

SENSITIVITY OF THE ^{40}Ar – ^{39}Ar METHOD: NEW POSSIBILITIES AND LIMITATIONS

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Abstract. The space resolution of the Ar-Ar method by laser spot evaporation is limited by the sensitivity of the mass spectrometer (MS). Commercially available noble gas MSs do not exploit the recent achievements of vacuum technology and do not use position sensitive detector for simultaneous detection of all Ar isotopes. A two-fold reduction of the spot-size can be expected from the use of properly designed MS. In spite of this, the sensitivity will be insufficient for dating fine-grained minerals of Alpine age, therefore efforts to separate < 40 μm minerals are important and useful.

Key words. Ar-Ar, sensitivity, extreme high vacuum, position sensitive detection, mineral separation

Introduction

Modern noble gas mass spectrometers (NGMS) allow the isotope analysis of very small amount of argon. The smallest Ar quantities must be measured when Ar-Ar dating is applied as a microprobe method. This techniques has been introduced by Megrue (1967) for lunar rocks and meteorites, where the old age and high Ar concentration reduced the need for a very high sensitivity. Recently the Ar-Ar laser microprobe techniques has been reviewed by Kelley (1995).

The most important figure of merit characterising the laser spot dating techniques is the available spatial resolution. This is determined by the minimum volume of Ar needed for isotope analysis with the NGMS: the age and K concentration of the mineral defines the size of mineral that must be evaporated by the laser pulse to liberate the required amount of Ar.

The sensitivity of a NGMS, i. e. the minimum volume of noble gas needed for isotope analysis depends on the efficiency of ion source, the intensity of background lines, i. e. the

final vacuum, volume of the MS and the efficiency of ion detection. In this work the possible improvement of the vacuum and the efficiency of ion counting will be discussed.

Increasing sensitivity by improving the vacuum system

A very important factor limiting the sensitivity of isotope analysis is the height of background lines, first of all at M=36. Namely (disregarding the Ca derived Ar isotope correction), (i) the radiogenic ^{40}Ar is obtained by the

$$^{40}\text{Ar}(\text{rad}) = ^{40}\text{Ar}(\text{total}) - 295.5x^{36}\text{Ar}(\text{atm})$$

equation, where 295.5 is the atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio. Thus, any error of the ^{36}Ar isotope will result 295.5 times greater error of the radiogenic ^{40}Ar and (ii) the background at M=36 is mostly $^1\text{H}^{35}\text{Cl}$, and this molecule could be distinguished from ^{36}Ar only with high resolution (over 4000), i. e. with less sensitive MS.

The background at M=36 for the most frequently used MSs is:

VG 3600	$< 3 \times 10^{-14} \text{ cm}^3 \text{ STP}$
VG 5400	$< 3 \times 10^{-13} \text{ cm}^3 \text{ STP}$
MAP 215, 216	$< 5 \times 10^{-14} \text{ cm}^3 \text{ STP}$

The background of the mass spectrometers is not stable. The Ar introduced into it is not absolutely clean and the energetic ion beams hitting the inner part of the vacuum system release molecules which contribute to the background. The resulting height of a background line will be obtained when the release and pumping away of its component molecules will be equal. Beside the introduced Ar, the H_2 background (H_2 is the most abundant component of rest gases in an ultra vacuum system) will generate the greatest part of the background. Thus, decreasing the H_2 background is a precondition to increase the sensitivity.

The final vacuum of a NGMS can be given by the equation $P = P_0 + Q/S$, where P is the final vacuum, P_0 is the vacuum limit of the sputter ion (SIP) or turbomolecular pump used, Q is the gas release into the vacuum chamber and S is the pumping speed of the non evaporable getter pump (NEG) used for pumping the active gases during the isotope analysis of noble gases. Even when the highest quality construction materials are used, Q is of the order of $\sim 10^{-14} \text{ Torr} \cdot \text{l} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$.

In the best MSs the partial pressure of H_2 is $\sim 10^{-9}$ mbar. This is surprisingly high, but estimating the total inner surface of the vacuum chamber and considering the gas release of surfaces and ion source, it is realistic: since the NEG pump is connected to the vacuum chamber through a valve of low cross section, no better vacuum can be expected. On the other hand, in accelerator/storage ring systems vacuum $\sim 10^{-12}$ mbar is achieved, e. g. at CRYRING,

Stockholm, $<5 \cdot 10^{-12}$ mbar (Bagge et al., 1993) and at the LEP, CERN, $<10^{-12}$ mbar (e. g. Benvenuti, Chiggiato, 1993). Vacuum of this quality is called Extreme High Vacuum (XHV). Before discussing the constructional causes of this great difference, the sensitivity of recently used mass spectrometers will be estimated.

Uncertainty of $(1-5) \cdot 10^{-15}$ is assumed for the background peak at $M=36$. this involves 295.5 times greater error of the $^{40}\text{Ar}(\text{rad})$. These are shown by 2 horizontal bands in Fig. 1. The amount of radiogenic Ar for minerals of different age and K content is plotted against the volume of mineral from which the Ar is extracted by the laser pulse. The extracted $^{40}\text{Ar}(\text{rad})$ must be greater than the uncertainty of the ^{40}Ar peak caused by the background (upper horizontal band). Even, if we assume only 10^{-15} cm^3 STP error for the background at $M=36$, almost $20 \mu\text{m}^3$ mineral of 1000 Ma age and 10 % K content, or more than $60 \mu\text{m}^3$ mineral of Hercynian age and 0.5 % K content has to be evaporated, if we intend to obtain the age with approximately 5 % accuracy. Accuracy can be increased, though, by performing a greater number of measurements and averaging the results, but it is clear, that every attempts to increase sensitivity is highly desirable.

In the accelerator/storage ring systems either a greater number of NEG pumps is connected to the vacuum chamber (e. g. CRYRING, Stockholm), or the inner wall of the vacuum chamber is covered with getter material (LEP, CERN). As getter material St707 (produced by SAES, Italy) is very suitable. It can be regenerated at lower temperatures (~ 350 °C: several hours; ~ 450 °C: 10 minutes), actually the baking temperature of the vacuum system is sufficient to regenerate the getter. St707 is composed of zirconium (70.0 %), vanadium (24.6 %) and iron (5.4 %) and it is available in the form of strip with ~ 0.3 mm thickness. As a test, the ion source of the mass spectrometer in the K/Ar laboratory in Debrecen has been surrounded with St707 strip and a 10-fold decrease of the background has been observed (Balogh, Simonits, 1998).

Position sensitive detection

Ar-Ar dating requires the detection of 5 Ar isotopes. Recently available NGMSs detect only one isotope at a time, i. e. the information carried by the other 4 isotopes is lost. 5 Ar isotopes could be measured simultaneously by 5 separate multipliers, but the size of multipliers would necessitate the use of greater mass spectrometers. Their great volume would involve the reduction of partial pressure of the Ar to be measured. Carrico et al. (1973) described a position sensitive detector based on 7100 channeltrons with 0.024 mm inner

diameter and 0.036 mm spacing. Applying a one dimensional resistive anode to collecting the electron pulses they obtained a resolution comparable to the spacing of channeltrons.

Development of the micro channel plates (MCP) opened new possibilities for the application of position sensitive detectors. In order to have sufficiently great electron pulses ($> 10^6$ electrons), usually 2 or 3 MCPs are stacked together with a two-dimensional resistive anode behind them. The space resolution of these two-dimensional detectors is $diameter/100$, if 2, or $diameter/400$, if 3 MCPs are stacked together. Counting rate of $< 10^5$ counts/s could be obtained without dramatic change of counting efficiency with the layout of the Quantar Technology (1991 Rev B). Counting rate is limited by the time needed for signal processing. Recently substantially higher counting rate ($\sim 10^6$ counts/sec) was reported by Shapira et al. (2000). For Ar-Ar dating counting a total of $\sim 10^7$ Ar ions appears sufficient to obtain age values with $< 1\%$ accuracy, if the enrichment of radiogenic Ar is over 50 %.

One dimensional position sensitivity is sufficient for mass spectrometric applications. It is likely that conventional electron multipliers with a one-dimensional resistive anode after them could be used too, since the electrons, which are hit out by the ions from the first dynode will keep their position along the dynodes while they reach the anode. The most important requirement for the MCPs or multipliers is the compatibility with XHV requirements.

In Fig. 2 a noble gas mass spectrometer is shown, where NEG strip surrounds the ion source, achieving this way a 10-50 times greater pumping speed for active gases, and position sensitive detection is used for simultaneous counting the Ar isotopes.

Limitations: need for separating fine-grained minerals

Estimating the available amount of radiogenic Ar, it appears that linear size of the evaporated spot can be decreased by a factor of ~ 2 . Observing Fig. 1, it will be clear that for 100 million years old minerals spot-sizes of $\sim 15\text{--}40\ \mu\text{m}$ are needed to obtain sufficient amount of Ar for K concentrations in the 0.5 – 10 % range. During metamorphic processes frequently finer-grained minerals are formed: their age relations will not be available for the laser spot dating techniques in foreseeable future. Therefore all efforts to separate finer-grained minerals will be essential for chronological studies of certain metamorphic processes.

Conclusions

1. Commercially available noble gas mass spectrometers do not exploit the results of modern vacuum technology and do not use position sensitive detectors for simultaneous measurement of Ar isotopes. This decreases their sensitivity with about one order of magnitude.

2. Even with the most sensitive mass spectrometer the minimum size of a 100 Ma old mineral needed for Ar analysis will be about 15-40 μm , therefore attempts to separate small-sized minerals are essential for chronological studies of certain metamorphic processes.

References

- Bagge, L., Danared, H., Ehrnstén, K., Herrlander, C. J., Hilke, J., Nilsson, A. and Rensfelt, K-G (1993): The ultra high vacuum system of CRYRING. *Vacuum*, **44** 497-499.
- Benvenuti, C. and Chiggiato, P. (1993): Obtention of pressures in the 10^{-14} torr range by means of Zr-V-Fe non evaporable getter. *Vacuum* **44** 511-513.
- Carrico, J. P., Johnson, M. C. and Somer, T. A. (1973): Position-sensitive charged particle detector for a miniature Mattauch-Herzog mass spectrometer. *Int. J. Mass Spectr. Ion Phys.* **11** 409-415.
- Kelley, S. P. (1995): Ar-Ar dating by laser microprobe. In: Potts, J. P. et al., (eds): *Microprobe techniques in the earth sciences*. Chapman & Hall, London, 327-358.
- Megrue, G. H. (1967): Isotopic analysis of rare gas with a laser microprobe. *Science*, **157** 1555-1556.
- Quantar Technology (1991): 3300/2400 series: System installation and operational manual, No. 9000-0131, Rev B.
- Shapira, D., Lewis, T. A., Hulett, L. D. (2000): A fast and accurate position-sensitive timing detector based on secondary electron emission. *Nucl. Instr. Meth. Phys. Res. A* **454** 409-420.

Fig. 1: Background of noble gas mass spectrometers at M=36 and M=40 and volume of $^{40}\text{Ar}(\text{rad})$ as a function of age, K content and size of the evaporated mineral.

Fig. 2: Scheme of noble gas mass spectrometer with effective pumping of active gases and position sensitive detection.

