

New Improved Delta Carbonate Method Used for Surface Geochemical Exploration for Petroleum

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ABSTRACT: The delta carbonate (ΔC) method is a common used surface geochemical exploration technique for oil and gas geochemical surveys in China. However, its application effectiveness is unsatisfactory because of the unidentified origins of CO_2 that form ΔC . In this study, a gold tube pyrolysis technique, coupled with gas chromatography (GC) and gas chromatography–isotope ratio mass spectrometry (GC–IRMS) detection, was employed to simultaneously measure the concentration and carbon isotopic composition of ΔC in surface soils. Experimental conditions for the ΔC analysis were determined by condition experiments, and the reproducibility and repeatability of the method were tested and found to be satisfactory. Subsequently, this new and improved ΔC method was applied to the Duoshiqiao area of the Jiyang depression in Bohai Bay Basin, China. Halo anomalies are found based on the concentrations and carbon isotopic compositions of ΔC . These are consistent with the actual distribution of known oil and gas accumulations in the region. The carbon isotopic composition of ΔC in the study area ranges from -4‰ to -8‰ [Vienna Peedee belemnite (VPDB)], possibly representing a special hydrocarbon seepage model with a relatively rapid leakage rate and partial chemical or biochemical oxidation of these migrated hydrocarbons from the subsurface. Combining concentration measurements of ΔC with its carbon isotopic values may be a promising method for accurately locating subsurface hydrocarbon seepage.

1. INTRODUCTION

Geochemical explorations for petroleum involve searching for chemically identifiable surface or near-surface occurrences of hydrocarbons and their alteration products.^{1,2} This has become an important auxiliary tool in oil and gas exploration.³ Geochemical explorations not only give direct and/or indirect evidence of hydrocarbon seepage but also provide more favorable drilling sites for oil or gas explorations. In comparison to more commonly used seismic explorations, geochemical methods have a marked advantage in terms of costs. Moreover, geochemical methods can reflect oil and gas accumulations that are hidden in stratigraphic traps.⁴

To date, various surface geochemical exploration methods and techniques have been established to identify the surface or near-surface occurrences of hydrocarbons.^{2,5–12} Among these methods, the delta carbonate (ΔC) method, first employed by Geochemical Survey, Inc. (GSI) in 1942, is the most obscure. The core of GSI's research has been reported to be a special carbonate formed by the oxidation of methane seeping from underlying oil or gas accumulations. The concentration of ΔC in a soil sample is obtained by measuring the amount of CO_2 released from the sample within the temperature window of $500\text{--}600\text{ °C}$.¹³ Briefly, a prepared soil sample is initially heated in an oxygen atmosphere at 500 °C to eliminate organic matter and low-decomposition–temperature carbonates or bicarbonates. The pre-combusted sample is then heated in a nitrogen atmosphere at 600 °C . This technique was kept as a trade secret until the analytical details were described by Duchscherer in

1980.¹³ From 1942 to 1984, the ΔC method initiated the exploration process, which conducted the drilling of 184 prospects, ultimately bringing in 39 new oil and gas fields, within which 1084 field wells were eventually drilled. The exploratory tests resulted in a 21% new field wildcat success rate.¹⁴

Although some successful cases were reported,^{15–22} the principle of the method could not be adequately taken into account. For example, the decomposition temperatures of common carbonates are either lower than 500 °C or higher than 600 °C , and no known carbonate minerals in soils or near-surface sediments can decompose within the $500\text{--}600\text{ °C}$ temperature range (Figure 1). Thus, some critics believe that CO_2 detected by this technique probably originated from organic materials in the soil rather than the inorganic carbonates created by vertically migrating hydrocarbons.^{9,14} Duchscherer's experiments have confirmed that the thermal combustion of soil samples at 500 °C in an atmosphere of oxygen for 1–2 h could effectively eliminate the effect of organic carbon (e.g., wood, coal, etc.) on the ΔC .²⁰ In addition, ΔC is not a very specific marker for thermogenic hydrocarbons.²³ Besides the microbial oxidation of hydrocarbons, CO_2 formed into ΔC may also be derived from several other processes, such as volcanic or geothermal activity, catagenesis of

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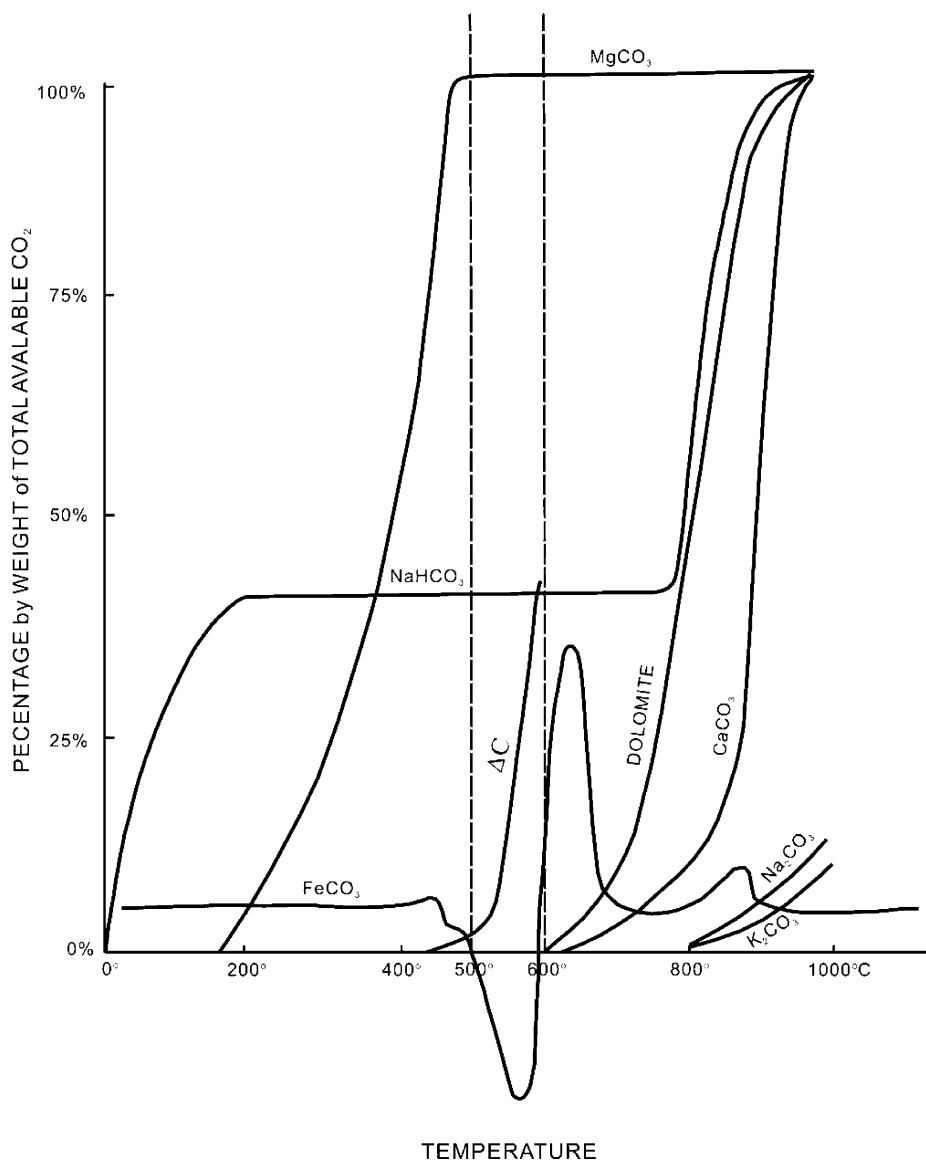


Figure 1. Thermal dissociation curves (adapted with permission from the study by Duchscherer¹⁶).

organic matter, micropore filtration, and thermochemical sulfate reduction.^{24–26} These factors may possibly result in multiple explanations for the origin of ΔC in soil.

Therefore, determining the anomalies of ΔC and identifying whether or not these anomalies are related to the microseepage of subsurface thermogenic hydrocarbons are necessary for the effective use of the ΔC method. However, more attention is currently focused on the former, and the latter is always ignored in actual applications. The purpose of this study is to improve the utility of the ΔC method by combining both approaches.

Stable carbon isotopic composition is an effective tool for tracing carbon sources. For example, the $\delta^{13}C$ value of hydrocarbons can provide more useful information on the origin of oils and gases. Therefore, it can be used for oil and gas explorations.^{27–33} Similarly, if hydrocarbons in soils are related to leakages from underlying petroleum accumulations, their carbon isotope values will be nearly identical to those from the actual reservoir.³⁴ Therefore, ΔC with relatively negative $\delta^{13}C$ values can be used to identify occurrences of subsurface thermogenic hydrocarbons. In this study, a gold tube pyrolysis technique, coupled with gas chromatography (GC) and gas

chromatography–isotope ratio mass spectrometry (GC–IRMS) analyses, is employed to determine the amount and carbon isotopic composition of ΔC in surface soils.

2. EXPERIMENTAL SECTION

To simultaneously achieve concentration and carbon isotopic analyses of soil ΔC , a closed gold tube system, used by Xiong et al.,³⁵ was introduced during the pyrolysis of soil samples in this study.

2.1. Sample and Pretreatment. The samples used in this study were collected from the Duoshiqiao area in the Jiyang depression of Bohai Bay Basin, China (Figure 2). The depth of each sample was 1.5–2 m (about 5–7 ft). In the laboratory, the samples were first dried in a ventilated area under room temperature, then pulverized with an agate mortar, and sieved, leaving the fraction with a particle size that is less than the 40 mesh for analysis. The powdered samples were then preheated in an oxygen atmosphere for 1 h at 500 °C and stored in a glassware desiccator for the following pyrolysis experiment.

The initial soil sample for extraction of adsorbed methane was milled to a fine-grained fraction (particle size is less than 63 μm).

2.2. Pyrolysis. The gold tube system has been employed in kinetic simulation experiments for kerogen and oil pyrolysis.^{35,38–40} However, instead of kerogen or oil samples, about 100 mg of the preheated soil samples was loaded into gold tubes (40 \times 4.2 mm inner diameter).

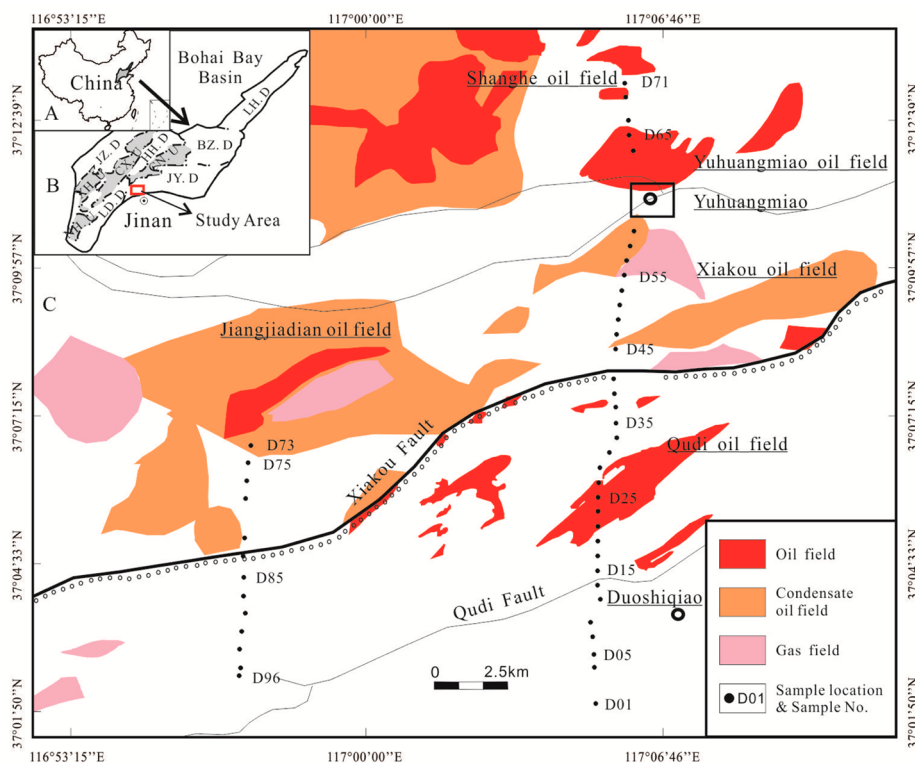


Figure 2. Map of the study area and sample locations. Panels A and B are modified with permission from the studies by Zhu et al.³⁶ and Zheng et al.,³⁷ respectively.

The loaded tubes were flushed with argon for several minutes to ensure the complete removal of air, and then they were sealed under an argon atmosphere. The gold tubes were enclosed in stainless-steel autoclaves and placed in an oven. A heat-circulating fan at the bottom of the oven ensured that the difference in temperature among the autoclaves was less than 1 °C. Adding water into the autoclaves by a high-pressure pump provided pressure to the gold tubes during the heating process. Connecting all autoclaves in parallel ensured that the pressure in each autoclave was identical. The pressure was kept at 50 MPa during the whole heating process. Setting a heating program ensured that the temperature of the oven was heated from room temperature to 250 °C within 10 h, then heated to 600 °C at a rate of 50 °C/h, and held at 600 °C for some time (the determination of exact held/pyrolyzed time is discussed later). The autoclaves were then removed from the oven when either the desired time or temperature was reached. Gaseous pyrolysates in the gold tubes were analyzed by GC and GC–IRMS.

2.3. Extraction of Adsorbed Methane. The adsorbed hydrocarbon gases were extracted from soil samples by heating approximately 5 g of each sample and a 50% solution of phosphoric acid at 50 °C for 2 h in a vacuum system. In this process, the released gases were passed through a 4 mol/L solution of sodium hydroxide to remove carbon dioxide produced from carbonates in the soil samples. The residual gases were then used for analyzing the carbon isotopic compositions of methane. More detailed information on the extraction of adsorbed methane was discussed in the study by Liang et al.⁴¹

2.4. Concentration and Carbon Isotopic Composition Determination of ΔC and Adsorbed Methane. After pyrolysis, the cleaned gold tube was placed in a piercing device attached to a vacuum glass pipe system equipped with a pump. The gas collection was initiated by puncturing the gold tube under vacuum. After about 30 s had passed for gas balance, the gases were directly injected into a gas chromatograph.

The quantities of CO₂ (ΔC) were measured using a gas chromatograph (6890 N, Agilent Technologies) fitted with a thermal conductivity detector (TCD). Quantification was performed using an

external standard method. The GC was operated using the following analytical materials and conditions: Wasson KC5 column (50 m × 0.53 mm inner diameter × 10 μm) and helium carrier gas with a minimum purity of 99.99%. The interface and GC inlet temperature were set at 300 °C. The GC oven temperature was programmed from 70 °C (6 min) to 130 °C at 15 °C/min and then to 180 °C at 25 °C/min.

Carbon isotopic compositions of CO₂ (ΔC) and adsorbed methane were measured with a gas chromatograph (5890 series II, Hewlett-Packard) equipped with a Poraplot Q column (30 m × 0.32 mm inner diameter × 0.25 μm) coupled to an isotope ratio monitoring mass spectrometer (VG Isochrom II). Helium gas was used as the carrier gas (8.5 psi head pressure). For CO₂, the GC oven temperature was programmed at a constant temperature of 50 °C. When measuring the carbon isotopic compositions of methane, the GC oven temperature was programmed from 50 °C (3 min) to 190 °C at 25 °C/min. Combustion was initiated via a combustion interface operated at 850 °C. Carbon isotope ratios were calculated using a CO₂ reference gas that was automatically introduced into IRMS at the beginning and end of each analysis. In addition, a standard mixture of gaseous hydrocarbon (C₁–C₃) and CO₂ with a known isotopic composition was used daily to test the performance of the instrument. The reported isotopic data represent the arithmetic means of at least four replicate analyses, and the repeatability is less than 0.3‰ [Vienna Pee Dee belemnite (VPDB)].

3. RESULTS AND DISCUSSION

3.1. Gold Tube Pyrolysis. A parallel experiment was performed to investigate the feasibility of using the gold tube pyrolysis system to analyze the ΔC . In the parallel experiment, five subsamples were prepared from the same treated sample, of which three weighed about 100 mg each and the other two weighed about 150 mg each. Gold tube pyrolysis was performed at 600 °C for 3 h.

Table 1 shows the data of the parallel experiment. Approximately equal ΔC values are obtained from the five

Table 1. Data of the Parallel Experiment

sample number	sample weight (mg)	CO ₂ yield (mL/g)	ΔC (%)	average ΔC (%)	relative deflection (%)
1	99.63	22.12	4.38	4.25	3.1
2	101.29	22.09	4.37		2.9
3	103.93	20.68	4.09		3.7
4	152.30	20.55	4.07		4.3
5	151.77	21.87	4.33		1.9

parallel determinations, with an average value of 4.25%. Relative deviations range from 1.9 to 4.3%, which is much lower than 10%, indicating that the gold tube pyrolysis system can be used for the quantitative analysis of ΔC .

3.2. Experimental Conditions of Pyrolysis. In Duchscherer's introduction to the ΔC method,^{9,13} the duration of time that the samples needed for heating at 600 °C was not mentioned. To obtain a better efficiency, a holding time of 1 h has been widely adopted in surface geochemical prospecting for hydrocarbons in China.^{42–46} Because the ΔC , as an index of surface geochemical prospecting, only needs to be a relative quantity,⁴³ the traditional method is acceptable for comparing relative concentrations of ΔC under uniform conditions. However, incomplete decomposition of ΔC can result in carbon isotopic fractionation, negatively influencing the accurate determination of carbon isotopic compositions of ΔC . On the basis of the thermal dissociation curve of ΔC ,¹³ over 6 or 7 h can be required for the complete decomposition of ΔC .⁴⁷ No document has reported on how long complete decomposition occurs in soil. In this study, experiments were performed to determine the time required for the complete decomposition of ΔC .

Two samples were chosen for this experiment. One sample, tagged as D01, came from a background area far away from any oil or gas reservoir. Another sample, tagged a D17, was sampled near a producing oil field (Figure 2). The analytical data are listed in Tables 2 and 3. As shown in Figure 3, the CO₂ yields of the two samples gradually increase with pyrolysis temperature and holding time. The main increase occurs between 520 and 600 °C. For D01, only a small quantity of CO₂ is released after heating for about 2 h at 600 °C. In comparison to D01, D17 has a relatively wider range of CO₂ generation. The amount of CO₂ slightly increases after heating for 6 h at 600 °C. Therefore, one can infer that most ΔC in soils can completely decompose after heating for 6 h at 600 °C.

Figure 4 presents the carbon isotopic composition of CO₂ generated by the two samples at different temperatures and holding times. A negative shift of $\delta^{13}C$ is observed in the early pyrolysis process (500–540 °C) of sample D17, which often occurs in kinetic simulation experiments of kerogen pyrolysis.⁴⁸ The $\delta^{13}C$ curve of CO₂ from the D17 pyrolysis becomes nearly horizontal after holding the sample for 1 h at 600 °C. For the

D01 sample, the $\delta^{13}C$ values of CO₂ display an approximate trend of enrichment in ¹³C with an increasing pyrolysis temperature. After heating for 4 h at 600 °C, its change is minimal and within the analytical error of 0.3‰ (VPDB).

Combining the concentrations and carbon isotopic compositions of CO₂ produced from samples D01 and D17, we infer that the complete decomposition of ΔC may require at least 6 h of heating at 600 °C. Therefore, pyrolysis was performed for 6 h at 600 °C for the other samples in this experiment.

On the basis of the above-mentioned parallel and condition experiments, an available method is established for determining the concentrations and carbon isotopic compositions of ΔC . Unlike the traditional ΔC method, the concentration and stable carbon isotopic composition of ΔC are simultaneously analyzed by coupling the gold tube pyrolysis system with the GC–IRMS technique.

3.3. Case Study. The Bohai Bay Basin is the largest petroleum-producing area in China and contains six depressions: Liaohe, Jizhong, Huanghua, Bozhong, Linqing, and Jiyang. The most important of the six depressions is the Jiyang depression, which is located in the southern Bohai Bay Basin and contains a number of oil and gas fields. The geological setting of the Jiyang depression is described in detail elsewhere.^{36,49–51} The study area in this work is located in Duoshiqiao, southwest of the Jiyang depression (Figure 2). This region was investigated previously and considered to be appropriate for the soil-gas-based investigation of surface geochemical prospecting for hydrocarbons.⁵² In the Shanghe oil field, nearly 25 km northwest of the Yuhuangmiao oil field, hydrocarbon microseepage anomalies have already been identified by the detection of soil-adsorbed light hydrocarbons using the vacuum desorption method.¹⁰ Hence, combined with the previous work on this area, one can safely conclude that hydrocarbon leakage is present in this area. The ΔC work discussed in this paper is one part of a study on new techniques of surface geochemical exploration for oils and gases.

A total of 48 near-surface soil samples (1.5–2 m depth) were collected at a spacing of about 250 m along two north–south sections in the Duoshiqiao area of the Jiyang depression (Figure 2): one is from D01 to D71, which crossed over the Qudi oil field, Xiakou oil field, Yuhuangmiao oil field, and Shanghe oil field, and another is from D73 to D96, located at the southern area of the Jiangjiadian oil field. The above-mentioned analytical method was used in this section. The results are presented in Table 4.

The carbon isotopic value of normal calcite, regardless of whether its carbon is derived from the atmosphere, freshwater, or marine environment, is usually between –10 and +5‰ [Peedee belemnite (PDB)].^{53,54} Hydrocarbon-induced alterations associated with petroleum seepage, which are formed principally as a byproduct of petroleum oxidation, particularly of methane, always have an isotopic signature that matches that of the parent hydrocarbon(s).²³ Thus, calcite formed from oxidized petroleum incorporates carbon from the organic source, which typically has an isotopic composition more

Table 2. CO₂ Yield and the $\delta^{13}C$ Value of Sample D01 at Different Temperatures and Times

temperature (°C)	500	520	540	560	580	600	600	600	600	600	600
holding time (h)	0	0	0	0	0	0	2	4	6	8	12
CO ₂ yield (mL/g)	3.24	5.45	11.42	17.07	18.74	22.69	26.12	26.63	28.03	28.57	28.66
$\delta^{13}C_{CO_2}$ (‰)		–8.2		–7.6	–7.3	–7.6	–7.1	–6.4	–6.2	–6.4	–6.2

Table 3. CO₂ Yield and the $\delta^{13}\text{C}$ Value of Sample D17 at Different Temperatures and Times

temperature (°C)	500	520	540	560	580	600	600	600	600	600	600	600	600	600	600	600	600	600	600
holding time (h)	0	0	0	0	0	0	1	2	3	4	5	6	7	8	9	10	12	12	12
CO ₂ yield (mL/g)	3.31	5.53	6.95	10.25	14.64	17.54	18.59	18.55	20.26	20.82	21.21	23.75	22.29	23.06	23.76	23.28	25.48	25.48	25.48
$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	-8.5	-9.2	-9.3	-9.1	-8.0	-8.4	-7.3	-7.2	-7.3	-7.2	-7.3	-7.3	-7.2	-7.3	-7.3	-7.2	-7.1	-7.1	-7.1

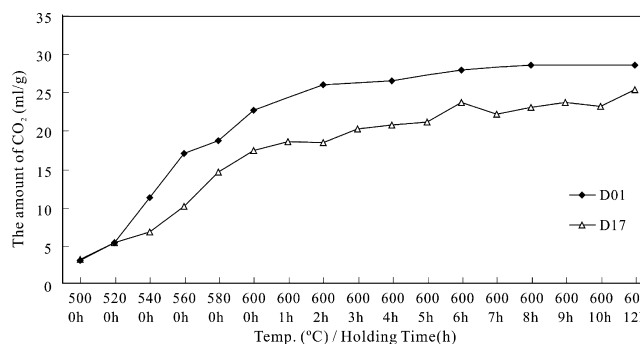
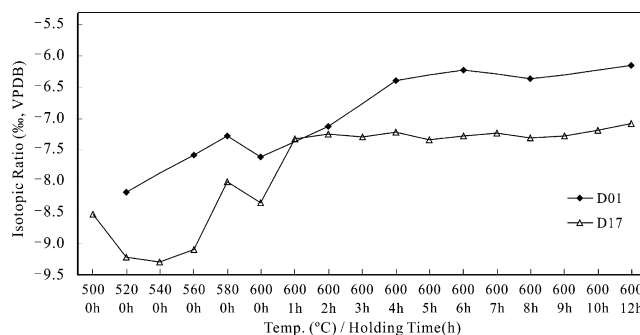


Figure 3. Thermal dissociation curves of D01 and D17.

Figure 4. Curves of the $\delta^{13}\text{C}_{\text{CO}_2}$ values of D01 and D17.

negative than -20‰ (PDB). The isotopic composition of the resulting carbonate can range from -10 to -60‰ (PDB), depending upon the proportion of oxidized hydrocarbon incorporated.²³

However, carbonate samples with heavier carbon isotopic ratios (heavier than -10‰ PDB) should not be simply ascribed to inorganic origins. The dolomitic sandstone of Permian age over the Davenport oil field in Oklahoma is a good example. The carbon isotopic ratios of the outcropping samples range from -5.1 to -11.3‰ (PDB) and result from the partial chemical or biochemical oxidation of the hydrocarbons that leak from the subsurface, further suggesting that the seepage rate is relatively rapid.⁵⁵ The carbon isotopic composition of ΔC in the Jiyang field ranges from 1.4 to -7.3‰ (VPDB), whereas the $\delta^{13}\text{C}$ values of the adsorbed methane range from -31.7 to -36.6‰ (Table 4). This narrow variation in isotopic composition of ΔC s indicates that the determined ΔC s have a predominant carbon source similar to that of normal calcite and that the carbon source from the oxidation of hydrocarbons (oil and gas) may be minor. One can further infer that a relatively rapid hydrocarbon seepage rate probably occurs in the area (Figure 5), similar to dry gas evaporation fractionation in the Davenport oil field, as suggested by Donovan et al.⁵⁵ Hydrocarbon seepage occurs rapidly, so that the hydrocarbons are not readily attacked before they escape to the atmosphere. Thus, only a partial minimal amount of hydrocarbons in the near surface can be chemically or biochemically oxidized, leading to a minor contribution from the oxidation of subsurface hydrocarbons in this seepage model.

In the geochemical exploration of both mineral resources and petroleum, general frequency plots and cumulative frequency plots are the statistical methods normally used to determine normal backgrounds and the most likely values for the contour interval.¹¹ A single contour is drawn at a value usually equal to the mean + 1.5σ . Sometimes, changing the contour value

Table 4. Concentration and $\delta^{13}\text{C}$ Values of ΔC and Adsorbed Methane (ACH_4)

sample number	concentration (mL/g)	concentration (%)	$\delta^{13}\text{C}_{\Delta\text{C}}$ [‰ (VPDB)]	$\delta^{13}\text{C}_{\text{ACH}_4}$ [‰ (VPDB)]	sample number	concentration (mL/g)	concentration (%)	$\delta^{13}\text{C}_{\Delta\text{C}}$ [‰ (VPDB)]	$\delta^{13}\text{C}_{\text{ACH}_4}$ [‰ (VPDB)]
D01	28.5	5.6	-5.8	-36.5	D51	27.8	5.5	-6.0	-36.6
D03	9.3	1.8	-6.2	-34.6	D53	26.5	5.2	-6.3	-35.2
D05	16.7	3.3	-4.5	-33.7	D55	30.3	6.0	-6.8	-35.0
D07	16.3	3.2	-5.3	-34.8	D57	3.4	0.7	-4.5	-33.2
D09	18.8	3.7	-7.1	-32.1	D59	12.1	2.4	-7.0	-33.6
D11	10.0	2.0	-7.2	-34.5	D61	8.2	1.6	-5.3	-34.3
D13	9.3	1.8	-6.2	-34.9	D63	13.5	2.7	-5.8	-33.5
D15	33.5	6.6	-6.7	-36.0	D65	2.4	0.5	-5.9	-34.2
D17	24.5	4.8	-7.2	-34.9	D67	14.3	2.8	-6.7	-33.9
D19	12.0	2.3	-5.6	-34.3	D69	26.5	5.2	-6.7	-35.2
D21	7.7	1.5	-6.5	-33.8	D71	32.9	6.5	-6.9	-34.2
D23	19.0	3.7	-5.1	-34.2	D73	19.8	3.9	-5.4	-33.4
D25	16.9	3.3	-5.7	-34.2	D75	27.1	5.3	-6.6	-34.6
D27	24.1	4.7	-6.1	-33.9	D77	2.9	0.6	-3.4	-33.0
D29	31.1	6.1	-7.3	-34.1	D79	9.2	1.8	-5.9	-33.5
D31	30.6	6.0	-6.7	-33.1	D81	17.9	3.5	-5.7	-33.8
D33	32.6	6.4	-7.1	-31.7	D83	16.3	3.2	-5.7	-33.5
D35	27.5	5.4	-6.8	-34.2	D85	4.7	0.9	-5.7	-34.0
D37	19.2	3.8	-5.6	-34.7	D87	1.2	0.2	1.4	-33.8
D39	15.8	3.1	-5.3	-34.6	D89	10.7	2.1	-4.8	-33.8
D41	11.5	2.3	-5.5	-33.7	D91	28.8	5.7	-6.2	-33.7
D45	16.0	3.1	-6.7	-35.2	D93	17.9	3.5	-6.3	-33.9
D47	23.1	4.5	-7.1	-35.0	D95	20.9	4.1	-5.5	-34.1
D49	17.1	3.4	-5.2	-34.7	D96	24.0	4.7	-5.2	-32.7

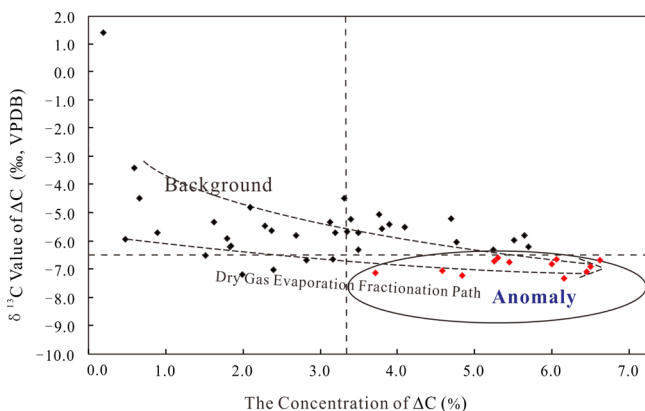


Figure 5. Cross-plot of stable carbon isotopes and concentrations of ΔC .

becomes necessary for different scale surveys.^{56–59} When data from 48 samples were processed with the iterative method, 3.3% is considered as the threshold for the concentration anomalies of ΔC . Because the survey was conducted in the oil and gas field at a small scale, less variation in the $\delta^{13}\text{C}$ values of ΔC probably resulted in unavailability of common statistical methods for obtaining the threshold of the carbon isotopic anomalies. With regard to the isotopic data of -6.5‰ (VPDB), the average carbon isotopic value (-5.9‰ VPDB) of ΔC from these samples plus the analytical error of isotopic determination (± 0.3 and 0.6‰ VPDB) is selected as the threshold of the carbon isotopic anomalies of ΔC .

Although the carbon source from the oxidation of hydrocarbons (oil and gas) may be minor, it can clearly identify anomalies over the thresholds of the concentration and isotopic ratio of ΔC . Figure 6 displays the profiles of the concentration and $\delta^{13}\text{C}$ values of ΔC along this sampling line. According to

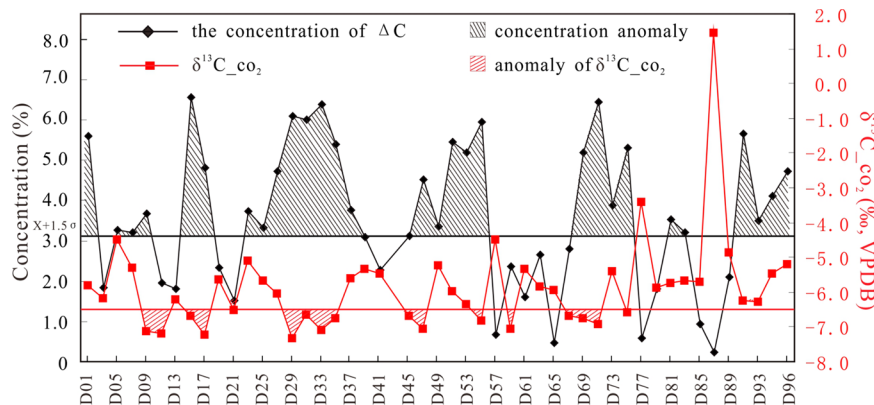


Figure 6. Contractive curves of the concentration and $\delta^{13}\text{C}_{\text{CO}_2}$ values of ΔC .

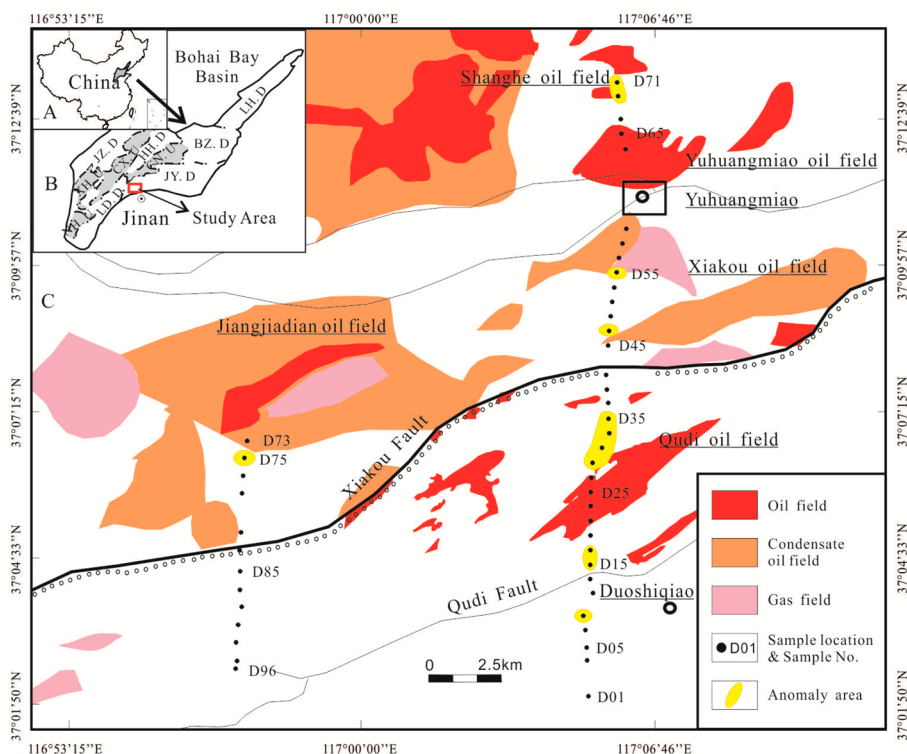


Figure 7. Anomalies determined by combining the concentration and isotopic ratios of ΔC . Panels A and B are modified with permission from the studies by Zhu et al.³⁶ and Zheng et al.,³⁷ respectively.

the traditional method, eight areas, which are D01, D05–D09, D15–D17, D23–D37, D47–D55, D69–D75, D81, and D91–D96, show anomalies of ΔC with ΔC concentrations greater than 3.8%. On the basis of the carbon isotopic composition of ΔC , the ΔC anomalies of relatively depleted ^{13}C (more negative than -6.5‰ VPDB) are observed at the following sites: D09–D11, D15–D17, D21, D29–D35, D45–D47, D55, D59, D67–D71, and D75. Combining the amounts and $\delta^{13}C$ values of ΔC , seven “real” anomalies are identified, which include D09, D15–D17, D29–D35, D47, D55, D69–D71 and D75. The anomaly characteristics of larger ΔC values and relatively negative $\delta^{13}C$ values are considered to be related to subsurface thermogenic hydrocarbons. The comparison indicates that the combination of the ΔC concentration and its $\delta^{13}C$ can effectively identify anomalies related to subsurface oil and gas accumulation and even determine some “false” anomalies. For example, in Figure 6, the values of ΔC for D01, D27, and D51–D53 are higher than 3.3%. These may be considered as anomalies if only the concentrations are evaluated. However, when isotopic compositions are taken into account, these samples are not found to be effective anomalies. In fact, they are consistent with the actual geological background in this region.

Geochemical exploration anomalies are always accompanied by the halo phenomenon. The halo type of anomalous patterns has been reported in many different types of surveys. Apical anomalies, as opposed to halo anomalies, usually represent smaller or narrower fields.¹⁴ The halo anomaly is a typical phenomenon related to the ΔC method in oil and gas geochemical exploration.^{9,13} It indicates that the area in the ring or annular region may contain oil or gas accumulation.⁶⁰ When the anomalies identified by the new ΔC method are marked on the map (Figure 7), all of the anomalies are clearly at the edges

of oil or gas fields. One can surmise that these anomalies will form the halo anomaly around the oil or gas fields if more samples are analyzed.

4. CONCLUSION

The ΔC method is a common surface geochemical exploration technique for oil and gas geochemical surveys in China. However, complex carbon sources hinder the application of this method. The carbon isotopic composition of ΔC in surface soils was introduced to identify carbon sources. The gold tube pyrolysis technique, coupled with GC and GC–IRMS detection, was employed to measure the amount and carbon isotopic composition of ΔC .

Experimental conditions for ΔC analysis were determined by condition experiments, and good reproducibility and repeatability were obtained for the experimental method used. Subsequently, this new method was applied to the Duoshiqiao area of the Jiyang depression in Bohai Bay Basin, China. The results indicated that the combination of the ΔC concentration and its $\delta^{13}C$ composition can effectively identify anomalies related to subsurface oil and gas accumulation and even determine some “false” anomalies. Halo anomalies identified by this new method are consistent with the actual distribution of known oil and gas accumulations in this region. Combining the concentrations and carbon isotopic values of ΔC may be a promising method for accurately locating subsurface hydrocarbon seepage.

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Notes

The authors declare no competing financial interest.

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