



Global mapping of carbon isotope ratios in coal

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ABSTRACT

We present stable carbon isotope ratios ($\delta^{13}\text{C}$) in 95 coals from 10 countries on a global $\delta^{13}\text{C}$ map and trace the relationship between $\delta^{13}\text{C}$ and coal production over geologic time. In addition, we compare $\delta^{13}\text{C}$ trends in coal as determined from samples and as calculated independently from trends in the $\delta^{13}\text{C}$ of atmospheric carbon dioxide (CO_2). We show that the $\delta^{13}\text{C}$ values measured in coal display a wide range (-27.4‰ to -23.7‰). Furthermore, the $\delta^{13}\text{C}$ values in Cenozoic coals are systematically lighter than those in Paleozoic coals. We made independent estimates of $\delta^{13}\text{C}$ values in coal by tracing the derivation of carbon from atmospheric CO_2 , from its incorporation in plants to the resulting coals. The resulting $\delta^{13}\text{C}$ histories in coal also show a trend toward lighter values. We suggest that the history of $\delta^{13}\text{C}$ in coal may reflect isotopic changes in atmospheric CO_2 caused by interactions of the short-term and long-term carbon cycles, in addition to factors in the photosynthetic process.

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1. Introduction

Coal is used worldwide as an energy source for its high combustion efficiency, relatively cheap cost, and large resource base. Coal is generally derived from decayed plants through geologic forces, including mild heat and pressure, and it has formed in every geologic time period since the Carboniferous, approximately 350 million years (Myr) ago (Walker, 2000; Thomas, 2012). The composition of coal is derived from polymeric hydrocarbon molecules, which vary in different areas. Coal is composed primarily of carbon with subsidiary amounts of hydrogen, oxygen, nitrogen, and sulfur. Limited research has been done on factors determining the isotope ratios of each of these elements. For example, stable hydrogen isotope ratios (δD) in coal have been shown to depend on differences in plant types (Schiegl and Vogel, 1970; Schoell, 1984) and differences in mean surface temperature at the time of plant growth (Schiegl and Vogel, 1970). Stable sulfur isotope ratios ($\delta^{34}\text{S}$) have been shown to be governed by the environment of the coalification process (Motoyama et al., 2011). However, there is no consensus on what may dominantly control isotope ratios of carbon in coal.

Over the past 60 years, stable carbon isotope ratios ($\delta^{13}\text{C}$) in coals have been measured in various areas (Craig, 1953; Wickman, 1953; Jeffery et al., 1955; Compston, 1960; Degens, 1969; Redding et al., 1980; Smith et al., 1982; Schwarzkopf and Schoell, 1985). Although some early studies found no correlation between $\delta^{13}\text{C}$ and coal age (Craig, 1953; Degens, 1969), others found that $\delta^{13}\text{C}$ is lighter in younger coals than in older coals (Wickman, 1953; Jeffery et al., 1955). More

recently, Gröcke (1998) reported that despite numerous studies, the relationship of $\delta^{13}\text{C}$ in coals to geologic time is still poorly known. Meanwhile, research has begun to address the global carbon cycle of the entire Phanerozoic and to assess the changing roles of burial of organic carbon, atmospheric composition, and mantle geochemical cycles since 550 Myr ago (Berner, 2003). In this paper, we present a large number of new $\delta^{13}\text{C}$ data from coal deposits around the world and address the global relationship between $\delta^{13}\text{C}$ and coal age. We conclude by discussing possible governing factors of the $\delta^{13}\text{C}$ values of coals.

2. Method

A total of 95 coal samples were investigated, representing 10 coal-producing countries (Table 1). Samples were supplied by the Coal Bank, jointly operated by the National Institute of Advanced Industrial Science and Technology (AIST) of Japan and the Japan Coal Energy Center (JCOAL: <http://www.jcoal.or.jp/coaldb/coaldb.html>; contact coalbank@aist.go.jp for information). All samples were crushed and then screened at 100 mesh before their $\delta^{13}\text{C}$ values were determined.

Carbon in coal comprises carbonate carbon (CC), organic carbon (OC), and black carbon (BC). In general, for aerosol studies, BC is separated from CC by using gaseous hydrochloric acid and separated from OC by combustion. In this study, we tested five coal samples (SS018 CHN, SS027 CHN, SS056 CHN, SS057 CHN, SS072 CHN) to determine the isotopic differences between BC and bulk carbon (CC + OC + BC). First, CC was removed by exposing the samples to gaseous hydrochloric acid (1 M) in a glass desiccator for approximately 24 h. Then OC was removed by the Interagency Monitor of Protected Visual Environments (IMPROVE) method, developed by the Desert Research Institute (DRI Operating Procedure, 2005); the samples were heated in a quartz tube in a ceramic combustion furnace (Asahirika Co. Ltd., Chiba, Japan) at 550 °C for 15 min

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Table 1
 $\delta^{13}\text{C}$ in coal from 10 producing countries.

Country	n	$\delta^{13}\text{C}$ (‰)			
		Average \pm S.D.	Median	Min	Max
Australia	27	-24.5 ± 0.6	-24.6	-25.6	-23.4
Indonesia	19	-27.4 ± 0.8	-27.6	-28.4	-26.3
China	16	-24.2 ± 0.5	-24.2	-24.9	-23.5
United States	10	-25.7 ± 0.4	-25.8	-26.1	-24.9
Russia	7	-24.4 ± 1.1	-24.3	-26.4	-22.7
South Africa	6	-23.7 ± 0.7	-23.5	-25.0	-23.2
Japan	4	-25.3 ± 0.5	-25.5	-25.6	-24.5
Canada	3	-24.3 ± 0.6	-24.4	-24.9	-23.7
Colombia	2	-25.4 ± 0.8		-26.0	-24.9
Vietnam	1	-24.3 ± 0.0		-24.3	-24.2

under ultrahigh purity helium (>99.99995%) at a flow rate of 50 mL/min to remove OC, then cooled under the same helium flow. The resulting differences in $\delta^{13}\text{C}$ between BC and bulk carbon were less than 0.5‰. Thus, we analyzed the coal samples directly without acid processing or IMPROVE combustion to separate these carbon types.

Because the carbon content of all coal samples except SS045 (carbon content 49%) exceeded 60% (Table S1), samples of approximately 0.5 mg were placed in a tin cup without further processing and analyzed with an elemental analyzer (EA; Flash EA 1112, Thermo Fisher Scientific Inc., Bremen, Germany) and an isotope ratio mass spectrometer (IRMS; MAT253, Thermo Fisher Scientific). The samples were combusted instantaneously in the EA, and the carbon was converted to carbon dioxide (CO_2) by using an oxidation catalyst and the reduction tube in the EA. The oxidation and reduction tubes in the EA were maintained at 1000 °C and 750 °C, respectively. The flow rate of ultrahigh purity helium during the analysis was 100 mL/min. The CO_2 from the EA was ionized and its $\delta^{13}\text{C}$ value was measured by IRMS using ISODAT NT 2.0 software (Thermo Fisher Scientific).

The stable isotope composition of the carbon, expressed in delta (δ) notation in permil (‰) units, was calculated as follows:

$$\delta^{13}\text{C} = \left(\frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{std}}} - 1 \right) \times 1000[\text{‰}]$$

where $^{13}\text{C}/^{12}\text{C}_{\text{sample}}$ and $^{13}\text{C}/^{12}\text{C}_{\text{std}}$ are the atomic ratios of ^{13}C to ^{12}C in the sample and in the Vienna Pee Dee Belemnite (VPDB) standard, respectively. All samples were measured in triplicate.

All data were averaged, and a two-point linear calibration was carried out for $\delta^{13}\text{C}$ against standards (Coplen et al., 2006). International isotopic standards, including IAEA-CH-3 (cellulose, $\delta^{13}\text{C} = -24.724\text{‰}$), IAEA-600 (caffeine, $\delta^{13}\text{C} = -27.771\text{‰}$), LSVEC (lithium carbonate, $\delta^{13}\text{C} = -46.6\text{‰}$), and USGS24 (graphite, $\delta^{13}\text{C} = -16.049\text{‰}$), were also used. As a check of instrumental stability, the SHOKO stable isotope working standard histidine (1-histidine, Shoko Co., Ltd., Tokyo, Japan; $\delta^{13}\text{C} = -9.8\text{‰}$) was analyzed after every nine coal samples. The analytical uncertainty (standard deviation) of the reported $\delta^{13}\text{C}$ values for the 95 coal samples in this study was within 0.74‰ (mean, 0.12‰).

3. Results and discussion

The $\delta^{13}\text{C}$ values we determined in our coals are listed in Table 1, in which national averages are used as a proxy for regional averages (all data are listed in Table S1). The global $\delta^{13}\text{C}$ maps shown in Fig. 1 present our data separately (Fig. 1a) and combined with previously published data (Fig. 1b) and are, to our knowledge, the first maps of their kind. They make it possible to see in one view the global distribution of $\delta^{13}\text{C}$ in coals, and they promise to clarify the relationships between the sources and $\delta^{13}\text{C}$ values of coals. These maps and the underlying data may enable isotopic studies similar to those being done using the δD and $\delta^{18}\text{O}$ values of water (West et al., 2010).

In our results, Indonesian coal is isotopically lightest (average $-27.4 \pm 0.8\text{‰}$) and South African coal is heaviest (average $-23.7 \pm 0.7\text{‰}$). The range represented by these results, approximately 4‰, is much greater than the analytical uncertainty (standard deviation) of 0.74‰ (mean, 0.12‰). With regard to isotopic variability within a single coal seam, Compston (1960) reported that the standard deviation of $\delta^{13}\text{C}$ in 11 coal samples collected over a distance of approximately 15 km from Artie's seam in Australia was 0.3‰. In other seams, including the St. Heliars ($n = 2$), Bulli ($n = 2$), and Wongawilli seams ($n = 3, 2$), the reported within-seam difference in $\delta^{13}\text{C}$ was approximately 1‰. These examples suggest that there is little difference in $\delta^{13}\text{C}$ within individual coal seams. Our $\delta^{13}\text{C}$ values for Australian coal averaged $-24.5 \pm 0.6\text{‰}$, nearly the same as previously reported values of $-24.0 \pm 1.8\text{‰}$ (Jeffery et al., 1955) and $-24.3 \pm 1.5\text{‰}$ (Compston, 1960). Our $\delta^{13}\text{C}$ results for the United States averaged $-25.7 \pm 0.4\text{‰}$, the same as or slightly lighter than previously reported values of $-23.9 \pm 1.1\text{‰}$ (Craig, 1953) and $-25.0 \pm 1.4\text{‰}$ (Redding et al., 1980). There was no correlation between $\delta^{13}\text{C}$ and the content of carbon, hydrogen, nitrogen, sulfur, or oxygen in our samples (Fig. 2).

Our data also revealed variations in $\delta^{13}\text{C}$ of coal within the larger coal-producing countries. For example, $\delta^{13}\text{C}$ of coal in China ranged from -24.9‰ to -23.5‰ , with the northern samples being isotopically heavier than the southern ones (Fig. 3). Domestic use of coal in China for cooking and heating (Bruce et al., 2000; Chen et al., 2005) is especially heavy in northern China during the “heating season” from November to March (Cao et al., 2007). The source of black carbon in winter aerosols in Japan has been traced by its $\delta^{13}\text{C}$ values to coal combustion in China (Kawashima and Haneishi, 2012), and our $\delta^{13}\text{C}$ map for coal supports a specific origin in northern China. Our measurements of $\delta^{13}\text{C}$ in coal from Russia showed a wide range of values from -26.4‰ to -22.7‰ (Fig. 1a). Coal from the United States can be differentiated between eastern and western sources when our data are combined with previously published data (Craig, 1953; Redding et al., 1980) (Fig. 1b).

The relationships between our $\delta^{13}\text{C}$ results and the ages of coals are summarized in Fig. 4, with coal-producing regions arranged in order of geologic age (Fig. 5 shows $\delta^{13}\text{C}$ maps for three age periods). The difference in $\delta^{13}\text{C}$ between coals from South Africa (290–250 Myr old) and Indonesia (30–10 Myr old) is approximately 4‰, consistent with the “age effect,” in which younger coal is isotopically lighter than older coal (Wickman, 1953; Jeffery et al., 1955). The H/C and O/C ratios of our samples (Van Krevelen, 1961) indicate that they comprised 80 bituminous coals and 15 subbituminous coals. The $\delta^{13}\text{C}$ of the bituminous and subbituminous coals ranged from -28.0‰ to -22.7‰ (average $-24.9\text{‰} \pm 1.1\text{‰}$) and -28.4‰ to -23.7‰ (average $-26.8\text{‰} \pm 1.6\text{‰}$), respectively; thus, the subbituminous coals were isotopically lighter than the bituminous coals. The $\delta^{13}\text{C}$ values of fossil plant became approximately 4‰ to 5‰ lighter during Cretaceous and Cenozoic time (Beerling et al., 2002; Tappert et al., 2013). The age effect is thought to arise from various factors involving the coalification process and the carbon cycle. As coalification progresses, the carbon content in coals increases as water, CO_2 , and the more volatile hydrocarbons such as methane are lost (Thomas, 2012). Because the $\delta^{13}\text{C}$ of methane is very light, from approximately -65.4‰ to -51.8‰ (Aravena et al., 2003), as the methane is lost, the $\delta^{13}\text{C}$ of the coal becomes correspondingly heavier (Whiticar, 1996). Thus, a relationship arising from the coalification process is plausible between the carbon content and the $\delta^{13}\text{C}$ of coals. However, our research found no correlation between $\delta^{13}\text{C}$ and the carbon content of the coal (Fig. 2). Thus, we sought an explanation for the age effect in factors other than the coalification process.

The $\delta^{13}\text{C}$ values of coals of Carboniferous and Permian age (350–250 Myr ago) were heavier than those of other coals (Fig. 4). To explain this result, we must distinguish between two different carbon cycles. The short-term carbon cycle, which operates at or near the earth's surface and comprises photosynthesis, respiration, and the air-sea exchange of CO_2 , has a time scale ranging from days to tens of thousands of years. The long-term carbon cycle consists of the exchange of

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