Dating petroleum emplacement by illite $^{40}Ar/^{39}Ar$ laser stepwise heating

Jian-Bing Yun, He-Sheng Shi, Jun-Zhang Zhu, Ling-Hao Zhao, and Hua-Ning Qiu

ABSTRACT

The timing of petroleum emplacement is crucial in understanding petroleum-forming processes and predicting new prospecting regions. This study investigates the possibility of determining the age of petroleum emplacement by an illite $^{40}Ar/^{39}Ar$ laser stepwise heating technique. A specially designed apparatus has been used to clean up the organic gases in samples contaminated with residues from oil or gas fields, resulting in credible $^{40}Ar/^{39}Ar$ data. The sandstone samples are from the Zhuhai and Zhujiang formations in the Huizhou sag in the Pearl River Mouth Basin, South China Sea. Illite $^{40}Ar/^{39}Ar$ laser stepwise heating consistently yields gradually rising age spectra at the low-temperature steps until reaching age plateaus at high-temperature steps. The first-step apparent ages of the six samples from the Zhujiang formation give a weighted mean age of 11.4 ± 0.5 Ma (1σ), in agreement with an age of 12.1 ± 1.1 Ma in the first three steps of the sample from the Zhuhai Formation. These dates are interpreted as being caused by the formation of fine authigenic illite and therefore indicative of the maximum age of petroleum emplacement in the Huizhou sag because illite is commonly one of the latest forming minerals prior to hydrocarbon accumulation. The plateau ages ranging from 58 to 276 Ma in high laser-output steps are interpreted as being caused by variable contributions from detrital K feldspar in the sandstones. The older total ages based on the illite $^{40}Ar/^{39}Ar$ stepwise heating results are equal to the K-Ar ages and are not usable in delineating petroleum emplacement

Manuscript received June 12, 2009; provisional acceptance September 2, 2009; revised manuscript received October 4, 2009; final acceptance October 21, 2009.
DOI:10.1306/10210909102

AUTHORS

Jian-Bing Yun ~ *Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS), Guangzhou 510640, China; present address: Graduate University of Chinese Academy of Sciences (GUCAS), Beijing 100049, China*

Jian-Bing Yun is a Ph.D. student at GIGCAS and GUCAS.

He-Sheng Shi ~ *School of Ocean and Earth Science, Tongji University, Shanghai 200092, China; present address: Research Institute, Shenzhen Subsidiary, China National Offshore Oil Corporation (CNOOC) Limited, 168 Jiangnan Road, Guangzhou 510240, China*

He-Sheng Shi is the general engineer of the Research Institute, Shenzhen Subsidiary, CNOOC Ltd. His research interests include sedimentary facies analysis and petroleum geology.

Jun-Zhang Zhu ~ *Research Institute, Shenzhen Subsidiary, CNOOC Ltd., 168 Jiangnan Road, Guangzhou 510240, China*

Jun-Zhang Zhu is an engineer of geochemistry in the Research Institute, Shenzhen Subsidiary, CNOOC Ltd.

Ling-Hao Zhao ~ *Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

Ling-Hao Zhao is an M.Sc. degree student at GIGCAS and GUCAS.

Hua-Ning Qiu ~ *Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China; present address: Key Laboratory of Tectonics and Petroleum Resources (China University of Geosciences Wuhan), Ministry of Education, Wuhan 430074, China; qiuhn@gig.ac.cn*

Hua-Ning Qiu is in charge of the argon laboratory in GIGCAS. His research interests include the techniques and applications of $^{40}Ar/^{39}Ar$ geochronology, especially in stepwise crushing techniques to determine the mineralization ages of hydrothermal deposits. Currently, his focus is on $^{40}Ar/^{39}Ar$ techniques to date oil or gas emplacement ages.

because they represent mixtures with variable contributions from authigenic illite and detrital K feldspar. The $^{40}Ar/^{39}Ar$ stepwise heating technique thus can be applied to resolve important petroleum emplacement age information from illite samples that otherwise cannot be provided by traditional K-Ar methods.

INTRODUCTION

Petroleum emplacement chronology is one of the frontier research subjects in both petroleum geology and isotope geochronology. Determining the oil or gas emplacement ages has important implications for oil or gas genesis and resource prediction. Typical relative chronology for oil or gas migration, emplacement, and accumulation is established by petrology, basin tectonic evolution, trap formation, and hydrocarbon generation from the source rock (Kelly et al., 2000; Middleton et al., 2000; Xiao et al., 2002). As we will show in this article, the $^{40}Ar/^{39}Ar$ stepwise heating technique holds significant promise in establishing absolute constraints on the maximum emplacement age of oil and gas in their parent reservoirs.

Illite is a nonexpanding, clay-size, micaceous phyllosilicate with the chemical formula $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2.H_2O$ and occurs as an alteration product of muscovite and feldspar in weathering and hydrothermal environments. Some illite is authigenic or could be derived from alteration of K feldspars or recrystallization of smectites. Illite is a common mineral in sediments, clays, marls, shales, and some slates. Interstratified illite-smectite converts to illite at depths. Since the middle of the 1980s, authigenic illite K-Ar dating has been applied to determine the ages of petroleum migration in the North Sea oil fields (Lee et al., 1985; Liewig et al., 1987; Hamilton et al., 1989; Robinson et al., 1993). The dating is based on the hypothesis that "illite is commonly the last or one of the latest mineral cements to form prior to hydrocarbon accumulation. Because the displacement of formation water by hydrocarbons will cause silicate diagenesis to cease, K-Ar ages for illite will constrain the timing of this event and also constrain the maximum age of formation of the trap structure" (Hamilton et al., 1989, p. 215–216). Wang et al. (1997, 1998) investigated oil or gas emplacement ages in the Tarim Basin by this technique. More illite K-Ar dating work has been done in the Exploration and Development Research Institute, China National Petroleum Corporation (Zhang et al., 2001; Zhang and Luo, 2004; Zou et al., 2007).

Dong et al. (1995) were the first to date authigenic illite by $^{40}Ar/^{39}Ar$ stepwise heating and Wang et al. (2005) performed

ACKNOWLEDGEMENTS

We are grateful to Anthony Koppers, Prasanta K. Mukhopadhyay, and Arthur E. Berman for their reviews that improved the manuscript. We also thank Bernard de Jong for his linguistic support. This study was supported by the National Natural Science Foundation of China (40772080) and the Research Institute, Shenzhen Subsidiary, China National Offshore Oil Corporation Limited (CNOOC 2004-37). This is contribution IS-1123 from Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS).

The AAPG Editor thanks the following reviewers for their work on this article: Arthur E. Berman, Anthony Koppers, and Prasanta K. Mukhopadhyay.

DATASHARE 35

Spreadsheets for the $^{40}Ar/^{39}Ar$ dating results of the samples in the study are available on the AAPG Website as Datashare 35 at www.aapg.org/datashare/index.html.

^{40}Ar/^{39}Ar dating of illite in a gas reservoir. Compared to the K-Ar total fusion methodology, the ^{40}Ar/^{39}Ar stepwise heating age dating technique has significant advantages. (1) It generally requires a much less amount of sample (~10 mg) and gives higher precision, in which a small amount of sample is important because authigenic illite is sparse in sandstone and requires much extraction time. (2) Dating only requires the isotope ratio determination of argon on one sample to obtain a well-defined age, avoiding the problem of inhomogeneity using two separate splits of a sample to measure potassium and argon contents separately. (3) By using the stepwise heating technique, the contributions to the age spectrum of different mineral components (e.g., detrital K feldspar) are distinguishable, whereas the total fusion K-Ar ages reflect the mixing contributions from different minerals in the separated samples.

One drawback is that illite is a fine-grained mineral on the order of microns, and ^{39}Ar will therefore be lost because of nuclear recoil during irradiation. Earlier workers used a microampoule encapsulation method (Hess and Lippolt, 1986; Smith et al., 1993) to monitor the ratio of ^{39}Ar lost by nuclear recoil to examine its influence on the age spectrum. Because the nuclear recoil gasses are typically a mixture from different sources (Dong et al., 1997, 2000), the encapsulation method was not used in this study.

Another drawback is the necessity of sampling pure illite; as with current technology, obtaining pure authigenic illite is difficult. However, as we show in this article, it is possible to get a reliable age date of impure illite samples from the ^{40}Ar/^{39}Ar age spectrum by careful stepwise heating, making the very important timing of petroleum emplacement feasible.

Qiu et al. (2009) summarized the difficulty and feasibility in determining the emplacement ages of oil or gas reservoirs by ^{40}Ar/^{39}Ar techniques. In the analysis of authigenic illite using the ^{40}Ar/^{39}Ar technique, two key problems must be confronted: (1) the separation and extraction of authigenic illite from their host rocks and (2) the purification of the extracted argon gasses from organic active gases. Proper experimentation requires high-purity authigenic illite. Liewig et al. (1987) proposed a repetitive freezing-heating method that breaks up fine grain-size sandstone along the grain borders or cleavages to prevent contamination of the illite samples with detrital K feldspar. Nevertheless, current illite separation techniques cannot practically avoid contamination with detrital minerals. Organic matter retained in illite samples is released during heating of organic gases, which, split into small fragments, will show the progressive outgassing mass-to-charge (m/e) ratios changing over the course of a single stepwise heating experiment and covering all argon isotopes and the components contributing to each of the argon isotopes. The presence of the fragments derived from the organic matter will alter the argon isotope compositions, resulting in misleading (and commonly wrong) age data in addition to seriously polluting the sample tubes, the mass spectrometer ion source, and its highly sensitive signal detectors.

In this study, we have researched a novel purification apparatus that can remove these harmful organic gases effectively, improving the quality of age results, preventing the mass spectrometer from contamination, and thus providing credible ^{40}Ar/^{39}Ar age data for illite samples in oil or gas reservoirs. The tasks of our first trial study were destined for illite ^{40}Ar/^{39}Ar dating, x-ray diffraction (XRD), and scanning electron microscopy (SEM) analyses related with the interpretations of the age spectra by the entrusting petroleum company. The novel purification technique and significant ^{40}Ar/^{39}Ar results are reported in this article.

GEOLOGICAL BACKGROUND AND SAMPLE CHARACTERISTICS

The study area, Huizhou sag, is located in the middle Pearl River Mouth Basin, South China Sea (Figure 1). All the sandstone samples are from the oil saturation zones marked by the petroleum geologists. Sample 06ZJ26 is from the Zhuhai Formation, the others are from the Zhujiang Formation. The reservoir sandstones of these two formations are about 1000–2000 m (3281–6562 ft) in thickness. Our illite samples were selected from oil-saturated sandstone intervals. According to the stratigraphic succession in the Pearl River Mouth Basin (Figure 2)

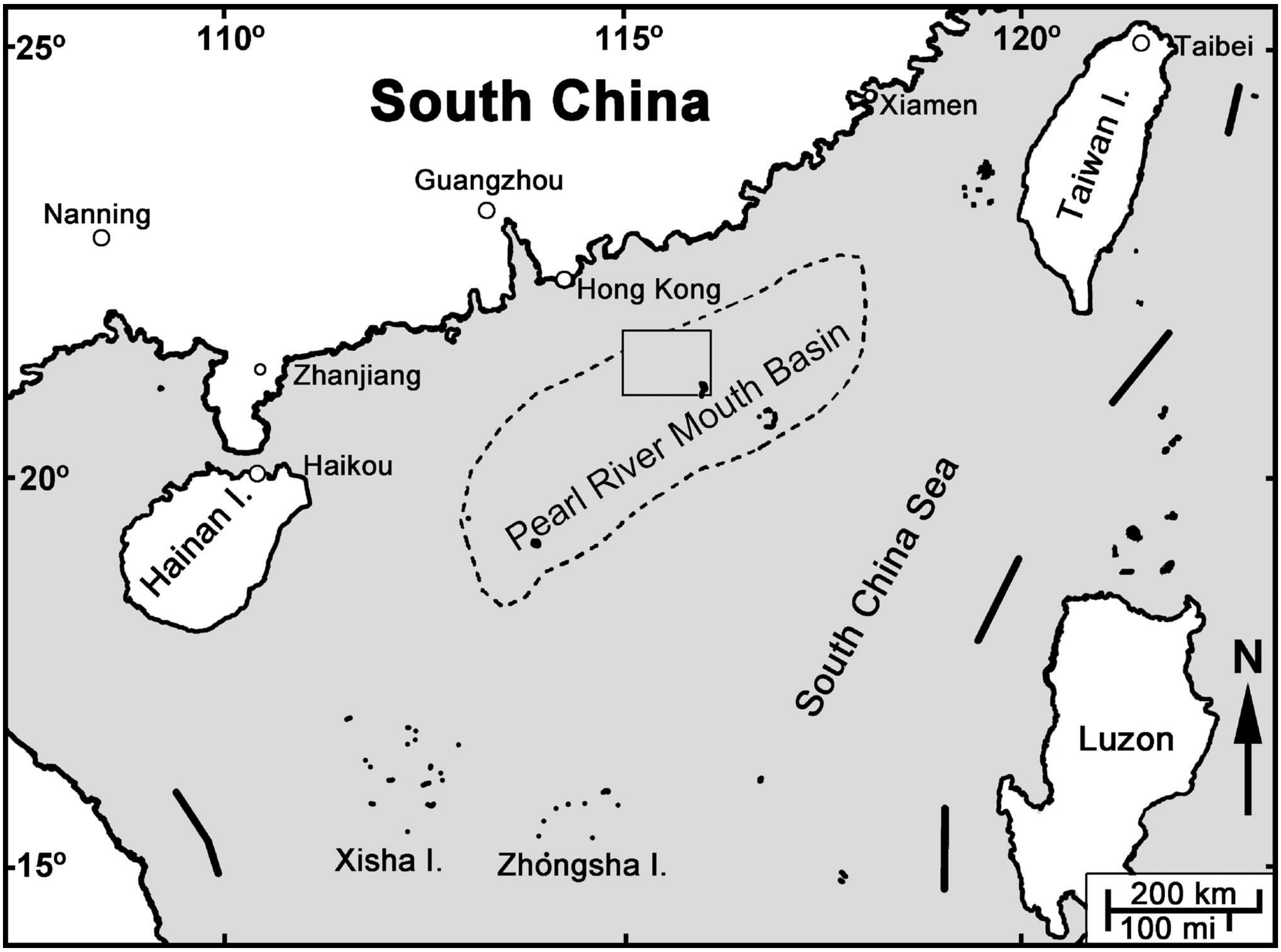

Figure 1. Geographic map of the South China Sea. Modified from Google Imagery ©2009. The study area is shown as a square in the Pearl River Mouth Basin.

(Wu, 1994; Yan et al., 2001; Yan et al., 2006) and the newest version of the international stratigraphic chart (ICS, 2009), the Zhuhai Formation ranges from 28.4 to 23.0 Ma in age and the Zhujiang formation ranges from 23.0 to 16.0 Ma.

Powder XRD and SEM will help us interpret the ^{40}Ar/^{39}Ar age spectra. For instance, the XRD analysis of 06ZJ26I from the Zhuhai Formation shows the presence of illite (11%), interstratified illite-montmorillonite (6%), kaolinite (22%), chlorite (1%), and K feldspar (15%), together with some unidentifiable minor components (19%) (Figure 3). The SEM analysis of 06ZJ26I shows widely distributed illite (Figure 4). Commonly filamentous illite occurs on particle surfaces, in intergranular pore and particle surface corrosion holes, or in intergranular paragenesis with authigenic quartz. Some flaky detrital illite is developed in secondary pores and in paragenesis with secondary quartz or kaolinite on particle surfaces. The other samples from the younger and shallower Zhujiang Formation (06ZJ06I, 06ZJ08I, 06ZJ14I, 06ZJ16I, 06ZJ17I, and 06ZJ22I) have less authigenic illite than 06ZJ26I. As a whole, authigenic illite is poorly developed in reservoir sandstones of the Pearl River Mouth Basin.

EXPERIMENTAL METHODS

Illite Sample Separation and Detection

The sandstone samples were crushed by a hammer to about 1 cm (0.4 in.) in size and cleaned in an ultrasonic bath with distilled water to remove surface dirt. The crushed fragments were placed in a stainless steel container with distilled water. The

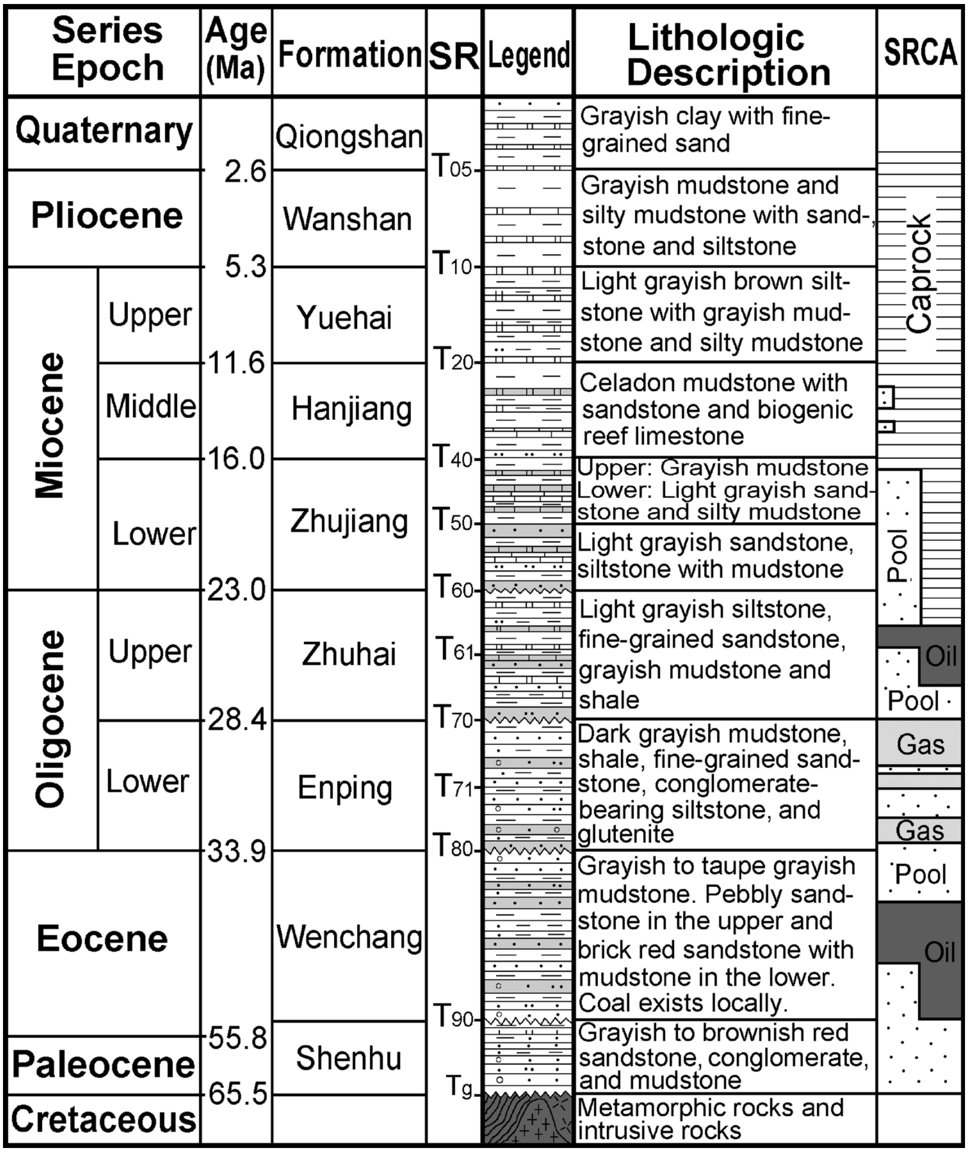

Figure 2. Stratigraphic succession of the Pearl River Mouth Basin based on He et al. (2008, with permission of the authors) and the latest international stratigraphic chart (ICS, 2009). The samples in this study were collected from the Zhuhai and Zhujiang formations. SR = seismic reflector; SRCA = source-reservoir-caprock assemblage.

container was alternately placed in a refrigerator (−18°C) and an oven (60°C) in repetitive freezing-heating cycles until the sample collapsed to fine grains, which was subsequently dried. To avoid chloride ion interference, a mixture of benzene and methanol with a volume ratio of 3:1 was used to extract organic matter for more than 72 hr until oil fluorescence disappeared.

Thirty grams of the sample grains were then placed with 1 L distilled water in a beaker in an ultrasonic bath. Ultrasonics removed the clay minerals from the surface of the grains and left a suspension with a grain size less than 0.5 μm. Acetic acid was used to remove carbonates, and H_2O_2 and acetone were used to remove residual organic matter from the grain surface. The liquid suspension was left for 110 hr at 25°C to separate illite from the detrital fraction, followed by siphoning the top 10 cm (3.9 in.) of the suspension liquid. The clay mineral (<0.5 μm) fraction was separated by centrifugation at a rotary speed of 5000 rpm for 1 h.

An XRD analysis was used to determine the purity and component of clay minerals. Scanning electron micrographs of rock-core specimens were used to examine the authigenic illite morphology.

Preliminary Tests of the Illite Samples

To determine the overall nature of the gases (i.e., argon and other reactive gasses) emanating from the

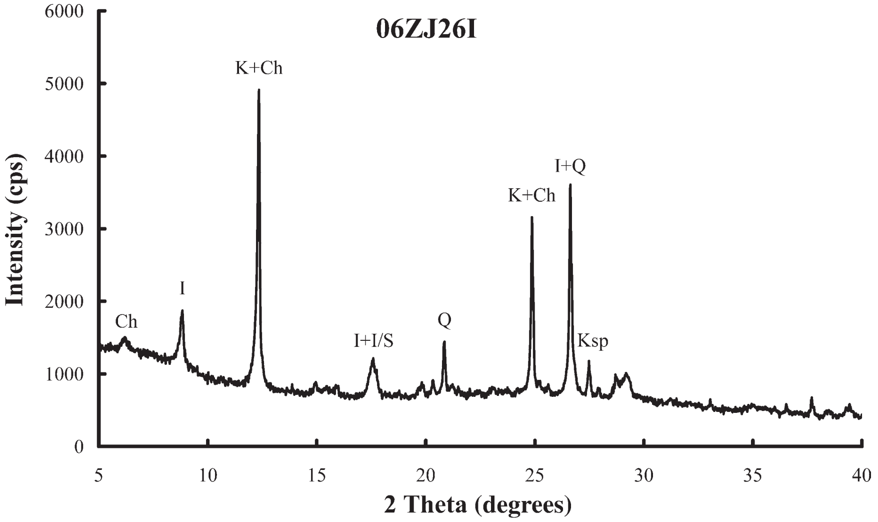

Figure 3. X-ray diffraction spectrum of 06ZJ26I. Q = quartz; K = kaolinite; Ksp = K feldspar; I = illite; I/S = interstratified illite-montmorillonite; Ch = chlorite; cps = counts per second. The Philips X'pert pro MPD x-ray diffractometer is courtesy of He-Jing Wang, Microstructure Analytical Lab, Peking University.

illite samples and the effectiveness of our purification line, two nonirradiated illite samples (~15 mg) were preliminarily tested with our old MM-1200 instrument after removal of residual organic matter with H_2O_2 and acetone. Prior to analysis, the samples were baked out at 250°C for 2 days to reduce the blanks.

The samples were heated at two steps of 600 and 900°C for 30 min. Gases released through a trap in liquid nitrogen were purified by a sponge Ti furnace (at 800°C for 20 min) and a Ti sublimation pump (two times at a current of 30 A for 45 s), followed by further purified purification with an SAES NP10 getter (operated at room temperature for 10 min). Then the gases were analyzed by an MM-1200 instrument with a Faraday cup and output to a recorder. The peak scan (Figure 5) shows

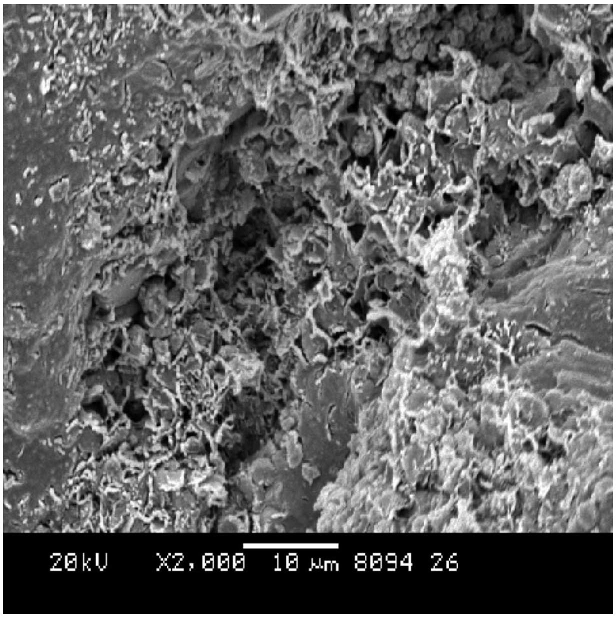

Figure 4. Scanning electron micrograph of 06ZJ26 showing authigenic illite in the pores among grains.

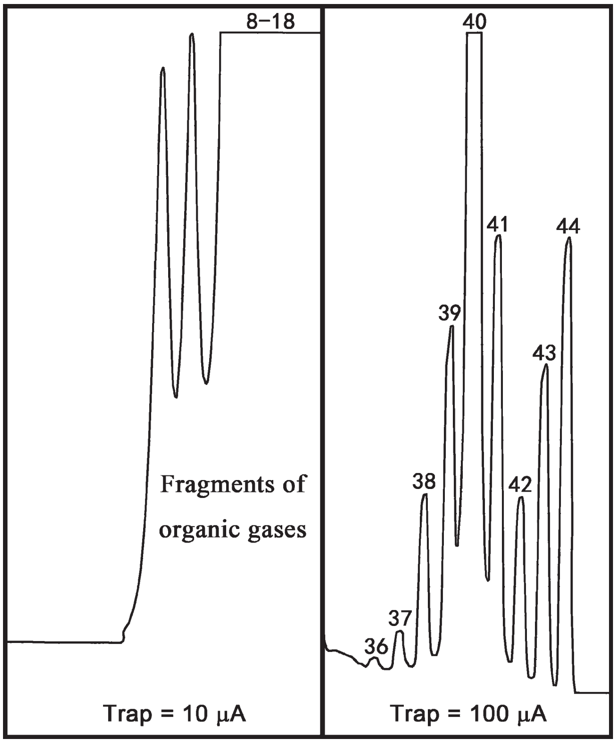

Figure 5. Peak scanning for the gases released from the non-irradiated illite sample 06ZJ40I at 600°C analyzed by an MM-1200 mass spectrometer, showing a variety of organic fragments within the illite sample.

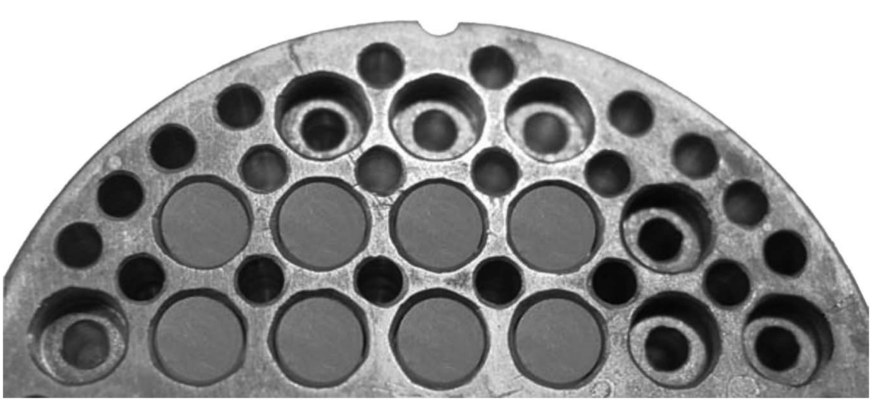

Figure 6. Illite sample holder and ZnS cover glass to avoid the powders from spurting out and contaminating the surroundings.

clearly that a considerable amount of organic gases, with carbon fragments of m/e = 8–18, was released from the samples, with some signals significantly outside the linear range at the lowest trap current of 10 μA. The m/e peaks between 36 and 44 were clearly affected by large signals from these organic gas components. Because the nonirradiated samples have no ^{37}Ar and ^{39}Ar, the peaks of 37, 39, and 41–43 must be from organic components in the released gasses, whereas peak 44 probably represents a mixture of both CO_2 and organic components. These preliminary tests indicated that the regular purification line did not suffice in cleaning up our oil-field illite samples. It therefore compelled us to manufacture a special purification apparatus to meet the specific needs of ^{40}Ar/^{39}Ar geochronology studies on oil or gas emplacements.

Experimental Procedure and Gas Purification

The samples and monitor samples were packed in aluminum and copper foil, respectively, in thin cylinders (about 5–7 mm [0.2–0.27 in.] in diameter, 2–4 mm [0.08–0.16 in.] in thickness) and placed in glass tubes. To obtain the irradiation parameter *J* values (the *J* value of a monitor standard sample is calculated with $J = \frac{e^{\lambda t_{\mathrm{ms}}}-1}{(^{40}\mathrm{Ar}^*/^{39}\mathrm{Ar_K})_{\mathrm{ms}}}$; ms is the monitor standard; the asterisk indicates radiogenic argon), the monitor standard samples with known age were inserted between every four unknown samples and both ends of glass tubes, and the positions (heights) of all unknown and monitor samples in the glass tube were recorded. Based on the *J* values and the positions of monitor sample, a regression line of each sample tube was obtained. Next, the *J* values of the unknown samples were calculated by interpolation from the regression line and their position. Cadmium, 0.5 mm (0.02 in.) thick, was employed to shield the samples and monitors from slow neutrons. The samples were irradiated for 48 hr in the 49-2 reactor in Beijing. The monitor sample was the DRA-1 sanidine used in the Vrije Universiteit University Amsterdam, with an age of 25.26 Ma (Qiu and Wijbrans, 2006). The correction factors for interfering Ar isotopes were $(^{39}\mathrm{Ar}/^{37}\mathrm{Ar})_{\mathrm{Ca}} = 8.984 \times 10^{-4}$, $(^{36}\mathrm{Ar}/^{37}\mathrm{Ar})_{\mathrm{Ca}} = 2.673 \times 10^{-4}$, and $(^{40}\mathrm{Ar}/^{39}\mathrm{Ar})_{\mathrm{K}} = 5.97 \times 10^{-3}$.

The argon isotopes were analyzed on a GVI–5400® mass spectrometer in the ^{40}Ar/^{39}Ar laboratory of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. A carbon dioxide infrared laser, MIR10-50W® (10.6 μm, 50 W), was used for stepwise heating.

To avoid illite powders from spurting out and contaminating the surrounding samples in the chamber, we proceeded as follows: (1) each sample was individually covered with a small ZnS cover glass (4.5 mm [0.18 in.] in diameter, Figure 6) and a big ZnS cover glass for all the samples in the chamber; (2) the sample was heated for 60 s in each step by increasing slowly the laser output from zero during the first 40 s followed by a fixed predetermined output during the last 20 s.

The released gases from illite samples by laser heating were first cleaned up in our new apparatus, which is specially designed to exclude organic gases. The apparatus consisted of a U-shaped trap, a Ti sublimation pump, a Zr-V-Fe pump, and a Zr-Al pump (Figure 7). The trap and pumps are operated at different temperatures: the U-shaped

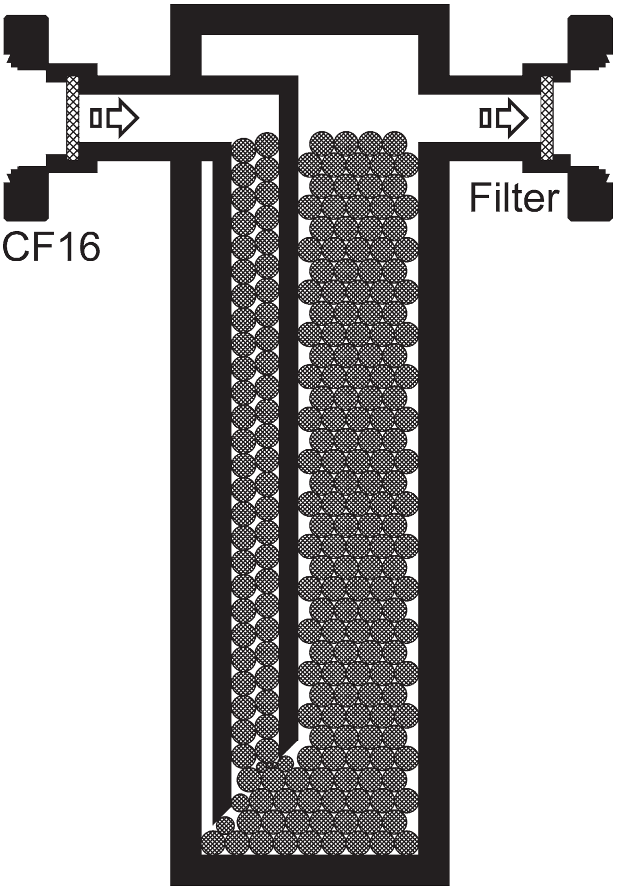

Figure 7. Schematic diagram of the Zr-V-Fe and Zr-Al pump. The Zr-V-Fe pump is operated at 250°C and the Zr-Ar pump at 400°C.

trap at a temperature from −150 to −50°C, the Ti sublimation pump at a current of 30 A for 45 s with a chiller outside, the Zr-V-Fe pump at 250° C, and the Zr-Al pump at 400°C. Then the gases were further purified by two SAES NP10 getters at approximately 400°C and room temperature, respectively (Qiu and Jiang, 2007). The resulting gases were sufficiently pure to be analyzed for Ar isotopes in the mass spectrometer (Figure 8). The ^{40}Ar/^{39}Ar dating results were calculated and plotted using the professional software ArArCALC version 2.4 (Koppers, 2002).

RESULTS

The ^{40}Ar/^{39}Ar dating results of all the samples in this study were summarized in a file in Microsoft Excel sheets that we supply with this article as an electronic supplement (see AAPG Datashare 35).

Zhuhai Formation

Sample 06ZJ26I is from the Zhuhai Formation at a depth of 3677 m (12,064 ft). Its illite ^{40}Ar/^{39}Ar laser stepwise heating yields a gradually rising age spectrum at low-temperature steps with a plateau at high-temperature steps (Figure 9). The apparent ages of the first three low-temperature steps agree with each other within experimental errors with a weighted mean age of 12.1 ± 1.1 Ma (1σ). From the 4th step onward, the apparent age gradually rises from 17.2 to 95.8 Ma at the 14th step. An age plateau is yielded from steps 15 to 19 with a plateau age of 98.0 ± 0.4 Ma. With further high temperature, the apparent ages decrease slightly.

The total age of a sample by incremental heating is given by Koppers (2002) in the software ArArCALC, calculated in terms of the ratio of the summary radiogenic ^{40}Ar ($\sum {}^{40}\mathrm{Ar_R}$) to the summary neutron-induced ^{39}Ar ($\sum {}^{39}\mathrm{Ar_K}$) of all steps.

$$t_{\mathrm{total}} = \frac{1}{\lambda}\ln\left(1 + J\frac{\sum {}^{40}\mathrm{Ar_R}}{\sum {}^{39}\mathrm{Ar_K}}\right)$$

Here, λ is the total decay constant of ^{40}K and J is the irradiation parameter. The total age of a sample should be equal to its traditional K-Ar age.

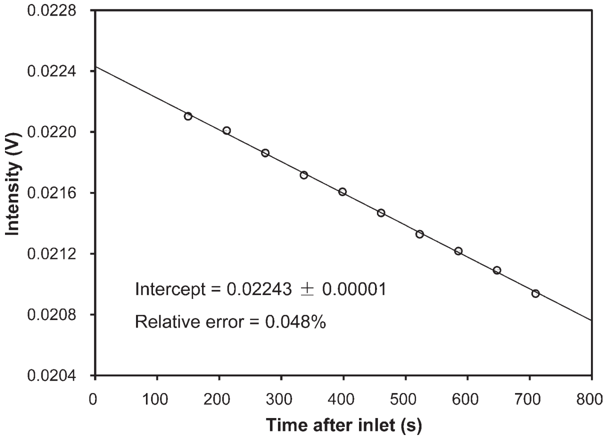

Figure 8. Plot of ^{40}Ar intensity vs. inlet time during mass spectrometer analyses for illite 06ZJ26I. The ^{40}Ar intensity decreased linearly with time, which suggested that no obvious amounts of organic fragments were present in the purified inlet gases. It indicated that our newly developed purification apparatus is effective in excluding organic contaminants from illite samples in oil-saturated sandstones.

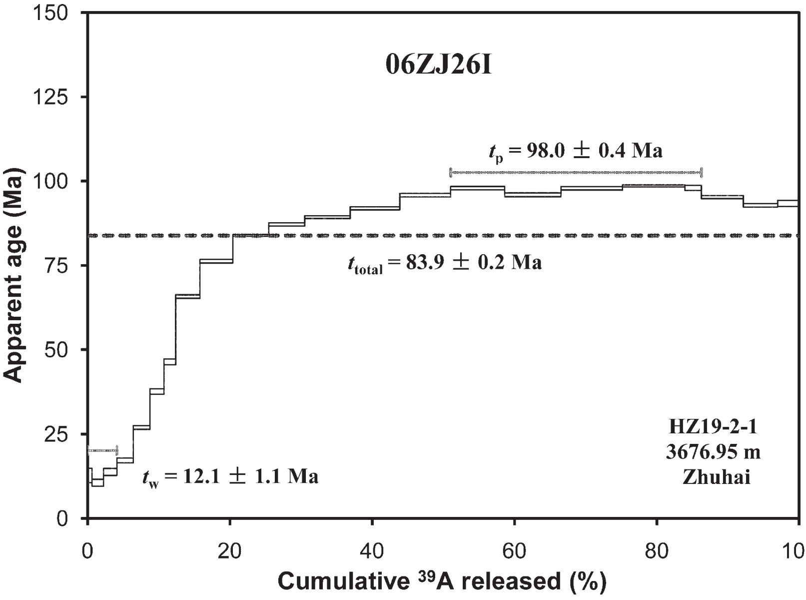

Figure 9. Age spectrum of illite 06ZJ26I based on the ^{40}Ar/^{39}Ar dating results by laser stepwise heating. The weighted mean age for the first three steps, t_w = 12.1 ± 1.1 Ma, is interpreted as the contribution of authigenic illite, representing the age of petroleum emplacement. The plateau age in the high-temperature steps, t_p = 98.0 ± 0.4 Ma, is interpreted as the contribution of the detrital feldspar in the sandstone. The total age of all steps, t_{total} = 83.9 ± 0.2 Ma, equal to K-Ar age, represents the contribution of all K and Ar minerals in the sample and has no process significance.

The total age of sample 06ZJ26I is 83.9 ± 0.2 Ma, which is much older than the age range of the upper Oligocene Zhuhai Formation.

Zhujiang Formation

The other six samples are from the Zhujiang Formation from 2950 to 1630 m (9678 to 5348 ft) in depth. This illite ^{40}Ar/^{39}Ar laser stepwise heating also yields gradually increasing stepping-age spectra (Figure 10) but without a short age plateau in the initial lowest temperature steps. Nonetheless, their first-step apparent ages are very similar and range only from 13.1 to 10.2 Ma (Table 1). They are reasonably younger than the top boundary age of 16.0 Ma of the Zhujiang Formation (Figure 2)

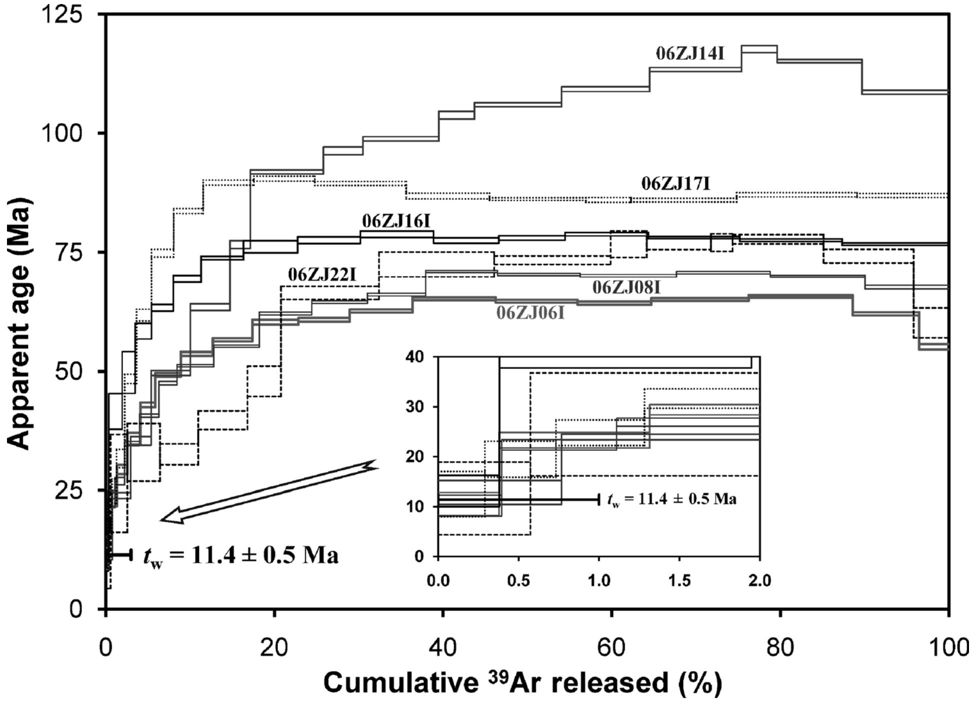

Figure 10. Age spectra of the six illite samples from the Zhujiang Formation by ^{40}Ar/^{39}Ar laser stepwise heating. t_w = weighted mean age calculated from the first-step apparent ages for the six illite samples.

Table 1. First-Step Ages of Illite Samples from the Zhujiang Formation*

Sample No.	Drill No.	Depth (m)	First-Step Age (Ma ± 1σ)	Weighted Mean Age (Ma ± 1σ)	Average Age (Ma ± 1σ)
06ZJ06I	HZ21-1-2	2941.2	10.5 ± 2.3	11.4 ± 0.5	11.7 ± 1.2
06ZJ08I	HZ21-1-2	2948.8	10.2 ± 2.1		
06ZJ14I	LF13-1-2	2506.1	12.8 ± 2.4		
06ZJ16I	LF13-1-2	2513.1	13.1 ± 3.1		
06ZJ17I	LF13-1-2	2521.5	12.1 ± 4.5		
06ZJ22I	LF22-1-3	1636.6	11.6 ± 3.6		

*The weighted mean age, t_{w}, and its error, $\sigma_{t_{\mathrm{w}}}$, are calculated with $t_{\mathrm{w}} = \frac{\sum(W_i t_i)}{\sum W_i}$ and $\sigma_{t_{\mathrm{w}}} = \left\{\sum\left([t_i - t_{\mathrm{w}}]^2 W_i\right)/(\sum W_i)\cdot(N-1)\right\}^{1/2}$. The weight, W_i, is obtained by $W_i = 1/(\sigma_{t_i})^2$. Here, N is the number of samples and t_i is the age of sample i.

(Yan et al., 2001). The weighted mean ages for the first steps of six samples, 11.4 ± 0.5 Ma (1σ) (Figure 10), are concordant with that of 06ZJ26I, 12.1 ± 1.1 Ma, from the Zhuhai Formation within analytical error.

DISCUSSION

Oil Emplacement Ages

The illite samples from both the Zhuhai and Zhujiang formations by ^{40}Ar/^{39}Ar laser stepwise heating yield similar gradually rising age spectra starting consistently at a low apparent age at the lowest temperature, then increasing in age until reaching a plateau. The low-temperature sections represent the contributions to the age spectrum from regions within the illite samples that most readily release the argon gas. Compared to detrital minerals, authigenic illite is the finest mineral and therefore releases argon the easiest by diffusion in the low-temperature steps of laser incremental heating. As a result, the apparent ages in the low-temperature steps are young, agreeing with the idea that authigenic illite represents the last mineral formed prior to petroleum emplacement. The weighted mean age of 12.1 ± 1.1 Ma for the three lowest temperature steps of 06ZJ26I from the Zhuhai Formation agrees with the age of 11.4 ± 0.5 Ma for the first steps of the six illite samples from the Zhujiang Formation. These first-step ages are younger than the top boundary age of the Zhujiang Formation and agree with the petroleum emplacement age deduced from basin simulation based on a variety of traditional techniques. We therefore conclude that the ages of 12–11 Ma represent the maximum age of petroleum emplacement of the Huizhou sag.

The homogeneity temperatures of the fluid inclusions in quartz of the Zhujiang Formation range from 160 to 100°C. Based on the homogeneity temperatures, burial history, and the temperature gradient of 3.6°C/100 m (328 ft) of the reservoirs, the geological engineers working in the oil fields in the South China Sea roughly estimated that the hydrocarbon fluid emplacements occurred in approximately 10 Ma (J. Z. Zhu, 2008, personal communication). Therefore, they agreed with our ^{40}Ar/^{39}Ar dating results because it coincides with results from their own emplacement assessment.

Detrital Source Ages

In the incremental heating experiments we conducted, gradually rising laser output increases the heating temperature, causing bigger detrital mineral grains to start releasing gas and thus causing a gradual increase in ages. The plateau age of 98.0 ± 0.4 Ma in medium- to high-temperature steps is much older than the bottom boundary age 28.4 Ma of the Zhuhai Formation, the lower reservoir sandstone, and thus must represent the age of the detrital feldspar in the source rocks.

The total age of a sample by the stepwise heating experiment based on the ratio of the summary argon isotopes of all steps is equivalent to its traditional K-Ar age. The total age of 83.9 ± 0.2 Ma of the 06ZJ26I illite, representing a mixture of authigenic illite and detrital K feldspar, is much older than the ages of the upper Oligocene Zhuhai Formation and is therefore geologically irrelevant. As a consequence, accurate K-Ar ages can only be obtained when analyzing very pure authigenic illite.

Technical Aspects

Dong et al. (1997, 2000) obtained $^{40}Ar/^{39}Ar$ age spectra of illite showing zero apparent ages for the initial 5–30% ^{39}Ar release in the low-temperature steps, which we argue might be caused by impurity of the argon gases measured because of inefficient cleanup and thus a high contribution of organic gases. Organic fragments with m/e = 36 might be considered as ^{36}Ar, causing some radiogenic ^{40}Ar to be incorrectly excluded as air argon according to the formula $^{40}Ar* = {}^{40}Ar_m - 295.5 \times {}^{36}Ar_m$ (m is the measured data) and thus lowering the apparent age calculated. We did not observe this zero age phenomena in any of our samples, further testifying to the effectiveness of our newly developed purification apparatus in removing organic gases.

Besides the thorough cleaning of the gasses released during stepwise heating, the dating of petroleum emplacement by the authigenic illite $^{40}Ar/^{39}Ar$ method requires the following prerequisites. First, oil saturation of the reservoir sandstone must be sufficiently high. If the reservoir sandstone does not contain sufficient oil and gas to displace the potassium-bearing aqueous solution, authigenic illite will continue to grow, and its $^{40}Ar/^{39}Ar$ age does not represent the time of oil intrusion in the reservoir. Second, the $^{40}Ar/^{39}Ar$ dating samples should have sufficient authigenic illite. The higher the content of authigenic illite, the higher the ratio of gas release and the larger the proportion of ^{39}Ar (K) from authigenic illite contributing to the $^{40}Ar/^{39}Ar$ age spectra at the very low temperature steps. Therefore, during illite separation, K-rich detrital minerals should not be ground to micron level to mix with the clay minerals.

Because the authigenic illite minerals in our study are only present on the micron size, the influence of nuclear recoil should be considered. The $^{40}Ar/^{39}Ar$ age dates may become older as a result of ^{39}Ar loss because of recoil. The age spectrum of the 06ZJ26I illite indicates that the although apparent age of the first step is slightly higher than that of the second step, both of them are still consistent within analytical error, and that the weighted mean age of 12.1 ± 1.1 Ma of the first three steps agrees with the geologically estimated oil emplacement age in the Huizhou sag. Thus, nuclear recoil does not affect our results.

Concordant first-step ages are obtained from the seven illite samples by $^{40}Ar/^{39}Ar$ laser stepwise heating in this study, which may be interpreted as the age of petroleum emplacement in the Huizhou sag. Although many difficulties exist at the frontier of oil or gas emplacement geochronological studies, authigenic illite $^{40}Ar/^{39}Ar$ laser stepwise heating is a feasible and potentially useful novel technique to be applied in prospecting studies.

CONCLUSIONS

The following findings were obtained by authigenic illite $^{40}Ar/^{39}Ar$ laser stepwise heating.

1. A novel purification apparatus that can effectively remove organic impurities resulting in gases pure enough for mass spectrometer analysis is crucial for reliable $^{40}Ar/^{39}Ar$ timing of petroleum emplacement.
2. Gradually rising age spectra are obtained by $^{40}Ar/^{39}Ar$ laser stepwise heating of the illite samples from the Tertiary reservoir sandstones in the Huizhou sag, Pearl River Mouth Basin. The youngest ages at the first steps are interpreted as being caused by contributions from authigenic illite, suggesting that the petroleum emplacement occurred after 11 Ma. The high plateau ages in the high-temperature steps that are rather variable between the seven samples are interpreted as being caused by contributions of detrital K feldspar in the sandstones.
3. Among the advantages of $^{40}Ar/^{39}Ar$ dating over traditional K-Ar methods are that stepwise

heating can distinguish contributions from authigenic illite and detrital K feldspar by interpreting their gas release characteristics. The K-Ar dating and total fusion $^{40}Ar/^{39}Ar$ dating, however, yield a meaningless mixing age of the authigenic illite and detrital K feldspar.

4. Illite separation techniques must be improved further to obtain higher illite contents and their wider proportions at low-temperature steps in age spectra. Also, higher sensitivity would be good, allowing for more steps at low temperatures to better image the shape of the spectra there. The wider the lowest age plateau, the better we can estimate the actual age of oil emplacement.

REFERENCES CITED

Dong, H. L., C. M. Hall, D. R. Peacor, and A. N. Halliday, 1995, Mechanisms of argon retention in clays revealed by laser ^{40}Ar-^{39}Ar dating: Science, v. 267, p. 355–359, doi:10.1126/science.267.5196.355.

Dong, H. L., C. M. Hall, A. N. Halliday, and D. R. Peacor, 1997, Laser ^{40}Ar-^{39}Ar dating of microgram-size illite samples and implications for thin section dating: Geochimica et Cosmochimica Acta, v. 61, p. 3803–3808, doi:10.1016/S0016-7037(97)00286-X.

Dong, H. L., C. M. Hall, D. R. Peacor, A. N. Halliday, and D. R. Pevear, 2000, Thermal $^{40}Ar/^{39}Ar$ separation of diagenetic from detrital illitic clays in Gulf Coast shales: Earth and Planetary Science Letters, v. 175, p. 309–325, doi:10.1016/S0012-821X(99)00294-0.

Hamilton, P. J., S. Kelley, and A. E. Fallick, 1989, K-Ar dating of illite in hydrocarbon reservoirs: Clay Minerals, v. 24, p. 215–231, doi:10.1180/claymin.1989.024.2.08.

He, J. X., H. L. Liu, Y. J. Yao, S. L. Zhang, X. W. Luan, and W. H. Ma, 2008, Petroleum geology and resource prospects in the northern marginal basins of the South China Sea: Beijing, Petroleum Industry Press, 185 p.

Hess, J. C., and H. J. Lippolt, 1986, Kinetics of Ar isotopes during neutron irradiation: ^{39}Ar loss from minerals as a source of error in $^{40}Ar/^{39}Ar$ dating: Chemical Geology (Isotope Geoscience Section), v. 59, p. 223–236, doi:10.1016/0168-9622(86)90073-4.

ICS (International Commission on Stratigraphy), 2009, The international stratigraphic chart: http://stratigraphy.science.purdue.edu/charts/stratchart.pdf (accessed September 26, 2009).

Kelly, J., J. Parnell, and H. H. Chen, 2000, Application of fluid inclusions to studies of fractured sandstone reservoirs: Journal of Geochemical Exploration, v. 69, p. 705–709, doi:10.1016/S0375-6742(00)00096-0.

Koppers, A. A. P., 2002, ArArCALC-software for $^{40}Ar/^{39}Ar$ age calculations: Computers and Geosciences, v. 28, p. 605–619, doi:10.1016/S0098-3004(01)00095-4.

Lee, M., J. L. Aronson, and S. M. Savin, 1985, K/Ar dating of time of gas emplacement in Rotliegendes sandstone, Netherlands: AAPG Bulletin, v. 69, p. 1381–1385.

Liewig, N., N. Clauer, and F. Sommer, 1987, Rb-Sr and K-Ar dating of clay diagenesis in Jurassic sandstone oil reservoir, North Sea: AAPG Bulletin, v. 71, p. 1467–1474.

Middleton, D., J. Parnell, P. Carey, and G. Xu, 2000, Reconstruction of fluid migration history in northwest Ireland using fluid inclusion studies: Journal of Geochemical Exploration, v. 69, p. 673–677, doi:10.1016/S0375-6742(00)00109-6.

Qiu, H. N., and Y. D. Jiang, 2007, Sphalerite $^{40}Ar/^{39}Ar$ progressive crushing and stepwise heating techniques: Earth and Planetary Science Letters, v. 256, p. 224–232, doi:10.1016/j.epsl.2007.01.028.

Qiu, H. N., and J. R. Wijbrans, 2006, Paleozoic ages and excess ^{40}Ar in garnets from the Bixiling eclogite in Dabieshan, China: New insights from $^{40}Ar/^{39}Ar$ dating by stepwise crushing: Geochimica et Cosmochimica Acta, v. 70, p. 2354–2370, doi:10.1016/j.gca.2005.11.030.

Qiu, H. N., H. Y. Wu, Z. H. Feng, H. S. Shi, J. B. Yun, Q. Wang, and L. H. Zhao, 2009, The puzzledom and feasibility in determining emplacement ages of oil/gas reservoirs by ^{40}Ar-^{39}Ar techniques: Geochimica, v. 38, p. 405–411.

Robinson, A. G., M. L. Coleman, and J. G. Gluyas, 1993, The age of illite cement growth, Village fields area, southern North Sea: Evidence from K-Ar ages and $^{18}O/^{16}O$ ratios: AAPG Bulletin, v. 77, p. 68–80.

Smith, P. E., N. M. Evensen, and D. York, 1993, First successful ^{40}Ar-^{39}Ar dating of glauconites: Argon recoil in single grains of cryptocrystalline material: Geology, v. 21, p. 41–44, doi:10.1130/0091-7613(1993)021<0041:FSAADO>2.3.CO;2.

Wang, F. Y., P. He, S. C. Zhang, M. J. Zhao, and J. J. Lei, 1997, The K-Ar isotopic dating of authigenic illites and timing of hydrocarbon fluid emplacement in sandstone reservoir: Geological Review, v. 43, p. 540–546.

Wang, F. Y., S. S. Hao, and J. J. Lei, 1998, The isotopic dating of authigenic illite and timing of hydrocarbon fluid emplacement in sandstone reservoir: Acta Petrolei Sinica, v. 19, p. 40–44.

Wang, L. Z., T. M. Dai, and P. A. Peng, 2005, $^{40}Ar/^{39}Ar$ dating of diagenetic illites and its application in timing gas emplacement in gas reservoirs: Earth Science-Journal of China University of Geosciences, v. 30, p. 78–82.

Wu, J. M., 1994, Evaluation and models of Cenozoic sedimentation in the South China Sea: Tectonophysics, v. 235, p. 77–98, doi:10.1016/0040-1951(94)90018-3.

Xiao, X. M., Z. F. Liu, J. K. Mi, D. H. Liu, J. G. Shen, and Z. G. Song, 2002, Dating formation of natural gas pools using fluid inclusion data from reservoirs: Chinese Science Bulletin, v. 47, p. 1567–1572, doi:10.1360/02tb9345.

Yan, P., D. Zhou, and Z. S. Liu, 2001, A crustal structure profile across the northern continental margin of the South China Sea: Tectonophysics, v. 338, p. 1–21, doi:10.1016/S0040-1951(01)00062-2.

Yan, P., H. Deng, H. L. Liu, Z. R. Zhang, and Y. K. Jiang, 2006, The temporal and spatial distribution of volcanism in the South China Sea region: Journal of Asian Earth Sciences, v. 27, p. 647–659, doi:10.1016/j.jseaes.2005.06.005.

Zhang, Y. Y., and X. Q. Luo, 2004, K-Ar isotopic chronological study of authigenic illite in reservoirs: Oil and Gas Geology, v. 25, p. 231–236.

Zhang, Y. Y., A. Z. Dong, and X. Q. Luo, 2001, Separation of authigenic illite in hydrocarbon reservoirs and its K-Ar dating techniques: Geoscience, v. 15, p. 315–320.

Zou, C. N., S. Z. Tao, and Y. Y. Zhang, 2007, Reservoir-forming age and its exploration significance to stratigraphic reservoirs in southern Songliao Basin: Chinese Science Bulletin, v. 52, p. 3239–3252, doi:10.1007/s11434-007-0424-5.