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Geological emission of methane from the Yakela condensed oil/gas field in Talimu Basin, Xinjiang, China

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Abstract

A static flux chamber method was applied to study natural emissions of methane into the atmosphere in the Yakela condensed oil/gas field in Talimu Basin, Xinjiang, China. Using an online method, which couples a gas chromatography/high-temperature conversion/isotope ratio mass spectrometry (GC/C/MS) together, the $^{13}C/^{12}C$ ratios of methane in the flux chambers were measured. The results demonstrated that methane gases were liable to migrate from deep oil/gas reservoir to the surface through microseepage and pervasion, and that a part of the migrated methane that remained unoxidized could emit into the atmosphere. Methane emission rates varied less in the oil/gas field because the whole region was homogeneous in geology and geography, with a standard deviation of less than 0.02 mg/(m^2·h). These were the differences in methane emission flux in the day and at night in the oil/gas field. The maximum methane emission flux reached 0.15 mg/(m^2·h) at 5:00–6:00 early in the morning, and then decreased gradually. The minimum was shown 0.10 mg/(m^2·h) at 17:00–18:00 in the afternoon, and then increased gradually. The daily methane released flux of the study area was 2.89 mg/(m^2·d), with a standard deviation of 0.43 mg/(m^2·d), using the average methane flux of every hour in a day for all chambers. $\delta^{13}C$ of methane increased with the increase of methane concentration in the flux chambers, further indicating that the pyrogenetic origin of methane was come from deep oil/gas reservoirs.

Key words: the Yakela condensed oil/gas field; methane emission; stable carbon isotopes; flux chamber

Introduction

Methane (CH_4), is a principal greenhouse gas and its content in the atmosphere has doubled its volume fraction in the past 300 years (Etheridge *et al*., 1992; Dlugokencky *et al*., 1994). Although the atmospheric methane concentration estimated by the global methane budget models is still believed to be growing, the annual growing rate has been reduced in recent decades (Dlugokencky *et al*., 1994, 1998) and has kept a steady value of about 1,751 mg/m^3 since 1999 (Dlugokencky, 2003). As the greenhouse effect of CH_4 of unit mass is 23 times that of CO_2 (EIA, 2003; Nickolas and Priscilla, 2007), the estimation and prediction of its content in the atmosphere have been the key aspect in the study of global environmental changes. Prediction of global CH_4 source strength and isotopic analysis of atmospheric CH_4 has revealed that the amount of CH_4 without ^{14}C, or "dead carbon", is about 100±50 Tg/year (1 Tg = 10^{12} g), constituting about 20%–30% of the total atmospheric CH_4 (Lowe *et al*., 1988; Manning *et al*., 1990; Lacroix, 1993), which is obviously higher than the statistical estimation according to the amount of burning fossil fuel, which accounts for only about 80 Tg/year (Fung *et al*., 1991; Quay *et al.*, 1991; Michael, 1990). This discrepancy is most possibly due either to an overestimation of the source of CH_4 with $\delta^{13}C$ lighter than –58‰, or to an underestimation of the source of heavy carbon CH_4 (Michael, 1990). Geologically originated methane release is an important component of such a loss of heavy carbon or dead carbon (Michael, 1990; Crutzen, 1991; Etiope and Klusman, 2002). However, until recently, only fossil fuel burning and hydrated methane have been considered as geological methane releases (Houghton *et al*., 2001).

Natural release of methane from oil/gas basins by upward microseepage from deep-buried reservoirs is thought to be an important source of CH_4, heavy carbon or dead carbon (Klusman and Jakel, 1998), which is a result of the heat release of volatile components of oil/gas from the long history of geology and a basis of geochemical exploration techniques for petroleum (Tissot and Welte, 1984; Hunt, 1996; Klusman, 1993). Such microseepage not only provides a source for atmospheric methane, but also a source for soil methane, and other light hydrocarbons necessary for methane bacteria. Previous studies of soil methane oxidation by methane-nourished bacteria under arid climate conditions, have been mainly limited to geological environment in which there were no underground

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oil/gas reservoirs and hence no methane microseepage from beneath is considered (Klusman and Jakel, 1998). Methane oxidation by soil is usually viewed as a sink for atmospheric methane, but an exception is given by Mosier *et al*. (1991, 1996, 1997) and Klusman and Jakel (1998) in their investigating of Denber-Julesburg oil basin in Colorado, USA, where, owing to the microseepage of methane from deep oil traps, the methane migrated to the surface failed to be completely oxidized or decomposed and hence emitted to the atmosphere by means of diffusion or air convection, with an estimated average flux of 0.57 mg/(m^2·d). This is representative of a natural or geologically originated source of methane in the global methane recycling processes.

Vast geochemical investigations have demonstrated that the methane from deep oil/gas traps is capable of migrating to the surface by diffusion and infiltration (Vermenlen, 1999; Klusman, 1993; Zhang *et al.*, 1999). The methane that has filtrated to the surface and failed to be oxidized or decomposed may be release into the atmosphere through diffusion and convection (Vermenlen, 1999; Klusman, 1993; Zhang *et al*., 1999). The known oil/gas basins on the globe comprise up to 8×10^7 km^2, which is about 15% of the whole continental area (Николай, 1996). Therefore, gas/oil basins must play a great role in the source-sink models of global atmospheric methane. The environmental issues caused by the natural release from deep oil/gas reservoirs have not created much interest until recently (Mosier *et al.*, 1991, 1996, 1997; Klusman and Jakel, 1998; Vice and Halleck, 1999). Therefore a careful measurement and correct assessment of the natural release of methane from different oil/gas basins are still of great value, for deeply comprehending the exchange of carbon between the lithosphere and the atmosphere, for improving the existing source-sink balance model, and for mastering the source-sink variation on a regional scale. In this study, by a static boxes technique, the methane fluxes have been measured in the Yakela condensed oil/gas field in Talimu Basin, Xingjiang, Northwest China, and the origin of the measured gases investigated through carbon isotope analysis of methane, with the purpose of assessing the possible contribution of methane release from oil/gas fields into the atmosphere, and having a better understanding of the source-sink relation in the methane budge models.

1 Basic features of the study area

As one of the major oil producer in the world, 33 large to medium sized oil fields have been discovered in China, among which the famous oil fields like Talimu and Junggar lie in the arid Northwest China, making it a distinctive oil accumulation area (Song *et al*., 1998). Since its arid climate, high evaporation and infiltration, strong salt-base reaction, low production of the land, the limited biogenetic release of CH_4 near the earth surface remarkably reduce the surface effect, usually severely affecting the study of microseepage of methane from deep reservoirs. Therefore, Northwest China is believed to be an ideal region for this kind of investigation.

In this study, the Yakela condensed oil/gas field was chosen as the study area. The field, tectonically located in the eastern part of Shaya Upwarping of the Luntai-Yakela faulted uplift zone in northern Talimu, is a large condensed oil field found in the recent decade. The zone is a mass block between Luntai Fault in the south and Yaha Fault in the north, with a range of 4,400 km (Fig.1). Three types of underling oil/gas reservoirs have been found in the region, namely, the condensed gas reservoir trapped in an anticline structure of the Kabushaliang Formation of the Cretaceous Period, rock-structure composite condensed oil/gas reservoir in Middle to Low Jurassic, and the condensed oil reservoirs of a buried-hill type in Low Ordovician, Upper Cambrian, and Sinian (Upper Proterozoic), respectively, and all these oil/gas traps are of carbonate and clastic rock types. Ordovician dolomite buried hill gas reservoir has been discovered in Well Shashen-2. Due to the influences of the Hercynian squeezing fold and squeezing uplift, the Luntai-Yakela faults, many dolomitic buried hills have developed, of which 20 have been proved. The Manjia'er depression to the south and the Kuqa depression to the north are favorable areas for hydrocarbon migration and accumulation, thus hydrocarbon resources are abundant (Yan *et al*., 2004). A soil geochemical survey had demonstrated that certain light hydrocarbon components are capable of migrating from a reservoir as deep as 4,000–6,000 m to the surface, that the lighter components transpose much faster and are more effective than the heavier ones, and such types of vertical micro-migrations have left evidence on the surface which is measurable as geochemical anomalies (Zhang *et al*., 1998; Hou and Su, 2001; Qian, 1998).

1.1 Sampling

The Yakela condensed oil/gas field is characterized by a homogeneous sedimentary basin in geology and geography, which consists of uncovered Quaternary terrene/arenaceous sediments, except scattered superxerophils, for example, instance jarrah, shrub, and so on. Research by Thomas *et al*. (2000) have proved in Ruhr Basin and Lower Rhine Embayment, in Germany, the spatial variability of methane consumption/emissions is low when the flux chamber experiments are conducted simultaneously for a wider area of identical soil type and utilization at a certain time. That is to say, methane con-

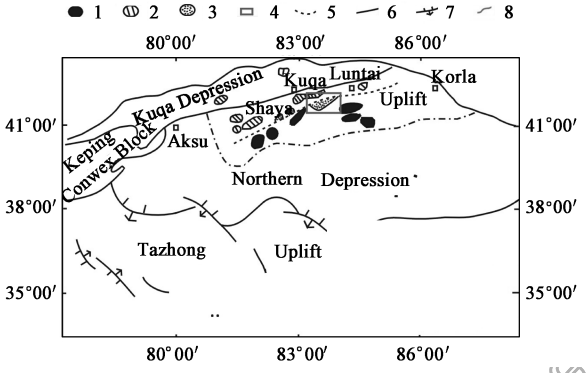

Fig. 1 Sketch geological map showing distribution of natural gas in the Talimu Basin, China (Huang, 1999).

sumption/emissions measured with several flux chamber experiments for a wider area of an identical soil type, and utilization at a certain time can represent characteristics of methane consumption/emissions in the whole region. Therefore, to study methane release from the deep oil/gas reservoir to the surface through microseepage and pervasion, a piece of bare land in the middle of the condensed oil/gas field was designed (Fig.2, 41°33′02″N, 83°31′11″E). Five chambers were arranged into a square lattice, with the one at the center, labeled as point M, and the other four at each corner, placed in the east, south, west, and north of point M, respectively, to monitor the methane release fluxes from each direction. The distance between point M and each corner was 5 m equally, so that the square covered an area of 50 square meters. The methane release fluxes in these boxes were monitored once every three hours for a whole day, that is, 8:00–9:10; 11:00–12:10; 14:00–15:10; 17:00–18:10; 20:00–21:10; 23:00–24:10; 2:00–3:10; 5:00–6:10, to monitor the daily variation. The methane fluxes were measured by fixed cylindrical chambers (Mosier *et al*., 1991). The static boxes made of transparent polyethylene of 8 mm in thickness, were composed of two parts, a cylindrical base with an inner diameter of 33 cm and a chamber height of 13 cm and a groove 3 cm deep in its upper brim, a chamber cover with an inner diameter of 37 cm with a thermometer in the box, and a small sampling hole was placed in the center, with 4 mm in diameter which was sealed by rubber of high quality (Fig.3). At each site, the cylindrical base was forcefully inserted into the ground to a depth of 7 cm, and the soil carefully pressed, sometimes with some water, to seal the lower edge of the box. The upper edge of each box was sealed by filling water in the groove and having the cover immersed in it. After the boxes were set, 100 ml gas samples were taken via a syringe through the sampling hole, at 0, 10, 30, 50, and 70 min, respectively, and filled into aluminum foil bags for methane analysis. The covers of the boxes were then removed to let the air in the boxes sufficiently mix with the atmosphere until the next sampling duration. In two durations, one in the afternoon, another at midnight, additional gas samples of 500 ml were taken for isotope analysis. The sampling time in each duration was the same as that in the common gas sampling scheme described previously.

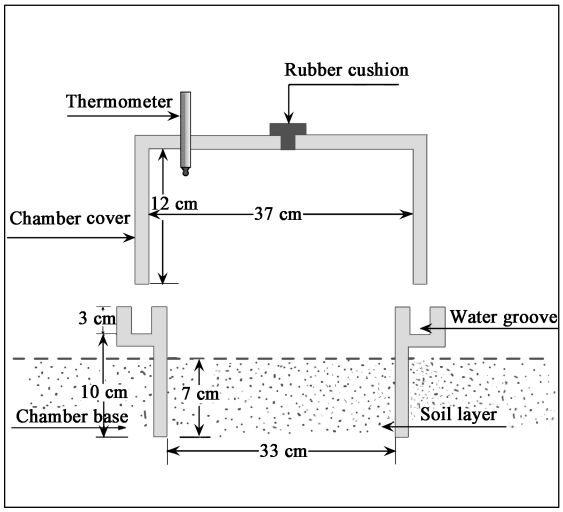

Fig. 3 Sampling chamber sealed by filling water in the groove.

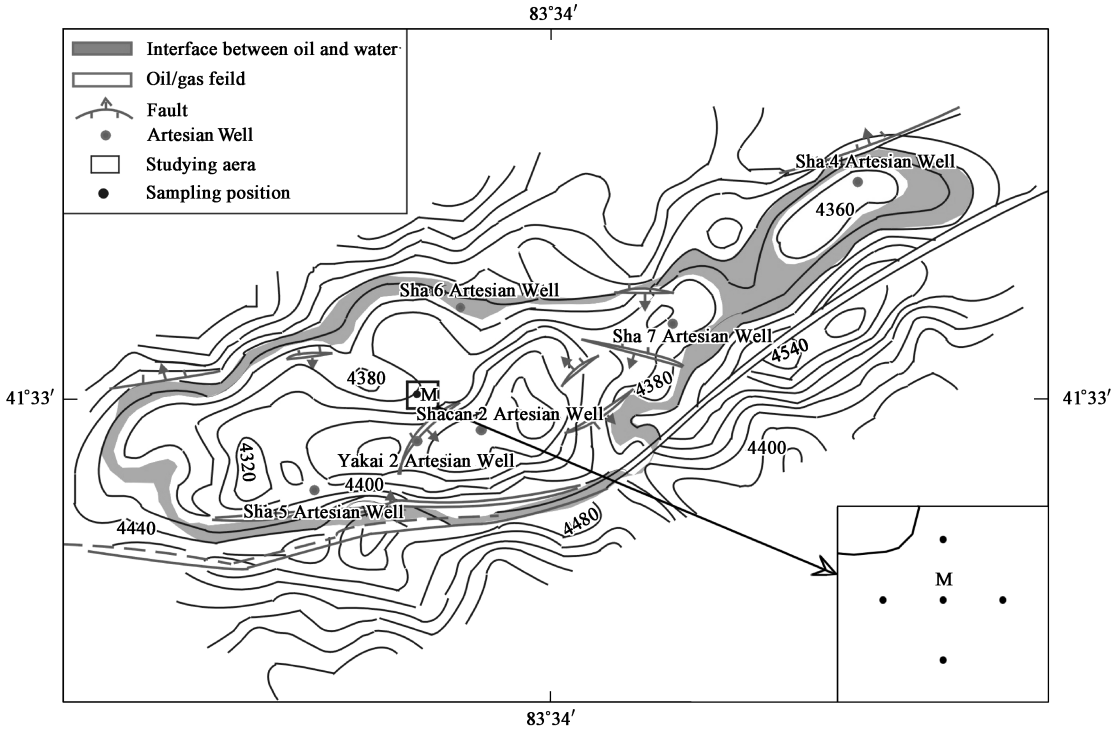

Fig. 2 Geological features of study area and flux chambers distribution in the Yakela condensed oil/gas field (modified from Xinjiang Bureau of SinoPec).

1.2 Analysis method

Methane concentrations in the gas samples were analyzed in the State Key Laboratory of Atmospheric Physics and Chemistry, China and the Institute of Atmospheric Physics of Chinese Academy of Sciences by a HP-5890 gas chromatographer (FID, America), which was calibrated by the national standard gas of 2.04×10^{-6} methane before and after each batch of measurements. The working conditions of the chromatographer were set as: a stainless steel column (2 mm × 2 m) filled with 13X molecular sieve of 60/80 meshes, N_2 (99.999%) as load gas with a flow of 30 ml/min, column temperature of 55°C, FID detector with a temperature of 200°C, and a measure error of 0.11%–0.25%.

Isotopic compositions of methane in the samples were measured in the Lanzhou Geological Institute of Chinese Academy of Sciences by an online analytic system of Delta Plus XP stable isotope mass spectrometer (GC/C/MS) by Thermo Finnigan, coupled with an online sample preprocessor designed by Tang *et al*. (2006). The working condition of the mass spectrometer was adjusted to an ion source pressure of 3.0 kV, and an ion source current of 1.5 mA, an ion source heating current of 6.0 mA. The chromatographer working with the mass spectrometer was settled as: C-2000 column (25 m × 0.53 mm × 20 μm). He (99.999%) as load gas with a flow of 12.0 ml/min. For the purpose of separating CH_4, CO_2 and CO, a program of temperature was as follows: 30°C for 10 min, rise to 200°C at 15°C/min and holding for 2 min at 200°C with an (NiO/CuO/Pt) temperature of 9°C. The measure error was less than 0.4‰.

The methane flux was calculated with Eq.(1) (Mosier *et al*., 1991).

$$E = \rho \times V/A \times \mathrm{d}c/\mathrm{d}t \quad (1)$$

where, E is the flux; ρ is the density of measured gas; V is the effective volume of the sample box; A is the bottom area of sample box; $\mathrm{d}c/\mathrm{d}t$ is the variation of concentration of methane with time.

2 Results and discussion

2.1 Daily variation of methane release from the Yekela condensed oil/gas field

The measurements of the natural release of methane from the Yekela condensed oil/gas field at eight time-durations in one day (8:00–9:10; 11:00–12:10; 14:00–15:10; 17:00–18:10; 20:00–21:10; 23:00–24:10; 2:00–3:10; 5:00–6:10), are shown in Fig.4 and Table 1. The results clearly demonstrated that the spatial variability of methane emission flux was quite small among the five chambers, with a standard deviation of less than 0.02 mg/(m^2·h), which is probably because of the fact that the Yakela oil/gas field is characterized by a homogeneous sedimentary basin in geology and geography and is consistent with the conclusion of Thomas *et al*. (2000). Furthermore, daily variation characteristics of the methane emission flux were similar in all boxes, that is, the methane emission flux at night was obviously higher than in the daytime and reached its maximum early in the morning. The characteristics are consistent with ones observed in

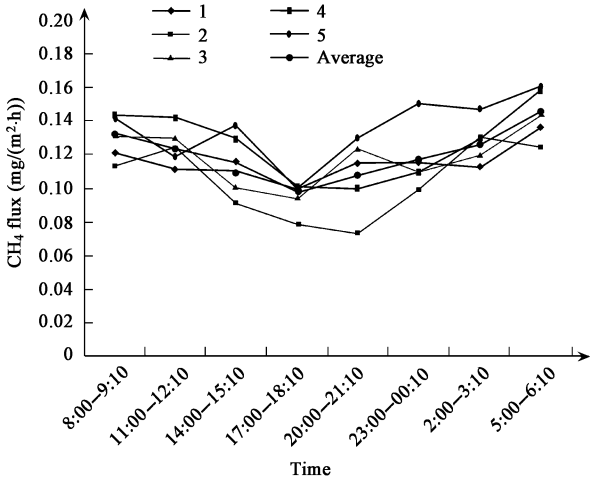

Fig. 4 Daily variation of methane emission from different flux boxes in the Yekela condensed oil/gas field.

Table 1 Flux of methane (CH_4) emission of five chambers in different times in Luntai area

Time	Flux of CH_4 emission (mg/(m^2·h))					Average flux of the five chambers[a] (mg/(m^2·h))	Standard deviation of average flux of the five chambers[a] (mg/(m^2·h))
	Chamber 1	Chamber 2	Chamber 3	Chamber 4	Chamber 5		
8:00–9:10	0.12	0.11	0.13	0.14	0.14	0.13	0.01
11:00–12:10	0.11	0.12	0.13	0.14	0.12	0.12	0.01
14:00–15:10	0.11	0.09	0.10	0.13	0.14	0.11	0.02
17:00–18:10	0.10	0.08	0.09	0.11	0.10	0.10	0.01
20:00–21:10	0.12	0.07	0.12	0.10	0.13	0.11	0.02
23:00–0:10	0.12	0.10	0.11	0.11	0.15	0.12	0.02
2:00–3:10	0.11	0.13	0.12	0.13	0.15	0.13	0.01
5:00–6:10	0.14	0.13	0.14	0.16	0.16	0.15	0.01
Average flux in each chamber[b] (mg/(m^2·h))	0.12	0.10	0.12	0.13	0.14	Average flux in all chambers[b] (mg/(m^2·h))	0.12
Standard deviation of average flux in each chamber[b] (mg/(m^2·h))	0.01	0.02	0.02	0.02	0.02	Standard deviation of average flux in all chambers[b] (mg/(m^2·h))	0.02
Daily flux[c] (mg/(m^2·d))			2.89			Standard deviation of daily flux[c] (mg/(m^2·d))	0.43

[a] In different time; [b] every hour in a day; [c] in every day.

the fault region in the Yakela oil/gas field (Tang *et al*., 2007). The average flux for all the five chambers was 0.15 mg/(m^2·h) early in the morning and decreased afterwards to a low value 0.10 mg/(m^2·h), an average flux in the five chambers in the afternoon, and gradually increased towards the night.

As soils play a role both as the source and sink of methane, their methane flux is decided by methanotrophic oxidation. Even though methanotrophic oxidation is affected by many factors, soil temperature is possibly the most important one (Nesbit and Breitenbeck, 1992). It is clearly demonstrated in Fig.5 that the relationship between methane emission flux and soil temperature was obviously inversely correlated. That is, in all the boxes, the methane flux decreased gradually in the day when the soil temperature rose, until reached its minimum at 17:00–18:00, and then gradually increased towards the evening when soil temperature fell, until the methane flux reached its maximum at 5:00–6:00. It is obvious that higher soil temperature was in favor of methanotrophic oxidation in soil (Nesbit and Breitenbeck, 1992). Thereby a part of the methane, which is diffused and infiltrated from the oil/gas reservoir to the surface, is absorbed and oxidized by the soil in the daytime. In addition, the soil temperature falls synchronously with the atmospheric temperature at night, which restrains methanotrophic oxidation in the soil and leads to more methane being diffused and infiltrated from the oil/gas reservoir to the surface where it emitted into the atmosphere.

Considering the geographical location, there are time differences between Xinjiang and Beijing. The highest sunlight intensity and atmospheric temperature in the day are about 15:00–16:00 in the afternoon. Thus soil temperature is the highest between 17:00–18:00 in the afternoon because it logs behind atmospheric temperature. Under this condition, methanotrophic oxidation in soil culminates during 17:00–18:00 leads to much of the methane which is microseepaged and infiltrated from oil/gas reservoir to the surface and absorbed and oxidized by the soil, thereby the methane emission is clearly the lowest (Fig.5). The Yekela condensed oil/gas field belongs to a dry desert area and is characterized by great difference above 25°C temperatures between the day and night. Soil temperature falls to its minimum in the wee hours, whereas, atmospheric temperature does so at midnight, which makes

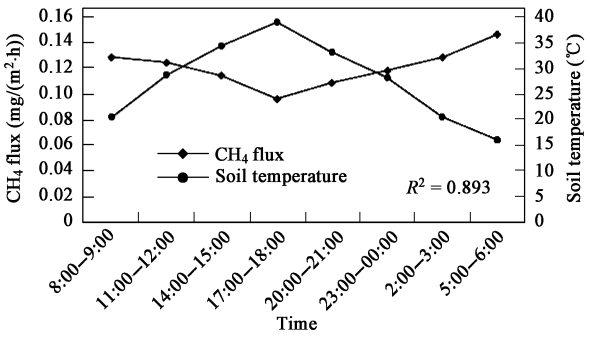

Fig. 5 Diagram of daily change of methane flux and soil temperature in the Yekela condensed oil/gas field.

methanotrophic oxidation declines noticeably in the soil. Therefore, a majority of methane, which is microseepaged and infiltrated from the oil/gas reservoir to the surface remains unoxidized and undegraded and is released into the atmosphere by means of diffusion and advection, which makes methane emission reach its maximum in the wee hours. It is obvious from this study that the Yekela condensed oil/gas field is a source of atmospheric methane (Table 1). The result is consistent with that of soil geochemical survey (Zhang *et al*., 1998; Qian, 1998; Hou and Su, 2001) which demonstrates that light hydrocarbons, methane in particular, could migrate from a reservoir as deep as 4,000–6,000 m to the surface, and such a type of vertical micro-migration had left evidence in the surface, which is measurable as geochemical anomalies.

Based on the fact that methane emission of each flux chamber varies little at the same time, it seems reasonable to calculate the daily methane release flux using the average hour methane flux in a day for all the chambers. The daily methane release flux of this area obtained was 2.89 mg/(m^2·d), with a standard deviation of 0.43 mg/(m^2·d).

2.2 Carbon isotope composition of released methane in the Yakela condensed oil/gas field

In recent years, many scientists have realized that the important role played by the isotopic tracing technique on the delineating environmental mechanisms of production, transport, and release of methane and on determining their relative contributions (Tyler *et al*., 1988; Rust, 1981). With the continuous improvement of isotope measurement, the techniques of stable carbon isotope composition ($^{13}C/^{12}C$), stable hydrogen isotope composition (D/H), and radioactive carbon isotope were widely applied to atmospheric methane and methane of various origins, for the purpose of tracing sinks/sources of the methane, and estimating the global or regional methane budget and source strength (Stevens and Rust, 1982; Stevens and Engelkemeir, 1988; Wahlen *et al*., 1989; Hilkert *et al*., 1999; Rice *et al*., 2001; Yamada *et al*., 2003). However, the weighted average of the carbon isotope composition from all known methane sources on the earth's surface seems lighter than that of the atmosphere (Michael, 1990; Etiope and Klusman, 2002) which has forced researchers to more accurately estimate the isotope fractionation coefficient of methane during its photochemical reactions. On the other hand, it asks for more detailed researches of the carbon isotope composition of methane on the earth surface, including a possible variation of isotope composition of known sources under various spatial and/or temporal conditions and possible unknown methane sources as well. As an important representative of a heavy carbon source, the influence caused by methane release from the oil/gas basins has caught the attention of researchers. Table 2 shows the methane emission flux and a change in the carbon isotopic composition of methane in the hydrocarbon-prone or coaly-prone areas, in recent years (Klusman and Jakel, 1998; Klusman *et al*., 2000; Klusman, 2003; Etiope and Klusman, 2002; Thomas *et al*, 2000).

To verify further, the origin of methane from under

Table 2 CH_4 flux data and change of carbon isotopic composition of methane from hydrocarbon-prone coaly-prone areas

Hydrocarbon-prone areas	Country	CH_4 flux (mg/(m^2·d))	Isotope (standard deviation) (‰)	Reference
Rangely Field Basin	Colorado	4.2–23.8	–	Klusman, 2003
Denver-Julesburg Basin	Colorado	–41–43.1	–	Klusman *et al*., 2000
Piceance	Colorado	–6.0–3.1	–	Klusman *et al*., 2000
Powder River	Wyoming	–14.9–19.1	–	Klusman and Jakel, 1998
Railroad Valley	Nevada	–6.1–4.8	–	Klusman and Jakel, 1998
Vincenzo Basin	Italy	–3–600	–	Etiope and Klusman, 2002
Ruhr Basin	Germany	4.3–99,830	–32.5 (±0.15–±0.4)	Thomas *et al*., 2000
This study area	China	2.89±0.43	–43.5 – –42.8 (±0.4)	

"–" means blank

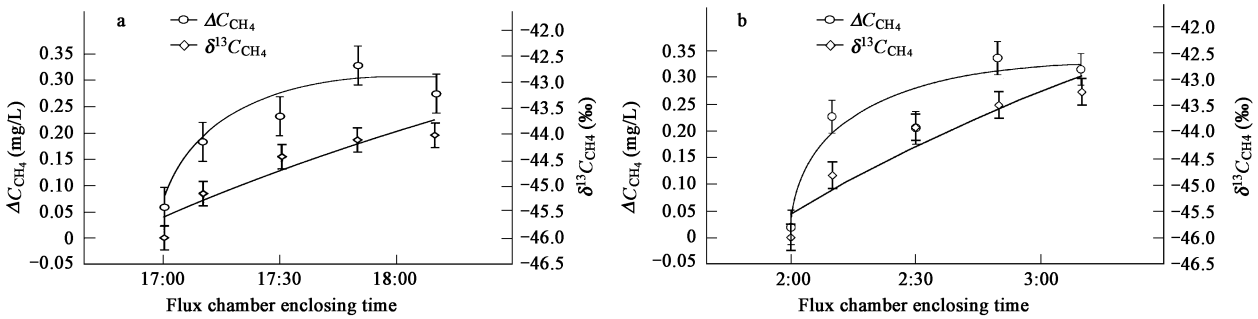

Fig. 6 Variation of carbon isotopic composition of methane in flux chambers with time in the Yekela condensed oil/gas field.

the oil/gas reservoirs in the Yekela condensed oil/gas field, the author simultaneously carried out the CH_4 flux measurement with static boxes, and measured the $\delta^{13}C$ variation of the methane during the day and the night. Shown in Figs.6a and 6b are the methane concentration and isotopic composition in the oil/gas reservoirs at 0, 10, 30, 50, 70 min, respectively, after the flux chambers were sealed during the day and the night. It is clearly demonstrated in Fig.6 that with an increase of methane concentration in the flux chambers, its carbon isotopic composition became heavier, a phenomenon similar to that observed by Thomas *et al.* (2000) in the subsidence troughs in the active and abandoned coal mining areas in the Ruhr Basin, Germany, where $\delta^{13}C$ increased with an increase in methane concentration in the flux chambers, indicating a the thermo-genetic origin of methane (Table 2). In contrast, the methane release by bacteria will cause a decrease in $\delta^{13}C$, or the carbon isotope becomes lighter with the increase in the methane concentration in the flux boxes. Petroleum geological studies have demonstrated that carbon isotopic composition of methane in deep natural gases in the Yekela condensed oil/gas field ranges from –42‰ to –31‰ and belongs to the pyrogenated gases (Tang and Liu, 2002). The fact that carbon isotopic composition become heavier with the increase of methane concentration in the flux chambers results obviously from the micro-leakage or diffusion/infiltration of methane in heavy carbon from the deep condensed gas reservoirs. Therefore, the methane released from the oil/gas field is believed to be mostly from the deep condensed oil/gas reservoirs.

3 Conclusions

Light hydrocarbons in the deep reservoirs, methane in particular, are liable to migrate upwards by microseepaging and infiltrating from beneath the oil/gas reservoir to the earth's surface in the Yakela condensed oil/gas field. As the speed of diffusion and infiltration of methane is much higher than that of its oxidation by bacteria, part of the methane will eventually be released into the atmosphere. Because the Yakela oil/gas field is characterized by a homogeneous sedimentary basin in geology and geography, methane emission flux changed little from sites to sites in the field. Daily variation characteristics of the methane emission flux were consistent in all boxes, that is, methane emission fluxes during the day were quite different from those during the night. Using the average hour methane flux in a day for all chambers, the daily methane release flux of the study area was 2.89 mg/(m^2·d). The $^{13}C/^{12}C$ ratios of methane in the flux chambers became heavier as methane concentrations in flux chambers increased gradually, which revealed that the methane emitted in the oil/gas field might come from the thermogenic methane of the deep condensed oil/gas reservoir.

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