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Occurrence of heavy carbon dioxide of organic origin: Evidence from confined dry pyrolysis of coal

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ABSTRACT

Although CO_2 is a common non-hydrocarbon gas in sedimentary basins and is significant in studying geofluid evolution, its origin is still a matter of debate. Light $\delta^{13}C_{CO2}$ values have been suggested as a good indicator for discriminating CO_2 of organic origin from that of inorganic origin (such as from the mantle or from carbonate mineral dissolution). However, here we present evidence suggesting that large quantities of isotopically heavy CO_2 can be liberated from deeply buried source rocks. An immature coal has been pyrolyzed in confined dry gold reactors at temperatures from 250 °C to 600 °C with different heating rates and under a pressure of 30 MPa. The results suggest that isotope fractionation and origin from various oxygenated functional groups with different $\delta^{13}C$ compositions make the late generated CO_2 (over 40% of potential) enriched in ^{13}C. The 44% of CO_2 late-produced from the coal has an average $\delta^{13}C$ value of −6.7‰ (VPDB); the latest 20% has an average $\delta^{13}C$ value of +1.5‰; and the latest 10% is most enriched in ^{13}C, with a $\delta^{13}C$ value of +5.0‰. This paper presents two cases highlighting organic, isotopically heavy CO_2 in natural gases occurring at variable concentrations in different sedimentary contexts.

1. Introduction

Carbon dioxide (CO_2) is one of the most common non-hydrocarbon gases found in sedimentary basins. It is of critical importance in investigating the evolution of volatile fluids (Ballentine et al., 2001) and in helping to develop regional strategies for natural gas exploration (Jenden et al., 1993), but its origins remain enigmatic (Wycherley et al., 1999). Carbon dioxide has several possible origins: thermal breakdown of kerogen, decarboxylation of organic acids by thermal or bacterial action, bacterial oxidation of hydrocarbons, dissolution of carbonate minerals, or mantle degassing (McKenzie, 1985; Hutcheon and Abercrombie, 1990; Andresen et al., 1994). For sedimentary rocks buried deeply at over 80 °C, three kinds of sources are significant: the mantle, carbonate dissolution, and organic substances (Andresen et al., 1994).

Evidence from carbon and noble gas isotope analyses has often been used to support a variety of interpretations for the origin of CO_2 (Clayton et al., 1990; Dai et al., 1996; Wycherley et al., 1999; Battani et al., 2000; Deines, 2002; Zhang et al., 2008). CO_2 which is highly depleted in ^{13}C ($\delta^{13}C < -8$‰ vs. VPDB) and of low abundance (<15 mol% of natural gas) is generally acknowledged to be derived from organic matter through diagenetic processes (Dai et al., 1996; Wycherley et al., 1999). Most mantle CO_2 is slightly heavy with $\delta^{13}C$ values between −8‰ and −4‰ and is usually one of the main constituents of natural gases (i.e., up to 90 mol%) (Des Marais and Moore, 1984; Javoy et al., 1986; Dai et al., 1996; Deines, 2002; Zhang et al., 2008). Carbon dioxide originating from thermal carbonate decomposition is characterized by much higher $\delta^{13}C$ values, ranging from −2‰ to +2‰ (Dallai et al., 2011).

However, the fact that heavy carbon dioxide can be liberated in large quantities from deeply buried source rocks has been generally ignored. In this research, immature coal samples have been pyrolyzed in confined dry gold reactors at temperatures from 250 °C to 600 °C with different heating rates. The purpose of the experiment was to investigate CO_2 generation and isotope evolution during artificial maturation of coal. These results could be useful to researchers attempting to explain the origin of certain mysterious CO_2 accumulations (Wycherley et al., 1999) in many sedimentary basins around the world.

2. Methods

An immature Jurassic coal (initial composition: $H/C = 0.75$, $O/C = 0.18$, TOC = 67.01%, vitrinite reflectance = 0.54% Ro, $\delta^{13}C_{coal} = -26.2$‰) was collected from the Cai 8 well (2257–2259 m) in the Junggar Basin, western China (e.g., Sun et al., 2010). To extract the

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purified kerogen, the coal was processed using a series of methods, as follows: 1) removal of minerals with HF/HCl, 2) removal of soluble organic matter by Soxhlet extraction (for 72 h) with MAB (methanol:acetone: benzene = 1:2.5:2.5) and 3) washing with distilled water followed by drying at low temperature (≤40 °C) (e.g., Durand and Nocaise, 1980). After purification, kerogen is only slightly more concentrated in organic matter than the original coal and has a TOC value of 68.74%.

The pyrolysis experiments were performed in confined dry gold reactors (e.g., Behar et al., 1989; Landais et al., 1989; Behar et al., 1995; Xiong et al., 2004; Shuai et al., 2006). Ten- to thirty-milligram samples were loaded into confined dry gold reactors (40 mm × 5 mm i.d.), and sealed in an argon atmosphere. The gold reactors were heated in stainless-steel autoclaves in a furnace programmed from 250 °C to 600 °C with two different heating rates, 2 °C/h and 20 °C/h, and under 30 MPa pressure. The autoclaves were removed from the oven immediately when the desired temperatures, ranging from 310 °C to 604 °C, were reached. The accuracy of temperature measurements was 1 °C, while the accuracy of pressure measurements was 1% (Xiong et al., 2004; Shuai et al., 2006).

After heating, the gold reactors were cleaned, put in a vacuum system and pierced with a needle. The released gas products were collected by a Toepler pump for quantification, and then compositional analysis was performed on line using HP5880A gas chromatography (GC) (Shuai et al., 2003; Xiong et al., 2004). The external standard method was applied to the quantification of gas components. The system setup has high sensitivity (as good as for the analysis of 0.01 ml volume of gas), and good accuracy (with the relative errors being less than 0.5%) (Xiong et al., 2004). The GC was equipped with a Poraplot Q column (30 m × 0.32 mm i.d). Helium was used as the carrier gas. Column head pressure was 8.5 psi. A temperature program of 50 °C (2 min) to 180 °C (8 min) at 25 °C/min was used. The carbon isotope composition of the CO_2 was determined using a VG Isochrom II instrument. The analytical error of isotope measurements is less than 0.3‰. Results for standards analyzed with our samples represented the arithmetic means of at least three duplicate analyses, and the repeatability was less than 0.3‰ (Table 1). Thus, the reproducibility of the experiments is very good, as indicated by many previous researchers using exactly the same experimental system (e.g., Pan et al., 2006).

Kinetic modeling of gas generation was conducted using the software Kinetics 2000, established by Burnham and Braun (1998) for kinetic parameter calculation. The modeling of isotopic composition of CO_2 was performed based on the methods of Cramer et al. (2001) and Xiong et al. (2004), which essentially treat both isotope species of CO_2, $^{12}CO_2$ and $^{13}CO_2$, as separate components (Shuai et al., 2003). The details can be found in Appendix A.

Stage yields and $\delta^{13}C$ values of CO_2 were calculated through mass balance evaluations. Based on the CO_2 yields at two temperatures (V_{T1} and V_{T2}), the stage yield between two temperature points was determined by the increase in yield ($V_{T2-T1} = V_{T2} - V_{T1}$). The $\delta^{13}C$ values of CO_2 ($\delta^{13}C_{T2-T1}$) at each stage were determined using the following equation:

$$\delta^{13}C_{T2-T1} = \left(\delta^{13}C_{T2} * V_{T2} - \delta^{13}C_{T1} * V_{T1}\right)/(V_{T2-T1}),$$

where $\delta^{13}C_{T2}$ and $\delta^{13}C_{T1}$ are the cumulative $\delta^{13}C$ values of CO_2 at temperatures T_1 and T_2.

In addition, the individual potentials of CO_2 and of methane (C_1) in coal were determined through mass balance evaluations. Because coal contains abundant carbon atoms, these potentials are probably limited by the initial contents of oxygen and hydrogen atoms. Because almost all the oxygen atoms can be combined with carbon atoms and converted into CO_2, the CO_2 potential was exactly the same as the mole content of O-atoms in the coal. When estimating the theoretical potential of C_1, it should be considered that not all H-atoms can be liberated, as a portion will be occluded in the coke indefinitely regardless of the maturity level. Usually, the residual coke can contain a ratio of H/C atoms of 0.25 and the remaining H-atoms in the coal can be used to determine the methane potential.

3. Results

3.1. Experimental results

The generation curves for C_1 and CO_2 obtained at the two heating rates, 2 °C/h and 20 °C/h, from 300 °C to 600 °C are shown in Fig. 1a. CO_2 generation generally starts at much lower temperatures than that of C_1 (Table 1). The onset of measurable C_1 occurs above 350 °C, while CO_2 yield amounts to 50 m^3/t TOC (equivalent to 50 ml/g TOC) below 310 °C. Initially, coal liberates CO_2 at a much higher rate and only slowly produces C_1. The yields of C_1 increase quickly and overbalance those of CO_2 at 470 °C. At even higher temperatures, yields of CO_2 increase

Table 1
Yields and $\delta^{13}C$ values of the cumulative carbon dioxide generated by kinetic pyrolysis of coal.

Initial composition of coal				TOC	H/C O/C	Ro	$\delta^{13}C_{coal}$
				67.01%	0.75 0.18	0.54%	−26.2‰
Heating rate (20 °C/h)				Heating rate (2 °C/h)			
T (°C)	CH_4 (m^3/t TOC)	CO_2 (m^3/t TOC)	$\delta^{13}C_{CO2}$ (‰)	T (°C)	CH_4 (m^3/t TOC)	CO_2 (m^3/t TOC)	$\delta^{13}C_{CO2}$ (‰)
311	1.3	43.9	n.d.	314	2.3	52.8	n.d.
335	2.2	55.6	n.d.	338	5.2	59.9	n.d.
360	4.5	57.6	n.d.	362	13	61.5	n.d.
384	9.2	61.8	n.d.	386	31.2	62.7	−27.4 ± 0.0
409	20.2	64.8	n.d.	411	60	64.2	−26.8 ± 0.3
433	40.9	68.2	−27.2 ± 0.1	423	77.8	65.5	−26.1 ± 0.0
445	53.3	69.5	−26.8 ± 0.2	435	97.5	67.4	−25.7 ± 0.3
458	71.6	72.3	−26.1 ± 0.2	445	113.2	73	−25.4 ± 0.2
469	82.3	74.5	−26.4 ± 0.0	459	127.1	78.8	−24.7 ± 0.1
482	96.4	77.9	−26.0 ± 0.0	483	154.1	86.8	−24.3 ± 0.2
509	128.8	87.6	−25.7 ± 0.0	507	182.5	111.4	−22.4 ± 0.1
531	150.3	98	−25.4 ± 0.2	532	209.8	129	−20.8 ± 0.2
555	176.5	110.8	−24.7 ± 0.0	556	229.8	147.9	−18.3 ± 0.0
579	209.1	134.5	−24.1 ± 0.2	581	244.9	157.9	−16.9 ± 0.0
603	224.5	139.8	−22.5 ± 0.0	604	250.7	165.1	−15.9 ± 0.1

n.d. = no data.