



## Effects of weathering on organic matter: I. Changes in molecular composition of extractable organic compounds caused by paleoweathering of a Lower Carboniferous (Tournaisian) marine black shale

Leszek Marynowski <sup>a,\*</sup>, Sławomir Kurkiewicz <sup>b</sup>, Michał Rakociński <sup>a</sup>, Bernd R.T. Simoneit <sup>c,d</sup>

<sup>a</sup> Faculty of Earth Sciences, University of Silesia, Będzińska 60, PL-41-200 Sosnowiec, Poland

<sup>b</sup> Department of Instrumental Analysis, Faculty of Pharmacy, Medical University of Silesia, PL-41-200 Sosnowiec, Poland

<sup>c</sup> COGER, King Saud University, 11451 Riyadh, Saudi Arabia

<sup>d</sup> Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA

### ARTICLE INFO

#### Article history:

Received 2 September 2010

Received in revised form 31 March 2011

Accepted 1 April 2011

Available online 9 April 2011

Edited by: J. Fein

#### Keywords:

Paleoweathering

Organic matter

Pyrite framboids

Black shale

Biomarkers

Maleimides

PAHs

### ABSTRACT

A detailed bulk and molecular study on paleoweathering of a Lower Carboniferous (Tournaisian) black shale from the Kowala quarry in the Holy Cross Mountains of Poland, revealed significant changes in total organic carbon (TOC), total sulfur (TS) and extract compositions. Paleoweathering resulted in a 97% decrease in TOC and total loss of sulfur, as well as changes in carbonate contents, extract yields and percentage yields of the organic fractions. Pyrite framboids, which are used extensively in paleoecological studies, decreased considerably in the partially weathered zone and totally vanished in the weathered zone. The decrease in TOC is accompanied by a pronounced reduction of organic compound concentrations, but the degradation range differs in the individual weathering zones. Here we show that less stable compounds such as low molecular weight aromatics (e.g. methylnaphthalenes, dibenzofuran, and dibenzothiophene), isorenieratane and its diagenetic products, or maleimides decrease significantly or disappear already in the partially weathered zone, while the more stable polycyclic aromatic hydrocarbons (PAHs) decrease (~90%) only in the weathered and highly weathered zones. Besides the organic matter (OM) content, the influence of paleoweathering on the distributions of organic compounds is important in the context of paleoenvironment, source and maturity interpretations. Almost all sterane and triterpane biomarker parameters change their values in the highly weathered zone, but some ratios, e.g. the 2-MeH index, are almost totally resistant to change. The aryl isoprenoid ratio (AIR) values decrease gradually with weathering. This modifies completely the potential interpretation of the nature of the photic zone anoxia. In addition to degradation of OM, some PAHs like benzo [b]fluoranthene increase in concentration in the partially weathered zone due to their formation from phenyl-derivatives. The correct recognition of paleoweathering in outcrop and drill core samples aids in the proper interpretation of biomarker parameters and contributes to a better understanding of the processes which took place during weathering.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Weathering of ancient organic matter (OM) is a major factor in the geochemical carbon cycle which controls the oxygen concentration in the atmosphere (Bolton et al., 2006; Chang and Berner, 1999; Hartnett et al., 1998; Wildman et al., 2004). Therefore, the understanding of how these processes took place during oxidative weathering and the estimation of all reaction rates is crucial for modeling atmospheric oxygen levels (Chang and Berner, 1999). One of the main factors controlling the rate of OM weathering, besides climate, is the OM source and maturity. For example, terrestrial OM is more resistant to oxidation

processes than marine OM (e.g. Prahl et al., 1997; Sinninghe Damsté et al., 2002), and highly carbonized material like charcoal, black carbon or graphite is more resistant to such processes than immature sedimentary OM (e.g. Scott, 2010; Haberstroh et al., 2006). Moreover, a new report shows that charcoals formed at lower temperatures are much more susceptible to chemical oxidation than those from higher temperature conditions (Ascough et al., 2010). This may result in more resistant OM accumulating in the weathered zones of sedimentary rocks or being re-worked and transported to sedimentary basins (e.g. Haberstroh et al., 2006). However, even in the case of highly metamorphosed OM in the anthracite stage of diagenesis, oxidative weathering is an effective and fast rock alteration process in view of geological time. For example, the total organic carbon content in low-grade metamorphic slates decreased from two- to seven-times during ~100 years of oxidation at ambient temperature (Fischer et al., 2007).

\* Corresponding author.

E-mail address: [leszek.marynowski@us.edu.pl](mailto:leszek.marynowski@us.edu.pl) (L. Marynowski).

There are several reports documenting recent natural weathering of black shale which can result in inorganic (Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002; Wildman et al., 2004; Fischer and Gaupp, 2005; Fischer et al., 2009), bulk organic (Leythaeuser, 1973; Clayton and Swetland, 1978; Littke et al., 1989; Lo and Cardott, 1995; Petsch et al., 2000, 2005; Wildman et al., 2004; Fischer and Gaupp, 2005; Fischer et al., 2009) isotopic (Van Os et al., 1996) and molecular (Clayton and King, 1987; Petsch et al., 2000, 2005) changes. In contrast, there is a lack of studies on terrestrial paleoweathering, especially in the context of OM composition and transformation during gradual natural oxidation. Only some preliminary results concerning early diagenetic OM oxidation of Triassic terrestrial green and red shales from Poland were reported recently showing that oxidation processes resulted in a significant decrease in OM content and changes in the *n*-alkane, triterpane, sterane and polycyclic aromatic hydrocarbon (PAH) distributions (Marynowski and Wyszomirski, 2008).

Here we report for the first time a thorough description of paleoweathering of a Lower Carboniferous (Tournaisian) marine black shale in the context of general OM transformations and pyrite framboid diameter interpretations, as well as important changes in extractable organic matter compositions and effects on most of the commonly used geochemical parameters. This problem seems to be especially relevant to cases of paleoenvironmental, source and maturity interpretations based on molecular parameters for not only surface samples, but also potentially those from drill cores, where rock sequences exposed to aerial paleoweathering processes may have occurred. In addition, subsurface weathering, which occurs preferentially along fault joints or bedding planes, may affect OM over a considerable part of such formations (see Van Os et al., 1996). The Lower Carboniferous shale investigated here has a relatively low maturity of the OM and macroscopically visible alteration caused by weathering processes (Fig. S-A, Supplemental On-line Material), and is an excellent example where the gradual change from non-oxidized to highly oxidized OM is visible within a few meters of section. The study focuses on the characterization of organic compound groups like: hopanes, methylhopanes, steranes, isorenieratane, aryl isoprenoids and PAHs in terms of their stability during oxidative weathering. These compounds are commonly used in reconstruction of sedimentary environments and OM maturity (e.g. Peters et al., 2005 and citations therein), but secondary weathering processes and especially paleoweathering are rarely taken into account in the interpretation of such results. Here we show that oxidative paleoweathering processes can substantially change the primary composition of extractable OM, which as a consequence may lead to erroneous maturity and paleoenvironmental interpretations. The detailed discussion of individual compounds and molecular parameter changes during the gradual paleoweathering of this black shale may aid in reliable future interpretations and conclusions based on sedimentary biomarkers.

## 2. Materials and methods

### 2.1. Samples

Nine samples were collected in August 2009 from the eastern part of the active Kowala Quarry, Holy Cross Mountains, Poland (Fig. S-A, Supplemental On-line Material). All samples belong to a 10 cm thick black shale horizon (Fig. S-A). This Tournaisian black shale is situated ca 40 cm above the Devonian/Carboniferous boundary and 2 m above the black Hangenberg shale (Fig. S-A, see Marynowski and Filipiak, 2007) and is the part of the Upper Devonian–Lower Carboniferous open marine sequence from the Holy Cross Mountains (Szulcowski, 1995). The sample horizon and other parts of the Lower Tournaisian section of the Kowala quarry are an excellent example of paleoweathering which took place after the Upper Carboniferous folding and before the Upper Permian deposition. This was affirmed by the observations on the unconformably overlying, non-weathered Upper

Permian conglomerates (Fig. S-A). Although the conglomerates are generally organic-poor, some of the Devonian, mainly limestone pebbles are enriched in OM and there is no evidence for their weathering. At least 2 m of intensively weathered shales occur below the conglomerates (see Fig. S-A), which suggests that oxidative weathering took place between the Lower Carboniferous and Upper Permian. The most severely weathered sample, KQ 136-1 was collected ca 2 m below the recent surface. Above this sample, the correct determination of the marker horizon was problematic (see Fig. S-A) due to the complete or almost complete mineralization of the weathered kerogen (see Berner, 1989) and furthermore, access to upper samples was difficult. The detailed geological description of the study area was provided elsewhere (Berkowski, 2002; Marynowski and Filipiak, 2007; Rakociński, 2009; Marynowski et al., 2010). Previous analyses revealed that Upper Devonian samples from the same quarry are generally immature, with Rock-Eval  $T_{\max}$  values ranging from 421 to 425 °C (Marynowski and Filipiak, 2007) and an average vitrinite reflectance value of 0.53%  $R_o$  (Marynowski et al., 2001). This indicates that the horizons investigated here have also similarly low maturities.

### 2.2. Vitrinite reflectance

For the vitrinite reflectance analysis, freshly polished rock fragments were used. Random reflectance was measured using an AXIOPLAN II microscope using 156 nm light and oil of 1.546 RI using a total magnification of 500×. The standards used were 0.42% and 0.898% reflectance ( $R_o$ ).

### 2.3. Total organic carbon

The total organic carbon (TOC) and total sulfur (TS) contents were determined using an Eltra Elemental Analyser (model CS530). For more details see Racka et al., (2010).

### 2.4. Pyrite framboid diameter analysis

Six samples were selected for pyrite framboid analysis, namely two samples from the unweathered part of the analyzed bed (KQ136-7 and KQ136-4), two samples from the partially weathered section (KQ136-3 and KQ136-2B) and two samples from the weathered region (KQ136-2A and KQ136-2) (cf. Fig. S-A). Samples in the form of small chips were polished, and framboid diameters were measured using a Philips Environmental Scanning Electron Microscope (ESEM) in the back-scattered electron (BSE) mode at the University of Silesia (Sosnowiec, Poland). Framboid diameters were measured using the ESEM internal measuring device (given in  $\mu\text{m}$ ). For each sample where frambooids occurred, minimum and maximum values, mean value and standard deviation were calculated, tabulated and shown as histograms (see Wignall and Newton, 1998).

### 2.5. Extraction and separation

Cleaned and powdered samples were Soxhlet-extracted with dichloromethane in pre-extracted thimbles. The extractable organic matter (EOM) was further separated by thin layer chromatography (TLC) using pre-washed plates coated with silica gel (Merck, 20×20×0.25 cm). Prior to separation, the TLC plates were activated at 120 °C for 1 h. Plates were then loaded with the dichloromethane soluble fraction and developed with *n*-hexane. Aliphatic hydrocarbon ( $R_f$  0.6–1.0), aromatic hydrocarbon ( $R_f$  0.05–0.6), and polar compound ( $R_f$  0.0–0.05) fractions were eluted and extracted from the silica with dichloromethane. The aliphatic and aromatic fractions of all samples were analysed in further detail by gas chromatography–mass spectrometry (GC–MS).

Download English Version:

<https://daneshyari.com/en/article/4699678>

Download Persian Version:

<https://daneshyari.com/article/4699678>

[Daneshyari.com](https://daneshyari.com)