



Differences in bitumen and kerogen-bound fatty acid fractions during diagenesis and early catagenesis in a maturity series of New Zealand coals



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ABSTRACT

Oxygen-bearing functional groups, in particular the carboxylic groups of acids and esters, are mainly responsible for the chemical reactivity of sedimentary organic matter. We have studied kerogen and bitumen fractions from a coalification series from the New Zealand Coal Band covering the rank range from 0.28% to 0.80% vitrinite reflectance. We investigated the composition of fatty acids separated from the bitumen, and compared this to the distribution of kerogen-bound fatty acids (esters) obtained after selective chemical degradation of the macromolecular organic matter. We found remarkable differences in the fatty acid composition between bitumen and kerogen-bound acids, both in the short ($<C_{20}$) and long chain ($\geq C_{20}$) fatty acid range. The compositions of these two acid fractions changed independently as a function of maturation. This points to the long and short chain fatty acids in bitumen and kerogen having different susceptibilities towards degradation, possibly as a result of their different solubilities in the pore water. The compositional differences may further reflect the occurrence of different types of bitumen e.g. if bitumen is trapped in organic micropores of the macromolecular network. Application of the carbon preference index for fatty acids (CPI_{FA}) of bitumen and kerogen-bound acids revealed a linear correlation to the T_{max} maturity parameter. This shows that the CPI_{FA} has a clear relation to thermal stability and, thus, reactivity of the buried organic matter. The difference in slopes of CPI_{FA} vs. T_{max} for short and long chain as well as bitumen and kerogen-bound acids may indicate their different degradation susceptibilities. The short chain fatty acids of the bitumen show the highest susceptibility whereas the kerogen-bound long chain fatty acids seem to be most resistant towards diagenetic degradation.

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1. Introduction

Fatty acids and esters are among the most reactive components of sedimentary organic matter (OM) (Fester and Robinson, 1966; Petersen et al., 2008; Vandenbroucke and Largeau, 2007). In terrestrial OM they consist predominantly of longer carbon chains (long chain fatty acids, LCFA, $\geq n-C_{20}$) originating from plant wax material (Eglinton and Hamilton, 1967; Goossens et al., 1989; Yamamoto et al., 2008). Additionally, some short chain fatty acids (SCFA, $<n-C_{20}$) can be present that derive mainly from algae (Cranwell, 1974; Shameel, 1990). Furthermore, palmitic acid ($n-C_{16}$) and stearic acid ($n-C_{18}$) are common in both microorganisms and higher plant material (Oldenburg et al., 2000). These compounds contribute to the formation of macromolecular OM during early stages of diagenesis and a significant fraction becomes part of the kerogen (Behar and Vandenbroucke, 1987; Vandenbroucke and Largeau, 2007). Some of the fatty acids

remain in free form in the bitumen, eventually adsorbed to the organic macromolecules or minerals, or they remain trapped in micropores of the formed macromolecular network (Valkova et al., 2009). Ongoing thermal maturation of kerogen alters its molecular structure thereby losing ester-bound fatty acids that become part of the soluble OM fraction. During main catagenesis, thermal breakdown of the organic macromolecules is the main process altering the kerogen. In maturation stages preceding main catagenesis, biotic degradation (microbial degradation) and abiotic degradation (e.g. by chemical equilibrium-reactions and hydrolysis within the pore water) play a fundamental role in altering the structure of macromolecular OM as well as the composition of the bitumen (Glombitza et al., 2009a; Hatcher, 1990; Hatcher and Clifford, 1997). An insight into such processes can be obtained by characterization and comparison of the molecular composition of both, kerogen and bitumen, in relation to different stages of OM maturation. The relation of bitumen and kerogen-bound constituents in selected samples has been subject of a number of recent studies (Disnar et al., 2005; Stefanova, 2013). They reveal for instance evidence of different types of bitumen associated to kerogen and mineral matrix (Bernard et al., 2012; Nabbefeld et al., 2010). However, understanding of the

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complex structural alterations during ongoing maturation is limited due to the rarely available sample material representing continuous maturation series covering the stages from diagenesis to catagenesis. Thus, most of the studies focus on single or few samples of similar maturity (e.g. Ambles et al., 1996; Djuricic et al., 1978; Grasset et al., 2002; Razvigorova et al., 2008; Xiong et al., 2007).

The New Zealand coal band provides one of the few continuous maturation series of similar OM type covering nearly all stages of maturation from peat to anthracite (Killops et al., 2002; Suggate, 2000; Sykes and Snowdon, 2002). Therefore, it represents a unique setting to investigate maturity related structural changes in OM. For the current study, we used a series of coal samples from the New Zealand coal band, carefully selected from coal mines and drill cores to represent a continuous maturation series of diagenetic to catagenetic maturation stage. This study is a contribution to the Deep Biosphere in Terrestrial Systems (DEBITS) project that aims to shed light into a microbial ecosystem re-laying on buried terrestrial OM and how geochemical alteration of OM during maturation is coupled to the occurrence of microbial life in the depth. Several biogeochemical data on these samples were previously reported (Fry et al., 2009; Glombitza et al., 2009a, 2009b, 2011; Vieth et al., 2008; Vu et al., 2008, 2009, 2013). All together, these studies point to the existence of a deep biosphere, which is associated to the coal bearing horizons forming the New Zealand coal band, and which is potentially sustained by the abundant substrates provided by these OM rich coal lithologies.

In a previous study we have investigated the composition of kerogen-bound fatty acids (KFA) in a maturity series of lignites and sub-bituminous coals from the New Zealand coals covering maturity intervals of diagenesis, early and main catagenesis (Glombitza et al., 2009a). The transition from diagenesis to early catagenesis was defined in Vu et al. (2009) by the slow but continuous start of thermal degradation processes in these coals at a vitrinite reflectance of R_0 0.40%. The main catagenesis started at R_0 0.60% with the massive generation of hydrocarbons. For the study of KFA, first we removed the bitumen from the coal samples by organic solvent extraction. Subsequently, we

applied saponification to the pre-extracted coal samples to obtain the fraction of fatty acids that were linked via ester-bonds to the macromolecular matrix (Fig. 1). We found that the amounts of KFA decrease with ongoing geological maturation of the coal samples, reflecting the loss of oxygen from the kerogen and concomitantly the decreasing reactivity of the organic material. With respect to their different origin, we separated the KFA into LCFA and SCFA. We found a more or less continuous decrease in the amounts of plant wax derived LCFA. Because the coals derived from different areas of New Zealand, the source facies may have been responsible for some variations in the abundance of the plant wax fatty acids. To overcome this uncertainty and getting a maturity dependent parameter we used the carbon preference index of the fatty acids (CPI_{FA}) (Glombitza et al., 2009a; Strauss et al., 2015). This parameter indicates the predominance of even fatty acids over odd fatty acids and was adapted from the carbon preference index for alkanes (Bray and Evans, 1961) which rates odd over even numbered alkanes. The CPI_{FA} was calculated according to Eq. (1):

$$CPI_{FA}(C_x \text{ to } C_y) = \frac{1}{2} \left(\frac{\sum_{n=x/2}^{y/2} C_{2n}}{\sum_{n=x/2}^{y/2} C_{2n-1}} + \frac{\sum_{n=x/2}^{y/2} C_{2n}}{\sum_{n=x/2}^{y/2} C_{2n+1}} \right) \quad (1)$$

where x and y represent the carbon numbers of the predominant even numbered fatty acids bordering the range for which the CPI_{FA} is calculated (i.e. for SCFA: $x = 14$, $y = 18$ and for LCFA: $x = 20$, $y = 30$).

For the LCFA, the CPI_{FA} vs. vitrinite reflectance plot showed a clear decreasing trend. Using the CPI_{FA} instead of the abundance, the facies variations were less pronounced and outliers fell on the trend line. In contrast to the LCFA, the SCFA fraction showed an intermittent increase in abundance and in the CPI_{FA} during the maturation stage of early diagenesis. We interpreted this as indication of less degraded fatty acids deriving from the input of fresh microbial biomass into the kerogen matrix during this maturity interval. We suggested that the slow release of hydrocarbons during the early catagenesis (Vu et al., 2009) might have stimulated microbial growth resulting in the contribution of less mature

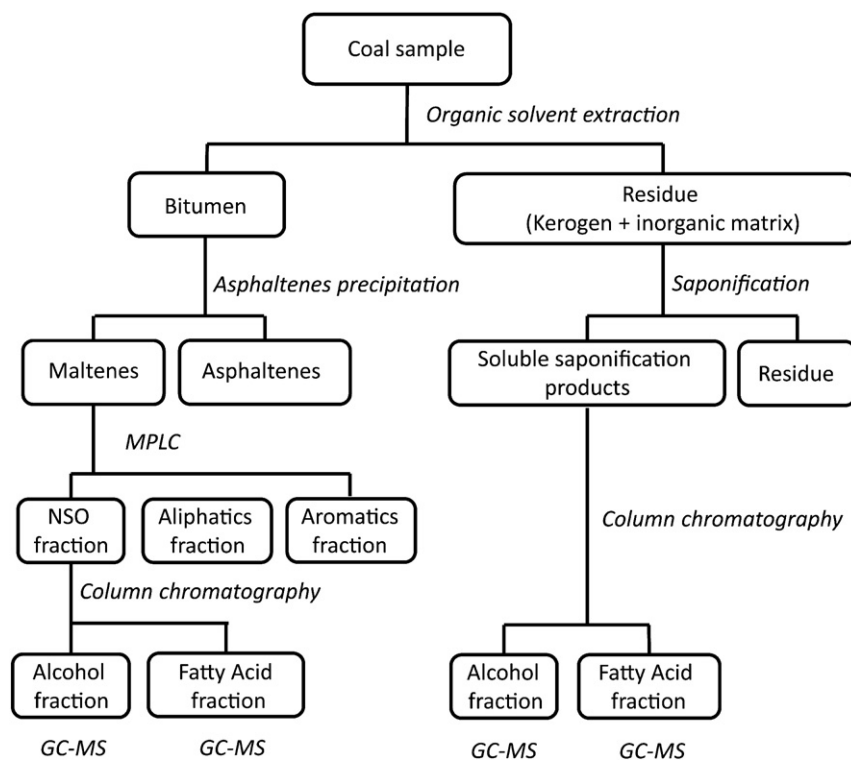


Fig. 1. Scheme of experimental procedure to obtain kerogen-bound and free fatty acids and alcohols. MPLC: medium pressure liquid chromatography (Radke et al., 1980; Willsch et al., 1997).

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