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THERMAL ANALYSIS OF HYDROCARBONS IN PALEOZOIC BLACK SHALES

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Abstract

Paleozoic black shales of the Saxothuringikum (Germany) with an average $C_{org.}$-content of 0.01 to 20 mass% were investigated with regard to the nature of organic matter. A special pyrolysis technique (DEGAS) was used for a temperature resolved analysis of different hydrocarbons (HC) and the simultaneous detection of inorganic volatiles during heating under vacuum up to 1450°C. The presented data indicate three different forms of organic matter occurring in the investigated black shales (bitumen, kerogen and pyrobitumen). Finally the influence of an igneous dyke intrusion on the alteration of the organic matter was examined.

Keywords: black shales and kerogen, DEGAS, pyrolysis

Introduction

Silurian graptolite-bearing black shales are the most important carrier rock of the largest uranium ore deposit in Europe (Ronneburg, Germany). Until 1990 over 110 000 tons uranium were produced in that location. Since the close-down of the mine in 1990 extensive redevelopment activities were realized to avoid acid mine drainage and pollution by heavy metals and radionuclides. One major problem of these activities is the occurrence of simultaneous ignition of the waste rock material caused by high contents of organic matter and sulfide. This process is strongly exothermal and leads to a rapid oxidation of the material and hence to an increased mobility of the pollutants.

The aim of this study is to distinguish different forms of organic matter present in the rock by thermal analysis and to determine their importance for the mobilisation and fixation of pollutants.

Sedimentary rocks usually contain organic matter in two different forms, finely disseminated macromolecular material (kerogen, insoluble in usual organic solvents) and free hydrocarbons (bitumen, soluble in usual organic solvents). Bitumen may be altered by thermal stress into an insoluble solid form (pyrobitumen, Fig. 1 [1]).

Laboratory heating under inert conditions up to 300°C yields volatile free hydrocarbons (bitumen) and between 300 and 850°C pyrolysis of the kerogen macro-

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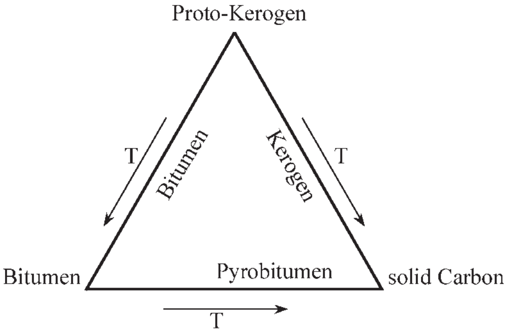

Fig. 1 Relationship between proto-kerogen, kerogen and bitumen (after Mossman 1999 [1])

molecule takes place [2]. The remaining graphite-like organic matter (dead carbon) may only be decomposed in the presence of oxygen.

Method

Evolved gas analyses were carried out using a special device of high-temperature mass-spectrometry (DEGAS, directly coupled evolved gas analyzing system, [3, 4]). The system consists of a NETZSCH STA 429 thermoanalyzer coupled directly to a Balzers QMG 421 quadrupole mass spectrometer. A schematic diagram of the used equipment is shown in Fig. 2. Measurements were carried out under vacuum of 10^{-4} to 10^{-3} Pa using a linear heating rate (10 K min^{-1}) in the temperature range from 20 to 1450°C. On-line taken mass spectra cover the range up to *m*/*z* 200. The mass spectrometer was operated at 100 eV in a multiple ion detection mode. The system runs under highly non-equilibrated conditions without the possibility of reverse reactions of the evolved volatiles.

We used 10 mg unground material from the inner part of the rock samples to avoid contamination.

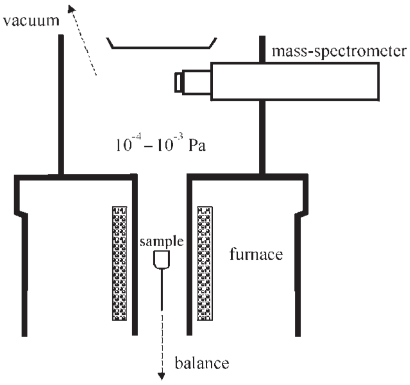

Fig. 2 DEGAS, directly coupled evolved gas analyzing system

A special problem results in the contamination of the system by oil from vacuum devices. To reduce the content of hydrocarbons in the background, turbomolecular pumps were used.

Results and discussion

The thermogravimetry curve and degassing profiles of a Silurian graptolite shale are represented in Figs 3–5. Three different ranges of mass loss can be recognized. The first step (20–250°C) is caused by a loss of water and volatile hydrocarbons (bitumen). In the second step (400–800°C) two processes overlap, dehydration of micas and/or iron hydroxides and pyrolysis of kerogen yielding water (*m*/*z* 18), CO (*m*/*z* 28)

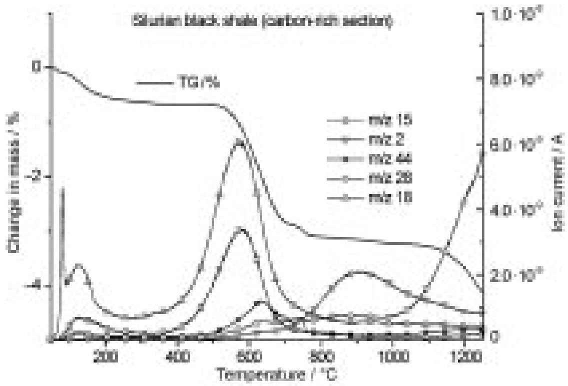

Fig. 3 Thermogravimetry in vacuum and release of hydrocarbons, H_2, CO_2, CO and water

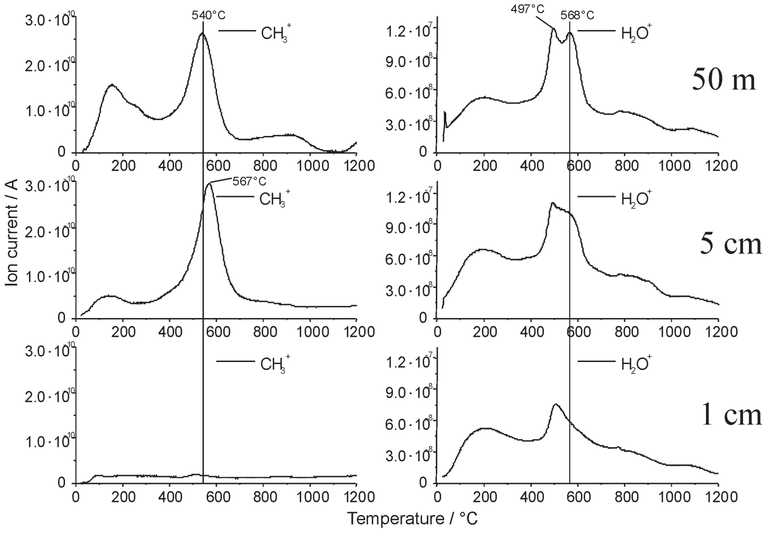

Fig. 4 Release of hydrocarbons (*m*/*z* 15) and water from a Silurian black shale (different distance to an igneous dyke intrusion)

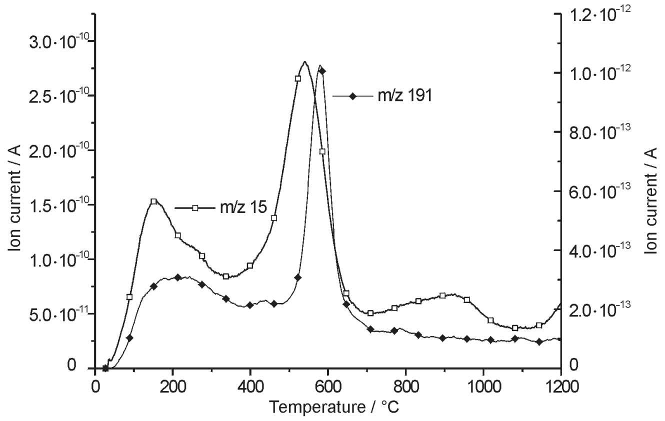

Fig. 5 Silurian black shale-release of *m*/*z* 15 and of a fragment *m*/*z* 191

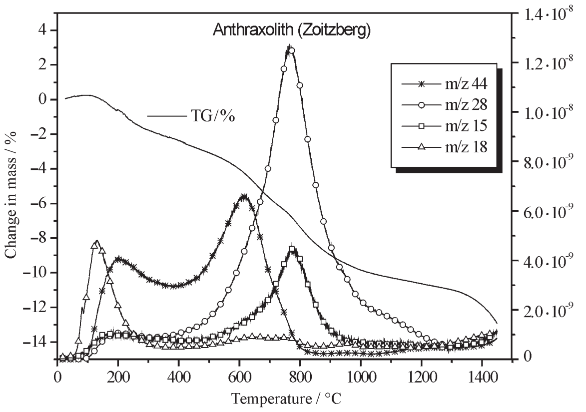

Fig. 6 Thermogravimetry in vacuum and release of water, CO, CO_2 and hydrocarbons

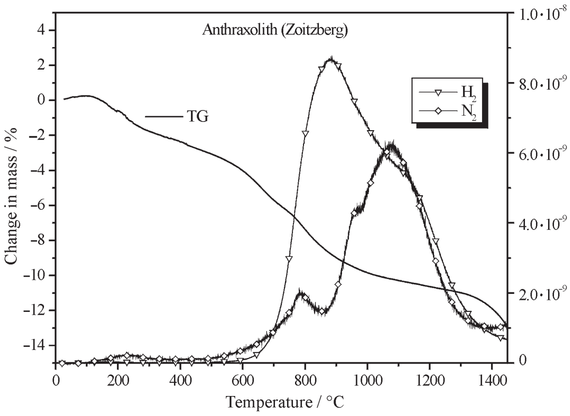

Fig. 7 Thermogravimetry in vacuum and release of hydrogen and nitrogen

and hydrocarbon fragments (*m*/*z* 15). The weak shoulder in the TG curve between 700°C and 800°C is caused by traces of carbonate (CO_2, *m*/*z* 44). Above 1100°C a third stage in the TG curve appears which is not finally completed. This corresponds to release of CO from the kerogen. The source of oxygen for this reaction is not clear but iron oxides are most likely.

Figure 4 illustrates the influence of an igneous dyke intrusion on the alteration of organic matter in black shales. Three different samples from the same Silurian graptolite shale were investigated with respect to their distance to a dyke intrusion (50 m, 5 cm, 1 cm). At 5 cm distance a weak effect on the hydrocarbons is detectable. There is a decrease in free hydrocarbons and an increase of $T_{\mathrm{max.}}$ of the pyrolysis peak, which describes the thermal maturity of the kerogen. The total amount of pyrolysable kerogen seems not to be affected. Only at 1 cm distance a full breakdown of the hydrocarbons is detectable.

The evolved gas profile of water shows two significant maxima at 497°C (clay minerals) and 568°C (iron hydroxides). Iron hydroxides disappear close to the dyke. Clay minerals seem not to be affected by the intrusion. Therefore it is concluded that the formation of these clays is a postintrusive process.

Figure 5 shows the ion trace of *m*/*z* 191 (maxima at 200 and 580°C) which is usually known to be a significant fragment of hopanes, a group of biomarker molecules, but in this case the signal is possibly caused by methylphenanthrenes (further studies in preparation).

Figures 6 and 7 illustrate the degassig behavior of a typical pyrobitumen (Anthraxolith). This material yields almost no free hydrocarbons but some water and CO_2 in the range of 20–300°C due to finely disseminated ironhydroxides. In the range of 400–1400°C appears a distinct sequence in the degassing of CO_2, CO and hydrogen.

In the range of 900 to 1400°C a release of nitrogen is detectable (Fig. 8). A possible source are nitrogen bearing aromatic structures. The peak at 800°C is a result of an overlapping with CO. To distinguish between nitrogen and carbon species which overlap in low resolution mass spectra the ratio of *m*/*z* 28 and *m*/*z* 14 is a useful crite-

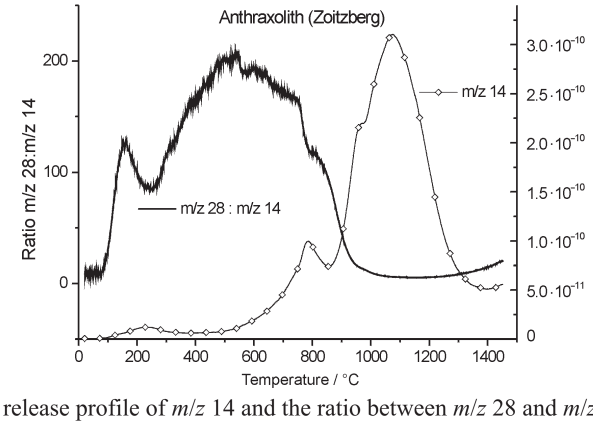

Fig. 8 Gas release profile of *m*/*z* 14 and the ratio between *m*/*z* 28 and *m*/*z* 14 for discrimination of nitrogen and carbon species

ria. In air as well as in blind measurements this ratio is determined by the fractionation and ionization probability of nitrogen and therefore constant. If any other source contributes to these signals the ratio changes.

Conclusions

DEGAS-analysis of Paleozoic black shales of the Saxothuringikum (Germany) indicates three different forms of organic matter in the shale (bitumen, kerogen and pyrobitumen). The thermal alteration in contact with an igneous dyke intrusion is detectable in a cm-scale. We have a clear evidence that the formation of clay minerals close to the dyke was a postintrusive process.

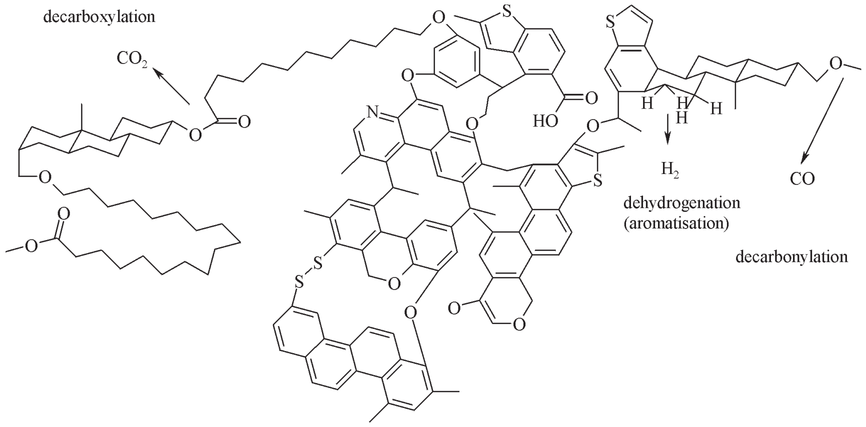

Fig. 9 Structural interpretation of the degassing behavior

The observed degassing profiles of hydrocarbons correspond to a structural model for kerogens [5] as shown in Fig. 9. We assume that the structure of pyrobitumina is similar to that of kerogens which is well correlated to our results.

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