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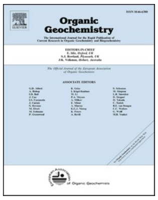

Discussion

Comment: Suppression of vitrinite reflectance by bitumen generated from liptinite during hydrous pyrolysis of artificial source rock by Peters et al. (2018)

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ABSTRACT

Peters et al. (2018) provide new hydrous pyrolysis data in defining the coal-reflectance and the suppressed-reflectance trends that source rocks may follow during their thermal maturation. The difference in the two trends is between hydrous pyrolysis temperatures of 300 to 360 °C for 72-hour durations. As implied in their title the suppressed-reflectance of vitrinite is a result of bitumen generation from liptinite during hydrous pyrolysis. Their experimental results do show that coal reflectance is lower when mixed with isolated liptinite encased in G-class Portland cement. However, there are published and omitted experimental data that they did not include in their interpretations. These are addressed as concerns and include early experiments of mixtures of Liptinite in source rocks mixed with coal that do not show a reduced reflectance of the coal. Earlier publications show that some source rocks with oil-prone Type-II kerogens also follow the suppressed-reflectance trend. Resinites did not cause reductions in coal reflectance. The validity of using G-class Portland cement as an artificial rock is not established and is unlikely to be an appropriate representative of natural shales. Reflectance suppression by free radicals are also feasible and more research is needed to better define the causes of the suppression.

1. Discussion

For the purposes of this discussion of Peters et al. (2018), two previously determined reflectance trends related to thermal stress induced by hydrous pyrolysis are discussed. One is the coal-trend and the other is the so-called suppressed-trend or solid-bitumen trend, which shows increases in reflectance less than that of the coal-trend with increasing hydrous pyrolysis temperatures (Fig. 1). The objective of this comment is to examine the data by Peters et al. (2018) in a broader context of previously and unreported hydrous pyrolysis data on the two reflectance trends. This discussion is not intended to be a review of the suppressed vitrinite topic, but rather a discussion of eight major concerns with Peters et al. (2018) that are discussed as follows.

As stated in the title of Peters et al. (2018), the suppressed-reflectance trend is a result of bitumen generated from the thermal maturation of liptinite, which may be classified as Type-I kerogen. The mere presence of bitumen does not appear to be the cause of the suppression. Instead, Peters et al. (2018) speculate that free radicals generated during thermal maturation of liptinite contribute to termination reactions that slow aromatization and rearrangement of polyaromatic sheets in vitrinite resulting in suppression of reflectance. Although the reflectance of vitrinite associated with Type-I kerogen does typically follow the suppressed-reflectance trend as also shown by hydrous pyrolysis of the Type-I kerogen bearing Brazilian Batateira Bed source rocks (Spigolon et al., 2015) plotted in Fig. 1A (i.e., solid red circle symbols). However, experimental results presented by Barker et al (2007) concerning the influence of bitumen on suppression of reflectance do not support the conclusion that bitumen is a likely causes of significant suppression of reflectance as implied by the subject paper's title. In addition, experimental work by Huwang (1996) and MacFarland (1981) concerning the influence of generated oil on suppression of reflectance also indicate that generated oil does not cause significant suppression of reflectance. However, high-hydrogen contents do appear to be associated with the suppressed-reflectance trend (Faiz et al. (2021).

Early hydrous pyrolysis experiments (HP-3838 through HP-3841) acknowledged but omitted by Peters et al (2018) showed that a rock containing Type-I kerogen mixed with coal at a similar 1 to 1 carbon ratio showed no suppressed reflectance (Hackley et al., 2023), but the reported experiments by Peters et al (2018) using isolated Type-I kerogen mixed with coal in a similar carbon ratio did show suppressed reflectance as they reported. This is interesting because their

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petrographic examination showed no apparent contact between the isolated Type-I kerogen and the coal or the presence of generated bitumen. Why were these early informative results omitted by Peters et al. (2018)? These are significant observations for future researchers to be aware of and to consider in subsequent experimental studies. It would also prevent confusion and unnecessary discussion by other investigators that may inadvertently use rock bearing liptinite rather than isolated liptinite.

Peters et al. (2018) briefly mentions earlier work by Lewan (1985 and 1993) but ignore the findings with respect to the suppressed reflectance trends observed in hydrous pyrolysis experiments of Type-II kerogen bearing source rocks (Fig. 1A). Lewan (1985) showed the suppressed-reflectance trend for Type-II kerogen in the Woodford Shale and for Type-IIS kerogen in a Phosphoria source rock (Fig. 1A). The association of Type-II kerogen with the suppressed-reflectance trend was also established by Price and Barker (1985) with natural data for the Type-II bearing kerogen of the Bakken shales in the Williston Basin. The Alum Shale with Type-II kerogen also followed the suppressed reflectance trend (Buchardt and Lewan (1990). Although the suppressed-reflectance trend was also associated with oil-prone Type-II kerogens showing suppression of reflectance is not exclusive to Type-I liptinite kerogens. A major exception to oil-prone Type-II kerogen bearing source rocks associated with the suppressed-reflectance trend was noted by Lewan (1993) for the Cretaceous Mowry Shale, which is the source of major oil accumulations in lower Cretaceous reservoirs of the Powder River Basin (Anna, 2010 and references there in). Lewan (1993) observed that the reflectance measurements of the oil-prone Mowry shale did not follow the suppressed-reflectance trend, but followed the coal-reflectance trend along with the overlying concentrated vitrinite of the Frontier coal and the dispersed vitrinite in the underlying Skull Creek Formation, which were also subjected to hydrous pyrolysis (Fig. 1B and 1C). Sometimes it is the exceptional cases or anomalies like the Mowry Shale in this case, that provide the insights that advance the understanding of an issue (Sturrock, 2007 and references there in). More detailed studies on the Mowry Shale reflectance trend are warranted. It remains unclear why this hydrous pyrolysis data by Lewan (1993) was ignored by Peters et al (2018) with emphasis only on liptinite as a cause of the suppressed-reflectance trend.

Suppressed reflectance in source rocks that have generated bitumen and expelled oil in hydrous pyrolysis occurs and was not addressed or mentioned by Peters et al. (2018). As previously noted, bitumen and oil do not appear to be the likely causes of the suppressed reflectance trend (Barker et al., 2007, Huwang (1996), and MacFarland, 1981, Price and Barker, 1985). The unlikelihood of oil causing the suppressed-reflectance trend is also evident in the hydrous pyrolysis experiments conducted on the Wilcox lignite and the Blackhawk Hiawatha coal. Both follow the coal-reflectance trend (Fig. 1A) and both generate bitumen and expel an oil. The Blackhawk coal from the King Coal mine in Utah generated oil (Lewan, 1985; 1990), which does not appear to suppress the reflectance of its vitrinite. Similarly, the lignite of the Tertiary Wilcox Formation, which is known to be a source of commercial waxy oils in the Gulf Coast (Philippi, 1974), and shown to generate an expelled waxy oil and bitumen during hydrous pyrolysis (Behar et al., 2003), does not follow the suppress-reflectance trend, but follows the coal-reflectance trend (Fig. 1A).

Peters et al. (2018) extend the effects of suppression by liptinite to other types of exinites including resinites. The Blackhawk Hiawatha coal seam from the King coal mine in Utah is enriched in resinite in sufficient quantities to be concentrated from the coal, by a froth-flotation process at the mine site as a commercial by-product (Tabet et al., 1995). The resinite concentrates contain minor amounts of coal-vitrinite impurities. Upon hydrous pyrolysis of these resinite concentrates, Lewan and Williams (1987) showed that during hydrous pyrolysis there was no suppression of reflectance of the minor vitrinite impurities in the resinite concentrates and that the reflectance followed the coal-reflectance trend.

It is also disconcerting that Peters et al. (2018) assume that the G-class Portland cement they encase the kerogen/coal mixtures is representative of natural shales. G-class Portland cement is made by heating limestone and clay minerals to temperatures as high as high as 1,450 °C forming a sintered material (i.e., a clinker), which is ground to a powder composed mostly of calcium silicates and calcium aluminates (Binici et al.2008; Broekmans and Pöllmann, 2012), which are high-temperature mineral assemblages not common in natural shales. In addition, they also lack shale textural fabrics as observed in the photomicrographs shown by Peters et al. (2018) compared to those observed during natural and hydrous-pyrolysis induced thermal maturation of source rocks (Lewan, 1987). Portland cements can also induce high alkalinities to contacted water. Chromkova and Čechmanek, (2018) report that Portland cement can raise the pH of distilled water from 5.6 to 12 within 14 days. The typical pH of recovered water from hydrous pyrolysis experiments of natural shales is between 5.8 and 7.2 (Lewan,

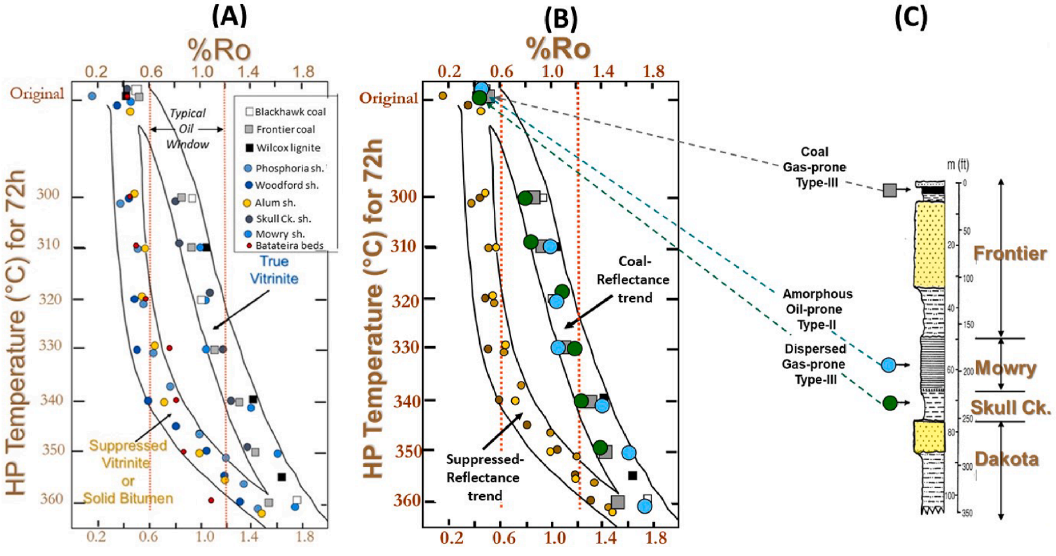

Fig. 1. (A) Relationships between reflectance readings at various hydrous pyrolysis temperatures after 72 h from Lewan, 1993 with data from Lewan, 1985, Buchardt and Lewan, 1990; and Spigolon et al., 2015); (B) Same as A but highlighting the relationships from Lewan (1993) for the samples from the Steinaker Mowry section in Utah. (C) composited generalized section showing stratigraphic position of samples collected along transit of outcrops on or near Highway 191 north of Vernal, Utah.

1997). Schumacher et al. (1960) showed through experimentation that pH of waters had an effect on the hydrogen content of artificial coalification. In particular, cellulose residues were shown to become enriched in hydrogen as the pH of the accompanying experimental water increased and only under acid conditions wood and cellulose approach the vitrinite track under artificial coalification. Making an artificial shale is desirable to control and study the effects of different mineral assemblages and their proportionalities, but requires a more rigorous and thoughtful effort. Luan et al. (2016) made artificial shales with geophysical properties similar to natural shales in an elaborate process. Peters et al. (2018) never establish that the Portland cement plugs before and after hydrous pyrolysis simulate petrographic textures, mineral assemblages, or geochemical properties resembling those of natural shales. The earlier hydrous pyrolysis experimental data by Hackley et al. (2023) also show that the vitrinite measurements in hydrous pyrolysis experiments at 330 °C for 72 h showed that the coal not encased in Portland cement (HP-3841) followed the coal trend with a vitrinite measurement of 1.2 %VR_o, but the same coal encased in Portland cement at 330 °C for 72 h (HP-3841) in the Portland cement had a significantly reduced measured reflectance of 0.9 ± 0.1%VR_o, which indicates that the Portland cement does suppress vitrinite reflectance intermediate to the coal- and suppressed-reflectance trends. Although the high pH induced to the hydrous pyrolysis water may be the cause, more study of the effects of Portland cement are required before it can be considered an appropriate substitute for natural shales.

Another concern is that Peters et al. (2018) observed convergence of the suppressed-reflectance and coal-reflectance trends to occur at 350 °C after 72 h and suggests that this convergence at this condition supports their interpretation that free radicals are the cause of the suppressed-reflectance trend, because of insufficient capacity to continue to generate radicals to further suppress vitrinite reflectance. However, published hydrous pyrolysis studies on Type-I kerogen bearing Brazilian Batateira bed and Green River source rocks show that oil generation does not cease at 350 °C for 72 h (Spigolon et al., 2015, and Ruble et al. 2001, respectively) as suggested by Peters et al. (2018). The hydrous pyrolysis studies on the Brazilian Type-I and Green River source rocks (Spigolon et al., 2015, and Ruble, 2001, respectively) show that oil and possibly associated free-radical generation continues up to 360 °C after 72 h as oil generation from thermal decomposition of bitumen continues. Again, these differences may be a result of using G-class Portland cement instead of natural rock, but this difference is not addressed by Peters et al. (2018).

It is enigmatic that the second author in Peters et al (2018) in an earlier paper (Hackley and Lewan, 2018) suggests the cause of the suppressed-reflectance trend may be the result of steric hindrance of the condensation of aromatic clusters by aliphatic functional groups resulting in suppressed reflectance. These authors suggest that this steric hindrance is a cause of the suppressed-reflectance trend until the aliphatic side chains are cracked from or crosslinked and aromatized into the aromatic clusters, resulting in the suppressed-reflectance trend converging with the coal-reflectance trend. This convergence starts as the intermediate bitumen is thermally cracked into a hydrocarbon-rich oil as described by Lewan (1985). Peters et al. (2018) speculate that the cause of the suppressed reflectance trend may be a result of aliphatic functional groups, but it is due instead to the free radicals generated by their cleavage of aliphatic groups that cause the suppressed reflectance trend by terminating reactions involved with aromatization and condensation of aromatic clusters related to reflectance. Once these aliphatic functional groups are cleaved and no more free radicals are formed at higher thermal maturities and temperatures, the resulting suppressed-reflectance trend converges with the coal-reflectance trend. More studies on whether free radical or aliphatic steric hindrance are responsible for reflectance suppression are needed. The loss of aliphatic functional groups is essential to both hypotheses with the one proposed by Hackley and Lewan (2018) caused by diminished steric hindrance of the aliphatic chains and that of Peters et al. (2018) caused by generating free radicals that hinder aromatization and condensation of the aromatic clusters. The free radical mechanism speculated by Peters et al. (2018) is conceivable, with concentration of generated free radicals from copyrolysis of coal and oil shale contributing to termination reactions that slow the aromatization and rearrangement of polyaromatic sheets in vitrinite and presumably resulting in a suppressed reflectance. In the excellent review of copyrolysis of coal and oil shale mixtures by Liu et al. (2020), free radicals generated from the oil shale do appear to inhibit polycondensation, which could be associated with a suppressed-reflectance. However, the temperatures at which free radicals are generated from the oil shale and coal are much higher than those associated with suppressed reflectance in hydrous pyrolysis (i.e., 300 to 360 °C). Li et al. (2020) cites that significant changes observed in copyrolysis experiments of coal and oil shale mixtures occur at 510 °C as cited by He (2006), and 400 to 550 °C as cited by Wang (2014). These high temperatures are beyond the range of the temperatures observed in hydrous pyrolysis for the suppressed-reflectance trend. Experimental work by Qui et al. (2012) is especially relevant in that these authors measured radical concentrations of pyrolyzed Type-I, -II, and -III kerogens with electron spin resonance spectroscopy (ESR). They reported maximum radical concentrations (N_g x10^{18} spins/gram) for Type-I kerogen to be 1.58 ± 0.22 at 450 °C after 180 min and an equivalent vitrinite reflectance of 2.07%. For Type-II kerogen the maximum radical concentration (N_g x10^{18} spins/gram) of 2.78 ± 0.22 occurs at 400 °C after 120 min and an equivalent vitrinite reflectance of 1.21%. Maximum radical concentrations for Type-III kerogen in coals is the highest at 6.14 ± 0.08 X10^{18} spins/g at 450 °C after 30 min and an equivalent vitrinite reflectance of 1.41%. Qiu et al. (2012) also shows that the radical concentrations for Type-II and -III kerogens are typically greater than that of Type-I kerogen at vitrinite reflectance values less than 1.21% and that free radical concentrations from Type-III kerogen in coals are consistently higher by a factor greater than 2 from vitrinite reflectance of 0.28 to 3.96. Therefore, the applicability of a free radical mechanism for suppression of reflectance needs further study based on actual measurements of radical concentrations measured by ESR spectroscopy rather than speculation or interpretive inferences (Peters et al., 2018). Both the aliphatic steric hinderance and free radical mechanisms can account in part for the suppressed-reflectance trend and the convergence of the suppressed-reflectance trend with the coal-reflectance trend. It is possible that both mechanisms are responsible and more spectroscopic studies are needed as suggested by Sanders et al (2022).

In conclusion, the causes that determine whether a source rock follows either the coal- or suppressed-reflectance trends is not exclusively the result of the presence of liptinite (Type-I) kerogen and more research as advocated in this discussion and that by Sanders et al. (2022) is needed. Although hydrogen content does appear to be a critical ingredient causing the suppressed-reflectance trend (Faiz et al. (2021), the specific mechanisms by which hydrogen causes suppressed reflectivity needs to be better understood. However, hydrous pyrolysis of immature source rocks at 330 °C for 72 h is a reliable method to determine, which of the two reflectance trends a source rock is likely to follow. This can be especially important in modeling burial temperature histories to determine timing and extent of oil and gas generation in an active pod of source rock of a petroleum system.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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