Ultra-violet laser probe measurement of $^{40}$Ar/$^{39}$Ar age profile in phlogopite

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Abstract Ultra-Violet Laser Ablation Microprobe (UVLAMP) extraction technique enables the direct investigation of Ar-Ar age profile in crystals, and yields more information on rates and durations of geological process than conventional single time snapshots. Phlogopite flakes from lamprophyre at Pishan dyke in western Kunlun were dated by using an UV laser ($\lambda = 213$ nm) microprobe with spot analyses. The results show good agreement with those from the conventional $^{39}$Ar/$^{38}$Ar step heating experiments. This indicates that the Ar isotopes are distributed homogeneously in the phlogopite and the UVLAMP can be a powerful tool in the study of thermal history.

Keywords: laser probe, lamprophyre, phlogopite, $^{40}$Ar/$^{39}$Ar.

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Argon mobility within minerals is usually modeled in terms of volume diffusion through the mineral lattice. For a pure mineral separate, low-temperature steps are dominated by gases release from sites with short diffusion paths (those close to grain boundary). Higher temperature steps are dominated by argon release from sites with longer diffusion paths (those close to the center of a grain). The natural argon diffusion profile and the thermal history can then be reconstructed from the Ar-Ar age spectrum$^{[1-2]}$. Unfortunately, recent investigations suggest that step heating experiments may not effectively reveal the internal distribution of radiogenic argon within single crystals due to the non-uniform heating, intrasample inhomogeneities and structural changes of hydrous minerals during heating in the vacuum system$^{[3-5]}$. Laser microprobe can vaporize samples of around 10 $\mu$g from a single laser pit, enables direct correlation of in-situ analyses with position in the grain, surmounts drawbacks of step heating and directly gives imaged age profile. Moreover, it is possible to retrieve the rate and duration of geological processes, and reconstruct thermal history of rocks by linking time with such parameters as temperature, pressure, composition or structural-textual data$^{[6,7]}$.

Laser microprobe includes the use of pulsed and continuous wave (CW) lasers in $^{40}$Ar/$^{39}$Ar geochronology. CW laser is commonly utilized in single crystal fusion and step-heating. Pulsed laser is mainly used to release gases from a small portion of a sample, giving the argon distribution. However, several important minerals including K-feldspar, plagioclase and quartz are very poor absorbers at visible/near IR laser wavelengths. In these minerals, beam reflection and refraction spread power for hundreds of microns from the focused laser spot, heating inclusions, imperfections and adjacent grains, making results very difficult to interpret$^{[5]}$. In recent years, many $^{39}$Ar/$^{39}$A labs have used Ultra-Violet Laser Ablation Microprobe (UVLAMP) technique to study the argon distribution within intra crystal and the wavelength used for UVLAMP is 266 nm$^{[15-21]}$. Because UV laser light is absorbed strongly by most silicates including feldspar and quartz, beam will not reflect and refract in these minerals. As a result, the spatial resolution can be improved.

Pickles et al.$^{[12]}$ successfully applied UVLAMP technique to investigating the age profile and reassessing the metamorphic history. By using UVLAMP technique and experimentally determined diffusion rates for Ar in phlogopite, Kelley et al.$^{[13]}$ obtained the age profile of phlogopite in Kimberlites and concluded that the magma transport time is less than 11.6 d. Based on detailed intra-grain profiling of phengites in situ, Sherlock et al.$^{[14]}$ presented a detailed picture of the spatial distribution of excess argon within the minerals. Although visible or near IR (694 nm$^{[15]}$ and 1064 nm$^{[16-18]}$) laser based Ar extraction has been applied to terrestrial rocks since 1994$^{[19-21]}$, no UVLAMP technique has been used in China. Here we report a study applying UVLAMP to phlogopite crystal from Pishan lamprophyre by using UP213 Nd-YAG laser ($\lambda = 213$ nm) and MM5400 mass spectrometer at $^{40}$Ar/$^{39}$Ar Geochronology Laboratory in Institute of Geology and Geophysics, Chinese Academy of Sciences. The good agreement of argon isotopic distributions measured by UVLAMP with those obtained from resistance-furnace step heating indicates that the newly established UVLAMP technique is an effective approach for $^{40}$Ar/$^{39}$Ar dating.

\section*{1 Sample and experimental methods}

\subsection*{(1) Sample description.} The Pishan lamprophyre dykes, which intruded in the Proterozoic hornblende schists, is exposed in the northern part of western Kunlun (N37°7’, E77°45’). Grey-black lamprophyres are characterized by massive structure and porphyritic texture. The phenocrysts (about 45%) consist of phlogopite and diopside. The matrix (about 55%) is composed of phlogopite, diopside, Fe-Ti oxides and carbonates. The phenocrysts in the lamprophyres characterized by clear edges and lack of chloritization show little alteration after their formation$^{[22]}$. Fresh phlogopite flakes Ps001L and Ps002 were removed from lamprophyre sample by knife for $^{40}$Ar/$^{39}$Ar measurements.
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(ii) Irradiation and J value calculation. Fresh phlogopite flakes were washed with acetone in an ultrasonic bath for 20 min. After drying, they were wrapped in Al foil, stacked in vacuum-sealed quartz vial (VUB22, VUB23) and irradiated with fast neutrons in the BR2 reactor of the Nuclear Research Center at Mol for 2 h. The vial was shielded with cadmium foil (0.5 mm thick) to limit neutron interactions on 40K. A piece of Fe-wire, which was cut into 5 equal parts, was put outside the vial. After irradiation, neutron flux was measured and flux gradient was calculated. For VUB22, dosimeter reading from top to bottom (0—45 mm) was 4.0889 × 10^{17} - 3.6768 × 10^{17} n.cm^{-2}. 85G003-sanidian standards were stacked on the top, middle and bottom of the quartz vial; the reference age is 28.34±0.28 Ma [23]. Three months after irradiation, argon total fusing analyses were performed on standards at the Geochronology Laboratory of the Vrije Universiteit Brussel on an MAP216 mass spectrometer operating in a static mode. Each standard yields a J-value, combined with neutron flux gradient and sample position, and all the J-values were calculated: for Ps002 J = 0.002937±0.000046, for Ps001L J = 0.002549±0.00002. The uncertainty of J-value is one standard deviation of mean and does not take account of uncertainties in the “absolute” age of the monitor mineral. K glass and CaF2 monitors were also stacked between the samples and Ca, K correction factors were calculated: (39Ar/39Ar)$_k$ = 8.95 × 10^{-4}, (39Ar/39Ar)$_K$ = 8.05 × 10^{-4}, (36Ar/39Ar)$_K$ = 3.33 × 10^{-4}, in accord with the summary of McDougall et al. [8]. Decay constant used throughout the calculations is $\lambda$ = (5.543 ± 0.010) × 10^{-10} a$^{-1}$, as recommended by Steiger et al. [24].

(iii) 40Ar/39Ar step heating. After irradiation and 4 months cooling, total fusing of standards and argon step-heating analyses of Ps002 were performed at the 40Ar/39Ar Geochronology Laboratory, Vrije Universiteit Brussel, Belgium, on an MAP216 mass spectrometer operating in a static mode. The 40Ar, 39Ar, 38Ar, 37Ar and 36Ar isotopic abundance is determined through linear extrapolation at time zero of peak intensities during fifteen sequential scans. The data were corrected for system blanks, mass discriminations, interfering Ca, K derived argon isotopes, and the decay of 37Ar since the time of irradiation. Plateau age was calculated by CHROPLOT from all the steps forming the age spectrum. A plateau age from an age spectrum is assigned when at least 3 successive incremental heating steps yield consistent apparent ages within error limits and cover a minimum of 50% of the total released argon. When these criteria are not met, a near-plateau age is assigned.

(iv) 40Ar/39Ar UVLAMP. After 33 months irradiation, UVLAMP analyses of Ps001L phlogopite flake were performed at the 40Ar/39Ar Geochronology Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences to examine the spatial distribution of argon in the phlogopite. The flake measured approximately 2.8 mm long by 1.9 mm wide and was oriented perpendicular to the (001) basal plane. Samples were loaded into fused silica sample chamber and degassed at 150°C for 60 h to reduce the system blank. The laser system consisted of a New Wave UP213 Nd-YAG laser ($\lambda$ = 213 nm) operating in pulse mode.

To ensure a precise measurement, the 160 μm diameter beam was used. After 4 min lasing, the gas released was purified using 2 SAES getters (operated at 350 and 100°C, respectively) for 3 min and expanded into an MM5400 mass spectrometer, which is equipped with a Nier source, a Faraday cup and an ion count multiplier. The MM5400 mass spectrometer has a resolution of 400, and the sensitivity is 1.251 × 10^{-3} A/Torr. From mass 40 to mass 36, every mass was measured eight times by multiplier; signals were extrapolated back to inlet time. Blanks were run after every three analyses and blank levels varied little. Thus, blank corrections for all Ar isotopes were based on daily averages (Table 1). The data were corrected for system blanks, mass discriminations, interfering K derived argon isotopes. Because there was little calcium in phlogopite and it was already 33 months after irradiation, we did not apply Ca correction to the data. The UVLAMP analyses are presented in Table 2. Their age profile and inverse isochron are showed in Figs. 1 and 2.

<table>
<thead>
<tr>
<th>40Ar</th>
<th>39Ar</th>
<th>38Ar</th>
<th>37Ar</th>
<th>36Ar</th>
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<tbody>
<tr>
<td>6.634 × 10^{-12}</td>
<td>5.354 × 10^{-14}</td>
<td>6.724 × 10^{-15}</td>
<td>4.101 × 10^{-14}</td>
<td>3.322 × 10^{-14}</td>
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2 Conclusion and discussion

(i) Results of 40Ar/39Ar step heating. Ps002 gives a plateau age of 233.5±1.5 Ma and isochronal age of 231.7±0.3 Ma, initial 40Ar/39Ar ratio of 280.3±1.7 [22], close to Nier value 295.5. We regard the inverse isochron age as being more objective because no assumptions are made about the initial 40Ar/39Ar ratio. Thus, 231.7±0.3 Ma represents the cooling age of phlogopite Ps002.

(ii) Results of 40Ar/39Ar UVLAMP. Fig. 1(a) shows the spatial distribution of the laser pits. Except laser pit b2, all other dates lie within 1SD of each (Table 2), and yield a relatively constant profile with a weighted mean age of 232.0±0.5 Ma (Fig. 1(b), (c)). Laser pit b2 (242.3±2.8 Ma), however, lies distinctly outside this range because there is a mistake in peak center and 36Ar peak is drifted. Except the anomalous age b2, other laser spot data yield a line on an inverse isochron diagram with an intercept age of 231.5±0.4 Ma and an 40Ar/36Ar initial ratio of 297.1±9.1 which is not distinguishable from the air ratio (Fig. 2). Homogenized argon distribution and initial value