

First Determination of the Isotopic Age of a Lunar Meteorite by the Uranium–Lead Zircon Method

E. M. Leont'eva¹, D. I. Matukov², M. A. Nazarov³,
S. A. Sergeev², Yu. A. Shukolyukov^{1,2,4}, and F. Brandstaetter⁵

¹Isotopic Geology Division, Faculty of Geology, St. Petersburg State University,
Universitetskaya nab. 7–9, St. Petersburg, 199034 Russia
e-mail: xekrarne@js10093.spb.edu

²Center for Isotopic Research, Karpinskii All-Russia Research Institute of Geology,
Srednii pr. B.O. 7, St. Petersburg, 199106 Russia
e-mail: sergeev@mail.wplus.net

³Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,
ul. Kosygina 19, Moscow, 119991 Russia
e-mail: nazarov@geokhi.ru

⁴Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences,
nab. Makarova 2, St. Petersburg, 199034 Russia
e-mail: xekrarne@js10093.spb.edu

⁵Natural History Museum,
Burgring 7, 1010 Vienna, Austria
e-mail: franz.brandstaetter@nhm-wien.ac.at

Received July 22, 2004

Abstract—The goal of this study was to evaluate the possibility of determining isotopic age for single accessory zircon grains from the new lunar meteorite Dhofar 025 using a SHRIMP II ion microprobe. The Dhofar 025 meteorite is an anorthosite regolith breccia with abundant fragments of a highland origin. Its rock-forming minerals are plagioclase, olivine, and pyroxene; and the accessory minerals are ilmenite, silica phases, zircon, Ti-rich aluminous chromite, troilite, and FeNi metal. Several zircon grains were found during the investigation of a polished section of the meteorite using reflected light optical microscopy and scanning electron microscopy, but only the largest of them, $20 \times 30 \mu\text{m}$ in size, appeared to be suitable for the determination of isotopic age. Ion currents were measured on the SHRIMP II mass spectrometer using a secondary electron multiplier operated in a mass scanning mode. Secondary ions were sputtered from the surface of the zircon grain by the bombardment with primary O_2^- ions of an analytical spot, $10 \times 15 \mu\text{m}$ in size. A mass resolution of more than 5200 eliminated all possible isobaric interferences in the mass range analyzed. Zircon SL13 was used as a concentration standard (accepted U concentration of 238 ppm). Zircon TEMORA (concordant and homogeneous in uranium–lead ratio) was used for the standardization of uranium–lead ratios. The ages calculated from the position of analytical points on the Ahrens–Wetherill diagram appeared to be discordant. The U–Pb system of Dhofar 025 zircon was most likely disturbed during the formation of the breccia as a result of a large meteorite impact. Possible variants of the interpretation of the data obtained led to the following conclusions. The zircon grain crystallized from a felsic melt more than 4360 ± 27 Ma ago, which supports the results of investigations of lunar samples suggesting the antiquity of lunar granitic rocks. The age of breccia formation is less than 2000 Ma and could be identical to the exposure age of the meteorite. Thus, the Dhofar 025 breccia is much younger than highland breccias from the near side of the Moon, which were produced by a lunar cataclysm (intense meteorite bombardment) 3900 Ma ago. This allowed us to suppose that Dhofar 025 probably represent a rock ejected from the far side of the Moon.

INTRODUCTION

Up to now, about 50 lunar meteorites from Antarctica, Africa, and Australia have been identified and investigated. These meteorites were analyzed for the isotopic composition of noble gases, oxygen, strontium, lead, and other chemical elements. Their ages were determined mainly by the rubidium–strontium and traditional uranium–lead and potassium–argon methods. However, only Mayer *et al.* (1996) managed

to date single grains of accessory zircon by ion microprobe techniques. The goal of our study was to evaluate the possibility of determining the isotopic age of single zircon grains from the new lunar meteorite Dhofar 025 using a SHRIMP II ion microprobe (housed in the Center for Isotopic Research, Karpinskii All-Russia Research Institute of Geology).

The meteorite is a brownish gray fragment weighing 751 g. It was found on March 5, 2000 in a desert in the

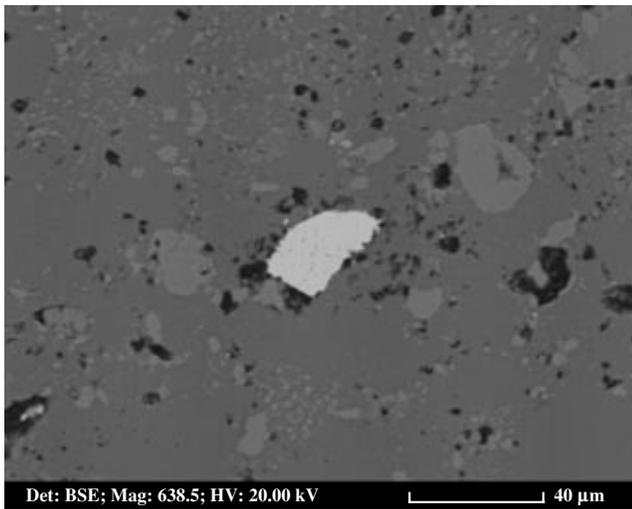


Fig. 1. Back-scattered electron image of the zircon grain studied.

Dhofar region (18°24.2' N and 54°09' E) of Oman. Dhofar 025 is an anorthosite regolith breccia with numerous clasts of a highland origin. Its matrix hosts fragments of rocks and minerals and contains abundant glass. The rock-forming minerals are plagioclase (An_{95-96}), olivine (Fo_{70-78} and Fe/Mn = 91–97 at.), and pyroxene (En_{74-84} , Wo_{3-6} , and Fe/Mn = 50–70 at.) (Cahill *et al.*, 2001). The accessory minerals are ilmenite, silica phases, zircon, Ti-rich aluminous chromite, troilite, and FeNi metal. Schlieren and vesicles are common. There is no molten crust, and products of terrestrial alteration were found in fractures impregnating the margins of the meteorite.

In order to determine the U–Pb age of single accessory zircon grains from Dhofar 025 by the ion microprobe method, an epoxy mount with a polished section of Dhofar 025 was preliminarily examined by means of reflected light optical and scanning electron microscopy. Among several zircon grains found in the meteorite, only one, 20 × 30 μm in size, appeared to be suitable for isotopic age determination. The other zircon grains were smaller in size.

The epoxy mount with the polished section was coated with gold (about 100 Å thickness) in an Emitech 450 vacuum cathode coater. The cathode luminescence imaging of the selected grain on a CamScan MX2500 electron microscope revealed the internal structural homogeneity of the grain. Ion currents were measured on the SHRIMP II mass spectrometer using a secondary electron multiplier operated in a mass scanning mode. Secondary ions were sputtered from the surface of the zircon grain by bombardment with primary O_2^- ions (Williams, 1998). The primary beam was focused using a 70 μm Kohler aperture to an elliptical spot 10 × 15 μm in size. The ion current of the primary beam was 0.9 nA. The secondary ions were accelerated to 10 keV. The width of the exit slit of the ion source was

80 μm, which provided a section of the beam of only 30 μm. Together with a 100-μm wide entrance slit of the amplifier, this yielded a mass resolution of more than 5200, which eliminated all possible isobaric interferences in the mass range studied.

A two-minute procedure of sample surface cleaning with a rocking primary beam was employed before each analysis to remove possible surface contamination (e.g., Pb) from the analytical spot area. The following ions were measured: $^{196}(Zr_2O^+)$, $^{204}Pb^+$, background (204.2 AMU), $^{206}Pb^+$, $^{207}Pb^+$, $^{208}Pb^+$, $^{238}U^+$, $^{248}ThO^+$, and $^{254}UO^+$. The masses of $^{196}(Zr_2O^+)$ and $^{254}UO^+$ were also used during analysis for the adjustment of the center of the ion current peak. Five spectra of the aforementioned masses were registered for each analysis. Zircon SL13 was used as a concentration standard (accepted U concentration is 238 ppm). Zircon TEMORA was used for the standardization of uranium–lead ratios. Zircon TEMORA was extracted from the Middledale leucocratic gabbro (Lahlan fold belt, eastern Australia) (Black and Kamo, 2003). Numerous investigations of many years of this zircon by both SHRIMP and classic isotope dilution (ID-TIMS) methods have shown that it is very concordant and homogeneous with respect to the uranium–lead ratio, i.e., it can be regarded as exemplifying a closed uranium–lead system. Because of the small size of the zircon grain (Fig. 1), only two series of measurements were conducted, and the size of the crater produced by the primary ion beam appeared to be comparable with the size of the grain. The results were processed using the SQUID v1.08 and ISOPLOT/Ex 3.0 programs (table).

The SQUID and ISOPLOT/Ex (K. Ludwig, www.bgc.org) programs are used to obtain a set of isotopic U–Pb ages from measured intensities with a comprehensive error estimate for each point of interest in the crystal studied and determine the concentrations of uranium, lead, and thorium.

The results are plotted in the Ahrens–Wetherill diagram (Fig. 2). Ages calculated from the analytical points appeared to be discordant. They can be interpreted in different ways.

It was experimentally shown that meteoritic material experiences in deserts various physical and chemical alterations, which are collectively termed weathering. The influence of climatic and geomorphologic factors promotes oxidation and hydrolysis processes in the material of many meteorites (Steltzner *et al.*, 1999). A two-stage history was proposed for meteorite weathering, with a rapid initial stage followed by a slower oxidation stage (Bland *et al.*, 1996). Some meteorites are strongly contaminated by terrestrial strontium and barium, which hampers the determination of their exposure ages. The intensity of weathering processes is also suggested by the capture of atmospheric noble gases into the structure of meteorites. For instance, we demonstrated experimentally that the concentrations of implanted terrestrial noble gases in the lunar meteorites

Results of the SHRIMP II U–Th–Pb isotopic dating of the zircon grain from the lunar meteorite Dhofar 025

Point	U, ppm	Th, ppm	$^{232}\text{Th}/^{238}\text{U}$	$^{206}\text{Pb}^*$, ppm	$^{206}\text{Pb}_c$, %	Atomic isotope ratio				Apparent age, Ma			
						$^{206}\text{Pb}^*/^{238}\text{U}$	$^{207}\text{Pb}^*/^{235}\text{U}$	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	$^{208}\text{Pb}^*/^{232}\text{Th}$	$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{232}\text{Th}$
ZR-MET2	48	18	0.38	34.2	0.18	0.823 ± 0.009	61.04 ± 0.98	0.538 ± 0.006	0.204 ± 0.008	3871 ± 32	4191 ± 35	4349 ± 18	3760 ± 160
ZR-MET1	51	19	0.38	36.9	0.57	0.831 ± 0.010	62.60 ± 1.06	0.547 ± 0.007	0.214 ± 0.015	3899 ± 34	4216 ± 36	4373 ± 18	3930 ± 280

Note: The errors correspond to 1σ ; Pb^* and Pb_c denote radiogenic and common captured lead, respectively; correction for common lead was introduced on the basis of ^{204}Pb ; and the probable error of standard calibration was 0.61%.

Dhofar 305, Dhofar 307, Dhofar 733, and Dhofar 731 are significantly higher than the concentrations of primary solar components (Shukolyukov *et al.*, 2004). Therefore, it could have been supposed that the U–Pb isotope geochemical system of the zircon studied was disturbed by interaction with water during the prolonged terrestrial residence of the meteorite (several tens of thousand years) under abrupt diurnal temperature variations in a desert environment. With such a model, the discordia line through the origin and experimental points yields an upper intercept age of 4360 ± 27 Ma. This value is identical to isotopic ages of 4300–4400 Ma obtained previously for some lunar rocks both returned by *Luna* and *Apollo* missions and sampled as lunar meteorites (e.g., Papanastasiou and Wasserburg, 1976; Dash *et al.*, 1987; Carlson and Lugmair, 1988). However, zircon is very resistant to chemical attacks. It is therefore rather improbable that the U–Pb isotopic system of zircon was disturbed under desert conditions. It is also questionable that the impact that ejected this rock from the Moon about 500 thousand years ago (Nishiizumi and Caffee, 2001), i.e., in the zero time, was accompanied by a temperature increase sufficiently high to disturb the U–Pb isotopic system. Therefore, the age of zircon crystallization (formation) should be higher than 4360 Ma.

Petrographic observations suggest the following scenario for the history of the zircon and material of the Dhofar 025 meteorite. Since the zircon is a fragment that occurred in the molten matrix of the breccia together with other mineral and rock fragments, it could not crystallize directly from the melt cementing the fragments, although some interaction with it could take place. Consequently, the zircon was formed from another melt, older than the melt of the breccia matrix. This melt had most likely a granitic composition, because all findings of lunar zircon were associated with granitic rocks (e.g., Meyer *et al.*, 1996). This was event no. 1 in the history of the zircon grain. It had to be followed by an impact event, which caused initial rock fragmentation, and the same or another event (or several events) resulted in the lithification of the heter-

ogeneous crushed material to form the Dhofar 025 breccia. This high-temperature episode in the history of the zircon is referred to as event no. 2, i.e., the event of breccia formation. Finally, event no. 3 was the impact that ejected the rock from the Moon about 500 thousand years ago, but this event could hardly cause melting in the breccia material.

As to the quantitative estimation of the timing of the aforementioned events, the upper limit of zircon age is reasonably constrained by the age of the Moon (4.5 Ga). An age identical to the age of the Moon was previously obtained for some lunar meteorites and lunar samples by the traditional U–Th–Pb method

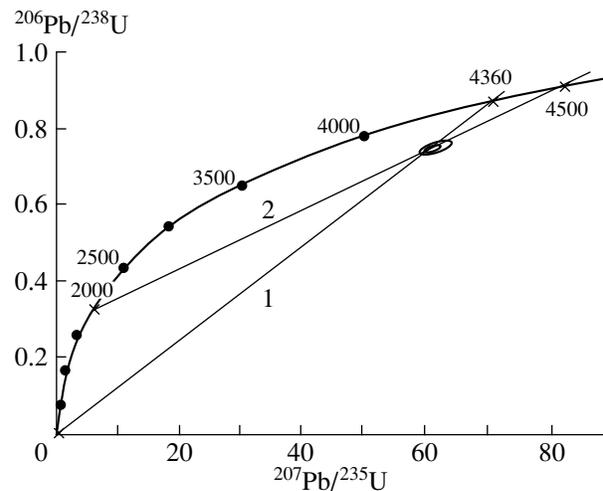


Fig. 2. Ahrens–Wetherill diagram with the measurement points. Two discordia lines correspond to two possible interpretations of our results. (1) The lower concordia intercept is 0 ± 300 Ma and the upper intercept is 4360 ± 27 Ma, which is the minimum age of the meteorite. (2) The lower concordia intercept is about 2000 Ma, which corresponds to the duration of meteorite irradiation on the lunar surface (cosmic-ray exposure age of the meteorite) and the time from the moment of breccia formation by a meteorite impact on the Moon; and the upper intercept is 4500 ± 30 Ma corresponding to the age of the oldest lunar meteorites.

(Takahashi and Masuda, 1987; Nakamura *et al.*, 1986; Wasserburg and Tera, 1974; Papanastasiou and Wasserburg, 1976, 1974; Oberli *et al.*, 1978; Wasserburg *et al.*, 1980). In such a case, using this value and the position of the experimental points in the Ahrens–Wetherill diagram, the lower concordia intercept yields the age of breccia formation as about 2000 Ma (this is the upper limit, because the zircon cannot be older than the age of the Moon). It is important that this value is supported by the cosmic-ray exposure age of Dhofar 025 calculated from cosmogenic noble gas isotopes, which is also close to 2000 Ma (Shukolyukov *et al.*, 2002), whereas common (not lunar or Martian) stony meteorites yield exposure ages of several millions to tens of millions of years. The very high exposure age is regarded as a result of the prolonged irradiation of the Dhofar 025 material on the lunar surface rather than the time of meteorite occurrence in interplanetary space. It is therefore reasonable to believe that the disturbance of the U–Pb system of zircon from the Dhofar 025 meteorite occurred during the formation of the breccia through a large meteorite impact and its transfer toward the lunar surface about 2000 Ma ago. Starting from this moment, cosmogenic noble gas isotopes have accumulated in this rock. Two conclusions can be drawn from these constraints.

(1) Felsic rocks were formed during the earliest stages of the history of the lunar crust (4360–4500 Ma).

(2) The breccia was formed \approx 2000 Ma ago, i.e., it is much younger than highland breccias from the near side of the Moon, which were produced by a lunar planetary cataclysm (intense meteorite bombardment) 3900 Ma ago (Tera *et al.*, 1974).

Consequently, Dhofar 025 probably represents a unique rock from the far side of the Moon.

ACKNOWLEDGMENTS

The authors thank A.V. Antonov and N.V. Rodionov (Center for Isotopic Research, Karpinskii All-Russia Research Institute of Geology) for their considerable help in high-precision measurements. This study was financially supported by the Russian Foundation for Basic Research, project nos. 04-05-64811 and 03-05-20008 BNTS-a.

REFERENCES

1. L. P. Black and S. L. Kamo, "TEMORA: A New Zircon Standard for U–Pb Geochronology," *Chem. Geol.* **200**, 155–170 (2003).
2. P. A. Bland, F. J. Berry, T. B. Smith, *et al.*, "The Flux of Meteorites to the Earth and Weathering in Hot Desert Ordinary Chondrite Finds," *Geochim. Cosmochim. Acta* **60**, 2053–2059 (1996).
3. J. Cahill, B. A. Cohen, L. A. Taylor, and M. A. Nazarov, "Mineralogy and Petrology of the 'New' Lunar Meteorite Dhofar 025," *Lunar Planet. Sci.* **XXXII**, 1840–1842 (2001).
4. R. W. Carlson and G. W. Lugmair, "The Age of Ferroan Anorthosite 60025: Oldest Crust on a Young Moon?," *Earth Planet. Sci. Lett.* **90** (2), 119–130 (1988).
5. E. J. Dash, C.-Y. Shih, B. M. Banzal, *et al.*, "Isotopic Analysis of Basaltic Fragments from Lunar Breccia 14321: Chronology and Petrogenesis of Pre-Imbrium Mare Volcanism," *Geochim. Cosmochim. Acta* **60**, 3241–3254 (1987).
6. C. Meyer, I. S. Williams, and W. Compston, "Uranium–Lead Ages for Lunar Zircons: Evidence for a Prolonged Period of Granophyre Formation from 4.32 to 3.88 Ga," *Meteorit. Planet. Sci.* **31** (3), 370–387 (1996).
7. N. Nakamura, D. M. Unruh, M. Tatsumoto, and T. Fujiwara, "REE Abundances and Pb–Pb Isotopic Systematics of the Lunar Meteorite, Yamato-82192," *Proc. Lunar Planet. Sci. Conf.* **17**, 601–610 (1986).
8. K. Nishiizumi and M. W. Caffee, "Exposure Histories of Lunar Meteorites Dhofar 025, 026, and Northwest Africa 482," *Meteorit. Planet. Sci.* **36**, A148 (2001).
9. F. Oberli, M. T. McCulloch, F. Tera, *et al.*, "Early Lunar Differentiation Constraints from U–Th–Pb and Rb–Sr Model Ages," *Proc. Lunar Planet. Sci. Conf.* **9**, 832–834 (1978).
10. D. A. Papanastasiou and G. J. Wasserburg, "Rb–Sr Age of Troctolite 76535," *Proc. Lunar Sci. Conf.* **7**, 2035–2054 (1976).
11. D. A. Papanastasiou and G. J. Wasserburg, "The Age of the Luna-16 Basalt and a Model Age of the Lunar Regolith," in *The Lunar Regolith from the Plenty Sea*, Ed. by A. P. Vinogradov (Nauka, Moscow, 1974), pp. 471–477 [in Russian].
12. Yu. A. Shukolyukov, M. A. Nazarov, and L. Shul'ts, "Noble Gases in Two Recently Found Lunar Meteorites: Dhofar 025 and Dhofar 026," *Geokhimiya*, No. 12, 1251–1263 (2002) [*Geochem. Int.* **40** (12), 1127–1138 (2002)].
13. Yu. A. Shukolyukov, M. A. Nazarov, and U. Ott, "Noble Gases in New Lunar Meteorites from Oman: Irradiation History, Trapped Gases, and Cosmic Ray Exposure and K–Ar Ages," *Geokhimiya*, No. 11, 1–18 (2004) [*Geochem. Int.* **42** (11), 1001–1017 (2004)].
14. Th. Stelzner, K. Heide, A. Bischoff, *et al.*, "An Interdisciplinary Study of Weathering Effects in Ordinary Chondrites from the Acfer Region, Algeria," *Meteorit. Planet. Sci.* **34**, 787–794 (1999).
15. K. Takahashi and A. Masuda, "Two Lunar Meteorites, Yamato 791197 and 82192: REE Abundances and Geochronological Dating," *Mem. Nat. Inst. Polar Res., Spec. Issue* **46**, 105–110 (1987).
16. F. Tera, D. A. Papanastasiou, and G. L. Wasserburg, "The Lunar Time Scale and a Summary of Isotopic Evidence for a Terminal Lunar Cataclysm," *Lunar Sci.*, 792–794 (1974).
17. G. J. Wasserburg and F. Tera, "U–Th–Pb Analyses of the Regolith from the Plenty Sea," in *The Lunar Regolith from the Plenty Sea*, Ed. by A. P. Vinogradov (Nauka, Moscow, 1974), pp. 478–487 [in Russian].
18. G. J. Wasserburg, D. A. Papanastasiou, M. T. McCulloch, *et al.*, "Samples by Luna-24: Petrology, Chemistry, Age, and Irradiation History," in *The Lunar Regolith from the Crisis Sea*, Ed. by V. L. Barsukov (Nauka, Moscow, 1980), pp. 219–230 [in Russian].
19. I. S. Williams, "U–Th–Pb Geochronology by Ion Microprobe," in: *Applications in Microanalytical Techniques to Understanding Mineralizing Processes*, *Rev. Econ. Geol.*, No. 7, 1–35 (1998).