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Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th birthday

EFFECTS OF MINERALS ON ROCK EVAL PYROLYSIS OF KEROGEN

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To define the effect of common sedimentary minerals on pyrolysis of kerogen, previously separated and purified kerogen concentrates of alginite, amorphous liptinite and vitrinite were mixed with the following minerals: quartz, calcite, pyrite, limonite, kaolinite, bentonite and illite in various kerogen to mineral ratios. Rock Eval pyrolysis of these mixtures which contain 0.5 to 6.6% organic carbon show systematic variations in the parameters; hydrogen index, oxygen index, production index and T_{max} and also in the amount of organic carbon consumed during the process. The variations for a given kerogen depend on the type of mineral and its proportion in the mixtures. The results of Rock Eval pyrolysis reflect the effect of the mineral matrix on the pyrolysis process of the sedimentary organic matter and its products. These effects are probably different from those caused by the same mineral during the natural oil and gas generation process. However, these analytical phenomena have to be recognized and accounted for in the interpretation of pyrolysis results.

Pyrolysis methods have become popular among geochemists and explorationists for the characterization of source rocks for oil and gas, oil shales and coals. The open system, anhydrous rapid pyrolysis (Rock Eval type) provides information on the yield of hydrocarbons at low temperature, yield of hydrocarbons during the programmed heating to high temperatures, yield of carbon dioxide of organic origin and the pyrolysis temperature at maximal hydrocarbon generation. These results are interpreted in terms of properties of the organic matter: free hydrocarbons, residual potential of the organic matter to generate hydrocarbons at higher maturity, type of organic matter and its maturity. Analogies were drawn between pyrolytic products of low temperatures regarded as free hydrocarbons and the solvent extractable or bitumen fraction of the organic matter and between the yield of hydrocarbons generated at elevated temperatures and the insoluble part

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of the organic matter, kerogen. Asphaltenes deviate from this scheme being extractable but pyrolysing in a temperature range overlapping with that of the kerogen. Correlations were established between the gross elemental composition (C, H, O) of sedimentary organic matter and the yield of hydrocarbons and carbon dioxide, thus providing an alternative to the tedious procedure of kerogen separation for elemental analysis. These features established this type of rapid method as screening tool and also as a method useful for detailed studies of sedimentary organic matter [1–8].

The mineral matrix was recognized as affecting the results of pyrolysis especially at high ratios of mineral to organic matter. Under these conditions the relative amount of hydrocarbons generated at high temperature decreases [5, 8, 9] and the relative amount of CO_2 seems to increase [5, 10]. Changes in the ratio between the quantities of product generated at low temperatures and at high temperatures of pyrolysis were observed in samples containing clay minerals [8, 11], while a change in the pyrolysis temperature of maximal hydrocarbon yield from nC_{20} alkane admixed with various minerals was observed by Dembicki *et al.* [12]. It seems therefore that the analytical results of this type of pyrolysis procedures are due to reactions of the organic matter which are not only thermally controlled but are affected by the mineral components. These latter effects are the subject of the present study. The effects observed with increasing proportion of the mineral components are studied for each one of seven different minerals which (apart from limonite) occur in source rocks. Three purified and homogeneous kerogen concentrates are used, which represent the three major kerogen types in source rocks. The study is focussed on kerogen as it represents the bulk of the organic matter in source rocks. The use of purified kerogen precludes the effects of bitumen on the pyrolysis procedure and results.

This comparative study, which uses three kerogen types and seven common sedimentary minerals admixed in various ratios, should demonstrate the specific effects of these variables on pyrolysis results and in turn assist in the interpretation of results of source rock pyrolysis.

Experimental

Kerogen concentrates were prepared from powdered rock samples by dissolving the carbonate minerals with 1N HCl and subsequently the silicate minerals with 48% HF. The residue was exhaustively extracted with methylene chloride using the modified flow blending technique [13]. The kerogen concentrate was further purified by heavy liquid centrifugation with aqueous CdI_2 solution of 1.95 g/ml density. The supernatant was filtered and subsequently fractionated by centrifugation with CdI_2 solutions of various densities.

In the present study three kerogen concentrates representing organic matter in source rocks of slightly different maturity levels (% R_o) were analysed: alginite from the Green River Formation (type I), (0.3% R_o), amorphous liptinite from the Irati Shale (type II), (0.5% R_o) and vitrinite from Madagascar (type III), 0.6% R_o. The samples used for the pyrolysis experiments contain more than 95% of the respective maceral as identified by transmitted and reflected white light and fluorescence microscopy.

Seven minerals were used: quartz, calcite, pyrite, limonite and the clay minerals; kaolinite, bentonite (montmorillonite) and illite. The minerals were sieved to pass 200 mesh. Their organic carbon content is less than 0.01%. The kerogen concentrates were mixed with the minerals in a mortar and a mixture of 1:10 wt:wt kerogen:mineral was prepared. Aliquots of these mixtures (except pyrite) were further diluted by addition of the respective minerals in the following ratios 1:1, 4:1 and 10:1. However, the actual content of organic carbon was determined in a Leco Carbon Analyzer. The content of organic carbon ranges between 0.5 and 6.6% in the four kerogen-mineral mixtures prepared from each kerogen and mineral. Results from pure kerogen concentrates are not presented as the analytical reproducibility is poor. This is probably due to small variations in the position of the sample material in the crucible and effects of the gas flow in the system designed for larger samples. As the content of organic carbon in the minerals (before mixing) is less than 2% of that of the kerogen mineral mixtures with the lowest C_{org} content and in view of the objectives of this study the possible effects of the trace amounts of the original organic matter present in the minerals [14] were not regarded as having a significantly quantitative effect on the pyrolysis results.

Pyrolysis was performed in a Rock Eval II (Geocom) using the standard procedure:

1) isothermal hold at 300° for 3 min yielding hydrocarbons included in the S_1 response.

2) heating to 550° at 25 deg/min yielding hydrocarbons included in the S_2 response.

3) isothermal hold at 550° for 1 min.

The evolved CO_2 was trapped between 300 and 390° yielding S_3. S_1 and S_2 have a reproducibility of ±5%, S_3 of 10% and T_{max} ±1°. After pyrolysis the residue was transferred to a Leco crucible for the determination of the residual organic carbon.

Results

Analytical pyrolysis of mixtures of kerogen and minerals gave rise to pyrograms having the following features. All programs show significant S_1 responses. This indicates that the kerogen concentrates of alginite, amorphous liptinite and vitrinite yield small amounts of hydrocarbons during pyrolysis at temperatures as low as 300 °. The S_2 responses are sharp for alginite and amorphous liptinites in contrast to vitrinite-mineral mixtures for

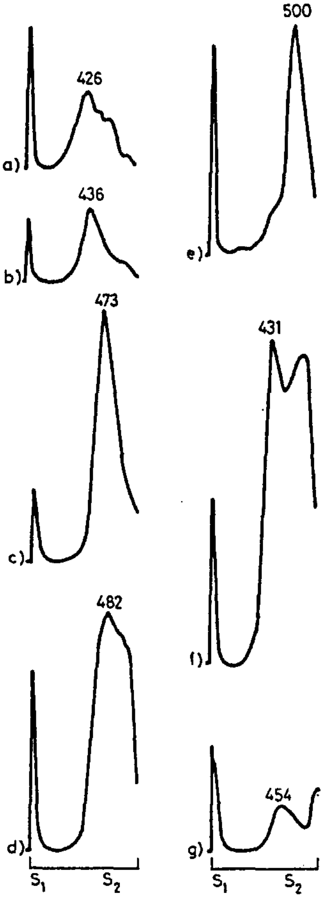

Fig. 1 Rock Eval pyrograms of mixtures of vitrinite with various minerals. The mixtures contain between 6.0 and 6.6% C_{org} *a*) pyrite *b*) calcite *c*) kaolinite *d*) bentonite *e*) illite *f*) quartz *g*) limonite

which it varies. The S_2 responses of the vitrinite-mineral mixtures are generally broad and have different profiles for the different mineral mixtures. This feature is particularly prominent for illite, bentonite and limonite. The pyrograms recorded from mixtures containing high proportion of vitrinite (6.0 –6.6% C_{org}) are shown in Fig. 1.

The results of analytical pyrolysis of kerogen concentrates of algae, amorphous liptinites and vitrinite mixed with quartz, kaolinite, bentonite, illite, calcite, limonite and pyrite are summarized in Figs 2, 3 and 4. These figures show the variation in the Hydrogen Index (*HI*), organic carbon consumed (C_{con}), temperature of maximal hydrocarbon generation T_{max}, Production Index (*IP*) and Oxygen Index (*IO*) *vs*. the content of organic carbon in the mixture. Alginite (type I kerogen), (Fig. 2) shows a systematic increase of the hydrogen index with increasing C_{org} for illite, bentonite, and limonite, while mixtures with quartz, calcite and kaolinite show this trend with a smaller effect, however. The difference between hydrogen index values of mixtures of various minerals with similar quantities of a single type of kerogen is significant. The variation in the proportion of organic carbon consumed during pyrolysis (C_{con}) shows the following features: consumption is high for quartz and calcite and does not show a systematic relationship with C_{org}. For kaolinite and illite the overall consumption is lower and increases with C_{org}. The behaviour of limonite has the opposite trend. Pyrite falls in the middle of that range for that level of C_{org}. These results demonstrate that whereas around 70–80% of the organic carbon is pyrolysed in the presence of calcite and quartz almost irrespective of its concentration, in the presence of kaolinite, bentonite and illite the proportion of pyrolysed organic carbon is lower. This effect is more pronounced in mixtures with low C_{org}. These results suggest that minerals affect the efficiency of the pyrolysis process. T_{max} varies in these mixtures between 430 and 470°. Illite and calcite mixtures give rise to higher temperatures than quartz and kaolinite. The variation in the production index (*IP*) shows two features: high values for limonite which increases at low C_{org} concentrations and a weaker trend of increase for bentonite, illite and kaolinite at low concentrations. The oxygen index (*IO*) is regarded as a measure of organic oxygen. The values of *IO* for limonite are higher than those of other minerals and are probably due to oxidation of the organic matter. The values for calcite are also high but show only a small variation with concentration of organic matter. Quartz and kaolinite show low values irrespective of C_{org} while illite and kaolinite show a slight increase towards low C_{org} levels.

The amorphous liptinite-mineral mixtures show in general the same features as the alginite-mineral mixtures. Notable are the strong decrease in *HI*

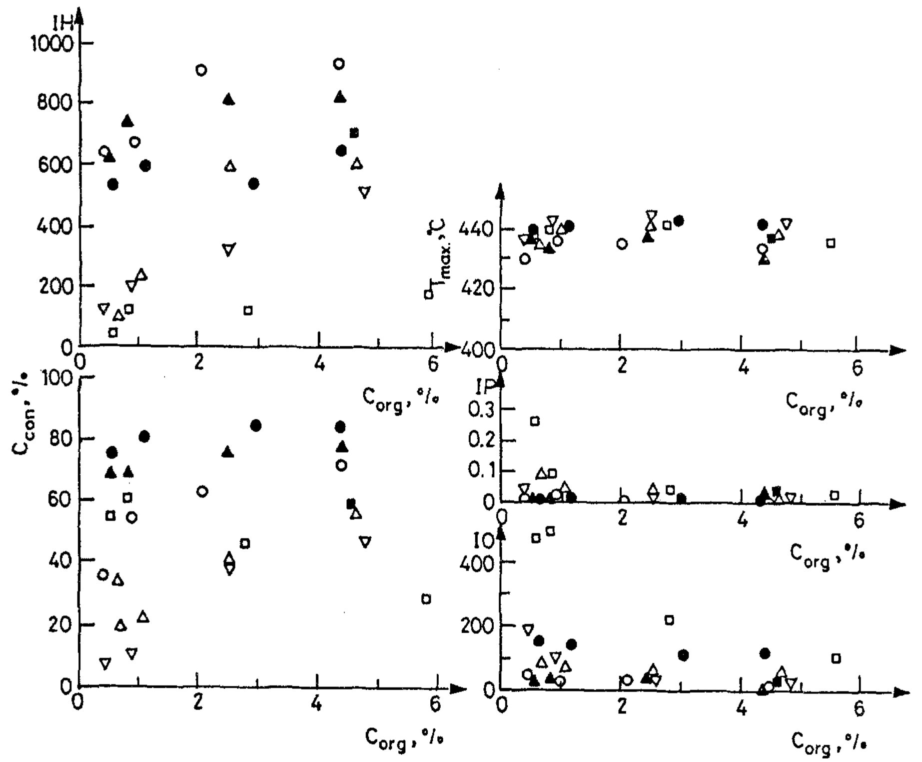

Fig. 2 Results of Rock Eval pyrolysis of mixtures of alginite with quartz ▲, kaolinite o, bentonite Δ, illite ∇, calcite •, limonite □ and pyrite ■. Note the variation of the pyrolysis parameters; Hydrogen Index (*IH*), temperature of maximal pyrolysis (T_{max}), Production Index (*IP*) and Oxygen Index (*IO*) as well as the proportion of organic carbon consumed during the experiment (C_{con}) as function of the organic matter content (C_{org})

and C_{con} for illite and bentonite with decrease in C_{org}. The spread of T_{max} is slightly larger (20°) and the features of *IP* and *OI* are even more pronounced than for the mixtures of alginite.

The vitrinite-mineral mixtures give rise to yet other results. The variation in *IH* shows a systematic decrease with decreasing C_{org} for all minerals. This effect is most pronounced for kaolinite, quartz and bentonite. The proportion of C_{con} is much lower than for alginite and amorphous liptinite in the different mixtures. Bentonite mixtures show lower values than quartz, calcite and limonite. The variation in T_{max} covers a large range of over 120 °. The variation follows the mineral composition whereby bentonite gives rise to the highest temperatures followed by illite, kaolinite, limonite, quartz, calcite and pyrite. The production index increases towards low levels of C_{org} for all minerals except calcite. The oxygen index varies in a manner similar to that observed for other maceral types i. e. systematic increase at

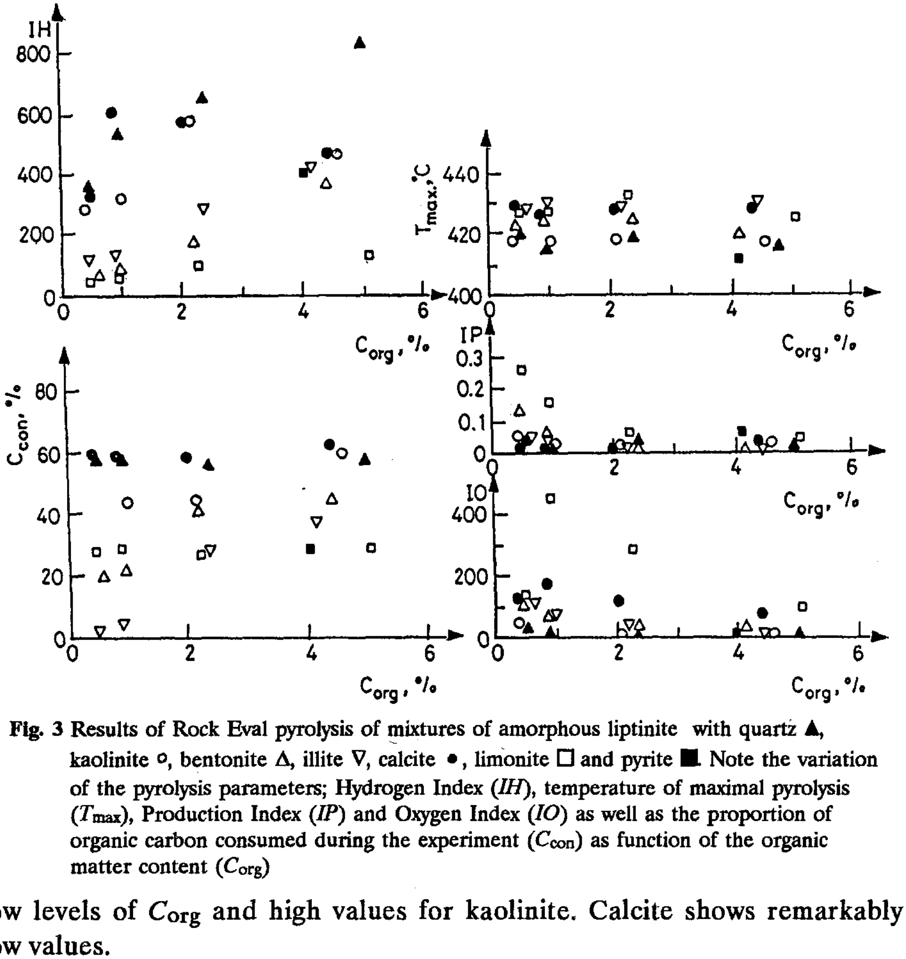

Fig. 3 Results of Rock Eval pyrolysis of mixtures of amorphous liptinite with quartz ▲, kaolinite ○, bentonite Δ, illite ∇, calcite •, limonite □ and pyrite ■. Note the variation of the pyrolysis parameters; Hydrogen Index (*IH*), temperature of maximal pyrolysis (T_{max}), Production Index (*IP*) and Oxygen Index (*IO*) as well as the proportion of organic carbon consumed during the experiment (C_{con}) as function of the organic matter content (C_{org})

low levels of C_{org} and high values for kaolinite. Calcite shows remarkably low values.

Discussion

The trends observed in the pyrolysis result for kerogen-clay mineral mixtures suggest that pyrolysis products are retained on the large active mineral surfaces [8–10].This was confirmed by the inverse trend observed for the amount of organic carbon consumed. This retention effect is related to the type of mineral and probably to other properties (e.g. specific area, crystallinity. The retention effect of the minerals are combined with the properties of the pyrolysis products with give rise to the observed systematic variations. The pyropoducts from vitrinite are probably richer in polar and aromatic compounds as compared with the products from alginite; consequently the variation reflects the stronger effect of minerals on the mobility of pyropoducts of vitrinite as compared with the other maceral types. These results and interpretation add to the large body of literature on mineral-organic matter interaction notably, Spiro [15], Huizinga *et al.* [16] and Heller-Kallai *et al.* [14]

The present results show that pyrolysis result are modified by the mineral composition and this modification depends on the type of kerogen

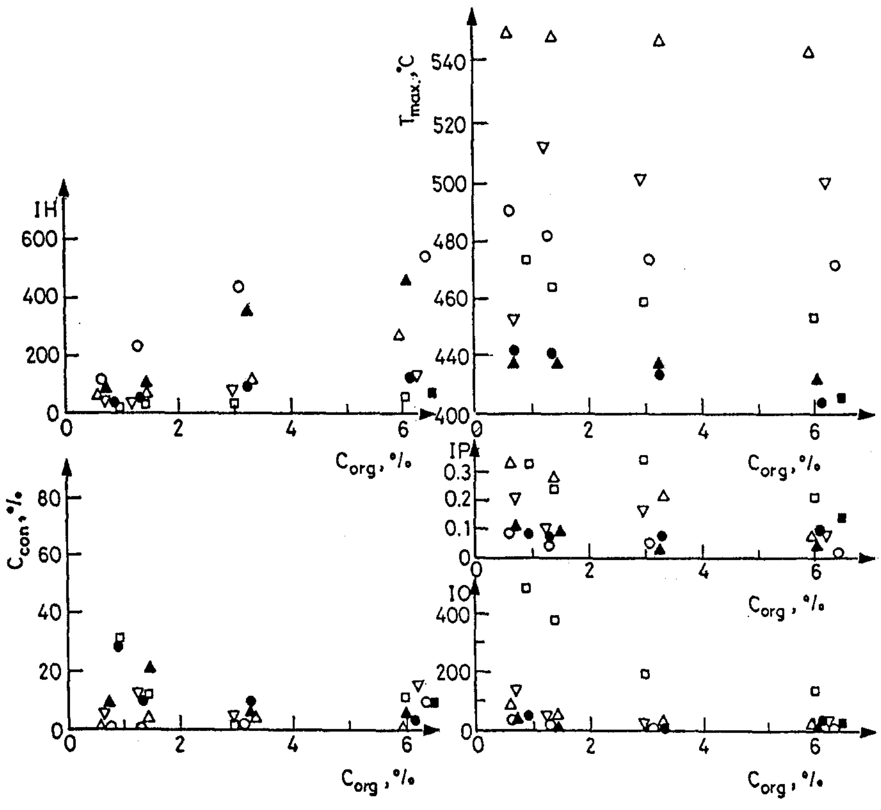

Fig. 4 Results of Rock Eval pyrolysis of mixtures of vitrinite (Fig. 4) with quartz ▲, kaolinite o, bentonite Δ, illite ∇, calcite •, limonite □ and pyrite ■. Note the variation of the pyrolysis parameters; Hydrogen Index (*IH*), temperature of maximal pyrolysis (T_{max}), Production Index (*IP*) and Oxygen Index (*IO*) as well as the proportion of organic carbon consumed during the experiment (C_{con}) as function of the organic matter content (C_{org})

pyrolysed. Therefore an attempt to calculate pyrolysis parameters 'free' from these effects has to take into account the two variables.

The amount of CO_2 recorded as oxygen index (*IO*) is generated only up to 390° whereas a substantial portion of CO_2 of organic origin is produced at higher temperatures. A shift of T_{max} to lower temperatures signifies that hydrocarbons are liberated from the kerogen in that particular mineral matrix at lower temperature, The sequence of generation of hydrocarbons and CO_2 from a given kerogen is probably irrespective of the mineral matrix. Therefore a smaller proportion of the generated CO_2 will be included in the range of pyrolysis temperatures used for the determination of the oxygen index which will be consequently smaller. This explains the relationship between low T_{max} and low *IO* values for quartz and kaolinite mixtures in contrast to illite and bentonite among the silicate minerals. The values recorded for the limonite mixtures are as a rule higher, probably due to an oxidation effect. The high values of calcite are possibly due to limited thermal decomposition of the mineral.

Conclusion

1) All pyrolysis parameters (hydrogen index, oxygen index, production index, T_{max}) vary in kerogen mineral mixtures with type of mineral and its proportion in the mixture. The variation also depends on the type of kerogen pyrolysed. Hence, this pyrolysis method does not characterize the organic matter only but the combined features of organic and inorganic components.

2) As the open system, rapid pyrolysis process differs from the process of hydrocarbon generation during burial diagenesis and katagenesis, also the interaction between minerals and kerogen and its pyrolytic products differ from those generated during natural maturation.

3) The interaction during pyrolysis is probably controlled by adsorption and secondary cracking reactions on the mineral surfaces. In the natural system, which is assumed to be water wet, different reactions probably take place.

4) Although pyrolysis differs from the natural hydrocarbon generation process, it can provide very useful information for screening purposes and for detailed studies, provided the effects of the minerals are recognized and accounted for. Hence, the use of pyrolysis data requires the determination of maceral and mineralogical composition.

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Zusammenfassung — Zur Bestimmung des Einflusses gewöhnlicher sedimentärer Mineralien auf die Pyrolyse von Kerogen wurden zuvor separierte und gereinigte Kerogenkonzentrate aus Alginit, amorphem Liptinit und Vitrinit mit folgenden Mineralien vermischt: Quarz, Kalzit, Pyrit, Limonit, Kaolinit, Bentonit und Illit in verschiedenen Kerogen/Mineral-Verhältnissen. Die Pyrolyse dieser Gemische mit einem organischen Kohlenstoffgehalt von 0.5 bis 6.6 % zeigt eine systematische Änderung der Parameter Wasserstoffindex, Sauerstoffindex, Bildungsindex und T_{max} sowie der Menge des bei dem Vorgang verbrauchten organischen Kohlenstoffes. Die Änderungen für ein bestimmtes Kerogen hängen von Art und Anteil des Minerales im Gemisch ab. Die Ergebnisse der Pyrolyse zeigen den Einfluß der Mineralmatrix auf die Pyrolyseprozesse sedimentären organischen Materiales und dessen Produkte.