

High-precision $^{40}\text{Ar}/^{39}\text{Ar}$ age of the gas emplacement into the Songliao Basin

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ABSTRACT

The problem of determining an exact isotopic age of hydrocarbon emplacement is complex because minerals suitable for dating with common isotopic methods are often lacking in the sedimentary domain. However, the igneous quartz from the Cretaceous volcanic rocks that host the gas reservoir in the Songliao Basin (northeastern China), contains abundant secondary fluid inclusions with high concentrations of K and high partial pressures of methane trapped during gas emplacement. Quartz with abundant K-rich fluid inclusions provides an excellent closed system well suited for $^{40}\text{Ar}/^{39}\text{Ar}$ dating. Three igneous quartz samples were measured by stepwise crushing to release the inclusion-based argon gas. All three samples yielded well-defined isochrons with ages in close agreement, precisely constraining the gas emplacement at 42.4 ± 0.5 Ma (2σ) below the Daqing oil field in the Songliao Basin, extending possible gas reservoirs from the upper Cretaceous to the middle Eocene.

INTRODUCTION

Reliable timing information for hydrocarbon emplacement is crucial for understanding reservoir-forming processes and for selecting regions suitable for further exploration. Constraining the timing of hydrocarbon migration and accumulation processes is a challenging research topic for both petroleum geology and isotope geochronology. The recent rise in demand for oil and gas has increased the need for predictive capabilities to detect new hydrocarbon reservoirs, thus stimulating geochronologists to develop dating techniques to directly constrain the oil or gas emplacement ages.

Historically, K–Ar ($^{40}\text{Ar}/^{39}\text{Ar}$) dating of authigenic illite or glauconite (Lee et al., 1985; Hamilton et al., 1989; Mossmann, 1991; Clauer et al., 1995; Dong et al., 1995; Meunier et al., 2004; Clauer et al., 2005; Zaitseva et al., 2005; Sandler and Harlavan, 2006; Tohver et al., 2008) has been the only isotope chronometer to constrain diagenesis. More recently, Mark et al. (2010) demonstrated that under favorable circumstances, growth rims of diagenetically grown K-feldspar can be used for dating diagenesis, and concomitant hydrocarbon mobility. Maximum ages for hydrocarbon emplacement can be estimated by dating diagenesis. In addition, some researchers have focused on dating bitumen from mineral deposits and oilfields using Pb–Pb and Re–Os methods (Parnell and Swainbank, 1990; Selby and Creaser, 2005). Diagenetic mineral growth stops when hydrocarbon accumulation has expelled formation water. Dating of authigenic minerals will therefore only record the maximum age, but not the exact age, of hydrocarbon emplacement. Moreover, pure illite and glauconite are difficult to concentrate using common separation techniques and have been shown to be relatively open structures that may easily lose radiogenic ^{40}Ar during subsequent overprinting. Soft bitumen also has disadvantages as it is not a closed system (Parnell and Swainbank, 1990). High spatial resolution UV-laser microprobe $^{40}\text{Ar}/^{39}\text{Ar}$ dating (Kelley and Wartho, 2000; Sherlock et al., 2005;

Mark et al., 2010; Qiu et al., 2010) of authigenic K-feldspar may easily exclude detrital minerals, and may become another useful approach to constrain the maximum ages of oil or gas emplacement.

Many $^{40}\text{Ar}/^{39}\text{Ar}$ studies applying the stepwise crushing technique have demonstrated that fluid inclusions in quartz act as a closed system. The technique has been used successfully to determine the mineralization ages of many hydrothermal deposits (Kelley et al., 1986; Turner, 1988; Qiu and Dai, 1989; Turner and Wang, 1992; Qiu, 1996; Qiu and Jiang, 2007) and the ages of ultrahigh-pressure metamorphism of the Dabieshan eclogites (Qiu and Wijbrans, 2006, 2008). We have improved the crushing device to effectively extract fluid from very fine inclusions (i.e., $<0.5 \mu\text{m}$) in quartz by using more than ten thousand cycles of lifting and gently dropping the pestle. This novel technique was validated recently when high-precision age data were obtained for sphalerite samples from the Fankou super-large Pb–Zn deposit in northern Guangdong Province, southern China (Qiu and Jiang, 2007), and ages for retrograde mineral assemblages of the Zhugiachong eclogite in southeastern Dabie-shan (Qiu et al., 2010).

Originally, the ages of gas-charging events in the Qingshen gas field were estimated at 100–65 Ma from the homogenization temperatures of fluid inclusions and the inferred burial history of the reservoir (Feng et al., 2003; Feng, 2008). In the present study, we show a novel approach to obtain precise gas emplacement ages by an $^{40}\text{Ar}/^{39}\text{Ar}$ stepwise crushing technique to extract argon from the secondary fluid inclusions (SFIs) within quartz samples from the reservoir volcanic rocks of the Qingshen gas field in the Songliao Basin, northeastern China. Because the SFIs were demonstrated by Raman microanalysis to contain substantial amounts of methane, the ages obtained by crushing document the migration of methane into these samples. The gas emplacement ages obtained in this study for the SFIs are much younger than those obtained from previous studies.

SAMPLE SUITE

The Qingshen gas field ('Qing' for Daqing and 'shen' for "deeply" below the oil reservoirs) was first discovered in 2002 with the Xushen-1 well in the Songliao Basin (Feng et al., 2008; Li et al., 2008), Heilongjiang Province, northeastern China. The $\sim 100 \times 10^9 \text{ m}^3$ gas reserves occur in deeply buried volcanics (>2880 m deep) below the Daqing oil field (Fig. 1). The source of the natural gas is currently controversial, with two opposing hypotheses: (1) deep abiogenic hydrocarbon (Wang et al., 2009), or (2) more traditional scenarios involving an organic source. A credible gas emplacement age will be central to a better understanding of the formation of the gas field. Sensitive high-resolution ion microprobe (SHRIMP) U/Pb ages of zircons from the reservoir volcanic rocks of the Yingcheng Formation (Zhang et al., 2009) date extrusion of the volcanics at 117–111 Ma.

Some calcite veins with minor pyrite occur in the drill cores, interpreted as the solid precipitates probably associated with diagenesis and hence gas emplacement. These veins are, however, unsuitable for isotopic dating with commonly used methods. The igneous quartz crystals

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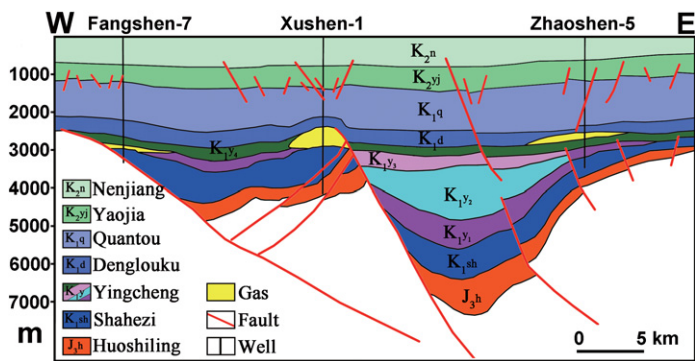


Figure 1. Cross section showing the gas reservoirs from wells Fangshe-7, Xushen-1 to Zhaoshen-5. Modified from Ren et al. (2004). The oil is reserved from the Nenjiang to Quantou Formations, and the gas is mainly from the Yingcheng to Houshiling Formations, beneath the oil reservoirs.

that are distributed in rhyolite and tuff in the volcanic Yingcheng Formation have a late igneous origin and were crystallized shortly after volcanic eruption. The quartz crystals contain some primary melt inclusions and abundant secondary fluid inclusions (Fig. 2), which were used for $^{40}\text{Ar}/^{39}\text{Ar}$ dating to constrain the gas emplacement age in the present study. The chemical and physical properties of these SFIs, including the composition, homogenization temperature, freezing-point temperature, and salinity, are described in the following. Three quartz samples were analyzed with the $^{40}\text{Ar}/^{39}\text{Ar}$ stepwise crushing technique: DQ-04 from the well Xushen-1 at 3451.4 m deep, and DQ-38 and DQ-39 from the well Zhaoshen-10 (~30 km south of Xushen-1) at 2948.7 m and 2950.8 m deep, respectively.

EXPERIMENTAL METHODS

The argon isotope ratios were analyzed using a GVI-5400[®] noble gas mass spectrometer in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, using the stepwise crushing technique (Qiu and Wijbrans, 2006; Qiu and Jiang, 2007). The improved crusher is made of a type 316L stainless steel tube (170 mm long \times 28 mm inner diameter) with a spherical curvature on the internal base. The pestle is made of magnetic 3Cr13 type stainless steel (or S42030), of 218 g. This new crusher is much smaller in diameter and length than the crusher tubes used previously in

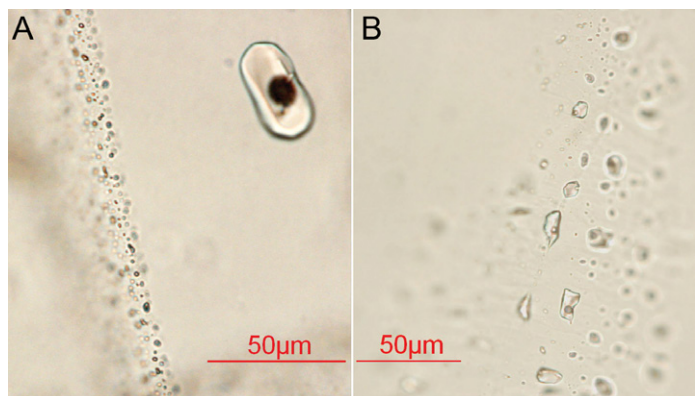


Figure 2. Photomicrographs showing abundant fluid inclusions in the volcanic quartz grains of the Yingcheng Formation. Their alignment is characteristic of secondary fluid inclusions associated with healed micro-cracks. Left one also shows a large primary volcanic bubble (~40 μm in length). This volcanic bubble is obviously much larger than the secondary fluid inclusions and more easily released in the early crushing steps.

Amsterdam and Guangzhou. We used quartz separates of 0.2–0.3 mm grain size and 126–164 mg in weight (~3–5 times more samples than used in previous experiments), in order to get sufficiently large signals from samples to reduce the relative contribution of the air component derived from the crusher, including the pestle.

Organic hydrocarbon gases will heavily contaminate the mass spectrometer and interfere isobarically with the argon isotopes during mass spectrometric measurement (see Yun et al., 2010, their figure 5). We developed a special apparatus that can effectively clean up the organic gasses (Yun et al., 2010; see the GSA Data Repository¹). The gases released by crushing were first cleaned up in the apparatus to exclude organic gases, then further purified using two SAES NP10 Zr-Al getters operated at ~400 $^{\circ}\text{C}$ and at room temperature, respectively, ensuring that the gases were sufficiently pure for argon isotope analyses. The $^{40}\text{Ar}/^{39}\text{Ar}$ dating results were calculated and plotted with the ArArCALC software version 2.4 (Koppers, 2002).

RESULTS

SFI Analyses

The igneous quartz in the reservoir volcanic rocks of the Yingcheng Formation contains some primary melt inclusions, bubbles, and abundant SFIs (Fig. 2). The results of laser Raman analysis indicate that the melt inclusions are quartz and the bubbles do not contain detectable methane, but the SFIs do contain obvious methane. The methane Raman shifts in the SFIs of DQ-04Q and DQ-39Q are 2915.89 and 2910.80 cm^{-1} , respectively (Fig. 3). According to the unified equation for calculating methane vapor pressures in the $\text{CH}_4\text{--H}_2\text{O}$ system with measured Raman shifts (Lu et al., 2007),

$$P(\text{MPa}) = -0.0148 \times D^5 - 0.1791 \times D^4 - 0.8479 \times D^3 - 1.765 \times D^2 - 5.876 \times D, \quad (1)$$

the methane vapor pressures within the SFIs of DQ-04Q and DQ-39Q are 9 MPa and 66 MPa, respectively. The high methane vapor pressures

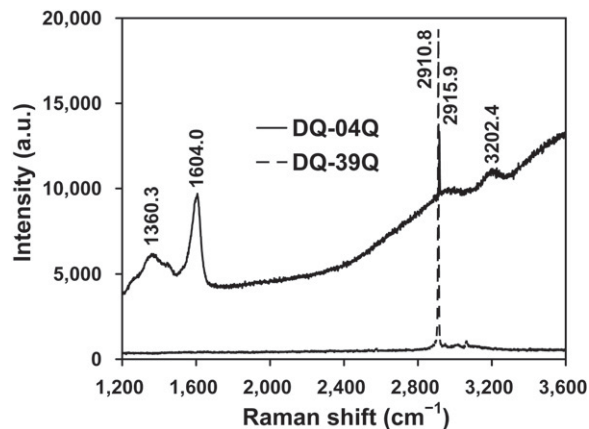


Figure 3. Raman spectra. Methane vapor pressures of 66–9 MPa inside the fluid inclusions are calculated in terms of the unified equation for the $\text{CH}_4\text{--H}_2\text{O}$ system by Lu et al. (2007), indicating the secondary fluid inclusions in quartz were trapped during the gas emplacement. Samples DQ-04Q and DQ-39Q were analyzed on a Renishaw RM-1000 at Sun Yat-Sen University and the China University of Geosciences (Wuhan), respectively.

¹GSA Data Repository item 2011147, $^{40}\text{Ar}/^{39}\text{Ar}$ dating results, is available online at www.geosociety.org/pubs/ft2011.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

strongly suggest that the SFIs were trapped during the phase of hydrocarbon gas emplacement.

The homogenization temperatures of the SFIs range from 165 to 175 °C in DQ-04Q, and from 135 to 145 °C in DQ-38Q and DQ-39Q. The freezing points of the SFIs in DQ-04Q range from -5.3 to -4.8 °C, in DQ-38Q from -1.2 to -0.9 °C, and in DQ-39Q from -0.5 to -0.2 °C. The corresponding salinities are calculated in terms of the equation based on the data of Hall et al. (1988):

$$W = 0.008 + 1.78|T_m| - 0.0442|T_m|^2 + 0.000557|T_m|^3. \quad (2)$$

The salinities of DQ-04Q range from 8.3 to 7.6 wt% with an average of 7.9 wt%, those of DQ-38Q range from 2.1 to 1.6 wt% with an average of 1.8 wt%, and those of DQ-39Q range from 0.9 to 0.4 wt% with an average of 0.6 wt%.

The differences of the methane pressures, homogenization and freezing temperatures, and the corresponding calculated salinities of DQ-04Q and DQ-39Q probably reflect the fact they come from different sectors of the field (~30 km apart) and from different tectonic settings.

The three quartz samples yielded substantial $^{39}\text{Ar}_k$ signals by crushing. The high $^{39}\text{Ar}_k$ signals and the salinities suggest high potassium contents inside the secondary fluid inclusions. However, the $^{38}\text{Ar}_{cl}$ signals are almost zero, indicating that no chlorine is present inside the secondary fluid inclusions. This is different from what is observed in hydrothermal fluids forming ore deposits (Kelley et al., 1986; Turner, 1988; Qiu, 1996) and the metamorphic fluids (Qiu and Wijbrans, 2006, 2008) where potassium is correlated with chlorine. We suggest that potassium is probably correlated with HCO_3^- and CO_3^{2-} in the fluids associated with the gas emplacement, based on the observation of ubiquitous carbonate veins accompanying the gas and oil accumulations, and calcite veins in the drill cores of the Qinshen gas field.

$^{40}\text{Ar}/^{39}\text{Ar}$ Dating Results

All the three samples analyzed by $^{40}\text{Ar}/^{39}\text{Ar}$ *in vacuo* crushing yield similar $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra, beginning with abnormally old apparent ages that decrease rapidly in several steps, to flat age plateaus in the final steps (Fig. 4A). The abnormally old ages observed in the first crushing steps are caused by the release of trapped excess ^{40}Ar from the much larger primary inclusions containing a hydrothermal gas phase originating from the magma chamber (Fig. 2A). The plateau ages obtained in the final crushing steps of these three quartz samples are, respectively, 42.9 ± 0.8 Ma (error in 2σ , MSWD = 1.2, plateau segment ^{39}Ar = 33.59%), 43.0 ± 0.4 Ma (MSWD = 3.7, plateau segment ^{39}Ar = 47.52%), and 41.3 ± 0.3 Ma (MSWD = 3.5, plateau segment ^{39}Ar = 46.80%), with an average of 42.4 ± 1.9 Ma (2σ , relative error <4.5%). The plateau data points define concordant isochrons (Fig. 4B) corresponding to 42.1 ± 1.9 Ma (MSWD = 1.2, $I_0 = 298 \pm 6$), 42.4 ± 1.9 Ma (MSWD = 4.1, $I_0 = 305 \pm 31$), and 42.6 ± 0.5 Ma (MSWD = 1.2, $I_0 = 280 \pm 5$), respectively, with an average of 42.4 ± 0.5 Ma (2σ , relative error <1.2%).

DISCUSSION

The presence of high-pressure methane inside the SFIs in the igneous quartz (Fig. 3) strongly suggests that the fluids in the SFIs were trapped during hydrocarbon emplacement, and therefore the SFI ages can be interpreted as dating the age of gas emplacement. The three quartz samples yielded age spectra with very similar features and concordant plateau and isochron ages within analytical uncertainty. Therefore, the average age of 42.4 ± 0.5 Ma found for these three experiments (Fig. 4) can be interpreted as the age of natural gas emplacement, constraining with great analytical precision (relative uncertainty of <1.2% at the 2σ level) the time when one period of gas emplacement occurred in the Songliao Basin.

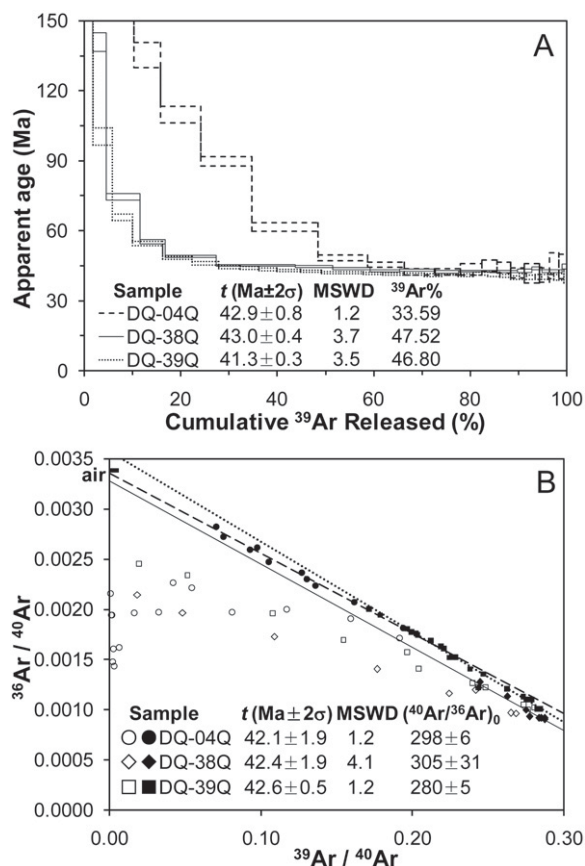


Figure 4. Age spectra and inverse isochrons of the quartz samples by $^{40}\text{Ar}/^{39}\text{Ar}$ stepwise crushing. Data points in solid symbols (circles, square, diamonds) define the isochrons corresponding to the respective final plateau steps, while those in open symbols are excluded from the isochrons corresponding to the initial steps with abnormally old apparent ages. $^{40}\text{Ar}/^{39}\text{Ar}$ isochron age is calculated using

$$t = \frac{1}{\lambda} \ln \left(1 + J \frac{^{40}\text{Ar}'}{^{39}\text{Ar}} \right)$$

Here J is the irradiation parameter, and $^{40}\text{Ar}'/^{39}\text{Ar}$ is the reciprocal of the x-axis intercept.

Previous estimates for the ages of the gas charging events range from 100 to 65 Ma (Feng et al., 2003), but were not obtained by isotopic dating methods and thus perhaps are somewhat suspect. Here we have demonstrated by high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the secondary fluid inclusions in igneous quartz that the actual emplacement age is 42.4 ± 0.5 Ma, which is substantially younger than the younger boundary of the previously published age range. Consequently, a complete new time window is opened for gas reservoir prognosis, extending possible resources from the upper Cretaceous into the middle Eocene in the Songliao Basin. We demonstrate that the $^{40}\text{Ar}/^{39}\text{Ar}$ progressive crushing technique provides a novel approach to obtain emplacement ages for natural gas mobility during diagenesis. Our approach has the potential for more wider use to constrain hydrocarbon mobility, and provides complementary information, when compared to the more commonly used authigenic mineral $^{40}\text{Ar}/^{39}\text{Ar}$ dating methods.

We have not obtained any evidence to support the hypotheses of abiogenic hydrocarbon. No detectable methane exists within the primary volcanic bubbles in quartz, and the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of the SFIs with high-pressure methane are close to the ratio of the modern atmosphere, indicating that the fluid accompanying the gas emplacement was indistinguishable from meteoric water. We therefore argue that the source of methane gas is unlikely to reside in the mantle or deep crust. The gas

emplacement ages (42.4 ± 0.5 Ma) are much younger than the ages of the volcanic rocks in the Yingcheng Formation (117–111 Ma), indicating that the source of methane had no genetic relationship with the emplacement of the Yingcheng volcanics.

A giant gas field such as the Qingshen gas field was probably formed by multiple periods of gas emplacement over a prolonged time span. A more substantial geochronological study will be necessary to more fully understand the history of gas emplacement and accumulation in the Songliao Basin.

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