

Sulfur-rich (Type II-S) source rocks and associated hydrocarbons

by Laura Garner

Sulfur-rich source intervals are associated with organic sulfur contents greater than 1% (Waldo *et al.*, 1990) and an atomic S/C >0.04. Sulfur content can be an important bulk parameter for interpretation, not only for correlating crude oils to their parent source rocks, but also to evaluate the viability of a discovery/field in economic terms.

Formation of sulfur-rich source rocks

Most primary sulfur in petroleum systems originates from early diagenetic reactions between deposited organic matter and aqueous sulfide species (Peters *et al.*, 2005). In environments where anoxic (low oxygen) conditions prevail, specific species of anaerobic microorganisms (sulfate-reducing bacteria) use the sulfate (SO_4^{2-}) within the water body to oxidise organic molecules, producing hydrogen sulfide (H_2S). Within siliclastic depositional environments, where dissolved iron species are usually in high abundance, the metals can remove the H_2S by the formation of iron monosulfides (FeS , and ultimately iron pyrite (FeS_2), resulting in low-sulfur kerogens and hydrocarbons. However, in less clastic facies such as carbonate muds for example, the low concentration of dissolved iron inhibits the removal of H_2S as iron sulfides, and the excess sulfide becomes incorporated into the kerogen. Lacustrine environments may contain sulfur-rich Type I and IIS kerogens, but these are generally not widespread, as such environments usually do not contain enough sulfate for the bacteria to utilise. The Miocene Monterey Formation in California is an extreme example of a euxinic marine source rock, with kerogen containing between 8-14 wt.% chemically bound sulfur (Baskin & Peters, 1992). It is this source interval that led Orr (1986) to propose a new 'Type II-S' kerogen.

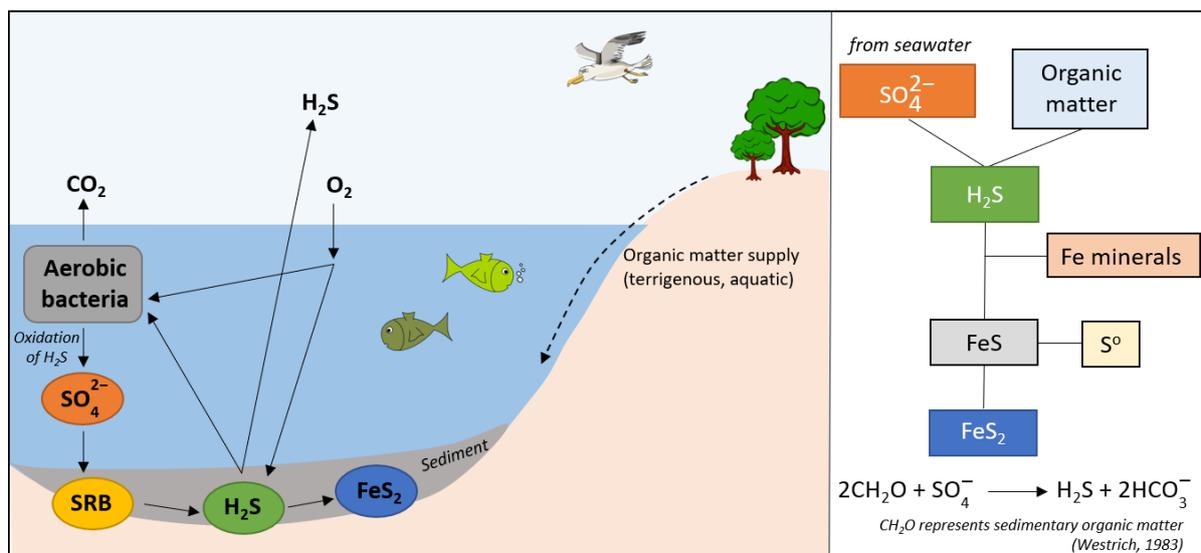


Figure 1: Model of sulfate reduction by sulfate-reducing bacteria and conversion of hydrogen sulfide into iron pyrite (SRB = sulfate-reducing bacteria). Image taken from ig.NET (IGI, 2019)

Low maturity petroleum generation and character

Sulfur-Sulfur (S-S) and Carbon-Sulfur (C-S) bonds are abundant in high sulfur kerogens and are more prone to cleavage at lower temperatures than Carbon-Carbon (C-C) bonds. This results in sulfur-rich source rocks generating petroleum at lower maturities than other kerogens (Martin, 1993). This corresponds to a shift in the average activation energy distribution (Figure 2) from a higher range (taking more energy to begin the chemical reaction) in a typical Type II kerogen (predominantly 52-55 kcal/mole) to a lower range of 48-51 kcal/mole for a Type II-S kerogen. It is also hypothesized by Lewan (1998), that the formation of active sulfur radicals generated during the initial stages of thermal maturation is the main controlling factor on increased petroleum formation rates, rather than the relative weakness of C-S bonds.

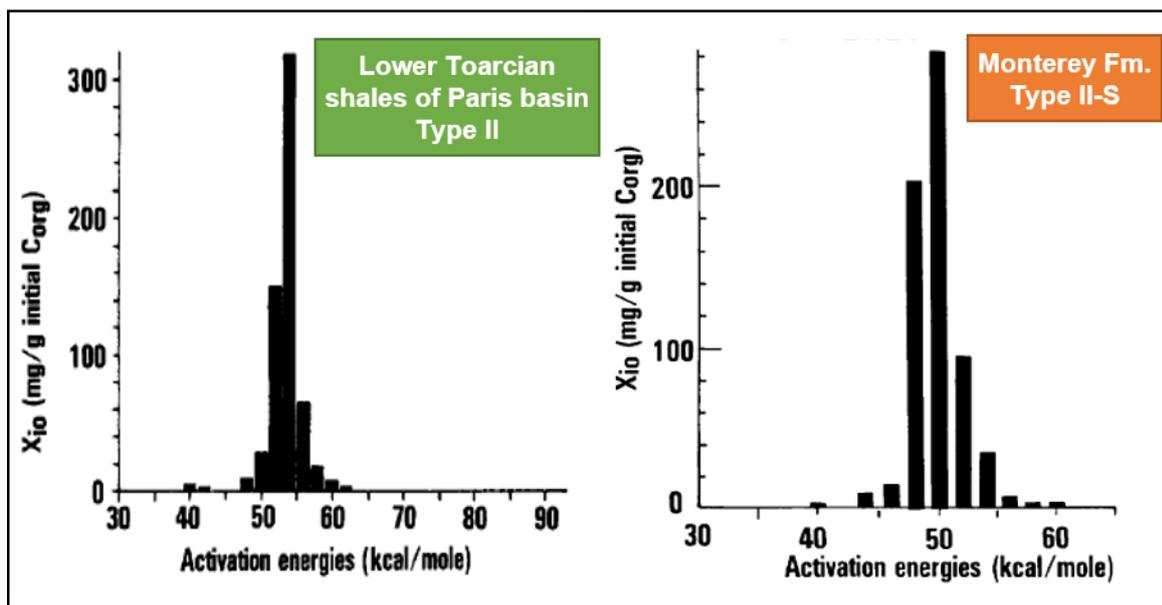


Figure 2: Distributions of activation energies for Type II and Type II-S kerogens (based upon Rock-Eval pyrolysis data (Tissot *et al.*, 1987))

The initial oil expelled will have the maximum sulfur content, with sulfur content decreasing with increasing source rock maturity as a result of dilution by further generation of non-sulfur compounds (Orr & White, 1990). Most sulfur in crude oils is organically bound (bound to carbon) and such organo-sulfur compounds are usually the most abundant NSO compounds in petroleum. In hydrocarbons expelled from Type IIS kerogens, the oil may contain in excess of 40% NSO compounds (Peters *et al.*, 2005). Organically bound sulfur compounds in petroleum can be subdivided into several chemical groups:

Chemical Group	Occurrence
Thiols	Abundant when high maturity condensates react with H ₂ S
Disulfides	Occur primarily in high-maturity condensates, and are generally alkylation products of thiols
Thiaalkanes	Normal branched alkyl compounds that contain a single sulfur atom within the structure (sulfur is commonly incorporated in these molecules during early diagenesis)
Thiacycloalkanes	Contains a single sulfur atom incorporated in a cycloalkyl structure, compounds generally form during early diagenesis
Thiophenes	Five-member unsaturated ring containing one sulfur and four carbon atoms (behave like aromatic hydrocarbons)
Benzothiophenes, dibenzothiophenes and polynuclear thiophenes	Have a thiophene unit condensed with one or more aromatic rings and behave chemically like aromatic hydrocarbons. Aromatic sulfur compounds are usually the most abundant class of non-hydrocarbons in crude oils.

Figure 3: Chemical groups of organic sulfur compounds in oil (taken from Peters et al., 2005)

High sulfur-oils are relatively undesirable for the industry as they can typically be very heavy and viscous (due to the early-mature nature of the expelled fluids), and thus, difficult and costly to refine. Sulfur species are also poisonous for all catalytic processes. These can be temporary, although the full effects can be permanent depending on process conditions (Grove, 2003). In addition, the reduction in sulfur oxide emissions from the energy production and distribution sector is a key target for environmental agencies. However, due to the large resources of heavy, sulfur-rich oils around the world, and as conventional, light-oil accumulations gradually become depleted, there may be a requirement to gain further insight into the most productive and environmentally friendly way to exploit these crudes.

References

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