



Effects of oxidative weathering on the composition of organic matter in coal and sedimentary rock



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ABSTRACT

The effect of oxidative weathering on the composition of sedimentary organic matter (SOM) of lignite, subbituminous coal, quartzose arenite, siliceous mudstone, siliceous shale and diatomaceous shale was investigated in Hokkaido, Japan, in a subarctic humid climate. For 15 samples in total, a humic substance extraction method was applied to divide SOM into lipid-C, humin-C and alkali soluble-C. The alkali soluble-C was further divided into fulvic acid (FA)-C, humic acid (HA)-C and a smaller molecular size fraction (SMSF)-C, which comprised organic molecules able to pass through a dialysis membrane (<1000 Da) during the HA and FA purification processes. The alkali soluble-C (8–750 g/kg) increased with the degree of sample weathering in compensation for lowering of humin-C. For the alkali soluble-C, HA-C (undetectable to 698 g/kg) became dominant with sample weathering, in contrast to FA-C and SMSF-C. These observations imply that oxidative weathering converts humin-C into alkali soluble-C (mainly HA-C). The ¹³C nuclear magnetic resonance (NMR) analysis (precision ±2.4%) revealed higher aromatic-C content of HA (average 40%) as compared to bulk humin (average 33%), suggesting that the re-generated HA was derived from condensed products (aromatic-C rich) in the humin, rather than from recalcitrant biomolecules (alkyl-C rich) in that fraction. The longer emission wavelength of the HA and FA from weathered samples in the excitation–emission matrix (EEM) spectra (precision ±1.0%) is ascribed to the abundance of oxidized aromatic moieties, with the higher O/C atomic ratio of HA and FA from the weathered samples.

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1. Introduction

Humic substances are macromolecular organic matter (OM) operationally classified into soluble fulvic acid (FA) at any pH, insoluble humic acid (HA) at pH ≤ 1 and insoluble humin at any pH (Kononova, 1966; Stevenson, 1994). While research into these substances has a historic origin in soil science (Kononova, 1966), the presence of HA and FA in sedimentary OM (SOM) has been reported more recently (Huc and Durand, 1977; Verheyen and Johns, 1981; Ibarra and Juan, 1985; Verheyen et al., 1985; Fengler et al., 1994). Although HA and FA in SOM tend to condense

Abbreviations: HA, humic acid; FA, fulvic acid; SMSF, small molecular size fraction; JAEA, Japan Atomic Energy Agency; URL, Underground Research Laboratory; MWCO, molecular weight cut-off; EEM, excitation–emission matrix.

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to humin during SOM diagenesis (Huc and Durand, 1977; Verheyen and Johns, 1981), oxidative weathering regenerates HA and FA in both surface (Berkowitz, 1979; Estévez et al., 1990; Klika and Kraussová, 1993; Martínez and Escobar, 1995; Kurková et al., 2004) and subsurface environments (Wassenaar et al., 1990; Aravena and Wassenaar, 1993; Grøn et al., 1996; Artinger et al., 2000; Buckau et al., 2000; Schäfer et al., 2005). The regeneration of HA and FA could aid the migration of toxic metals in aquatic systems via complexation (Choppin, 1988; Moulin et al., 1992; Kim and Czerwinski, 1996; Tipping, 2002), or could be coupled with substrate production for methanogens in groundwater (Aravena and Wassenaar, 1993; Ahmed and Smith, 2001; Formolo et al., 2008), yielding economic methane deposits (e.g., Scott et al., 1994; Martini et al., 1996; Strapoć et al., 2011). These examples signify the importance of oxidative weathering of SOM from both scientific (e.g., Fischer and Gaupp, 2005; Petsch, 2014)

and engineering viewpoints. However, evolutionary routes of SOM during oxidative weathering have been poorly resolved. For example, what components of SOM are evolved to re-generate HA and FA and how they are evolved in response to oxidative weathering are still uncertain. The lack of this understanding has hindered better assessment of dissolved organic matter (DOM) formation from SOM via oxidative weathering and consequential environmental impacts.

In this context, SOM composition subject to differing degrees of oxidative weathering was revealed using the method of Ishiwatari et al. (1977). Both coal (lignite and subbituminous coal) and sedimentary rocks (quartzose arenite, siliceous mudstone, siliceous shale and diatomaceous shale) were selected as a prevalent source of DOM. For humic extraction, organic molecules permeable through a dialysis membrane during HA and FA purification processes were often neglected in their quantification. In this study, we defined this permeable fraction (<1000 Da) as smaller molecular size fraction (SMSF), and quantified it along with humin, HA and FA. To the author's knowledge, this study is the first to suggest evolutionary routes of SOM through quantifications of lipid-carbon(C), humin-C, alkali soluble-C, HA-C, FA-C and SMSF-C. The extracted fractions were characterized by elemental analysis (precision $\pm 1.5\%$), ^{13}C nuclear magnetic resonance (NMR) spectroscopy (precision $\pm 2.4\%$) and excitation-emission matrix (EEM) spectroscopy (precision $\pm 1.0\%$). The humic composition of brecciated quartzose arenite derived from an anoxic environment and vein-populated siliceous mudstone were also analyzed for comparison.

2. Material and methods

2.1. Material

Hokkaido is the northernmost island of Japan (Fig. 1), and is located relatively near the Asian continent in the northwestern Pacific Ocean. The basement of the western part of Hokkaido developed in part as an island arc-trench system in the Jurassic to Cretaceous, which extends southwards to Japan's main island. On the other hand, the basement of the eastern part of Hokkaido belongs to the Okhotsk land block of the Cretaceous. Hokkaido has the largest coal resources (14.8 billion metric tons) in Japan and shares this feature with Kyusyu Island. These resources formed in the Paleogene–Neogene, ranging rank from lignite to bituminous coal.

The sampling locations (Horonobe, Monomanai and Kushiro) in Hokkaido were chosen as those where both weathered and unweathered samples were recoverable (Fig. 1, Table 1). The climate in the research area is considered humid subarctic, with

average annual temperature and precipitation of about 6°C (temperature range: about -15°C to $+30^\circ\text{C}$), and 950–1400 mm, respectively. The relevant geology of the collected samples is briefly summarized as follows. In Horonobe, Miocene lignite in the Soyakyotan Formation is distributed in the Tempoku coalfield (Fig. 1). Its total organic carbon (TOC) content, volatile matter content and calorific value are about 69%, 47–53% and 6900–7200 kcal/kg, respectively on a dry, ash free basis. The Soyakyotan Fm. is unconformably overlain by massive marine sediments (~ 3 km) dating to the Miocene–Pliocene, which transits from older (hence deeper) shallow marine sediments to younger (hence shallower) deep marine sediments. The deep marine sediments are composed of the Miocene Wakkanai Fm. consisting of siliceous shale, and the Miocene–Pliocene Koetoi Fm. consisting of diatomaceous shale. The Koetoi Fm. is characterized by the presence of opal-A, which is diagenetically transformed into opal-CT in the Wakkanai Fm. (Iijima and Tada, 1981).

In Kushiro, Eocene subbituminous coal in the Harutori Fm. is distributed in the Kushiro coalfield (Fig. 1). The TOC content, volatile matter content and calorific value are about 73%, 43–58% and 7500–8000 kcal/kg, respectively on a dry, ash free basis. Under the Harutori Fm. is located the Cretaceous Shiomi Fm., sandy siltstone and sandstone that forms a part of the eastern basement of Hokkaido.

The basement of Monomanai is Cretaceous Yezo Group, forming a part of the western basement of Hokkaido. The Yezo Group consists of mudstone, sandstone and conglomerate.

The degree of oxidative weathering of the samples was basically judged by relative color and physical strength of the samples, using authorized methods (e.g., ISRM, 1978; ISO 14689-1, 2003). With regards to the color alteration of sedimentary rocks, whitening due to leaching of organic carbon (Petsch et al., 2005; Fischer et al., 2007) and yellow-browning due to iron oxide and hydroxide formation (Schwertmann and Cornell, 1991; Hu et al., 2014) are commonly observed during oxidative weathering.

In this study, we did not need to obtain absolutely “unweathered” samples, because the focus was to reveal humic compositional differences between two or more samples of the same origin, owing to the differing degrees of oxidative weathering. Hence the terms “unweathered” and “weathered” were used in a relative sense. For example, even somewhat weathered samples were designated as “unweathered” if the sample was the least weathered among the others of the same origin. For the samples that were altered in a differing manner as compared to oxidative weathering effects, the term “weathered” was not used. The details of the sample labeling of the 15 samples are given below.

In Horonobe, a black, hard lignite in the Soyakyotan Fm. (Miocene) from a riverbed outcrop was collected and labeled as “unweathered lignite.” Dark brown, and somewhat fragile lignite from a slope outcrop alongside the river was collected and labeled as “moderately weathered lignite.” Red-yellowish, highly fragile lignite from a slope outcrop, uncovered by road construction, was collected and labeled as “extensively weathered lignite.”

In Kushiro, a blackish, hard subbituminous coal in the Harutori Fm. (Eocene) was obtained at an underground coal mine, immediately after having been mined. This sample was labeled as “unweathered subbituminous coal.” On the tunnel wall of the mine, densely fractured coal was exposed to air for about two years after tunnel construction (September 2010). This sample was collected and labeled as “weathered subbituminous coal.” In Monomanai, recently excavated waste rocks in the Yezo Group (Cretaceous) from tunnel construction were accumulated at interim storage sites. Among the waste rocks, a hard, light olive grayish quartzose arenite was collected and labeled as “unweathered sandstone.” Similarly, a hard grayish siliceous mudstone was collected and labeled as “unweathered mudstone.” The

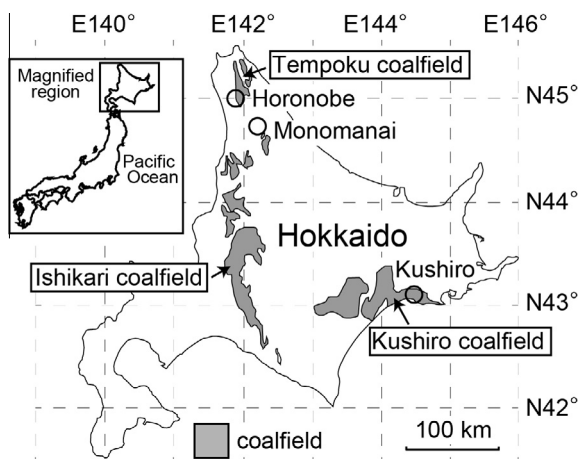


Fig. 1. Sampling locations.

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