Palaeogeography, Palaeoclimatology, Palaeoecology 371 (2013) 54–61

Contents lists available at SciVerse ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Contributions of soot to $\delta^{13}C$ of organic matter in Cretaceous lacustrine deposits, Gyeongsang Basin, Korea: Implication for paleoenvironmental reconstructions

Sung Kyung Hong [a], Yong Il Lee [b,*]

[a] Petroleum and Marine Resource Division, Korea Institute of Geoscience and Mineral Resources, 124 Gwahang-no, Yuseong-gu, Daejeon, 305-350, Republic of Korea
[b] School of Earth and Environmental Sciences, Seoul National University, 1 Gwanak-no, Gwanak-gu, Seoul, 151-747, Republic of Korea

A R T I C L E I N F O

Article history:
Received 18 April 2012
Received in revised form 4 December 2012
Accepted 8 December 2012
Available online 31 December 2012

Keywords:
Organic matter
Soot
Paleoenvironment
Gyeongsang Basin
Carbon isotope composition

A B S T R A C T

This study reports that soot carbon (SC) derived from biomass burning is an important constituent of total organic carbon (TOC) (30–90%) in two Cretaceous lacustrine deposits (Middle Albian Jinju Formation and Early Cenomanian Banyaweol Formation) of the Gyeongsang Basin, Korea and that SC contributed significantly to the carbon isotope composition ($\delta^{13}C$) of the TOC. $\delta^{13}C$ of the TOC and $\delta^{13}C$ of the SC-corrected (non-SC) organic matter range from −24.7‰ to −21.9‰ and −25.1‰ to −20.7‰ in the Jinju Formation, and −24.7‰ to −23.0‰ and from −26.4‰ to −21.7‰ in the Banyaweol Formation, respectively. Based on the $\delta^{13}C$ values of coeval charcoal, the calculated $\delta^{13}C$ of the original plant material in the surrounding watershed of the paleo-Jinju lake ranged from −21.8‰ to −17.8‰ (av. −19.3‰). These values are considerably different from $\delta^{13}C$ of vegetation (av.−24.3‰) estimated from SC. The estimated $\delta^{13}C$ values of non-SC organic carbon are different from those of the TOC, by up to 3.5‰ (either an enrichment or depletion across this value). This discrepancy indicates that the presence of SC in sedimentary organic carbon affected carbon isotope composition of TOC in the studied lacustrine deposits and led to increase uncertainty of interpretation of paleoenvironment of the watershed. For improving the paleoenvironmental reconstructions by utilizing the $\delta^{13}C$ values of TOC in ancient lacustrine sediments, a correction for the contribution of SC to TOC needs to be considered.

1. Introduction

Total organic carbon (TOC) in lacustrine sediments comprises a mixture of carbon from two sources: a terrestrial source and lacustrine source. Plant tissues in the watershed of lakes have been shown to be the principal source of terrestrial carbon in lakes (Tablot and Johannessen, 1992). The carbon isotope composition of plant organic matter is primarily controlled by three main factors: 1) the photosynthetic pathway (C_3, C_4, and CAM), 2) carbon isotope composition of atmospheric CO_2, and 3) environmental factors, such as water availability, canopy effect, temperature, and difference in pCO_2 with altitude (Körner et al., 1988; Tieszen, 1991). C_3 plants dominated the history of terrestrial vegetation, as C_4 plants became abundant only in the last 7–8 Ma (Kohn, 2010). The carbon isotope compositions of C_3 plant exhibit a large range from −20‰ to −37‰, reflecting diverse environmental conditions under which they grow (Tieszen, 1991; Arens et al., 2000; Kohn, 2010). Most studies of $\delta^{13}C_{TOC}$ of lacustrine deposits have considered local plants as a primary source for the terrestrial organic matter (i.e., Tablot and Johannessen, 1992; Meyers and Ishiwatari, 1993). Accordingly, when organic matter in lacustrine sediments consists mainly of terrestrial plant material supported by C/N ratios, the carbon isotopic values of total organic carbon ($\delta^{13}C_{TOC}$) in ancient lacustrine sediments have been used to reconstruct paleoenvironments in the surrounding watershed (i.e., Tablot and Johannessen, 1992; Meyers and Ishiwatari, 1993; Gröcke, 1998; Sifeddine et al., 2004; Street-Perrott et al., 2004; Wei et al., 2010).

Black (pyrogenic) carbon (BC) represents a group of recalcitrant carbonaceous material produced by incomplete combustion of biomass and fossil fuels (Goldberg, 1985). BC is described as continuum from charred materials to charcoal, soot and graphite (Preston and Schmidt, 2006). Soot has significantly different properties from charcoal due to different production mechanisms (Masiello, 2004; Brid and Ascough, 2011). Soot is formed from condensation of small volatile particles in the gas phase of a fire, whereas solid residues of combustion form charcoal (Schimidt and Noack, 2000; Preston and Schmidt, 2006). Charcoal particles are larger than 2 μm and thus charcoal may indicate the burning history of local forest due to their very short range transport (Clark and Patterson, 1997). In contrast, soot is characterized by submicron-sized particles (<1 μm) that can be transported thousands of kilometers once they become airborne (Masiello, 2004) and thus soot may reflect burning of far-distant source areas.

* Corresponding author at: School of Earth and Environmental Sciences, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-747, Republic of Korea. Tel.: +82 2 880 6736; fax: +82 2 878 0252.
E-mail address: lee2602@plaza.snu.ac.kr (Y.I. Lee).

0031-0182/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.palaeo.2012.12.016

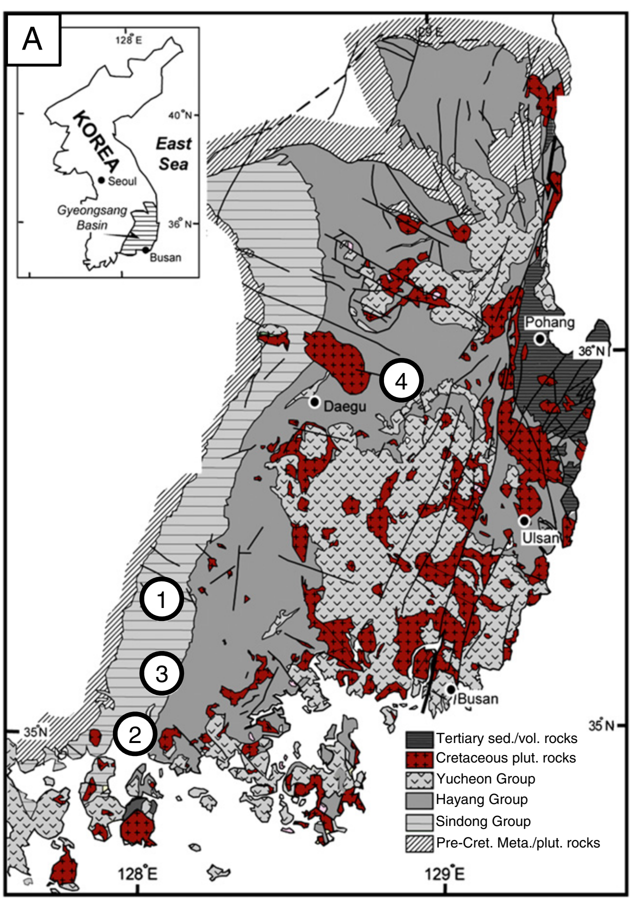
Natural vegetation burns and forest fires have occurred frequently during geological time (Scott, 2000; Glasspool et al., 2004). Soot and charcoal have been reported from lacustrine and marine sediments over a range of geological time periods (Wolbach and Anders, 1989; Lim and Cachier, 1996; Verardo and Ruddiman, 1996; Masiello and Druffel, 1998; Jia et al., 2003; Liu et al., 2007). The $\delta^{13}C$ measurements of charcoal and soot in sediments have been used to reconstruct paleovegetation and paleoclimatic conditions of watershed area and large-scale continental source areas, respectively (Jia et al., 2003; Liu et al., 2007; Hall et al., 2008).

When soot particles are originated from the burning of plants growing beyond the watershed or catchment basin, the $\delta^{13}C_{TOC}$ values may be affected by the carbon isotope composition of SC and/or the fraction of SC in TOC. In deep ocean sediments, the BC concentration of TOC was measured up to 90% (Verardo and Ruddiman, 1996), whereas SC is present as up to 10% of the organic carbon in modern and Holocene terrestrial sediments (Muri et al., 2002; Thevenon et al., 2003; Bogdal et al., 2011). Because post-depositional changes of SC are generally assumed to be minor (Masiello, 2004), the SC fraction of TOC in ancient sediments may increase with geological time. However, data on the SC content of pre-Quaternary terrestrial sedimentary rocks are sparse. Furthermore, until now no, systematic study has been carried out to determine how the presence of SC affects the carbon isotopic values of bulk TOC measurements in ancient terrestrial deposits. Therefore, the purpose of this study is to identify the relative contributions of SC to the bulk $\delta^{13}C$ signal of TOC in Cretaceous lacustrine sediments. This study reports first the occurrence of the oldest fossil soot in sedimentary rock.

We focus on the Gyeongsang Basin, the largest Cretaceous nonmarine basin in Korea (Fig. 1A), which is filled with cyclical alluvial, fluvial, and lacustrine deposits. Two lacustrine deposits selected in this study, the Jinju Formation in the lower sequence and the Banyaweol Formation in the middle sequence (Fig. 1B), contain a significant organic matter component. Charcoal fragments are also observed in the Jinju Formation. We analyzed the contents of TOC and SC of the two lacustrine successions and measured the carbon isotope composition of TOC ($\delta^{13}C_{TOC}$), SC ($\delta^{13}C_{SC}$), and Jinju charcoal samples ($\delta^{13}C_{charcoal}$). Using these data, we assess the contribution of SC to the measured bulk $\delta^{13}C_{TOC}$ and its subsequent implications for paleoenvironmental reconstruction and interpretation.

2. Geological setting

Cretaceous rocks of the Gyeongsang Basin, the Gyeongsang Supergroup, are divided into the Sindong, Hayang, and Yucheon groups with decreasing age (Fig. 1A). The Sindong Group comprises the Nakdong (alluvial fan), Hasandong (fluvial plan), and Jinju (lake) formations with decreasing age (Chang, 1975). The Hayang Group near Daegu is subdivided into the Chilgok, Sila, Hakbong volcanics, Hanman, Banyaweol, Songnaedong, Chaeyaksan, and Geoncheonri formations in ascending order (Fig. 1B; Chang, 1975; Choi, 1986). Except for volcanic rocks, the sedimentary rocks of the Hayang Group were deposited in fluvial plain (Chilgok, Haman, and Songnaedong formations) and lacustrine (Banyaweol and Geoncheonri formations) environments (Choi, 1985). The Jinju Formation is about 1200 m thick and is composed of dark gray to black marginal lake shales, black open lake shales, and channel sandstones (Choi, 1985). The Banyaweol Formation is 1100 m thick and is composed of gray to black shale and siltstone, and sandstone with intercalations of thin



B

Gyeongsang Supergroup		Age
Yucheon Group	Volcanic rocks	Campanian~
	Goseong Fm.	
Hayang Group	Geoncheonri Fm.	Turonian~ Santonian
	Chaeyaksan vol.	Cenomanian
	Songnaedong Fm.	
	Banyaweol Fm. (4)	
	Haman Fm.	Albian
	Hakbong vol.	
	Silla Conglomerate	
	Chilgok Fm.	
Sindong Group	Jinju Fm. (1, 2, 3)	
	Hasandong Fm.	
	Nakdong Fm.	Aptian

Fig. 1. A. Geological map of the Gyeongsang Basin and sampling sites (modified after Lee and Lee, 2001). B. Stratigraphic classification of the northern part of the Milyang Subbasin (modified after Chang, 1988). Circled numbers on the map correspond to the stratigraphic unit from which samples were collected. Lacustrine shale samples were collected from the Jinju (①) and Banyaweol (④) formations, and charcoal samples from the Jinju Formation (②, ③).