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Characterization of water-soluble organic compounds released from black shales and coals

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ABSTRACT

Knowledge of the composition of dissolved organic compounds as well as the main controls on their mobilization from natural organic matter is prerequisite for a comprehensive understanding of the fluid–rock interactions taking place in shale environments and coal seams over both geological and human timescales. In this study, black shales and coals from five different geological settings and covering the maturity range Ro = 0.3–2.6% were extracted with deionized water. The dissolved organic carbon (DOC) yields were found to decrease rapidly with increasing diagenesis and remain low throughout catagenesis. Four different fractions of DOC have been qualitatively and quantitatively characterized in the study using size exclusion chromatography (SEC). Acetate is the dominant low molecular weight organic acid (LMWOA) in all extracts of shales and coals of bituminous rank. The concentrations of individual LMWOA also decrease with increasing maturity of the samples except for acetate extracted from the overmature Posidonia shale from the Haddessen well, which was influenced by hydrothermal brines. The positive correlation between the Oxygen Index (OI) and respective LMWOA yield indicates that OI is a significant factor influencing the extraction of organic acids from shales. The yields of both DOC and individual organic acids normalized to TOC are in the same order of magnitude for coals and shales with the same maturity. However, the extracts of coals tend to contain more aromatic compounds and the molecular masses of most constituents included in macromolecular fractions are higher than for shale extracts. These results suggested that different kerogen types show comparable amounts of DOC being extracted, but different DOC composition. Thus, both the origin of organic matter and thermal maturation progress during deposition has significant influence on water extract composition.

1. Introduction

Dissolved organic carbon (DOC) is defined as the fraction of organic matter in water that passes through a filter with pore size 0.45 μm (Herbert and Bertsch, 1995). DOC in near-surface groundwater and natural formation waters like oil field brines has been studied for years (Leenheer and Croué, 2003; Lepane et al., 2004; Schmidt et al., 2009) and the first insights into the molecular composition have been provided. Special attention has been paid to the abundance and origin of low molecular weight organic acids (LMWOAs) in subsurface brines (Means and Hubbard, 1987). LMWOAs have been proposed as tracers or proximity indicators of hydrocarbons (Zinger and Kravchik, 1973), and Kharaka et al. (1983) argued that acid anions are important precursors of natural gas via thermal cracking. LMWOAs are assumed to create secondary porosity in the subsurface by increasing the dissolution of aluminosilicates and carbonates (Surdam et al., 1984). Additionally, LMWOAs can act as feedstock for the deep terrestrial biosphere (Horsfield et al., 2006; Vieth et al., 2008). As far as oil and gas production is concerned, it has been reported that LMWOAs make up a dominant fraction of DOC in waters utilized during oil shale retorting (Dobson et al., 1985; Leenheer et al., 1982). High concentrations of formate and acetate in flowback waters were previously reported in fracturing flowback (Lester et al., 2015; Olsson et al., 2013). The amount and composition of other organic compounds in flowback and produced waters from hydraulic fracturing of shales have been reported in recent years (Maguire-Boyle and Barron, 2014; Orem et al., 2014). Although the occurrence of DOC and LMWOAs in different types of natural waters is well documented, only little work has been done to elucidate the relation between their quantitative and qualitative occurrence in water and the properties of the rock they have been in contact with.

Black shales and coals usually contain high concentrations of organic matter. During progressive burial over geological times, reactive functional groups within the organic material are thermally degraded. It is well known that during diagenesis, with vitrinite reflectance (R_o) below 0.5%, biopolymers such as polysaccharides, proteins and amino sugars are initially degraded by microorganisms in the water column and in young sediments, after which a loss of hydrolysable moieties takes place during continuing subsidence (Tissot and Welte, 1984). Catagenesis (R_o = 0.5–2.0%) is characterized by the progressive

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cracking of carbon-carbon and carbon-oxygen bonds accompanied by aromatization and condensation of the kerogen (Kelemen et al., 2007; Lis et al., 2005; Petersen et al., 2008; Robin and Rouxhet, 1978; Werner-Zwanziger et al., 2005). The generation of LMWOAs in sedimentary basins has been attributed to the cleavage of kerogen fragments containing carboxylic functional groups during the early stage of thermal maturation (Cooles et al., 1987). Decreasing yields of ester-bound LMWOA generated with increasing maturity of coals has been reported (Glombitza et al., 2009). In addition, oxidation reactions involving mineral oxidants may also produce organic acids during thermal maturation (Borgund and Barth, 1994; Seewald, 2001a, 2001b; Surdam et al., 1993).

Knowing the composition, molecular size and structure of the DOC as well as the main controls on the release of DOC are prerequisites for a better understanding of the fluid–rock interactions taking place in shale environments over both geological and human timescales. Soxhlet extraction of marine sediments accesses a larger and more complex pool of organic matter than that contained in interstitial pore water (Schmidt et al., 2014). Hot water extraction of organic matter has also been previously applied to soils to examine the labile organic fractions (Bu et al., 2010; Ghani et al., 2003; Gregorich et al., 2003; Sarkhot et al., 2011). Thus, water extraction is an appropriate tool for studying the soluble organic matter released during the interaction between water and rock. As far as we are aware, leaching experiments have only rarely been applied to black shales and coals (Bou-Raad et al., 2000; Vieth et al., 2008) and little attention has been paid to how DOC composition varies as a function of organofacies, organic matter type and maturity. In the present contribution, we report the composition of DOC in water extracts from shales and coals not only of different geological ages and depositional settings, thereby covering different kerogen types, but also different thermal maturation levels, enabling the controls of progressive thermal maturation on composition of water extracts to be documented.

2. Materials

Thirty-two organic-rich black shales and coals from around the world, representing a wide range of depositional settings and ages (Paleozoic through Cenozoic age) were selected for this study (Table 1). The samples cover a maturity range from immature ($R_o = 0.29$; $T_{max} = 409$ °C) to overmature ($R_o = 2.6$; $T_{max} = 602$ °C) with TOC contents of shales and coals extending up to 15% and 67%, respectively. The chain length distribution of n-alkyl moieties ($C_{1\text{-}5}$ total, n-$C_{6\text{-}14}$, n-C_{15+}) in pyrolysates of the original samples is illustrated in the ternary diagram of Horsfield (1989) (Fig. 1). The pyrolysate compositions of shale samples indicate Paraffinic-Naphthenic-Aromatic Low Wax Oil petroleum type as well as Gas and Condensate petroleum type organofacies. The chain length distributions of the macromolecular organic matter in shale samples are closely similar despite their diverse origins. The three bituminous coals (C3, C4 and C5) fall in the High Wax, Paraffinic-Naphthenic-Aromatic Oil petroleum type and the two lignites C1and C2 fall in Paraffinic Oil High Wax organofacies. Relative percentages of the three main minerals of the shale samples are shown in Fig. 2. The Posidonia and Duvernay shales are dominated by carbonate, whereas the Bakken and Alum shales are characterized by higher contents of quartz and clays, respectively.

Table 1
Sample origin and Rock–Eval pyrolysis characteristics. Hydrogen Index (HI) and Oxygen Index (OI) are measured in mg hydrocarbons/g organic carbon and mg CO_2/g organic carbon, respectively. TOC and Rock–Eval data of Duvernay shales and New Zealand coals were taken from (Dieckmann, 1999) and Glombitza (2011), respectively. Posidonia, Bakken and Alum shale samples were analyzed in this study. R_o values of Posidonia, Bakken, Alum and New Zealand samples were taken from Rullkötter et al. (1988), Dembicki and Pirkle (1985), Buchardt and Lewan (1990), and Glombitza (2011) respectively. Ro of Duvernay shales was calculated using the empirical formula $\%R_o = 0.018 * T_{max} - 7.16$ (%) (Jarvie et al., 2007).

ID	Well	Depth (m)	TOC (%)	Tmax (°C)	OI	HI	R_o (%)
(A) Black shale, Posidonia Formation, Germany, Lower Jurassic, Type II							
P1	Wickensen	58.2	9.9	430	14	664	0.53
P2*	Wickensen	42.2	9.0	432	16	658	0.53
P3	Wickensen	30.2	11.4	433	14	634	0.53
P4	Harderode	77.3	4.8	447	7	340	0.88
P5*	Harderode	42.5	7.2	449	7	384	0.88
P6	Harderode	55.7	11.0	449	5	282	0.88
P7	Haddessen	36.6	9.2	466	9	87	1.45
P8*	Haddessen	51.0	5.0	466	16	79	1.45
P9	Haddessen	60.6	7.7	469	8	66	1.45
(B) Black shale, Bakken Formation, USA, Mississippian, Type II							
B1*	Daniel Anderson 1	1012.1	9.4	409	28	360	0.35
B2	Dobrinski 18–44	2631.7	14.9	423	12	420	0.45
B3	Nordstog 14–23–161–98 H	2651.6	12.1	440	3	462	0.7
B4	Loucks 44–30	2350.8	15.0	440	2	460	0.75
B5*	Titan E-Gierke 20–1-H	3351.6	11.9	452	3	118	0.86
B6	BR 12-29	3253.7	8.4	452	4	93	1.1
(C) Black shale, Duvernay formation, Canada, Late Devonian, Type II							
D1*	Sarcee et al. Pibroc	1395.9	6.4	418	19	619	0.36
D2	Imperial Kingman	1404.2	2.4	427	32	412	0.53
D3	Bangg Imperial	1677.9	5.5	431	6	621	0,6
D4	Tomahawk	2337.5	4.8	435	7	620	0.67
D5*	Imperial Cynthia	2976.1	1.9	447	12	92	0.89
D6*	Banff Aguit Ram River	4623.9	2.0	542	17	4	2.6
(D) Black shale, Alum Formation, Denmark, Lower Ordovician to Middle Cambrian, Type II							
A1	Skelbro-2	39.6	6.3	564	2	3	2.3
A2*	Skelbro-2	27.0	10.1	591	8	4	2.3
A3	Skelbro-2	38.7	8.1	591	2	3	2.3
A4	Skelbro-2	15.0	11.2	599	1	7	2.3
A5	Skelbro-2	11.8	7.7	600	4	3	2.3
A6	Skelbro-2	21.1	11.4	602	34	10	2.3
(E) Coal, New Zealand, Cenozoic, Type III							
C1*	DEBITS-1	18.9	45.1	414	95	192	0.29
C2*	DEBITS-1	62.5	35.9	414	80	366	0.29
C3*	DEBITS-1	140.5	58.2	419	26	172	0.39
C4*	Rotowaro Mine	Outcrop	61.2	422	32	154	0.45
C5*	Welcome Mine	Outcrop	67.4	424	15	209	0.52

* Samples selected for display in Figs. 4 and 5 are covering the whole range of maturity from each location.

2.1. Posidonia shale

The Lower Toarcian Posidonia shale samples are from three shallow boreholes (Wickensen, Harderode, Haddessen) located in the Hils Syncline of Northwest Germany and cover a large maturity range from immature to overmature (Rullkötter et al., 1988). The shale was deposited in a restricted epicontinental sea with prevailing anoxic conditions, and the organic matter originates mostly from marine phytoplankton with minor terrigenous input (Littke et al., 1991). Comprehensive studies on the Posidonia shales have been presented by several authors, on nanoscale structure (Bernard et al., 2010; Bernard et al., 2012), petrophysical characteristics (Mann and Müller, 1988) and biogeochemistry (Wilkes et al., 1998). The depositional conditions and the preservation of organic matter are considered to be uniform for the three sampling sites (Littke et al., 1988; Littke et al., 1991; Rullkötter et al., 1988).

2.2. Bakken shale

The Devonian–Mississippian Bakken shale samples from six wells located in the Williston Basin in North Dakota, USA and covering the immature to mature range, were supplied by the North Dakota Geological Survey. The Bakken shale was deposited in an epicontinental setting (Jiang et al., 2001) under anoxic and uniformly quiet conditions, judging by the widespread occurrence of planar and thin laminations (Webster, 1984). Amorphous organic matter derived from marine algae dominates, and terrestrial contributions are minor (Smith and