



Global mapping of carbon isotope ratios in coal

Nana Suto¹, Hiroto Kawashima*

Department of Management Science and Engineering, Faculty of Systems Science and Technology, Akita Prefectural University, Japan



ARTICLE INFO

Article history:

Received 23 November 2015

Revised 19 April 2016

Accepted 1 May 2016

Available online 3 May 2016

Keywords:

Coal
Carbon isotope
Carbon cycle
Organic carbon

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.

© 2016 Elsevier B.V. All rights reserved.

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

* Corresponding author.

E-mail address: kawashima@akita-pu.ac.jp (H. Kawashima).

¹ Present address: Energy and Environment Research Division, Japan Automobile Research Institute, Japan.

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 (l-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

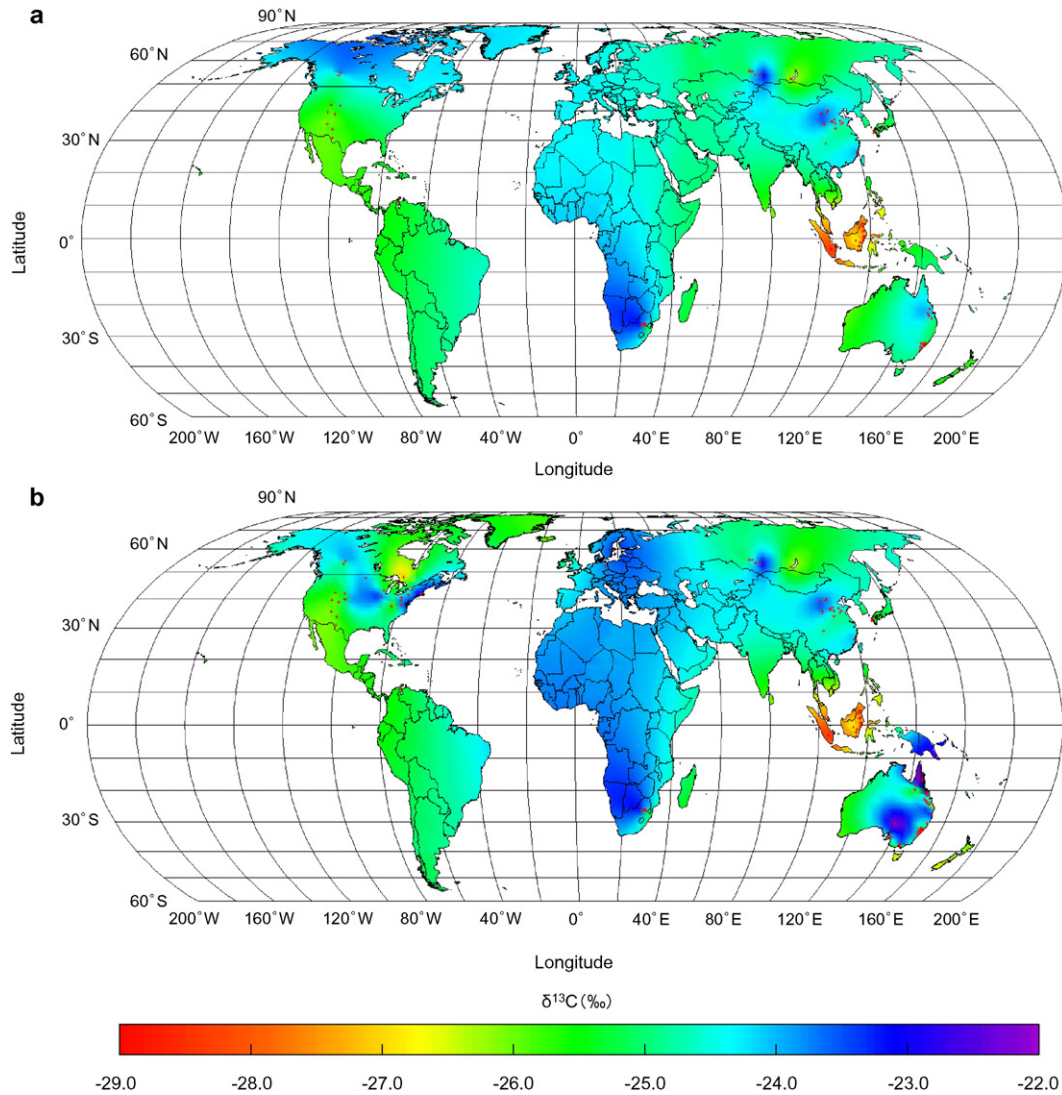


Fig. 1. Global distribution of carbon isotope ratios in coal. (a) Coal samples from 80 localities in 10 countries. Since 10 of the 95 coal samples were from the same lots, their samples were averaged. Precise locations were not available for five coal samples (SS006 AUS, SS061 USA, SS076 RUS, SS091 USA and SS096 CHN). Results for South America are based on a single value from Colombia. (b) Coal samples from 121 localities in 13 countries (including samples shown in a): Australia (48 samples) (Jeffery et al., 1955; Compston, 1960; Redding et al., 1980), Indonesia (15 samples), China (15 samples), Western U.S.A. (10 samples) (Craig, 1953; Redding et al., 1980), Eastern U.S.A. (9 samples) (Craig, 1953; Redding et al., 1980), Russia (6 samples), South Africa (6 samples), Canada (4 samples) (Craig, 1953), Japan (3 samples), Colombia (1 sample), Germany (1 sample) (Craig, 1953; Redding et al., 1980; Schwarzkopf and Schoell, 1985), Iceland (1 sample) (Craig, 1953), Sweden (1 sample) (Craig, 1953), and Vietnam (1 sample). Figure created using Map Viewer 7 (Golden Software Inc., Golden, CO, U.S.A.).

carbon between rocks and the earth's surface (i.e., the short-term cycle) over millions of years, and it is this cycle that is of interest with respect to the origin of fossil fuels (Berner, 2003, 2004). We consider coal to be an important carbon reservoir over long time scales. The $\delta^{13}\text{C}$ of atmospheric CO_2 was heaviest in Carboniferous and Permian time, and it has gradually become lighter until the present day (Beerling and Woodward, 2001). In the photosynthetic process, the RuBisCO carboxylation path in C3 plants favors $^{12}\text{CO}_2$ over $^{13}\text{CO}_2$. During Carboniferous and Permian time, atmospheric CO_2 and light carbon were removed from the atmosphere and the atmospheric O_2 concentration was raised as a consequence of massive burial of organic carbon. Subsequently, C3 plants took in heavier atmospheric CO_2 in the short-term cycle, and their remains formed isotopically heavier coal. Thus, the short-term carbon cycle has been intimately connected to the long-term carbon cycle.

Coal was produced from C3 plants, which derive their carbon from atmospheric CO_2 . However, the $\delta^{13}\text{C}$ values of modern C3 plants vary widely (from approximately -35% to -25%) (Wickman, 1952; Craig, 1953; Smith and Epstein, 1971) and cannot be used directly. Here, we assumed that ^{13}C in atmospheric CO_2 was taken up by C3 plants without regard to species, and then the plants were converted

into coal. Peters-Kottig et al. (2006) reported that the $\delta^{13}\text{C}$ values of four C3 plant groups from the Carboniferous Euramerican Phytogeographic Province lie within a remarkably narrow range around 1.5% . The $\delta^{13}\text{C}$ history of atmospheric CO_2 over geologic time and the various isotope fractionations that take place during the conversion from CO_2 to coal are well determined. Therefore, we made an independent calculation of $\delta^{13}\text{C}$ in coal during the Phanerozoic as follows.

(1) The $\delta^{13}\text{C}$ values of atmospheric CO_2 have been calculated from values in marine limestone for the past 350 Myr (e.g., Isozaki, 2009). Those data show that the $\delta^{13}\text{C}$ value in limestone from Carboniferous and Permian time (350–250 Myr ago) grew slightly heavier by approximately 3% to 4%, and from the Permian to the present (250–0 Myr ago) it grew lighter by 4% to 0%. The fractionation of ^{13}C in marine limestone relative to atmospheric CO_2 is -7% (Mora et al., 1996). Thus, since the Carboniferous, the estimated $\delta^{13}\text{C}$ in atmospheric CO_2 has decreased from approximately -3% to -7% . (2) The ^{13}C fractionation from atmospheric CO_2 to C3 plants during photosynthesis is negative at -20% (Smith and Epstein, 1971). (3) As described above, the coalification process from C3 plants to coal is apparently isotopically neutral.

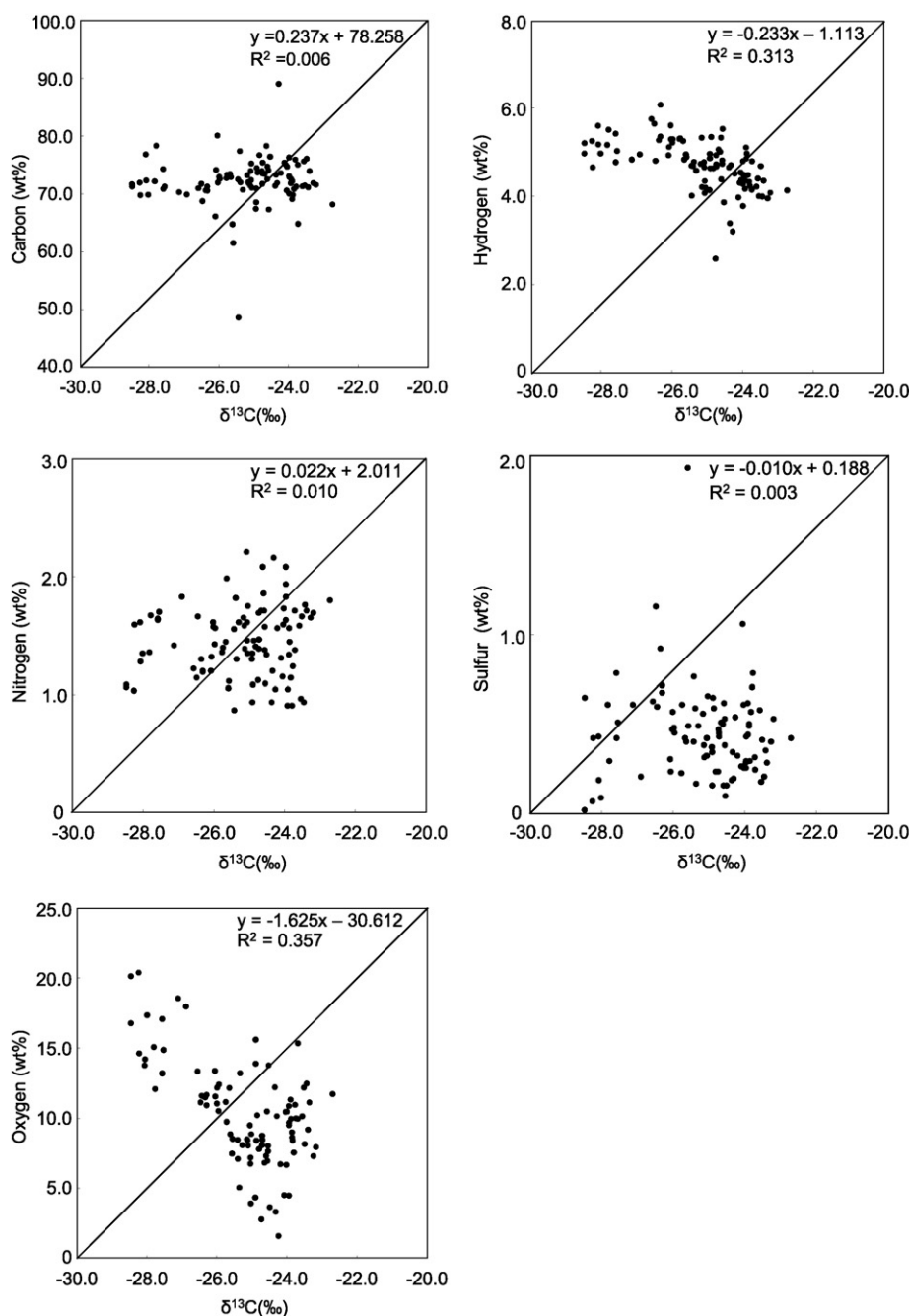


Fig. 2. Correlations between $\delta^{13}\text{C}$ in coal and carbon, hydrogen, nitrogen, sulfur, and oxygen content.

In sum, the measured $\delta^{13}\text{C}$ values of Cenozoic coals are systematically lighter than those in Paleozoic coals, and the estimated $\delta^{13}\text{C}$ values of coals calculated independently from atmospheric CO_2 values show the same trend (Fig. 6). The correlation coefficient between these two estimates of $\delta^{13}\text{C}$ in coal is 0.51, and if the three samples from Canada and the two samples from Colombia are excluded from the comparison, the correlation coefficient is 0.76 (Fig. 7). Angiosperms generally exhibit a greater degree of isotopic discrimination than gymnosperms (Chikaraishi and Naraoka, 2003; Flanagan et al., 1997; Holdgate et al., 2009). Specifically, the $\delta^{13}\text{C}$ range of angiosperms is -37.5‰ to -28.5‰ (average -32.8‰ , $n = 18$), and the range for gymnosperms is -28.3‰ to -26.0‰ (average -27.1‰ , $n = 4$) (Chikaraishi and Naraoka, 2003). Thus, the isotopic trend of coals may reflect the rise in abundance of angiosperms. We did not test this hypothesis, however, but considered gymnosperms and angiosperms together as C3 plants.

The evidence suggests that the $\delta^{13}\text{C}$ values of coal are affected by the changing $\delta^{13}\text{C}$ values in atmospheric CO_2 over geologic time.

In addition, Beerling and Woodward (2001) reported that $\delta^{13}\text{C}$ values of plants and coal of Carboniferous and Permian age are heavier owing to effects of the photosynthetic process. For this reason, we added a red line to Fig. 6 representing the $\delta^{13}\text{C}$ trend in plants over the last 350 Myr (Beerling and Woodward, 2001). The correlation coefficient between the $\delta^{13}\text{C}$ trend in coals as determined from samples and the $\delta^{13}\text{C}$ trend in plants over the last 350 Myr (Beerling and Woodward, 2001) is 0.70 if the coal samples from Canada and Colombia are excluded.

For simplicity, our independent calculation used a constant value of -20‰ for the fractionation of ^{13}C during photosynthesis. As shown in Fig. 6, the $\delta^{13}\text{C}$ of coals calculated from $\delta^{13}\text{C}$ in atmospheric CO_2 during the Carboniferous and Permian was approximately 3‰ heavier than

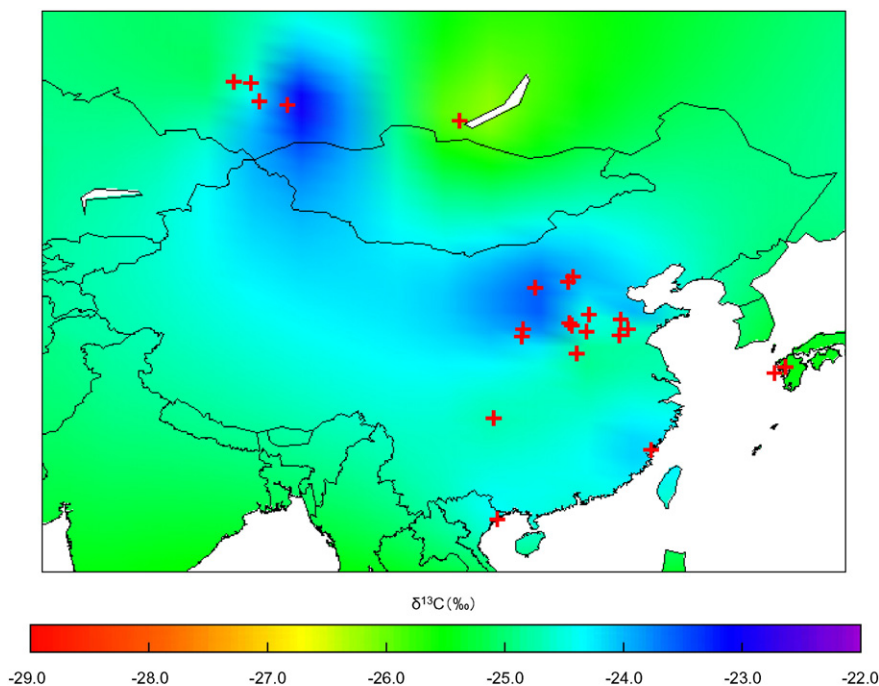


Fig. 3. Map of $\delta^{13}\text{C}$ in coals from China ($n = 15$) and surrounding countries.

the $\delta^{13}\text{C}$ determined from coal samples. Carbon isotope discrimination during photosynthesis is determined by several factors that we discuss next.

Carbon isotope discrimination during photosynthesis has been shown to have ranged between approximately -24% and -18% over the past 400 Myr (Beerling et al., 2002) and between

approximately -22.5% and -18% over the past 420 Myr (Strauss and Peters-Kottig, 2003) in response to changes in the atmospheric O_2/CO_2 ratio. Recently, it has been shown that the degree of carbon isotope discrimination during photosynthesis rises with increasing $p\text{CO}_2$ (Schubert and Jahren, 2012). During Carboniferous and Permian time, when the CO_2 concentration was low (Graham et al., 1995), stomatal

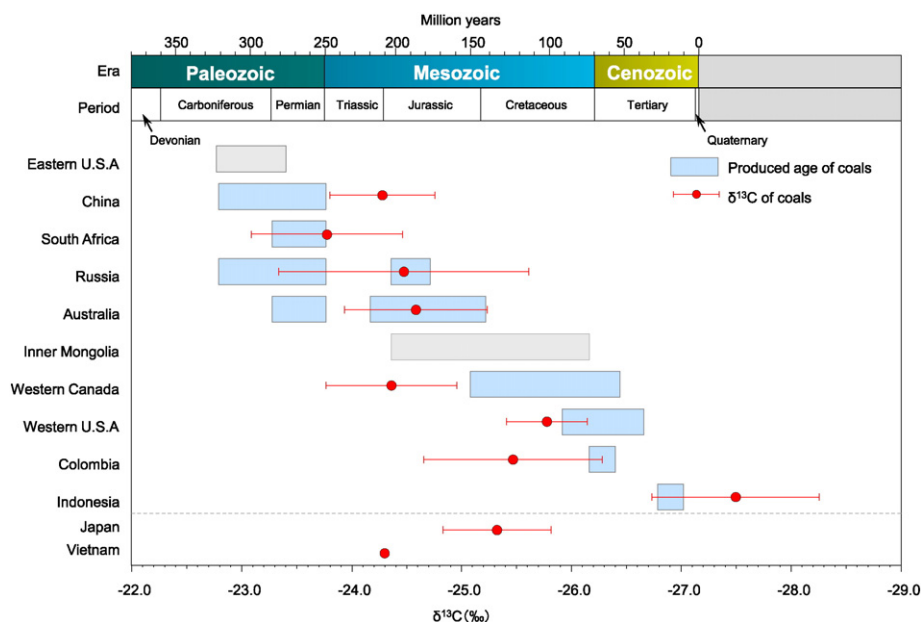


Fig. 4. Geologic age and carbon isotope ratios in coal. The blue and gray blocks show the age range of coals in the producing region (Walker, 2000; Thomas, 2012). The figure was made by fitting the $\delta^{13}\text{C}$ values and age of coals (excluding Japan and Vietnam) using the least squares method. Coal from the U.S.A. can be differentiated between eastern and western (Walker, 2000; Thomas, 2012). Although coals in Russia and Australia were divided into two ages (Russia, Carboniferous to Permian and Jurassic; Australia, Permian and Triassic to Jurassic) (Walker, 2000; Thomas, 2012), we did not have enough information to divide them by location. Coal from China was divided into two ages (Carboniferous to Permian and Triassic to Cretaceous), but it was also possible to distinguish them by location (Fig. S2). Coals from Japan and Vietnam had no age information (Walker, 2000; Thomas, 2012).

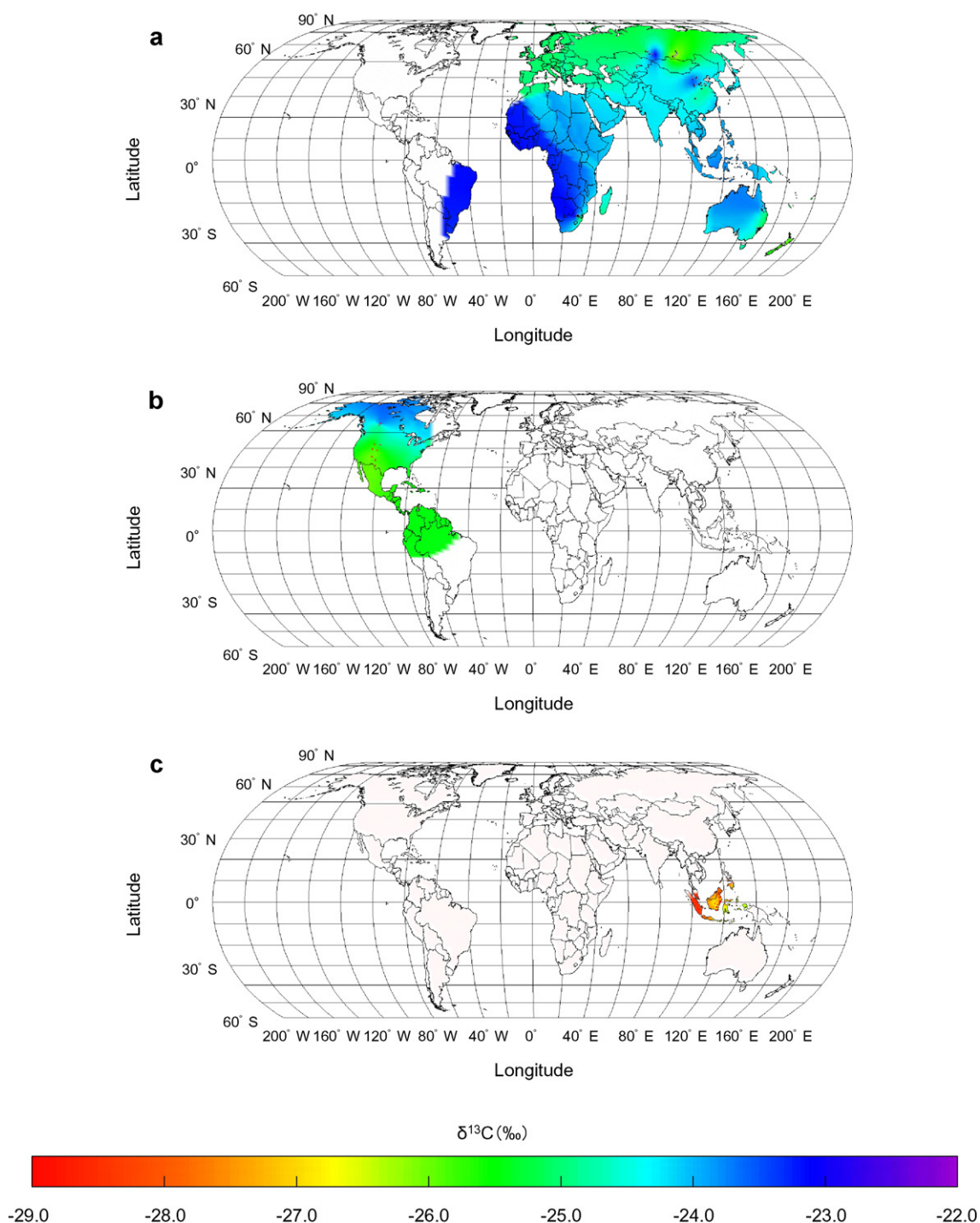


Fig. 5. Map of $\delta^{13}\text{C}$ in coals of the three age ranges in Fig. 1a. (a) Carboniferous to Jurassic, (b) Cretaceous to early Tertiary, and (c) late Tertiary.

density and stomatal conductance were high (Beerling and Woodward, 2001). Carbon isotope discrimination during photosynthesis generally is affected by the stomatal opening rate. Efficient mixing of CO_2 between the atmosphere and the intercellular space of plants raises the ratio of intercellular to ambient CO_2 partial pressures (Lloyd and Farquhar, 1994) and thus would have promoted efficient RuBisCO carboxylation during Carboniferous and Permian time. These factors would have nudged $\delta^{13}\text{C}$ toward lighter values (Beerling and Woodward, 2001; Beerling et al., 2002; Tappert et al., 2013). In addition, the O_2 concentration was high during Carboniferous and Permian time (Graham et al., 1995). This environment led to low photosynthetic rates and high photorespiration rates, favoring the development of leaves with high

stomatal densities. These high stomatal densities also would have influenced carbon isotope discrimination during photosynthesis, leading to lighter $\delta^{13}\text{C}$ values. The resulting high O_2/CO_2 ratios led to $\delta^{13}\text{C}$ values of -24% by carbon isotope discrimination during photosynthesis (Beerling and Woodward, 2001; Beerling et al., 2002). Wetland soils were probably an important factor in terrestrial carbon storage during Carboniferous and Permian time (Beerling and Woodward, 2001; Peters-Kottig et al., 2006), and massive burial of organic carbon during coal formation in the Carboniferous simultaneously removed CO_2 from the atmosphere and raised atmospheric O_2 (Berner and Canfield, 1989).

If a photosynthetic fractionation value of -24% during Carboniferous and Permian time is used instead of -20% , as we assumed in our

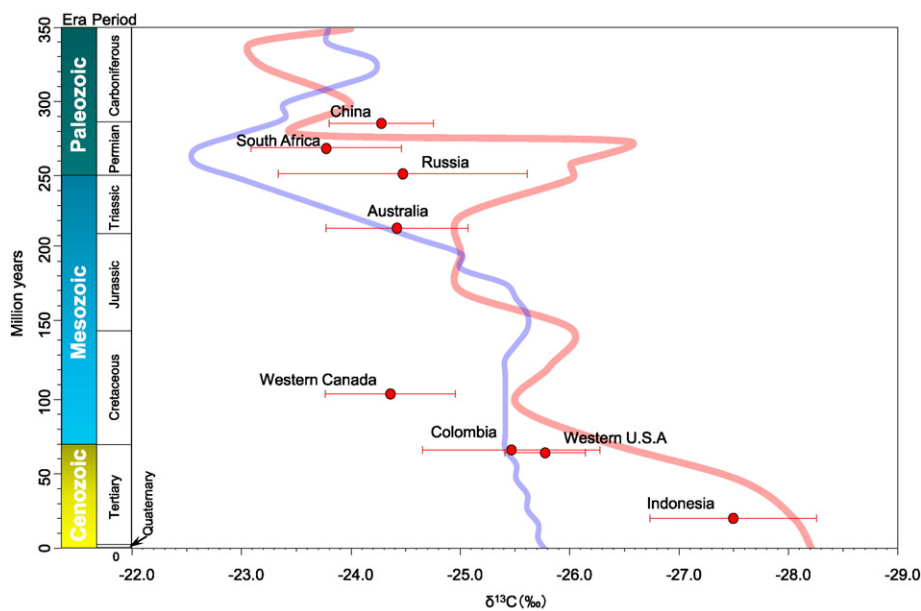


Fig. 6.

Fig. 6. Measurements of $\delta^{13}\text{C}$ in coal (red circle), estimated $\delta^{13}\text{C}$ trend in coals calculated from atmospheric CO_2 (blue line), and $\delta^{13}\text{C}$ trend in plants (red line) (Beerling and Woodward, 2001).

calculations, then the estimated $\delta^{13}\text{C}$ would be closer to the $\delta^{13}\text{C}$ determined from coal samples. If a photosynthetic fractionation value of -18% during Cretaceous time (Strauss and Peters-Kottig, 2003) is used, the estimated $\delta^{13}\text{C}$ would shift to heavier values. We suggest that the history of $\delta^{13}\text{C}$ in coal may reflect isotopic changes in atmospheric CO_2 due to interactions of the short-term and long-term carbon cycles. This study thus offers an alternative explanation for the age effect in coal.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.gexplo.2016.05.001>.

Acknowledgments

This research was partially supported by Grant-in-Aid for Scientific Research on Innovative Areas 23120704 (2011–2013) and Scientific

Research (B) 15H05121 (2015–2017) from the Ministry of Education, Culture, Sports, Science and Technology and by Akita Prefectural University, Independent Student Research (2011–2012). The support of these organizations was vital for this research and their contributions are greatly appreciated. The data for this paper are available upon request from the corresponding author. We thank anonymous reviewers whose helpful comments improved the quality of the manuscript.

References

- Aravena, R., Harrison, S.M., Barker, J.F., Abercrombie, H., Rudolph, D., 2003. Origin of methane in the Elk Valley coalfield, southeastern British Columbia. *Canada Chem. Geol.* 195, 219–227.
- Beerling, D.J., Woodward, F.I., 2001. *Vegetation and the Terrestrial Carbon Cycle*. United Kingdom at the University, Cambridge.
- Beerling, D.J., Lake, J.A., Berner, R.A., Hickey, L.J., Taylor, D.W., Royer, D.L., 2002. Carbon isotope evidence implying high O_2/CO_2 ratios in the Permo-Carboniferous atmosphere. *Geochim. Cosmochim. Acta* 66, 3757–3767.
- Berner, R.A., 2003. The long-term carbon cycle, fossil fuels and atmospheric composition. *Nature* 426, 323–326.
- Berner, R.A., 2004. *The Phanerozoic Carbon Cycle: CO_2 and O_2* . Oxford University, New York.
- Berner, R.A., Canfield, D.E., 1989. A new model for atmospheric oxygen over Phanerozoic time. *Am. J. Sci.* 289, 333–361.
- Bruce, N., Perez-Padilla, Y., Albalak, R., 2000. Indoor air pollution in developing countries: a major environmental and public health challenge. *Bull. World Health Organ.* 78, 1078–1092.
- Cao, J., Lee, S.C., Chow, J.C., Watson, J.G., Ho, K.F., Zhang, R.J., Jin, Z.D., Shen, Z.X., Chen, G.C., Kang, Y.M., Zhou, S.C., Zhang, L.Z., Qi, S.H., Dai, M.H., Cheng, Y., Hu, K., 2007. Spatial and seasonal distributions of carbonaceous aerosols over China. *J. Geophys. Res. Atmos.* 112, D22511.
- Chen, Y., Sheng, G., Bi, X., Feng, Y., Mai, B., Fu, J., 2005. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environ. Sci. Technol.* 9, 1861–1867.
- Chikaraishi, Y., Naraoka, H., 2003. Compound-Specific $\delta\text{D}-\delta^{13}\text{C}$ Analyses of N-Alkanes extracted from terrestrial and aquatic plants. *Phytochemistry* 63, 361–371.
- Compston, W., 1960. The carbon isotopic compositions of certain marine invertebrates and coals from the Australian Permian. *Geochim. Cosmochim. Acta* 18, 1–22.
- Coplen, T.B., Brand, W.A., Gehre, M., Gröning, M., Meijer, H.A.J., Toman, B., Verkouteren, R.M., 2006. New guidelines for $\delta^{13}\text{C}$ measurements. *Anal. Chem.* 78, 2439–2441.
- Craig, H., 1953. The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta* 3, 53–92.
- Degens, E.T., 1969. *Biogeochemistry of Stable Carbon Isotopes*. U.S. Geological Survey Open-File Report Organic Geochemistry. Springer, New York, pp. 304–329.
- DRI Operating Procedure, 2005. DRI Model Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples-Method IMPROVE_A, SOP #2–216.1. Desert Research Institute.

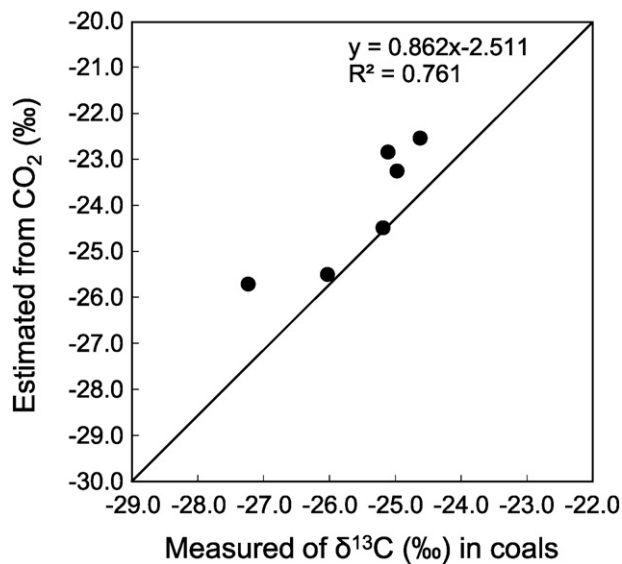


Fig. 7. Coefficients of correlation of $\delta^{13}\text{C}$ in coal from six countries (China, South Africa, Russia, Australia, Western U.S.A., and Indonesia) as measured in the laboratory and as estimated from atmospheric CO_2 .

- Flanagan, L.B., Brooks, J.R., Ehleringer, J.R., 1997. Photosynthesis and carbon isotope discrimination in boreal forest ecosystems: a comparison of functional characteristics in plants from three mature forest types. *J. Geophys. Res.* 102, 861–869.
- Graham, J.B., Dudley, R., Aguilar, N.M., Gans, C., 1995. Implications of the late Palaeozoic oxygen pulse for physiology and evolution. *Nature* 375, 117–120.
- Gröcke, D.R., 1998. Carbon-isotope analyses of fossil plants as a chemostratigraphic and palaeoenvironmental tool. *Lethaia* 31, 1–13.
- Holdgate, G.R., McGowran, B., Fromhold, T., Wagstaff, B.E., Gallagher, S.J., Wallace, M.W., Sluiter, I.K., Whitelaw, M., 2009. Eocene–Miocene carbon-isotope and floral record from brown coal seams in the Gippsland Basin of southeast Australia. *Glob. Planet. Chang.* 65, 89–103.
- Isozaki, Y., 2009. Illawarra Reversal: the fingerprint of a superplume that triggered Pangean breakup and the end-Guadalupian (Permian) mass extinction. *Gondwana Res.* 15, 421–432.
- Jeffery, P.M., Compston, W., Greenhalgh, D., DeLeaeter, J., 1955. On the carbon-13 abundance of limestones and coals. *Geochim. Cosmochim. Acta* 7, 255–286.
- Kawashima, H., Haneishi, Y., 2012. Effects of combustion emissions from the Eurasian continent in winter on seasonal $\delta^{13}\text{C}$ of elemental carbon in aerosols in Japan. *Atmos. Environ.* 46, 568–579.
- Lloyd, J., Farquhar, G.D., 1994. ^{13}C discrimination during CO_2 assimilation by the terrestrial biosphere. *Oecologia* 99, 201–215.
- Mora, C.I., Dtieste, S.G., Colarusso, L.A., 1996. Middle to late Paleozoic atmospheric CO_2 levels from soil carbonate and organic matter. *Science* 271, 1105–1107.
- Motoyama, R., Yanagisawa, F., Ueda, A., Suzuki, Y., Kanai, Y., Ohsawa, E., Kojima, T., Akata, N., 2011. Spatial distribution of stable sulfur isotope ratio in coal samples in East Asian region. *Radiat. Isot.* 60, 27–33.
- Peters-Kottig, W., Strauss, H., Kerp, H., 2006. The land plant $\delta^{13}\text{C}$ record and plant evolution in the Late Palaeozoic. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 240, 237–252.
- Redding, C.E., Schoel, M., Monin, J.C., Durand, B., 1980. Hydrogen and carbon isotopic composition of coals and kerogens. *Phys. Chem. Earth* 12, 711–723.
- Schiegl, W.E., Vogel, J.C., 1970. Deuterium content of organic matter. *Earth Planet. Sci. Lett.* 7, 307–313.
- Schoell, M., 1984. Recent advances in petroleum isotope geochemistry. *Org. Geochem.* 6, 645–663.
- Schubert, B.A., Jahren, A.H., 2012. The effect of atmospheric CO_2 concentration on carbon isotope fractionation in C3 land plants. *Geochim. Cosmochim. Acta* 96, 29–43.
- Schwarzkopf, V.T., Schoell, M., 1985. Die Variation der C- und H-Isotopenverhältnisse in Kohlen und Maceralzusammensetzungen und Inkohlungsgrad. *Fortschr. Fortschr. Geol. Rheinl. Westfalen* 33, 161–168 (Abstract in English).
- Smith, B.N., Epstein, S., 1971. Two categories of $^{13}\text{C}/^{12}\text{C}$ ratios for higher plants. *Plant Physiol.* 47, 380–384.
- Smith, J.W., Gould, K.W., Rigby, D., 1982. The stable isotope geochemistry of Australian coals. *Org. Geochem.* 3, 111–131.
- Strauss, H., Peters-Kottig, W., 2003. The Paleozoic to Mesozoic carbon cycle revisited: the carbon isotopic composition of terrestrial organic matter. *Geochem. Geophys. Geosyst.* 4, 1–15.
- Tappert, R., McKellar, R.C., Wolfe, A.P., Tappert, M.C., Ortega-Blanco, J., Muehlenbachs, K., 2013. Stable carbon isotopes of C3 plant resins and ambers record changes in atmospheric oxygen since the Triassic. *Geochim. Cosmochim. Acta* 121, 240–262.
- Thomas, L., 2012. *Coal Geology, Coal research*. International Energy Agency, Paris.
- Van Krevelen, D.W., 1961. *Coal*. Elsevier, Amsterdam.
- Walker, S., 2000. *Major Coalfields of the World*. IEA Coal Research, Paris.
- West, J.B., Bowen, G.J., Dawson, T.E., Tu, K.P., 2010. *Isoscapes*. Springer, New York.
- Whiticar, M.J., 1996. Stable isotope geochemistry of coals, humic kerogens and related natural gases. *Int. J. Coal Geol.* 32, 191–215.
- Wickman, F.E., 1952. Variations in the relative abundance of the carbon isotopes in plants. *Geochim. Cosmochim. Acta* 2, 243–254.
- Wickman, F.E., 1953. Wird das Häufigkeitsverhältnis der Kohlenstoffisotopen bei der Inkohlung verändert? *Geochim. Cosmochim. Acta.* 3, 244–252 (Abstract in English).