

The most common and best known metal sulfides that form as by-products of TSR are galena, sphalerite, subordinately pyrite, often as Mississippi-Valley-Type deposits (Sangster, 1996). Typical textures are banded galena-saddle dolomite (Fig. 20) and colloform masses of sphalerite associated with white saddle dolomite or calcite (Fig. 21). For economically viable amounts of these sulfides to form, the settings must be open or semi-open, to allow for sufficient mass transfer of metals into the TSR site, or for H_2S

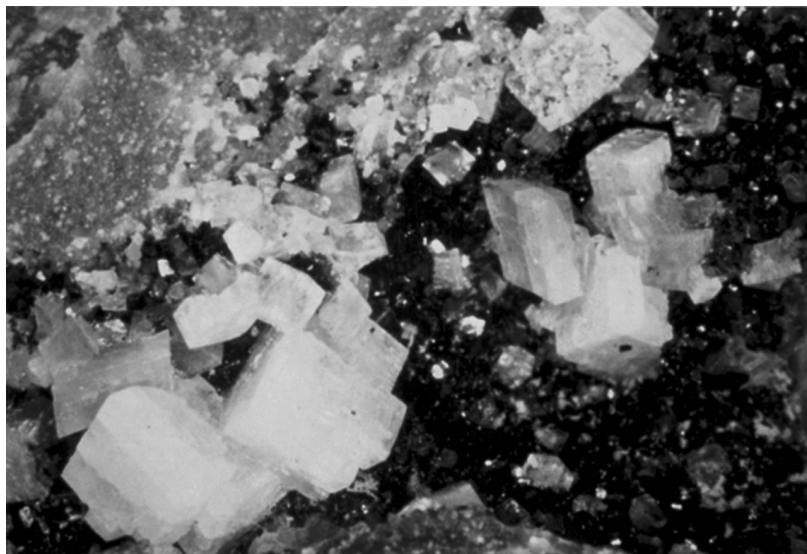


Fig. 15. Core specimen of milky-white TSR saddle dolomite cement in vug that is coated with solid bitumen. Devonian Leduc Formation, Alberta, Canada. Width of photograph is about 4 cm.

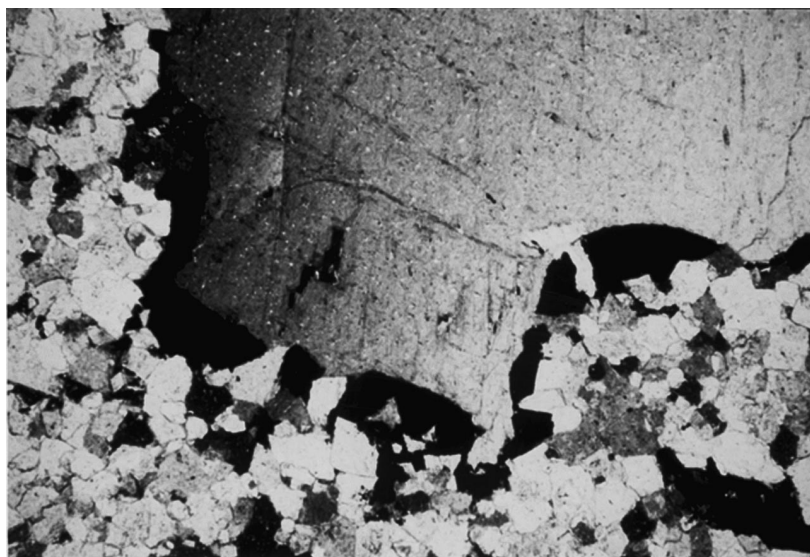


Fig. 16. Thin section photomicrograph, transmitted light — crossed polarizers, of TSR dolomite cement and solid bitumen shown in Fig. 15. Note that most of the bitumen displays round/convex surfaces toward the center of the pore, mimicking formerly liquid oil droplets that clung to the margins of this pore. This bitumen may have formed as a by-product of thermal cracking or from TSR. Saddle dolomite appears as large crystal with undulous extinction. Width of photograph is about 800 μm .

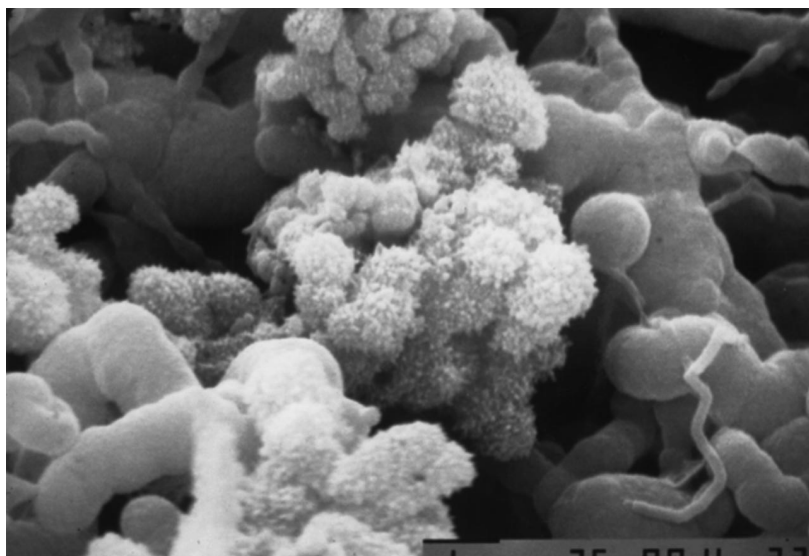


Fig. 17. SEM photomicrograph of framboidal pyrite in association with bacteria from a US Gulf coast oil seep. This pyrite is a by-product of BSR. Scale bar = 1 μm . Photo courtesy of Roger Sassen.

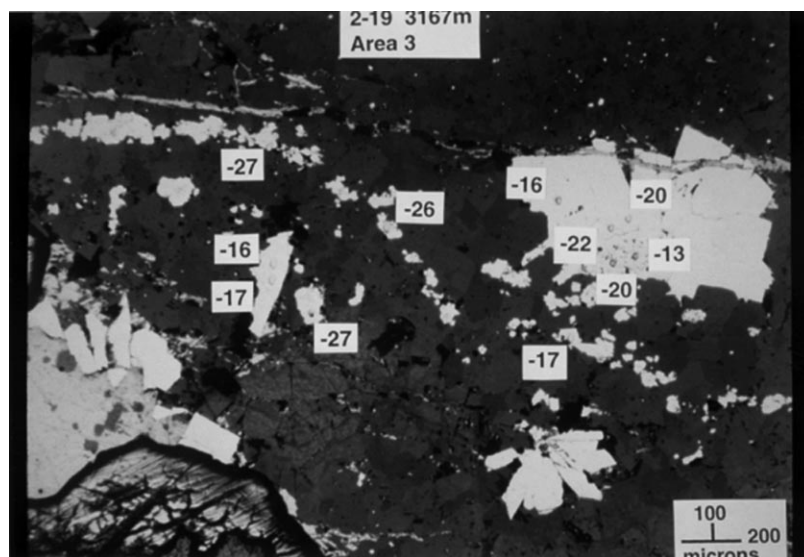


Fig. 18. Thin section photomicrograph, reflected light, of BSR pyrite clusters that formed directly from solution or from recrystallization of framboidal pyrite soon after formation of the framboids. Beam pits (roundish light spots) and corresponding $\delta^{34}\text{S}$ values (‰ CDT) are from ion microprobe analysis. This sample illustrates large variations in $\delta^{34}\text{S}$ within individual thin sections and clusters of crystals, which is typical for BSR (Machel et al., 1997). Devonian Nisku Formation, Alberta, Canada. Scale bar in 100/200 μm .

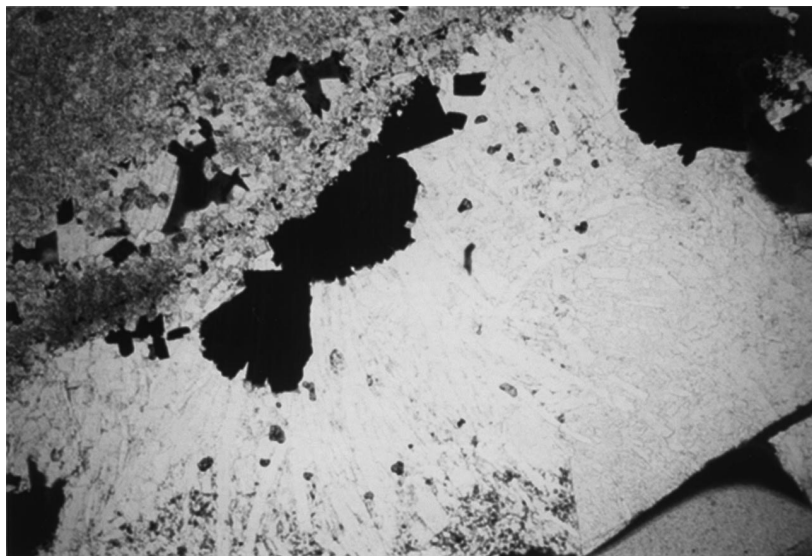


Fig. 19. Thin section photomicrograph, transmitted light — one polarizer, of TSR marcasite (black) pseudomorphically replacing splays of late diagenetic anhydrite cement (white/colorless). Dolostone host rock at top left. Devonian Nisku Formation, Alberta, Canada. Width of photograph is about 2.5 mm.

migration to the site of metal abundance (Garven, 1995). This is in marked contrast to typical sour gas reservoir settings, which typically are nearly or completely closed hydrodynamically (Machel et al., 1995b; Hutcheon et al., 1995).

3.9.4. *Elemental sulfur*

Elemental sulfur may accumulate as a net reaction product, if the system runs out of reactive hydrocarbons, or if the reactive hydrocarbons are not supplied fast enough to the reaction site and Reaction 8 cannot proceed

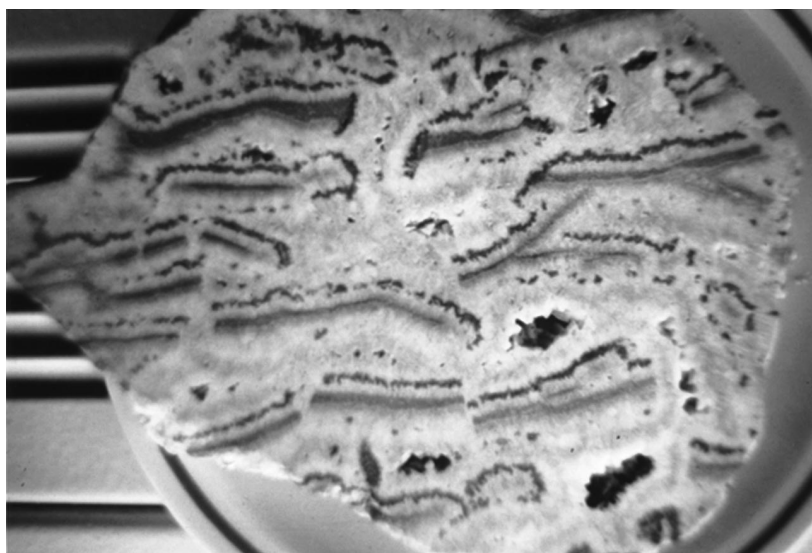


Fig. 20. Hand specimen of milky-white, coarse crystalline TSR saddle dolomite intergrown with bands of galena. Typical MVT- paragenesis, Pine Point, N.W.T., Canada. Width of photograph is about 14 cm.

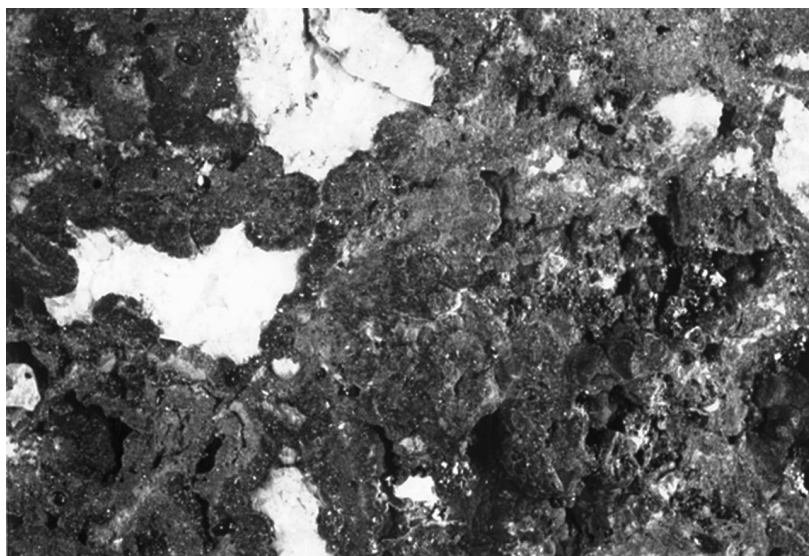


Fig. 21. Hand specimen of colloform sphalerite masses intergrown with milky-white, coarse crystalline TSR calcite cement. MVT- paragenesis, Pine Point, NWT, Canada. Width of photograph is about 7 cm.

(Orr, 1990). These aspects place certain constraints on the amounts and distribution of elemental sulfur that can accumulate as a by-product of BSR and TSR.

In BSR settings, elemental sulfur often occurs intergrown with authigenic calcite and may form massive, economically viable sulfur deposits. A large number

of metabolically and environmentally diverse microbes can form sulfur, either intracellularly or extracellularly (Machel, 1992, and references therein). Intracellularly formed sulfur tends to be granular with grain sizes reflecting those of the microbes (Fig. 22). Sulfur formed in this way usually

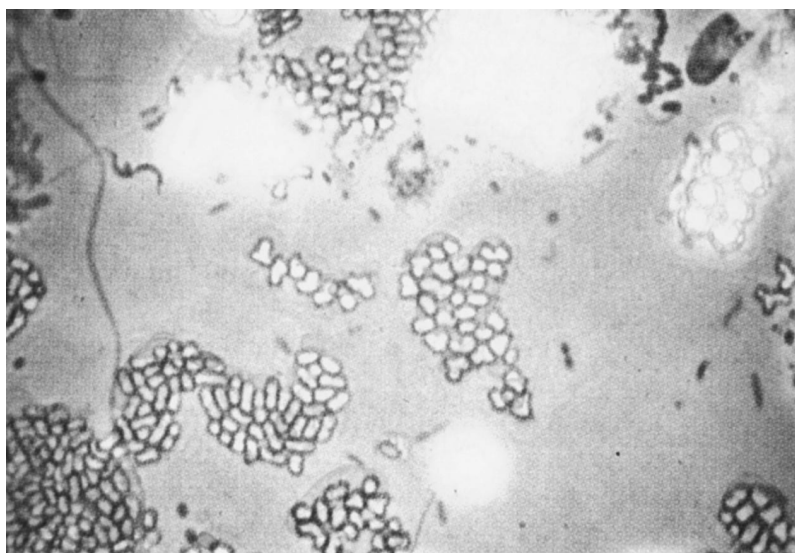


Fig. 22. Phase contrast photomicrograph of microbial, intracellularly formed, elemental sulfur granules from a lake next to Miette Hot Springs, Alberta, Canada. Width of photograph is ca. 100 μm .



Fig. 23. Core specimen of an elemental sulfur crystal that is fused to a limpid calcite crystal, both formed as by-products of BSR. Permian McElroy oil field, Texas. Width of photograph is about 2.5 mm.

form economically insignificant, stratiform and/or disseminated deposits. By contrast, extracellularly formed microbial sulfur crystals can be up to several cm in size (Figs. 11 and 23), and such sulfur may form coarse-crystalline masses that are volumetrically abundant enough to form minable deposits (Pawlowski et al., 1979). Extracellularly formed sulfur crystals are inorganic precipitates *sensu strictu*, because the microbes certainly are not consciously capable of forming crystals that have orthorhombic symmetry and are many times their own size. However, these crystals can be said to form biogenically/microbially, because the microbes are found to colonize them, facilitating their precipitation by changing the microenvironment in such a way as to supersaturate the boundary layer of the crystals with respect to elemental sulfur.

In TSR settings with well-defined gas (condensate) — water contacts, i.e. where the irreducible water saturation in the gas (condensate) column is very low, elemental sulfur tends to form at the gas (condensate) — water contact. This is because here the hydrocarbons are in physical contact with water that is needed for calcium sulfate dissolution. Alternatively, elemental sulfur may form throughout a gas column, where the latter contains significant amounts of water, i.e. where the irreducible water saturation is relatively

high. Sulfur normally does not form in the water leg below a gas column because the water leg usually is devoid of hydrocarbons. Where sulfur does occur within a water leg, this typically indicates a rise of the gas–water contact after TSR, which may happen when the top seal ruptures and gas escapes. All these spatial relationships have been found in sour gas reservoirs in western Canada (Machel et al., 1995a,b; Patey, 1995).

TSR sulfur most commonly occurs in vugs as blobs that resemble chewing gum, with round surfaces that mimic fluid–fluid interfaces (Figs. 24 and 25). This texture undoubtedly reflects the fact that many TSR settings are hotter than the melting point of elemental sulfur, which commonly ranges from about 116–119°C (liquid sulfur may persist metastably at temperatures as low as 90°C: Woll, 1983). Another common occurrence is TSR sulfur intergrown with anhydrite, as milky-white masses with a slight yellow tinge in hand specimens. A relatively rare occurrence is elemental sulfur as minute crystals embedded in solid bitumen (Fig. 26) that are only visible after dissolution of the bitumen.

3.10. Solid bitumen

Both BSR and TSR form numerous organic

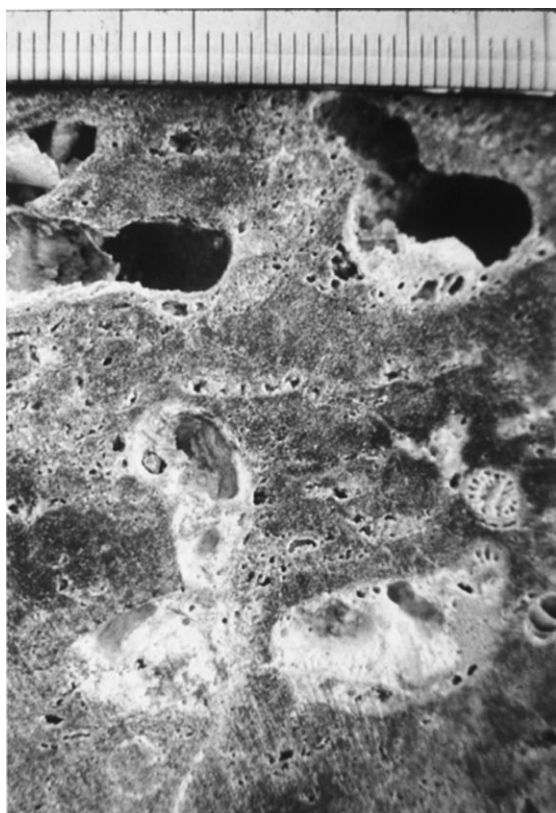


Fig. 24. Core specimen of dolostone with vuggy porosity that is partially filled with TSR 'chewing gum sulfur'. Note the round and mostly concave (with respect to void margins) surfaces of the sulfur, indicating that it was liquid in the reservoir, with the remaining pore spaces occupied by gas and/or water. Devonian Nisku Formation, Alberta, Canada. Scale bar in centimeter/millimeter at stratigraphic top.

compounds, some of which polymerize and precipitate as solid bitumen. In contrast, no solid bitumen is formed where methane is the main or the only available reactive hydrocarbon. This situation occurs in settings where microbial gas (chiefly methane) is the principal nutrient for BSR (e.g. Kirkland and Evans, 1976), or where thermogenic methane is the main or only hydrocarbon available for TSR. The latter probably is very rare in nature because, as discussed above, TSR typically takes place during wet gas maturation, and gases with higher molecular weight are much more reactive than methane. Methane is expected to act as the chief hydrocarbon source for TSR only where TSR is kinetically inhibited until the

wet gas is cracked to dry gas. This probably happened in some very deep sour gas reservoirs of the Jurassic Smackover Formation, United States, as shown by isotope and gas compositional data (Claypool and Mancini, 1989; Rooney, 1996). Another example may be the Permian Khuff Formation of Abu Dhabi (Worden et al., 1996). However, the evidence for methane as the chief reactive hydrocarbon for TSR in the Khuff Formation is circumstantial, and the TSR-reactive hydrocarbons have not been properly determined via analysis of the gases, as in the studies by Manzano (1995) and Rooney (1996).

Solid bitumen from BSR often displays no distinctive petrographic characteristics and can be mistaken for bitumen generated by aerobic biodegradation, inspissation (evaporation), or water-washing. Hence, without geochemical analysis such bitumens may best be addressed as 'low-temperature' bitumens. Similarly, solid bitumen from TSR often displays ambiguous petrographic characteristics and may not be unambiguously distinguishable from bitumen that formed via gas deasphalting (Curiale, 1985). Collectively such bitumens may best be called 'high-temperature' bitumen, or pyrobitumen. In at least some cases, however, microscopy and elemental analysis of solid bitumens may yield discriminating clues regarding their origin. Stasiuk (1997) showed that pyrobitumen with fine-grained mosaic needle coke that hosts euhedral calcite and sulfide inclusions probably formed as a by-product of TSR. Low- and high-temperature bitumens can be distinguished petrographically in most cases via their paragenesis. Bitumens that occur intergrown with deep-burial nodular or pile-of-brick anhydrite (Figs. 5 and 8), that are associated with TSR calcite or saddle dolomite (Figs. 14–16), that occur in a sour gas reservoir and contain inclusions of elemental sulfur (Fig. 26) or authigenic calcite, that coat late-diagenetic vugs (Fig. 27), or that occur in intercrystalline spaces and within fluid inclusions of late-diagenetic anhydrite (Fig. 28), most certainly are high-temperature bitumens.

3.11. Other organic compounds

Those organic compounds that remain after and/or are formed via BSR and TSR, and that are not solid but liquid or gaseous, can only be characterized by physical and geochemical methods, especially chromatography and mass spectroscopy. Most of these

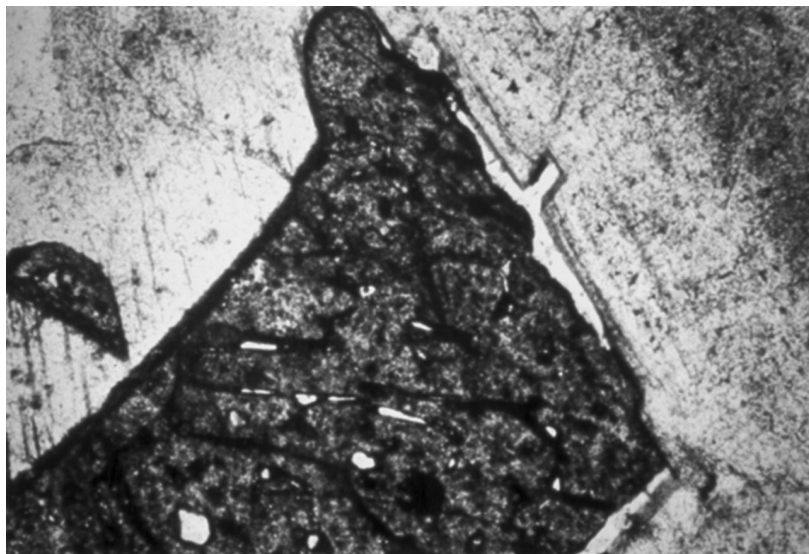


Fig. 25. Thin section photomicrograph, transmitted light — one polarizer, of TSR sulfur (dark) in void next to saddle dolomite (light grey, cloudy). The sulfur was liquid in the reservoir. Note the convex surface of the sulfur at the top, and the elongate, open space between sulfur and dolomite (center right), which originated from shrinkage of the sulfur during its solidification. Devonian Leduc Formation, Alberta, Canada. Width of photograph is ca. 1 cm.

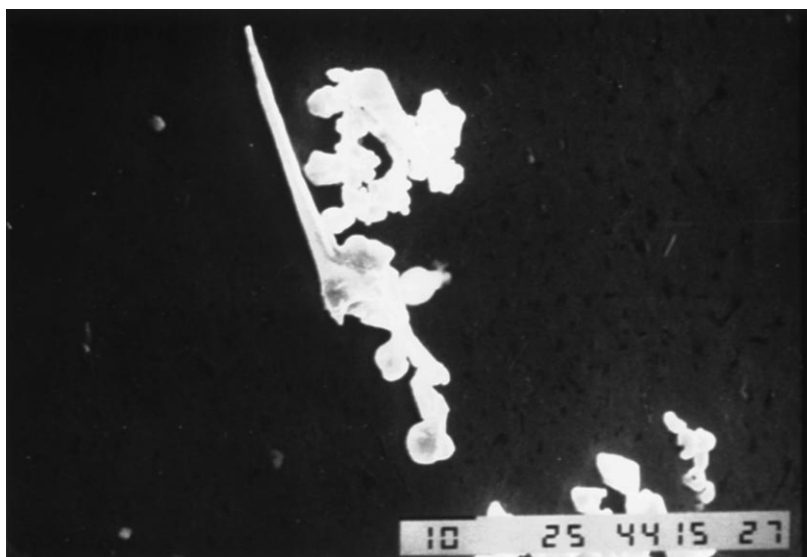


Fig. 26. SEM photomicrograph of crystal aggregate of elemental sulfur extracted from solid bitumen via dissolution of the latter. Jurassic Smackover Formation, USA. Scale bar = 10 μm . Photo courtesy of Roger Sassen.

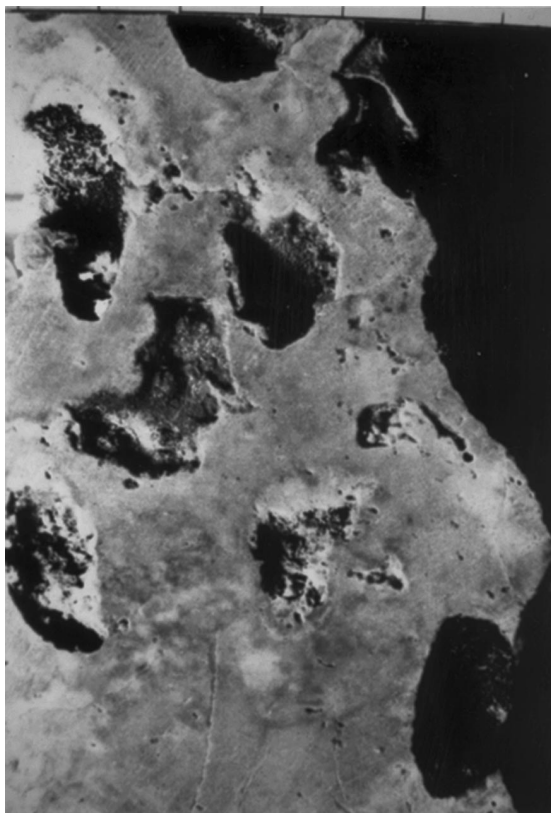


Fig. 27. Core specimen of dolostone with moldic and vuggy porosity that is coated with solid bitumen formed during TSR. Devonian Nisku Formation, Alberta, Canada. Scale bar in cm at stratigraphic top.

characteristics are summarized and discussed by Machel et al. (1995a,b) and not repeated here except for, as an example for the complexity involved, the compositional changes of condensates that have undergone TSR (Table 1).

3.12. Water

The amount of water generated and/or released during BSR is unknown and usually ignored, presumably because BSR settings often are located within or near active meteoric groundwater systems and/or in near-surface marine settings. Any water released in such settings is of little to no concern scientifically or economically.

By contrast, the amount of water released during TSR is potentially important and controversial. Considering that TSR settings are often closed

hydrodynamically, water, if released in significant amounts, may dilute the formation water, and this may have a number of significant side-effects, such as increasing or decreasing the rate of TSR, changing the wettability, changing the gas/oil ratio or the position of the gas–water contact. These effects could significantly alter the reservoir characteristics.

One can write numerous mass-balance reactions for TSR without water being released in the process, and some of the involved sub-reactions actually consume water (Toland, 1960; Goldstein and Aizenshtat, 1994). Furthermore, the particular stoichiometry realized as a net mass balance reaction in a given setting, and whether water is a volumetrically significant net reaction product, can usually not be ascertained in field studies. Only two studies have provided evidence for the release of ‘measurable’ amounts of water during TSR. Worden et al. (1996) provided fluid inclusion and isotope evidence for the formation of water during the precipitation of TSR calcites (formed as a by-product of TSR) of the Khuff Formation, Abu Dhabi. Using the same methodology, a similar argument was made for a Devonian sour gas reservoir by Simpson et al. (1996). However, Worden et al. (1996) provided no data to support the claim that enough water was formed to significantly dilute the bulk formation water in the TSR-affected part of the Khuff Formation. It is much more likely that the water released during TSR (and trapped in the fluid inclusions of the Khuff TSR calcites) represents local anomalies that were confined to relatively small TSR reaction sites, and that the bulk solution salinity was not affected to any significant degree after mixing (Machel, 1998b).

Conversely, there are at least two studies in western Canada that have shown that no measurable amounts of water are released and/or accumulate during TSR. Fluid inclusions of saddle dolomites formed as a by-product of TSR in the gas–water transition zone of the Nisku sour gas play, Alberta, Canada, have salinities of about 19 wt% eq. NaCl, which are identical (within the margin of error) to the salinities determined for the present formation brines that were retrieved at the wellheads (Machel, 1987b; Machel et al., 1995a). Similarly, fluid inclusions from TSR calcites in the Devonian Peace River Arch Leduc reef trend, Alberta, Canada, have salinities of about 18–20 wt% eq. NaCl (McKenzie, 1999). Furthermore, it is well known that

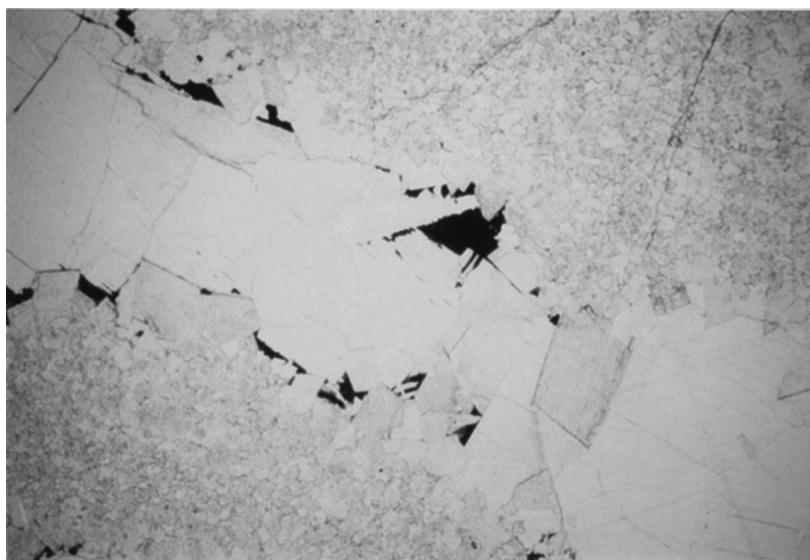


Fig. 28. Thin section photomicrograph, transmitted light — one polarizer, of late diagenetic anhydrite cement (white/colorless, across center) in moldic pore of dolostone (light grey, top and bottom). The anhydrite contains dark brown oil and/or solid bitumen in fluid inclusions and remnant intercrystalline pores. Devonian Leduc Formation, Alberta, Canada. Width of photograph is ca. 1 cm.

sour gas reservoirs commonly do not (co-)produce any water, or only so little that it is hardly enough for chemical/isotopic analysis and a proper evaluation of the formation water chemistry (Krouse, pers. comm.).

Taking all available evidence together, the

amounts of water released during TSR are likely to be very small and, in most cases, negligible (Machel, 1998b). It is not clear at this time whether there are any reservoirs where the amounts of water formed are of more than local significance.

Table 1

Distinguishing geochemical criteria for condensates. Observed total ranges are extracted from the literature, and deviations have been calculated from the same sources (after Machel et al., 1995b). sat = saturates; arom = aromatics. All deviations are normalized to condensates that have *not* participated in TSR, i.e. the deviations result when 'No-TSR' condensates participate in TSR

	Gas condensates	
	TSR, observed deviation from No-TSR condensate	TSR, observed total range
S (%)	+0.8 to +1.3	+0.1 to +1.4
$\delta^{13}\text{C}[\text{CH}_4]\text{‰ PDB}$	−1.4 to −2.9	−46 to −35
$\delta^{13}\text{C}[\text{C}_2\text{H}_6]\text{‰ PDB}$	Up to +10	−26 to −18
$\delta^{13}\text{C}[\text{C}_3\text{H}_8]\text{‰ PDB}$	Up to +10	−22 to −18
$\delta^{34}\text{S}\text{‰ CDT}$	+5.0 to +23.7	+2.4 to +24.1
sat/arom	−5.1 to −8.6 (not always)	+0.2 to +8.8
C_{15+} (%)	−9.3 to −29.1	+11.3 to +40.4
Gas conversion (%)	+11 to +37	+48 to +85
$^{\circ}\text{API}$	−3.1 to −9.3	+42.3 to +56.0
CO_2 (%)	+0 to +10	2.4–50.1
H_2S (%)	Up to 95	Up to 95

3.13. Porosity and pressure

As in the case of water, the amount of porosity formed or destroyed as a by product of sulfate reduction is usually of no importance or interest in the case of BSR, but little understood and/or somewhat controversial in the case of TSR. The amount of porosity generated or destroyed obviously is of great importance in sour gas reserve assessments and reservoir development.

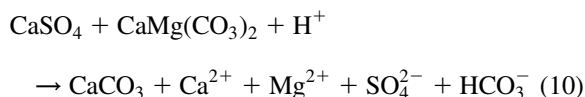
Porosity is necessarily produced from the dissolution of calcium sulfate, which has to dissolve in order to yield SO_4^{2-} for TSR, and may additionally be generated due to the generation of CO_2 when pH is controlled by the carbonate system (the latter may or may not be the case). However, porosity can also be generated by a host of other factors, i.e. release of organic acids from thermal maturation of organic matter, and certain mineral reactions including metal sulfide precipitation (Giles and Marshall, 1986; Hutcheon and Abercrombie, 1990; Mazzullo and Harris, 1992). On the other hand, porosity is lost due to the precipitation of authigenic carbonates and/or sulfides. Any porosity gain is the net result of all of these processes combined. If the net reaction (9) (above) is balanced in such a way that the ratios of $\text{CaSO}_4\text{:CaCO}_3\text{:H}_2\text{S} = 1\text{:}1\text{:}1$ and no sulfides are formed, the net porosity development as a result of TSR is positive. For every mole of CaSO_4 that is converted to CaCO_3 and H_2S , there is a loss in rock volume of about 10 cm^3 . Expressed as volumes, 1 m^3 of CaSO_4 results in 0.78 m^3 of CaCO_3 and 0.22 m^3 (22%) of additional porosity, which is the maximum possible porosity gain.

Calculations using the ideal gas law ($PV = nRT$) further imply that the pressure in the reservoir may increase considerably, unless the generated H_2S escapes, because the porosity gain (above) is exceeded by the amount of gas generated. Indeed, many sour gas reservoirs are significantly overpressured relative to hydrostatic pressures and relative to sweet reservoirs at comparable depths (Hutcheon et al., 1995; Machel et al., 1995a).

The net effect of the pressure increase via TSR depends on the moles of hydrocarbons that are destroyed in the overall process relative to the moles of H_2S that are generated. One cubic meter of $\text{CaSO}_4 = 21,739\text{ mol}$. Therefore, 21,739 is also the number of moles of CaCO_3 and H_2S generated,

using reaction (9). One mole of gas occupies 24.5 l ($= 0.02447\text{ m}^3$) at 25°C and 1 atm . Therefore, $21,739\text{ mol}$ occupy 532 m^3 at these P/T conditions. Extending the range up to 200°C and 600 atm , 1 mol of gas occupies 0.0647 l ($= 6.47 \times 10^{-5}\text{ m}^3$), and $21,739\text{ mol}$ occupy 1.4 m^3 . Hence, even under these extreme temperature and pressure conditions, equivalent to $5\text{--}7\text{ km}$ of depth, the amount of H_2S generated exceeds the amount of porosity generated via anhydrite–calcite conversion. Once again, the net effect depends on the stoichiometry of the net reaction. Related to these considerations, the amount of H_2S that is generated from a given amount of CaSO_4 can also be derived from the molar volumes. Assuming a conversion of $\text{CaSO}_4\text{:H}_2\text{S}$ in the proportion $1\text{:}1$ ($1\text{ mol H}_2\text{S} \times 34\text{ g/mol}$):($1\text{ mol CaSO}_4 \times 136.1\text{ g/mol}$) $= 0.25\text{ g H}_2\text{S/g CaSO}_4$. This approach can be used to approximate the potential gains in porosity, pressure, and H_2S through TSR.

Furthermore, one can write a reaction between anhydrite and dolomite to generate porosity according to:



In other words, if the pH is low enough, host rock dolomite may dissolve.

It becomes obvious that a quantitative prediction of porosity, pressure, and H_2S through TSR requires the use of computer models where the involved variables (e.g. reaction stoichiometry, fluid composition) can be fixed at different values (Nicholson and Goldhaber, 1991; Nicholson, 1992). The argument can be extended to other diagenetic reactions or processes that may be caused by TSR or may be related to it. In particular, if metal sulfides precipitate, acid is generated and the pH of the system drops, at least initially until carbonate (host rock) dissolution buffers the pH (Anderson and Garven, 1987). The amount of porosity gained in this way obviously depends on the amount of metal sulfide precipitated, as well as on the other fluid parameters. In any case, the porosity initially gained via metal sulfide precipitation appears to be significant, considering the widespread presence of solution collapse brecciation in MVT-deposits (Anderson and Garven, 1987).

In summary, porosity can be produced, directly or indirectly, via TSR in at least two ways: (a) conversion

of CaSO_4 to CaCO_3 [or other carbonates]; and (b) metal sulfide precipitation. However, the complexity of the system requires the use of computer models for quantitative prediction of porosity development during TSR. Considering the available petrographic evidence from various sour gas fields especially in western Canada and the US (Machel et al., 1995a,b; Heydari, 1997), it appears that in most locations porosity generation as a result of TSR is minor to negligible. Although porosity was significantly enhanced in some locations, there is no apparent significant porosity gain in many other locations, and there are no known examples of gas/oil pools that owe their existence to secondary porosity produced by TSR. Conversely, in some locations there is considerably occlusion of porosity via anhydrite cements that appear to have formed after TSR (Machel and Burton, 1991, plus unpublished data). Anhydrite appears to be quite mobile and can invade sour gas reservoirs even after the TSR reactions have ceased.

3.14. Sizes and locations of TSR zones

The sizes and locations of TSR zones are governed by the necessity of physical contact between hydrocarbons and sulfate, and by the fact that sulfate does not react in the solid state. There must be enough water to facilitate sulfate dissolution and to instigate or sustain TSR.

The available data (Machel, 1987b; Machel et al., 1995a) demonstrate that TSR is likely to take place in fairly narrow reaction zones, rather than throughout an entire formation with a thickness of some 100 or more meters. In the case of the Nisku Formation, the TSR reaction site was only about 10–20 m in thickness and coincided with the past and present gas–water transition zone. In this zone, the TSR saddle dolomites display distinctive upward decreasing trends for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (but no trends in the fluid inclusion salinity or homogenization temperature data), with fixation of oxidized organic carbon in the saddle dolomite lattices ($\delta^{13}\text{C}$ -values are as low as about -12‰ PDB close to the top of the gas–water transition zone where the proportion of incorporated oxidized organic carbon is greatest). Depleted $\delta^{18}\text{O}$ values do not indicate the formation of TSR water in this case, as the fluid inclusions contain the bulk formation water brines. Rather, the depleted $\delta^{18}\text{O}$ values originated from elevated temperatures and/or transfer of oxygen from the SO_4^{2-} into the CO_3^{2-}

groups (Machel et al., 1995a). There is no saddle dolomite above the gas–water transition zone, evidently because there is and was no water, except for irrelevantly small amounts in the form of irreducible water saturation and/or steam. Petrographically similar dolomites in the fully water-saturated zone below, where saddle dolomite formed mainly due to chemical compaction, have normal-marine $\delta^{13}\text{C}$ values (ca. $+1$ to $+2\text{‰}$ PDB) and do not contain oxidized organic carbon. Hence, the mineralogical (saddle dolomite) and geochemical (isotopic) influence of TSR is confined to the gas–water transition zone.

The Nisku Formation may be quite typical of TSR reservoirs in general, in that TSR is likely confined to the gas–water transition zone where one exists, i.e. where the irreducible water saturation in the gas column is very low. However, this zone need not be as narrow as 10–20 m elsewhere, and it most certainly can be wider than that. Furthermore, where gas columns have significant irreducible water saturation, TSR may take place throughout the entire gas-containing part of a reservoir.

4. Geochemical criteria

The mere presence of any of the above reaction products does not permit discrimination of BSR from TSR. It is desirable, however, to distinguish between these two processes because products of BSR can subsequently be buried into the thermal regime of TSR, and products of TSR can be uplifted into the thermal regime of BSR. As shown above, petrographic relationships may be sufficient to establish paragenetic relationships, but additional stable isotope and gas-chromatographic data are often needed.

The compositions of kerogens, crude oils, condensates, solid bitumens, and minerals formed by BSR and/or TSR, offer a plethora of criteria for discrimination among genetic processes. In particular, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, elemental, and chromatographic analysis can be used to differentiate products of BSR from TSR as well as from related processes, such as thermal maturation (Machel et al., 1995b). Regarding the inorganic phases, the carbon isotopes of carbonates and the sulfur isotopes of elemental sulfur and sulfides appear to yield the best discriminating criteria. Solid reservoir bitumens and gas

condensates also display several distinctive isotopic and compositional differences, depending on low-temperature or high-temperature alteration.

The most reliable geologic interpretations can be obtained by combining several geochemical methods. One example would be the combined occurrence in solid bitumen of a high total sulfur content, $\delta^{34}\text{S}$ enrichment, $\delta^{13}\text{C}$ depletion, admixed elemental sulfur, and insolubility in common organic solvents, which would suggest an origin by TSR. Another example would be the combined occurrence of formation waters that have relatively high $\delta^{34}\text{S}_{\text{dissolved sulfate}}$ values and relatively low $\delta^{18}\text{O}_{\text{water}}$ values, and to have the paraffins missing in associated crude oil that also has a fairly high content of dissolved or organically bound sulfur. In this case, aerobic biodegradation of crude oil with concomitant bacterial sulfate reduction in a meteoric environment is indicated. Obviously, one should combine as many petrographic and geochemical criteria as possible.

5. Conclusions

BSR takes place in a multitude of diagenetic settings that range in temperature from 0 to about 80°C. TSR takes place as soon as a geologic environment with the right ‘ingredients’ is buried to depths that correspond to temperatures of about 100–140°C. In some cases even these temperatures are not sufficient. The lowest confirmed temperature for TSR to date is 127°C, with questionable evidence pointing to a temperature as low as perhaps 100°C.

BSR is geologically instantaneous in most geologic settings. Kinetic data from experiments suggest that TSR may occur at rates in the order of hundreds of thousands of years in the most probable temperature range of 100–140°C in geologic environments. Although much slower than BSR, even TSR appears to be a geologically fairly fast process.

A heat anomaly of perhaps 5–10°C could originate from TSR, if the reactions are exothermic and as long as TSR is occurring. However, the little heat that could be generated quickly dissipates. Hence, a temperature anomaly in a sour gas pool measured today would indicate that TSR is occurring at present or has ceased very recently (less than about 160 years ago). Alternatively, the measured temperature anom-

ally could be unrelated to TSR but caused by hydrodynamics (hot formation waters flowing upwards relatively rapidly), or by increased heat flow (from the basement).

Both BSR and TSR can be represented by a single set of simplified mass and charge balanced reactions that contain various organic compounds and dissolved sulfate as reactants, and that yield H_2S , CO_2 , carbonates, elemental sulfur and metal sulfides as the main products or by-products. The reactive organic compounds differ for BSR and TSR, with aerobic biodegradation and thermal maturation yielding reactive organic compounds for BSR and TSR, respectively.

The relative amounts of the products of BSR and TSR vary widely and are determined by a number of locally variable factors, including availability of reactants, formation water chemistry, and wettability. The amounts of water released during TSR are likely to be very small and, in most cases, negligible. It is not clear at this time, however, whether there are any reservoirs where the amounts of water formed are of more than local significance. Porosity can be produced, directly or indirectly, via TSR. However, it appears that in most locations porosity generation as a result of TSR is relatively minor, and there are no known examples of gas/oil pools that owe their existence to secondary porosity produced by TSR. Most solid products of BSR and TSR, although similar in gross composition, can be distinguished petrographically and, in some cases, geochemically (isotopes, fluid inclusions). The sizes and locations of TSR zones are governed by the necessity of physical contact between hydrocarbons and sulfate, and by the fact that sulfates do not react in the solid state. Where the irreducible water saturation is low, TSR is likely to take place in fairly narrow reaction zones, in one well known case about 10–20 m thick. However, where the irreducible water saturation is high, TSR may take place throughout an entire gas column.

The mere presence of any of the above reaction products does not permit discrimination of BSR from TSR. Petrographic relationships may be sufficient to establish paragenetic relationships, but additional stable isotope and gas-chromatographic data are

often needed. The compositions of kerogens, crude oils, condensates, solid bitumens, and minerals formed by BSR and/or TSR, offer a plethora of criteria for discrimination among genetic processes. In particular, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, elemental, and chromatographic analysis can be used to differentiate products of BSR from TSR as well as from related processes, such as thermal maturation.

Acknowledgements

I wish to thank many colleagues, especially Roy Krouse, Roger Sassen, and Julia Foght, for numerous discussions over the last 15 years that have sharpened my understanding of BSR and TSR. The constructive reviews of this paper by Ian Hutcheon, Pat Cavell, and an anonymous reviewer are much appreciated. Funding was provided by the Natural Science and Engineering Research Council of Canada (NSERC), MOBIL Canada, AMOCO Canada, and the Alexander von Humboldt Foundation.

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