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A novel purification technique for noble gas isotope analyses of authigenic minerals

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Abstract Noble and active gases are released from geological samples during gas extraction for noble gas isotope analyses. The active gases should be removed before inletting to mass spectrometers for the analyses. The normal noble gas preparation systems can clean up most geological samples. However, authigenic minerals from sedimentary rocks in oil/gas fields contain organic matter, which cannot be cleaned up by the normal preparation systems and thus influence the noble gas analyses. We introduce a novel gas purification system (PRC patent No. ZL201320117751.2), which includes several reversible purification pumps with different absorbing and degassing temperatures. It can well clean up water steam, carbon dioxide and organic gases. Mica minerals are often used for $^{40}Ar/^{39}Ar$ dating. A muscovite sample (2082MS) which could not be cleaned up by the normal preparation system with two SAES NP10® getters, becomes the test sample for a comparative experiment in this study. The experiment is assigned into 4 sections with the organic gas removal system (OGRS) "Closed/Opened" in turn. When the OGRS is closed only with two NP10 getters for purification, the ^{40}Ar intensities increase in curves with inlet time because of impurities, the $^{40}Ar/^{39}Ar$ dating results yield age errors about ±2%–±1% (2σ) . When the OGRS is opened for purification, in contrast, the ^{40}Ar intensities decrease linearly with inlet time. This indicates that the gases have been cleaned up effectively, and the $^{40}Ar/^{39}Ar$ results yield ages with errors in ±0.4%. The OGRS is very helpful to obtain high-quality analysis data.

Keywords $^{40}Ar/^{39}Ar$ dating, Gas purification technique, Organic impurity, Noble gas

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1. Introduction

In $^{40}Ar/^{39}Ar$ dating and noble gas isotope analyses, noble and active gases are released from geological samples by gas extraction methods. The active gases should be removed prior to gas inlet for mass spectrometer analyses. The normal gas preparation systems can clean up most geological samples for argon isotope analyses.

The normal noble gas preparation systems probably include sponge titanium furnace, titanium sublimation pump, copper oxide, active metals and getters made by SAES Group©. Sponge titanium furnace is reversible with large surface and high adsorptive rate. Titanium reacts with all non-noble gases at high temperature, for example, it can react with steam, carbon dioxide and organic volatile above

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700°C. It would not react with noble gases and degas effectively at 800–900°C (Zhang, 1981; Quan, 1987; Wang et al., 1990; Qiu and Peng, 1997). Using the active properties of titanium, the Ti sublimation pump forms a titania layer on the surface in the reactor wall under vacuum. The new titania membrane could be saturated in a few seconds and lose its ability to absorb gases. In order to keep the adsorptive rate, the titanium sublimation pump needs to evaporate continuously. Titanium wires in the pump will be replaced after consumption. Through the hot copper oxide (normally at 500–550°C), combustible gases are oxidized as CO_2 and H_2O and then absorbed by cryotraps. The active metals are also good absorbers. Calcium can absorb CO_2, CO, H_2, O_2, N_2 and water vapor effectively at 400–650°C (Qiu and Peng, 1997).

Micromass1200 mass spectrometer is equipped with a sponge Ti furnace, a Ti sublimation pump and a SAES NP10® Zr/Al getter for purification prior to argon isotopic analyses. As the improvement of the mass spectrometer sensitivities as well as less sample volumes is needed, the purification systems are getting simpler. The GVI-5400® noble gas mass spectrometer in the State Key Laboratory of Isotope Geochemistry, GIGCAS, is only equipped with two reversible NP10 Zr/Al getters (one is operating at ~400°C and the other at room temperature). The main absorptive materials of Zr/Al getters are Zr_5Al_4, Zr_5Al_3, Zr_3Al_2, Zr_2Al and other multiply metal components. These materials are reversible with high activity, high adsorptive rate and inspiratory capacity. The activation temperature is about 750°C. The getters can absorb O_2, N_2, CO_2, CO, H_2, CH_4 and water vapor efficiently without reaction with noble gases.

The normal preparation systems made by the instrument companies can clean up most geological samples for $^{40}Ar/^{39}Ar$ dating. However, some basalt whole rocks, minerals from sedimentary rocks (i.e. illite and glauconite), and even some mica and tourmaline formed in special environments bearing organic materials, could not be effectively cleaned up using the normal preparation systems. The impure gases influence the argon isotopic analyses. A granitic tourmaline was once analysed by stepwise heating. It released large amount of impurity gases at ~900°C and took a week to recover the system blank by two ion pumps of 30 L/s in the MM-1200 instrument.

During hydrocarbon emplacement, the organic matter could be trapped in the fluid inclusions, cracks and mineral defects, which cannot be washed out completely, resulting in the organic gases released during heating. The organic gases will be split into small organic fragments which would interfere the Ar isotopic analyses. An illite sample from the Zhuhai Formation in the Pearl River Mouth Basin, South China Sea was tested. After soaked in H_2O_2 and acetone to remove the residual organic matter, the unirradiated illite sample was baked out at 300°C for 24 h with a turbopump unit. The gases released at 600°C by the electrobombardment furnace were purified in the Ti sponge pump at 800°C for 15 min, in the Ti sublimation pump at a current of 30 A for 90 s and in the NP10 Zr-Al getter for 10 min. The purified gases were analysed on the MM-1200 mass spectrometer. Peak scan (Figure 1) indicated that there were still a large amount of organic impurities, especially for the fragments of *m*/*e*=8–18. Peaks of *m*/*e*=36–44 were obviously influenced by organic fragments, causing the baseline uplift in different degrees. The peaks of *m*/*e*=37, 39, 41, 42 and 43 should be organic fragments, which will inevi- tably affect the analyses of argon isotopes of 36, 38 and 40. In other words, the organic fragments cover all argon isotopes, resulting in wrong argon analyses (Qiu et al., 2009). Therefore the organic gases should be removed thoroughly prior to the mass spectrometer analyses.

The normal preparation systems cannot effectively remove the organic gases. In order to develop a new technique to determine the gas/oil emplacement ages by $^{40}Ar/^{39}Ar$ dating, we designed a novel purification system called as "the organic gas removal system (OGRS)" in this paper, PRC patent No.201320117751.2. This purification system showed the ability to remove the organic impurities *m*/*e*=37 effectively from the illite samples from the oil fields (Figure 2). Using this purification system, the oil/gas emplacement ages were successfully obtained for the oilfields in Pearl River Mouth Basin, South China sea (Yun et al., 2009, 2010a; Shi et al., 2011) and for the gas fields in the Songliao Basin (Yun et al., 2010b; Qiu et al., 2011) by $^{40}Ar/^{39}Ar$ dating.

Because the illite released a large amount of organic im-

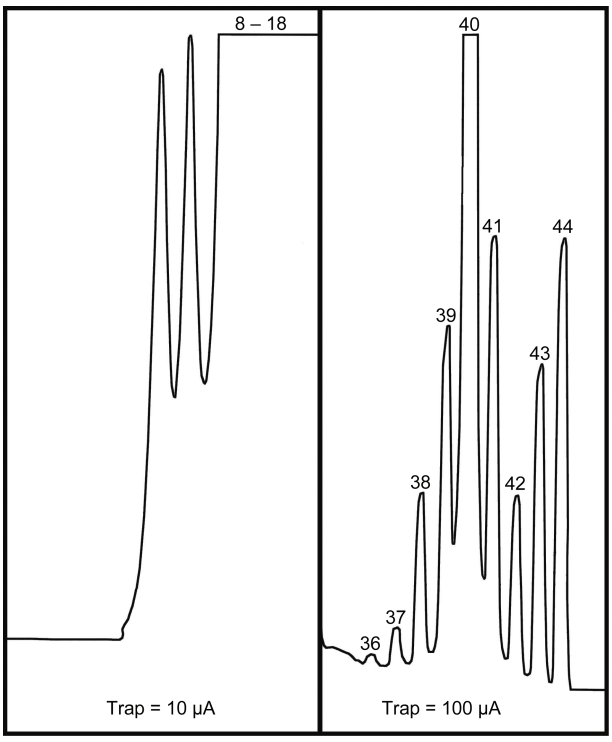

Figure 1 Peak scanning for unirradiated illite purified by a normal preparation system of the MM-1200 instrument in Guangzhou (Qiu et al., 2009).

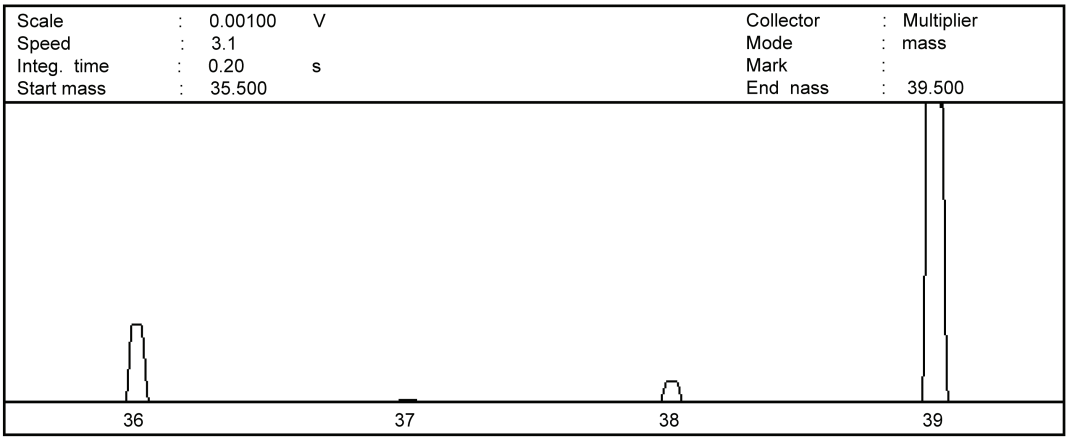

Figure 2 The peak scanning of irradiated illite purified by the novel OGRS connected to the GVI-5400 instruments in Guangzhou. The M37 was very low, indicating that the organic gases had been effectively removed.

purity gases during the test on the MM-1200 instrument, it might be a risk to use illite to verify the effectivity of the organic gas removal system on new GVI-5400 instrument, in order to prevent the instrument from contamination. Therefore, it needs a suitable sample to test the effectivity of the OGRS. Mica minerals are often used for $^{40}Ar/^{39}Ar$ dating. A muscovite 2082MS which could not be cleaned up by the normal preparation system with two SAES NP10 getters, becomes the test sample for a comparative experiment in this study.

2. Diagram of intensity vs. inlet time and gas purification

Gas purification can be evaluated by the plot of ^{40}Ar (*m*/*e*=40) intensity *vs.* inlet time (Figure 3). Three cases are shown as following.

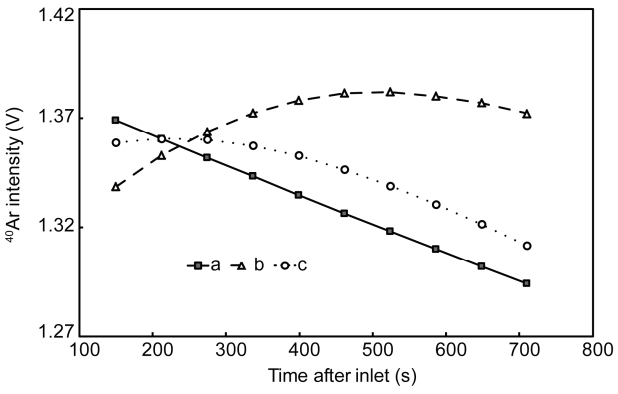

Figure 3 Plot of ^{40}Ar intensity *vs.* inlet time, showing three cases about gas purification. a, Pure noble gases for analyses; b, a lot of impurity gases, requiring a powerful system for purification; c, impure noble gases, prolonging the purification time can improve well. The argon isotopes were measured on the GVI-5400 mass spectrometer in 10 cycles with peak jumping.

(1) The ^{40}Ar intensity decreases linearly with the inlet time, indicating that the gases have been cleaned up effectively, no detectable impurity interferes the ^{40}Ar analysis (Figure 3, a). The ^{40}Ar is consumed by the ion source filament during analysis, resulting in the signal declining linearly. Usually most geological samples can been cleaned up for $^{40}Ar/^{39}Ar$ dating, i.e., Figure 4 showing the case of the ZBH-25 biotite, one of the Chinese standard samples for K-Ar dating (Wang, 1983).

(2) The ^{40}Ar intensity increases with the inlet time in a rising curve (Figure 3, b), demonstrating that there are still a lot of impurity gases after the normal preparation system, which are further absorbed by two NP10 getters within the mass spectrometer. The further purification causes the argon partial pressure to increase. In this case, a new powerful purification system is needed to clean up this kind of samples.

(3) The ^{40}Ar intensity slowly increases and then declines with the inlet time (Figure 3, c), indicating incomplete purification. In this case, prolonging the purification time can

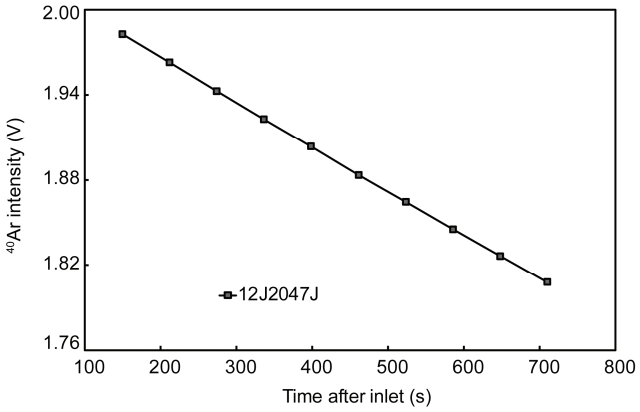

Figure 4 Plot of ^{40}Ar intensity *vs.* inlet time of ZBH-25 biotite (a Chinese standard sample for K-Ar dating), showing pure noble gases obtained for mass spectrometer analyses.

obtain pure noble gases for analyses.

3. Experimental procedure

The argon isotopes were analyzed by GVI-5400® noble gas mass spectrometer in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The samples were packed in aluminum foil for irradiation with the flux monitor the Chinese standard sample of ZBH-25 biotite (Wang, 1983) packed in copper foil. In order to obtain the irradiation parameters (*J*-values) for the samples, the monitors standard ZBH-25 biotite (with an age of 132.7 Ma) inserted between each 2–4 samples and both ends of the sample tubes. The packet thicknesses of all samples and monitors were recorded. The *J*-value of each sample was calculated by interpolation from the line (or curve) of *J*-value vs. height. The *J*-value uncertainty of 0.15% (1σ) was incorporated in the age uncertainty. The samples were irradiated for 48 h in the 49-2 reactor in Beijing, China Institute of Atomic Energy. The $^{40}Ar/^{39}Ar$ dating results were calculated and plotted with the ArArCALC software version 2.4 (Koppers, 2002).

For normal samples, the OGRS is set as a selectable bypass, appending to the two NP10 getters from the GV Instruments© (Figure 5). For special samples from oil/gas fields, the released gases are first going through the OGRS to exclude most organic and active gases and then passing the two NP10 getters for further purification. This OGRS (Qiu et al., 2013) includes a cryotrap, a high temperature pump and several reversible purification pumps of Zr-Al and Fe-V-Zr (Figure 6). The working procedure are as follows: (1) The released gases are kept in the cryotrap at −120°C for 8 min to absorb most macromolecule organic gases; (2) through the high temperature reaction furnace, the macromolecule organic gases will be split or react with high pure oxidizing agent yielding CO_2 and H_2O absorbed by the cryotrap; (3) the residual gases react in Zr-Al pump (400°C) and Fe-V-Zr pump (200°C); (4) if necessary, charcoal finger can be used for further absorption of residual gases at −120°C. With this procedure we obtained pure enough noble gases for Ar isotopic analyses. After an experiment, each part can be degassed by heating to recover the ability of purification. In order to keep the whole system in very low level blanks, the degassing temperature is set to 450°C for the cryotrap, 800°C for the Zr-Al pump and 500°C for

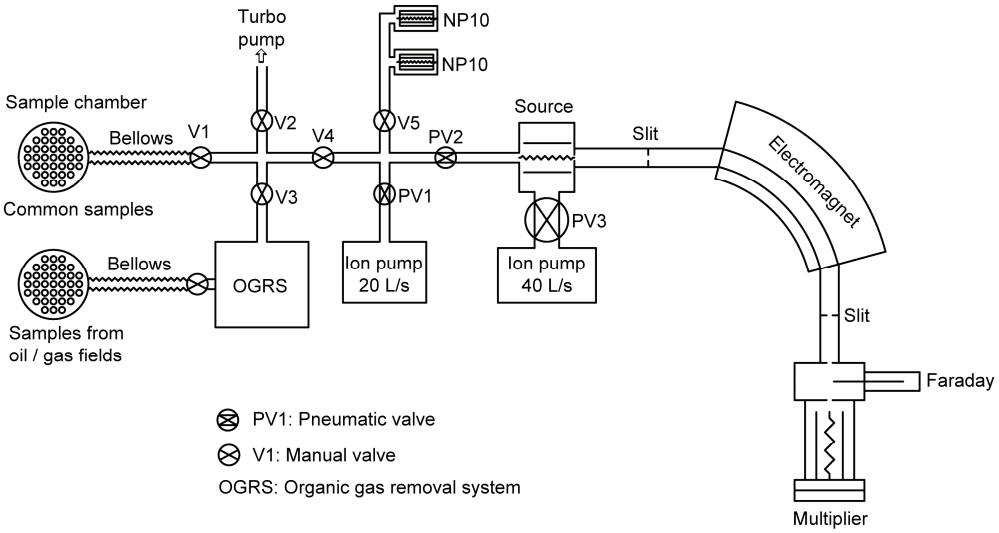

Figure 5 Schematic diagram of an argon extraction system with the GVI-5400 mass spectrometer in Guangzhou.

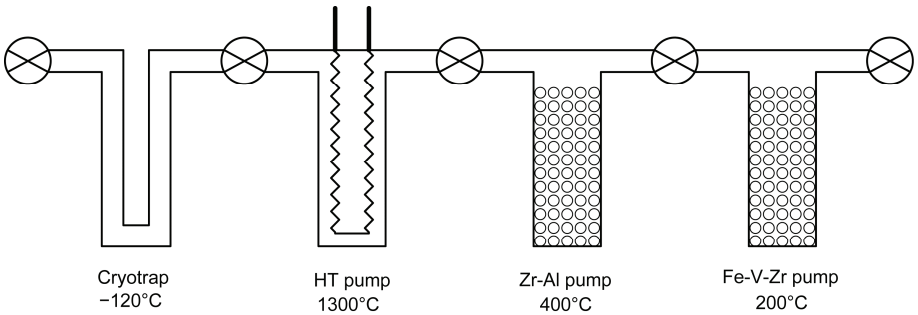

Figure 6 Schematic diagram of the organic gas removal system (OGRS), including a cryotrap, a high temperature (HT) pump and reversible Zr-Al and Fe-V-Zr pumps. PRC Patent No. ZL201320117751.2.

the Fe-V-Zr pump.

The GVI© purification system has two SAES NP10® (one operated at room temperature and the other at ~400°C) can meet the demand of most geological samples. During experiments if the gases are found not pure enough for argon isotopic analyses, the organic gas removal system can be opened to get rid of the most impurities in advance, then the NP10 getters are used for further purification.

A muscovite 2082MS, which could not be cleaned up by the normal preparation system with two NP10 getters, is used as a test sample for a comparative experiment in this study. The experiment is assigned into 4 sections with the OGRS "Closed/Opened" in turn. Each section includes 6 steps of laser stepwise heating. In order to correct the system blanks, cool blanks are carried out at the start and end of each section. After each section the whole purification system including the two NP10 getters are degased to keep low blank levels. It is worth to mention that we use the muscovite 2082MS for this experiment because it contains suitable amount of impurities and will not contaminate the instrument seriously. The whole system blanks can be easily recovered by the routine degasing procedure. Illites from oil fields contain a large amount of organic matter which might severely contaminate the instrument, thus unsuitable for a comparative test.

4. Results and discussion

The K-rich mica is a kind of the most common minerals for $^{40}Ar/^{39}Ar$ dating. Usually the gases from a mica can be cleaned up effectively, and the $^{40}Ar/^{39}Ar$ analyses yield small errors. The ^{40}Ar intensities increased in curves during the analyses of muscovite 2082MS-1 in the first six steps, showing that two NP10 getters failed to clean up the gases. The $^{40}Ar/^{39}Ar$ data yielded large analytical errors (Figure 7). This muscovite released so much impure gases that a powerful purification system would be necessary to obtain pure noble gases for mass spectrometer analyses. Therefore, the OGRS was put into use for all the subsequent heating steps, causing that the argon intensities decreased linearly with inlet time, which indicated that pure noble gases had been obtained for analyses. The $^{40}Ar/^{39}Ar$ data yield a flat age plateau with small analytical errors (Figure 7). With the OGRS, we obtained high-quality $^{40}Ar/^{39}Ar$ data. There might be two possibilities: (1) the OGRS had indeed played an important role to remove the impurities; (2) all the impurities on the surface had already been released completely for the first six laser heating steps. In order to demonstrate the effectiveness of the OGRS, a further comparative experiment on this muscovite 2082MS-2 was assigned into 4 sections with the OGRS "Closed/Opened" in turn (Figure 8).

Now we discuss the age spectrum of 2082MS-2 (Figure 8)

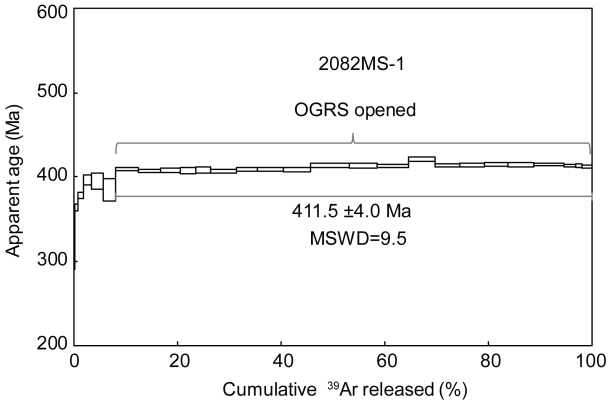

Figure 7 Age spectrum of muscovite (MS) 2082MS-1 by laser stepwise heating. The organic gas removal system (OGRS) was put into use for the gas purification except for the first six steps.

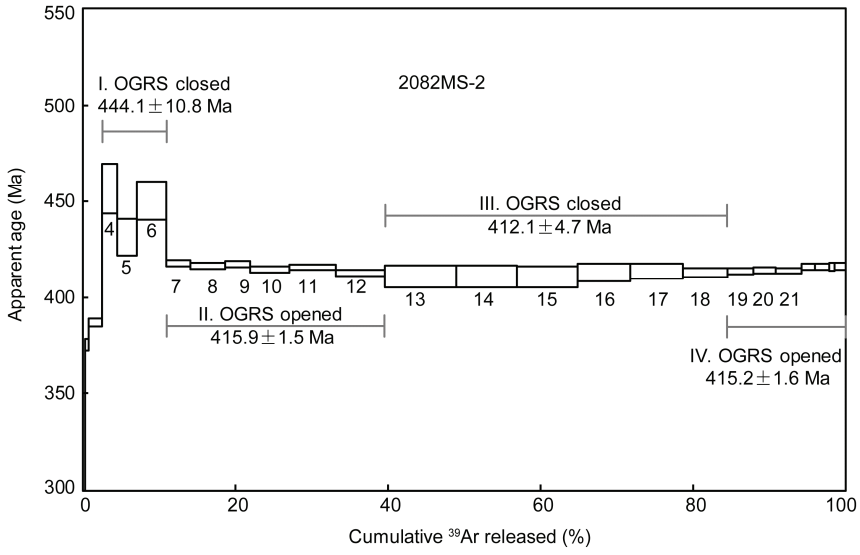

Figure 8 Age spectrum of muscovite 2082MS-2 for comparative test with the OGRS "Closed/Opened" in turn. OGRS was closed in section I and III, opened in section II and IV. The weighted mean age errors are marked in average values.

in detail. Section I of steps 1–6 with the OGRS closed. Using only two NP10 getters for purification, the $^{40}Ar/^{39}Ar$ data yield a weighted mean age of 444.1±10.8 Ma for this section. The gases released by low laser-output heating are most probably from the surface of the muscovite. Taking the data of step 6 (marked as 2082-6) for example, the ^{40}Ar intensity increases and then decreases in curves (Figure 9), showing that two NP10 getters cannot clean up the gases completely for high precision $^{40}Ar/^{39}Ar$ analyses.

Section II of steps 7–12 with the OGRS opened. The gases were firstly cleaned up in the OGRS and then transferred into the two NP10 getters. A weighted mean age of 415.9±1.5 Ma is obtained for this section. Taking step 7 (2082-7) for example, its ^{40}Ar intensity decreases with the inlet time linearly, indicating that the gases have been cleaned up well for $^{40}Ar/^{39}Ar$ dating (Figure 9).

Section III of steps 13–18, with the OGRS closed again, yields a weighted mean age of 412.7±4.7 Ma. The gases were purified only by two NP10 getters. In order to show the signal variation trends from steps 13 to 18, we homogenize the ^{40}Ar intensities in this way: the signals of the fifth cycle (X_5) are assigned to 2 V, and the other signals are multiplied by $2/X_5$. Figure 10 illustrates that the ^{40}Ar intensities of steps 13–16 slowly increase and then decline in total rising trends, indicating the impurities are still obvious resulting in large analytical errors. While the ^{40}Ar intensities of steps 17 and 18 slightly increase and then decline in total declining trends, showing that the impurities are lower than the previous steps and further purification is still necessary. When the heating temperatures might reach as high as 1000°C in steps 17 and 18, the sample was still releasing the impure gases, indicating that the impurities were probably trapped inside the muscovite lattices.

Section IV of steps 19–24, with the OGRS opened, has a weighted mean age of 415.2±1.6 Ma. Similar to those of section II, the ^{40}Ar intensities decline with the inlet time linearly again (Figure 11).

When the OGRS was closed in sections I and III, only using two NP10 getters for purification, the data yield large analytical errors of 10.8 and 4.7 Ma respectively. When the OGRS was opened in section II and IV, the data yield small analytical errors of ~1.5 Ma. Therefore, our OGRS is very effective to clean up the active and impurity gases to obtain pure noble gases for high-quality argon isotopic analyses, which is worth to be popularized.

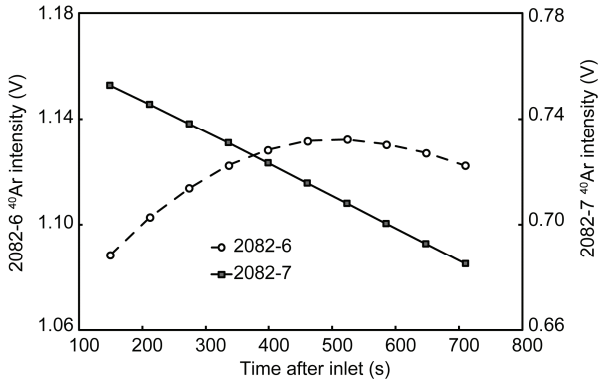

Figure 9 Plot of ^{40}Ar intensity *vs*. inlet time of muscovite 2082MS-2 in steps 6 and 7.

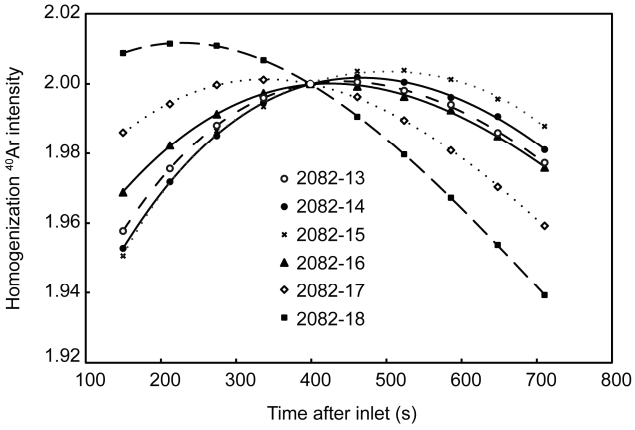

Figure 10 Plot of homogenization ^{40}Ar intensity *vs.* inlet time of muscovite 2082MS-2 of steps 13–18.

5. Conclusion

The normal purification systems, probably consisting of some of sponge Ti pump, titanium sublimation pump, Zr-Al pump (NP10) and copper oxide pump, can clean up most geological samples for $^{40}Ar/^{39}Ar$ dating or noble gas analyses. We have often got some samples hard to be purified by normal purification systems. The OGRS introduced in this study can clean up the active and organic gases very effectively even though the samples are from gas/oil fields, therefore, it is worth to be widely promoted. It will be more helpful to combine this new technique into the routine purification systems for all minerals and rock samples for the $^{40}Ar/^{39}Ar$ analyses.

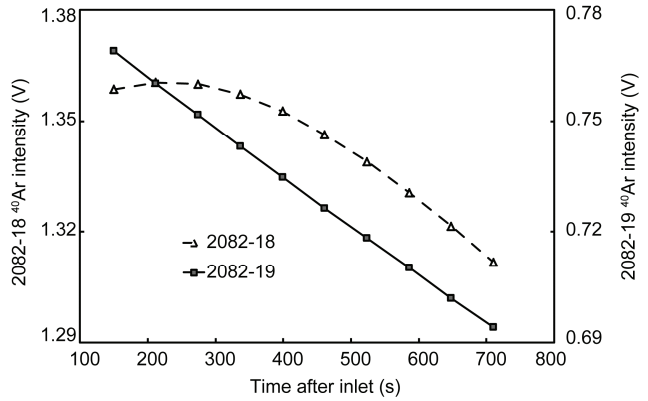

Figure 11 Plot of ^{40}Ar intensity *vs.* inlet time of muscovite 2082MS-2 of steps 18–19.

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