Preservation of Radiogenic Argon in Mantle Micas in situ: Dating of Deep Seated Inclusions from the Shavaryn–Tsaram Paleovolcano, Mongolia

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Abstract—This article presents new data on isotopic (K/Ar) dating of a series of volcanic units of the Shavaryn–Tsaram Volcano based on rocks and minerals and the chemical composition of deep seated micas. Four age intervals have been identified, one of which is pertinent to the Middle Miocene (15.5–12.2 Ma) and the other three, to the Quaternary (1.87–1.82, 1.44-1.33, and 0.54–0.44 Ma). The age intervals correlate with the known volcanic events. The xenolites examined are most similar to fragments of a deep seated alkaline–ultramafic rock complex whose formation proceeded during the last 15.5 myr and was accompanied by sporadic effusion of alkali–basaltoid lavas onto the surface. The micas from the inclusions of the Shavaryn–Tsaram Volcano had a high activation energy of migration of radiogenic argon, which ensured argon accumulation during the radioactive transformation of ^{40}K and preservation in situ. The high equilibrium temperature of garnet lherzolite (1050–1150°C) and the calculated pressure (20–22 kbar) played the role of mutually compensating factors in argon diffusion; high temperatures enhanced diffusion, while pressure suppressed it.

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It is well known that radiogenic argon that does not form chemical bonds is removed from crystalline structures at high temperatures as a result of diffusion according to Fick's and Arrhenius laws [1]. At relatively shallow depths (middle and upper crust), rocks and minerals exposed to elevated temperatures constantly lose radiogenic argon in the Laplace regime [2]. This leads to distortion of the actual age of the units examined in the K/Ar isotope system. However, increasing pressure hinders diffusion, so radiogenic argon can be completely preserved in minerals in the context of high lithostatic pressure in the lower crust and the upper mantle.

Deep seated inclusions are normally carried out to the Earth's surface with melts or gas flows. In the course of long term crystallization of a high temperature melt, a deep seated mineral inclusion loses argon. However, during rapid melt crystallization (chilling) or in emissions of the resurgent material of volcanoes, the inclusions are not exposed to long term heat action and preserve the radiogenic argon that had accumulated at depth in situ. An example of such a phenomenon is the micas of deep seated inclusions of the Shavaryn–Tsaram Volcano.

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The alkali basalt Shavaryn–Tsaram Volcano is located on the southern extension to the Terkhin–Tsagannur Depression (Khangai Highland), at the water divide between the Angarkhai and Shavaryn–Gol rivers (coordinates 48°02′48″ N, 99°59′30″ E) and is represented by an eroded neck and a low cinder cone on the edge of a laval basalt field. Amongst basaltoid debris and in the cinder, there are numerous fragments of spinel and garnet lherzolites, wehrlites, websterites, pyroxenites, and phlogopite peridotites, and megacrytals of garnet, pyroxene, feldspars, micas, and other minerals [3–5].

According to the samarium–neodymium geochronology data, the spinel lherzolites of the Khangai Highland formed no later than 1 billion years ago. However, the age estimates obtained for the phlogopite lherzolite in the Sm–Nd and Rb–Sr systems are within the last 20 myr [6]. The assumption was made that the age of the metasomatic alteration of the mantle that led to the formation of the phlogopite is close to that of alkali basalt magmatism [7]. The determined age of the rocks of Shavaryn–Tsaram that host inclusions is within the range of 1.2 ± 0.3 Ma [3] to 0.4 ± 0.1 Ma [8].

We made an attempt to use the K/Ar method in order to determine the age of a series of volcanic units of Shavaryn–Tsaram based on rocks and minerals. Due to the peculiar technique developed by the workers of the Laboratory of Stable Isotopes of the Far East Geological Institute, Far East Branch, Russian Academy of Sciences [9], K/Ar dating of the samples was
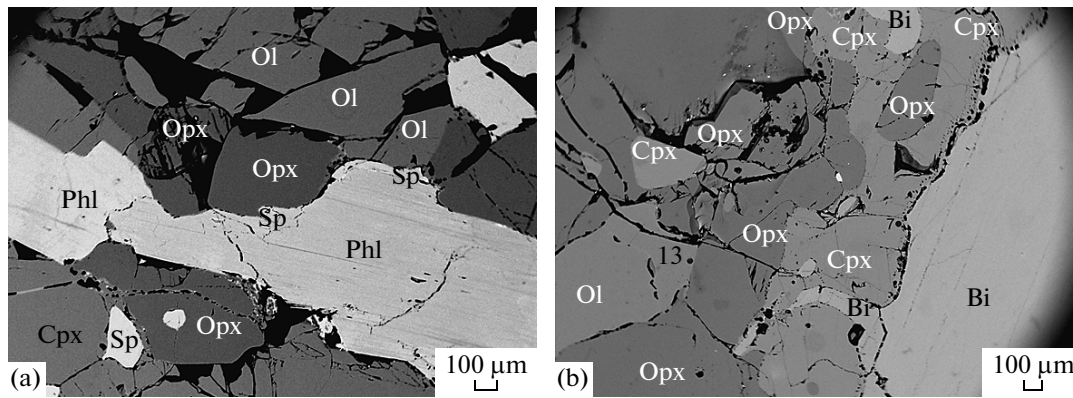
Fig. 1. The relationship between minerals in micaceous peridotites. (a) Spinel lherzolite; coarse phlogopite crystals are situated inside the rock and contact all minerals with no visible reactions. (b) Garnet lherzolite; biotite crystals are separated from the minerals of the bulk of lherzolite with interbeds of clinopyroxenes and orthopyroxenes. Backscattered electron image, JXA−8100 microanalyzer. Opx is orthopyroxene; Cpx, clinopyroxene; Ol, olivine; Phl, phologopite; Bi, biotite; and Sp, spinel.

conducted on very small aliquots (1.5−4.0 mg). Isolation, collection, cleaning, and measuring of the isotopic composition of argon was carried out in a continuous flow of superpure helium. A CO_2 laser (10.6 μm) was used for argon isolation from the samples. The isotopic composition of argon was measured using a MAT−253 mass spectrometer (Thermo Scientific). The content of potassium was determined by inductively coupled plasma atomic emission spectrometry (ICP−AES) using an iCAP 6500Duo spectrometer (Thermo Scientific) and a JXA−8100 microanalyzer.

From the various ultramafic xenoliths of Shavaryn−Tsaram, the following were selected for investigation: spinel lherzolite and chrome−diopside pyroxenite that contained titanian phlogopite, a clinopyroxene−phlogopite−apatite rock (jacupirangite?), and garnet lherzolite with interbedded titanian biotite. Megacrysts (up to 2 cm long) of titanian biotite were collected from basalt lavas and cinders. The sample also contained fragments of sanidine megacrysts and lavas that hosted them.

As noted previously [3], the primary nature of the phlogopite in the spinel lherzolites, garnet lherzolites, and chrome−diopside pyroxenites is confirmed first of all by the lack of a reactionary relationship with other associating minerals (Fig. 1a). In addition, the phlo-

Table 1. Average chemical compositions of the examined micas of inclusions of the Shavaryn−Tsaram Volcano (wt %)

Compo-nent	Megacryst				Garnet lherzolite	Clinopyrox-enite	Spinel lherzolite	Phlogopite clinopyroxenite (jacupirangite?)
	ShchTs07-8A, $n = 11$	ShchTs07-17, $n = 11$	ShchTs07-22, $n = 11$	ShchTs07-5, $n = 11$	ShchTs07-12, $n = 11$	ShchTs07-22a, $n = 12$	ShchTs07-19, $n = 5$	ShchTs07-29, $n = 11$
SiO_2	35.60	36.29	35.15	35.45	35.65	36.35	37.4	37.9
TiO_2	11.47	11.19	11.32	11.67	11.21	6.13	5.38	2.96
Al_2O_3	14.99	15.35	14.89	15.01	15.03	14.63	15.85	16.02
FeO	13.08	12.17	12.51	12.84	10.94	5.32	4.15	7.67
MgO	12.00	12.71	11.84	12.17	13.72	18.59	19.98	20.31
Na_2O	0.44	0.40	0.47	0.40	0.50	0.26	0.81	0.30
K_2O	9.97	9.85	9.79	9.89	10.04	9.99	9.46	10.54
Cr_2O_3	–	–	–	–	–	1.28	0.62	–
F	–	–	–	–	–	–	–	2.13
Ba	–	0.72	–	–	–	–	–	–
Total	97.55	98.68	95.97	97.43	97.10	92.60	93.70	97.83
f	37.92	34.92	37.19	37.16	30.89	13.82	10.44	17.47

Note: The dashes denote below the detection limit, $f = Fe/(Fe + Mg)$ (mol %), n is the number of analyses.

Table 2. Results of K−Ar dating of rocks and minerals of the Shavaryn−Tsaram Paleovolcano

Sample	Material	K (wt %)	$^{40}Ar_{rad}$ (ng/g)	$^{40}Ar_{air}$ (%)	Age (myr)
ShchTs07-3	Lava flow (bulk composition)	3.11*	0.104 ± 0.009	72	0.50 ± 0.04
ShchTs07-9	Volcanic glass	3.81*	0.126 ± 0.009	84	0.49 ± 0.04
ShchTs07-4a	Sanidine megacryst	7.58*	0.241 ± 0.018	70	0.47 ± 0.04
ShchTs07-4б	Ditto	8.67*	0.32 ± 0.02	66	0.54 ± 0.04
ShchTs07-4	Ditto	8.33*	0.25 ± 0.07	85	0.44 ± 0.12
ShchTs07-8a	Biotite megacryst	7.48*	0.73 ± 0.03	93	1.44 ± 0.02
ShchTs07-12	Biotite interbed from garnet lherzolite	7.66*	0.72 ± 0.03	62	1.38 ± 0.09
ShchTs07-17	Phlogopite from pyroxenite	7.76*	0.7 ± 0.03	67	1.33 ± 0.06
ShchTs07-22	Ditto	7.67*	0.97 ± 0.04	71	1.87 ± 0.08
ShchTs07-05	Ditto	7.60*	0.94 ± 0.04	93	1.82 ± 0.15
ShchTs07-22a	Phlogopite from pyroxenite	8.28*	1.05 ± 0.04	76	1.87 ± 0.08
ShchTs07-29	Phlogopite from phlogopite clinopyroxen-ite (jacupirangite?)	8.00*	8.5 ± 0.4	61	15.5 ± 0.7
ShchTs07-19	Phlogopite from spinel lherzolite	7.85**	6.5 ± 0.3	19.4	12.2 ± 0.6

* Detected via inductively coupled plasma atomic emission spectrometry (ICP−AES) using an iCAP 6500Duo spectrometer (Thermo Scientific), ** − detected using a JXA-8100 microanalyzer. When calculating the ages, it was accepted that $\lambda_k = 0.581 \times 10^{-10}$ year^{-1} and $\lambda_\beta = 4.962 \times 10^{-10}$ year^{-1}.

gopites have a high magnesium content and an elevated chrome content, which is also typical of the minerals of this association (Table 1).

The contact between interbedded biotite and garnet lherzolite has a zonal structure: the biotite directly contacts the clinopyroxene bed, which gives way to orthopyroxene followed by lherzolite (Fig. 1b). Small biotite crystals are encountered inside the clinopyroxene interbed and partly go beyond it into orthopyroxene. In this sample, no mica was observed inside the garnet lherzolite proper. The pyroxenes of the near-contact portion are insignificantly more magnesian than similar minerals inside the lherzolite. At the same time, all minerals of this sample are the most ferriferous amongst the peridotites examined, while the composition of the biotite is close to that of the megacrysts (Table 1).

Jacupirangite is represented by an oval fragment of a clinopyroxene−phlogopite rock with interbedded coarsely scaled phlogopite and apatite on one of the sides. The micas in the interbedded scale are up to 1.5 cm in size; their shapes and dimensions are similar to those of megacrysts in basalts, but their compositions are different. The jacupirangite phlogopite in the interbed and inside the rock (just like apatite) contains a considerable quantity of fluorine, which is quite typical of alkaline intrusions.

The estimates of the pressure and temperature of the formation of the samples examined according to the mineral thermobarometry data are widely scattered, but are still within the limits of the existence parameters of garnet−spinel paragenesis. The calculated temperature (depending on the type of geothermometer used) varies from 1050 to 1150°C, while the pressure does not exceed 20−22 kbar [10]. These results do not contradict the previously published data [7, 11, 12] and correspond to the conditions of the lower horizons of the crust and the upper portion of the mantle.

The results of K/Ar dating are shown in Table 2. There are four age intervals, one of which is related to the Middle Miocene (15.5−12.2 Ma) and the other three, to the Quaternary (1.87−1.82, 1.44−1.33, and 0.54−0.44 Ma).

The youngest interval (0.54−0.44 Ma) probably corresponds to the time of effusion of the lavas of Shavaryn−Tsaram. These ages coincide with the K−Ar ages of the basalt [8] and the Ar−Ar age of the sanidine [13]. The ages of the sanidine megacrysts correspond to the ages of the lava flow and a fragment of volcanic glass from the resurgent material of the edifice, which indicates that sanidine does not contain excessive argon due to complete degassing of the megacrysts as a result of the heat action of magmatic melts and gases and the absence of trapped magmatic gases (including argon 40) during crystallization. Sanidine probably crystallized in the course of the final volcanic eruption.

Unlike sanidines, the micas in the form of megacrysts and those incorporated into holocrystalline inclusions contain excessive (inherited) argon. A Middle Miocene and two Quaternary episodes of mica crystallization are interpreted based on grouping of the ages.

The oldest episode (15.5−12.2 Ma) was determined based on phlogopites of spinel lherzolite and jacupirangite. It correlates with the initial stage of

effusions of potassium basalts in the Ugei−Nur volcanic field within the Orkhon−Selenga Middle Mountains.

The Quaternary episodes (1.44−1.33 and 1.87−1.82 Ma) were determined based on phlogopite in pyroxenite, interbedded biotite in garnet lherzolite, and biotite megacrysts. The episodes correlate with early Quaternary eruptions in the Taryat−Chulutyn field. Lavas with ages of 1.9 ± 0.1 and 1.2 ± 0.1 Ma were described in this field not far from the Shavaryn−Tsaram Volcano [14].

Analysis of the data presented indicates that the xenolites examined are most similar to fragments of a deep seated alkaline−ultramafic rock complex whose formation proceeded during the last 15.5 myr and was accompanied by sporadic effusion of alkali−basaltoid lavas onto the surface. The grouping of the ages into intervals is not accidental, but reflects the known volcanic events. Therefore, the micas from the inclusions of the Shavaryn−Tsaram Volcano had a high activation energy of migration of radiogenic argon, which ensured argon accumulation during the radioactive transformation of ^{40}K and preservation in situ. The data presented indicate that kinematically the high equilibrium temperature of garnet lherzolite (1050−1150°C) and the calculated pressure (20−22 kbar) played the role of mutually compensating factors in argon diffusion; high temperature enhanced diffusion, while pressure suppressed it.

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