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The production rate of cosmogenic ^{38}Ar from calcium in terrestrial pyroxene

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Abstract

Pyroxene separated from dolerite surfaces, which were exposed to cosmic ray irradiation for millions of years in the Antarctic Dry Valleys, contains considerable amounts of cosmogenic ^{38}Ar , as evident from $^{38}\text{Ar}/^{36}\text{Ar}$ ratios up to 0.2887 (air: 0.1880). In five out of eight mineral separates the concentrations of K, Ti and Cl are low enough to enable us to deduce the terrestrial production rate of ^{38}Ar from Ca (the remaining relevant target element) by relating cosmogenic ^{38}Ar concentrations to ^3He and ^{21}Ne exposure ages. Correlations of cosmogenic ^{38}Ar (normalized to Ca) to total ^3He and to cosmogenic ^{21}Ne normalized to Mg, respectively, are excellent. However, various currently used methods to derive the ^3He and ^{21}Ne production rates in pyroxene lack consistency. Depending on the method chosen, the ^{38}Ar production rate derived here ranges between $(191 \pm 21) \text{ atoms (g Ca)}^{-1} \text{ a}^{-1}$ and $(254 \pm 28) \text{ atoms (g Ca)}^{-1} \text{ a}^{-1}$ at sea level (standard atmospheric pressure) and high latitude. A more accurate value may be calculated from our data as soon as the He and Ne production rates from pyroxene are known more reliably. Our production rate determination is largely independent of past geomagnetic field variations and of the scaling method used.

Keywords: terrestrial cosmogenic nuclides; surface exposure dating; argon; helium; neon; production rates

1. Introduction

Nuclear interactions of cosmic ray particles with terrestrial surface matter produce a variety of “cosmogenic” nuclides, some of which can be used to decipher surface exposure histories of rocks and, thereby, date surface features or quantify denudation rates [e.g. 1,2]. For such studies the radionuclides ^{10}Be , ^{26}Al and ^{36}Cl , with half lives of 1.5, 0.7 and 0.3 Ma, respectively, and the stable noble gas isotopes ^3He and ^{21}Ne have mainly been used in the last two decades. More recently, ^{14}C has been added as a reliable tool to in situ cosmogenic nuclide studies [3], extending the range of applications owing to its relatively short half-life of 5730 a. However, there are still a number of nuclides which have proven invaluable in extraterrestrial cosmic ray exposure studies, but have not been applied to terrestrial rocks so far, due to low production rates or high background concentrations for instance. One of these nuclides is ^{53}Mn ($t_{1/2} = 3.7$ Ma), whose terrestrial production rate has recently been determined [4]. Another one is ^{38}Ar , a stable noble gas isotope which is mainly produced by spallation of the target elements K and Ca. Therefore, it could provide a complementary alternative to conventionally used nuclides especially in K- and Ca-rich minerals which do not quantitatively retain the lighter noble gases and are not suitable for ^{10}Be and ^{26}Al dating, such as feldspar.

The presence of cosmogenic ^{38}Ar in terrestrial samples was first shown by Renne et al. [5], who studied mainly apatite, as well as fluorite, sphene and plagioclase. They did, however, not succeed in deriving a consistent ^{38}Ar production rate. Knight et al. [6] reported more cosmogenic Ar data, involving additional minerals such as diopside, clinopyroxene, and garnet, and estimated an ^{38}Ar production rate from Ca of ~ 100 atoms $(\text{g Ca})^{-1} \text{ a}^{-1}$ at sea level and high latitude. This value is a factor of 2 lower than the theoretical estimate of Lal [7] of 200 atoms $(\text{g Ca})^{-1} \text{ a}^{-1}$.

One of the main obstacles to accurate determinations of cosmogenic ^{38}Ar in terrestrial rocks is the high background of atmospheric Ar, corresponding to ~ 6 ppm ^{38}Ar in air, while those contributions are two and six orders of magnitude less for ^{21}Ne and ^3He , respectively. Another major difficulty in getting a reliable ^{38}Ar production rate is the fact that cosmogenic Ar is not only produced by spallation of K, Ca and, to a minor extent, Ti and Fe, but also by thermal neutron capture of ^{35}Cl , producing ^{36}Cl which decays to ^{36}Ar with a half life of 3×10^5 a. The production systematics of neutron capture reactions is considerably more complex than that of spallation reactions [e.g. 8], so that an accurate assessment of the contribution to the total ^{36}Ar production is difficult for Cl-rich minerals. Therefore it is essential to choose minerals with low enough Cl concentrations in order to resolve the cosmogenic Ar production rate from major target elements such as Ca or K.

In this paper we report concentrations of cosmogenic Ar in pyroxene minerals separated from dolerites which were exposed to cosmic ray irradiation for several million years in the Antarctic Dry Valleys [9]. The pyroxenes are low in both K and Cl, enabling us to deduce the ^{38}Ar production rate from Ca by relating the cosmogenic ^{38}Ar concentrations to ^3He and ^{21}Ne exposure ages.

2. Samples and experimental method

Boulder and bedrock samples were taken from Ferrar Dolerite surfaces in the Antarctic Dry Valleys region. Information on sampling and geological setting can be found in [9] and references therein. Eight samples were selected for this study based on their long surface residence times of several million years at elevations of up to 2600 m [9], which make them well-suited for a precise determination of cosmogenic ^{38}Ar excesses. Erosion rates on the sampled surfaces were below a few tens of centimeters per Ma [9], and the consistency

between the concentrations of stable ^3He and radioactive ^{53}Mn in these samples indicates continuous exposure without significant periods of burial by sediment, ice, or snow [4]. Beyond that, both erosion and burial do not affect the concentration ratios of the stable cosmogenic nuclides ^3He , ^{21}Ne and ^{38}Ar on which our production rate determination is based. An influence on the $^{38}\text{Ar}/^{36}\text{Ar}$ ratio could possibly occur if the burial was recent enough to affect the secular equilibrium between ^{36}Cl production and decay. Also, snow or ice cover might change the thermal neutron flux in the rock and, therefore, the production rate of ^{36}Ar via $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$, but given the low Cl concentrations in our samples (see section 3.1) this is not a significant issue.

Except for samples NXP and 318, pyroxene separates were not left in large enough quantity from the earlier investigation, therefore we prepared new separates from the original whole rock material by etching in concentrated HCl, applying magnetic separation and density separation techniques, and handpicking. The quality of the mineral separates was inspected by X-ray diffraction (XRD) analysis, though only after noble gas analysis in some cases. It turned out that three separates (403, 444, 446) contained less than 80% pyroxene, making their results less reliable. Major element compositions were determined by X-ray fluorescence (XRF) analysis, using splits of ~400 mg of each separate. Cl concentrations were checked by microprobe analysis at the University of Kiel.

The concentrations and isotopic compositions of all stable noble gases have been determined in the noble gas laboratory of GFZ Potsdam. Samples of ~0.6 to 1.1 g were wrapped in Al or Mo foil and placed in the sample carousel above the extraction furnace, where they were baked for about one week at 100°C. Noble gases were extracted in two or three heating steps up to 1750°C, in order to achieve a better separation of atmospheric and radiogenic from cosmogenic components. Analytical blanks were quite variable, depending on the extraction temperature, the type of foil used, and the history of the crucible; they were monitored regularly between sample measurements. In units of $10^{-12} \text{ cm}^3 \text{ STP}$, the blank ranges were 8-

30 for ^4He , 0.5-6 for ^{20}Ne , 2-23 for ^{36}Ar , 0.05-0.35 for ^{84}Kr , and 0.01-0.12 for ^{132}Xe , with atmospheric isotopic compositions. In one case (sample NXP), the He blank was considerably higher ($\sim 250 \times 10^{-12} \text{ cm}^3 \text{ STP } ^4\text{He}$) with a $^3\text{He}/^4\text{He}$ ratio of $\sim 1 \times 10^{-5}$, possibly due to a tiny leak not affecting the heavier noble gases or to passive degassing of He-rich MORB glasses loaded in the same sample suite, but still the ^3He blank was five orders of magnitude less than the ^3He in the sample. More details about the experimental procedure and the methods of data reduction can be found in [10].

A recent redetermination of the isotopic composition of Ar [11] has yielded somewhat higher ratios of $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{38}\text{Ar}/^{36}\text{Ar}$ than the classic ones given by Nier [12] (298.56 ± 0.31 vs. 295.5 ± 0.5 and 0.1885 ± 0.0005 vs. 0.1880 ± 0.0003 , respectively). The data presented here are still based on the earlier determination because all our mass spectrometer calibrations have been performed using those values. Since we determine the instrumental mass discrimination independently for the $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{38}\text{Ar}/^{36}\text{Ar}$ ratios, a change in the underlying atmospheric values would only marginally affect the results of this study: Using the composition of [11] instead of [12], all $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{38}\text{Ar}/^{36}\text{Ar}$ ratios would come out 1.04% and 0.27% higher than reported here, respectively, while the concentrations of cosmogenic ^{38}Ar would decrease by $\sim 0.77\%$, which is about an order of magnitude less than the analytical uncertainties.

3. Results

The concentrations and isotopic compositions of He, Ne and Ar are presented in Table 1. Kr and Xe data are given in the background data set (Tables A1 and A2); they show atmospheric compositions in general except for a few contributions of fission Xe. The only case where cosmogenic ^{124}Xe and ^{126}Xe excesses are indicated is the 1700°C step of sample 446. All error limits given in this paper correspond to 95% confidence level.

3.1. Chemical and mineralogical composition

Table 2 gives the results of XRF and XRD analyses. It shows that the applied mineral separation procedures did not yield clean enough pyroxene separates for three out of the eight samples, as pyroxene contents are <80% for 403, 444, and 446. These three samples also have elevated concentrations of elements that are not expected to be abundant in pyroxene: Na, Al, K, and Ti (Table 2). The difficulty of obtaining pure pyroxene separates from Ferrar dolerite has been reported before [13,14]. The ^{38}Ar production rate will be derived from the five pure separates (NXP, 435, 439, 464, 318) only, which contain at least 92% pyroxene and have K contents of <0.02% (Table 2). The impure samples will only be used for reference.

Cl concentrations have been determined for a few spots in electron microprobe mounts of six pyroxene separates. Due to the small number of measurements the statistical errors are quite large, but this method allowed us to establish an upper limit of ~100 ppm Cl. We assume that the Cl content of the other two samples is equally small and will show below that such concentrations do not affect the accuracy of our production rate determination.

3.2. Helium and neon

There are distinct differences in how prominent the ^3He , ^{21}Ne and ^{22}Ne excesses are, depending on the temperature fraction and on the concentration of trapped (or radiogenic) ^4He and ^{20}Ne . $^3\text{He}/^4\text{He}$ ratios vary from 0.859×10^{-6} to 331×10^{-6} ; they typically decrease with increasing temperature, confirming the predominant release of cosmogenic He from pyroxene below 600°C [15]. To calculate the concentration of cosmogenic ^3He , the contributions of trapped and radiogenic He have to be known. The isotopic composition of trapped He was checked by crushing sample 444 (the sample with the lowest cosmogenic ^3He concentration) in vacuo, yielding a $^3\text{He}/^4\text{He}$ ratio of $0.112 \pm 0.010 \times 10^{-6}$ (Table 1). This value is probably an upper limit, since some release of cosmogenic He during crushing cannot be excluded [16].

Radiogenic He, which is expected to be present in the crystal lattice, will have a much lower $^3\text{He}/^4\text{He}$ ratio; Margerison et al. [13] estimated $\sim 0.003 \times 10^{-6}$ for pyroxene from the the same Ferrar dolerite lithology. They also determined the total (non-cosmogenic) ^3He concentration in a shielded Ferrar dolerite pyroxene to 6.8×10^6 atoms/g [13], which corresponds to $\sim 1\%$ of total ^3He in sample 444 and less than that in all other samples. We conclude that non-cosmogenic ^3He fractions are negligible and report total ^3He as the cosmogenic component in Table 3.

$^{22}\text{Ne}/^{20}\text{Ne}$ and $^{21}\text{Ne}/^{20}\text{Ne}$ ratios are higher than atmospheric throughout, ranging from 0.1043 to 0.951 and from 0.00443 to 0.801, respectively, and generally increasing with extraction temperature, again in agreement with the degassing systematics reported in [15]. Trapped Ne is very similar to atmospheric, as shown by the crushing extraction of sample 444. The small excess in $^{21}\text{Ne}/^{20}\text{Ne}$ may be due to a minor release of cosmogenic ^{21}Ne by crushing; it corresponds to $\sim 0.2\%$ of the total cosmogenic ^{21}Ne in this sample. The Ne three-isotope plot (Fig. 1) shows that the data are well aligned along the “spallation line”, i.e. the mixing line between atmospheric and cosmogenic Ne typical for pyroxene [9]. Deviations from the spallation line occur only for two of the impure pyroxene separates with significant contributions of quartz and feldspar (403 and 446; Table 2). Hence it is justified to assume two-component mixtures of atmospheric and cosmogenic Ne in all samples for calculating the cosmogenic ^{21}Ne concentrations, which are reported in Table 3.

In most cases, the cosmogenic ^3He and ^{21}Ne concentrations obtained here agree within error limits with those determined at ETH Zurich [9] and the Lamont-Doherty Earth Observatory [4], respectively, which were reported earlier (Table 3). Slight deviations may be due to differences in target element chemistry among different pyroxene separates from the same rocks. Substantial deficiencies of both ^3He and ^{21}Ne with regard to the data of [4] and [9] occur for samples 403 and 446, with combined plagioclase and quartz fractions of 28 and 77 %, respectively (Table 2). The ^3He and ^{21}Ne deficiencies are thus easily explained by

diffusion loss from such less retentive minerals. On the other hand, minor deficiencies of ^3He in samples 435, 439, and 464 in the data of [9] compared to those reported here may indicate a poorer quality of the earlier separates in case of those samples.

3.2. Argon

In general, $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are only moderately elevated over the atmospheric reference value of 295.5 (Table 1) except for the samples 403 and 446 with higher K contents (Table 2).

$^{38}\text{Ar}/^{36}\text{Ar}$ ratios range from close to atmospheric (0.1880) up to a maximum of 0.2887 ± 0.0018 , clearly indicating the presence of cosmogenic ^{38}Ar excesses in most heating steps of all samples. The composition of trapped Ar is assumed to be atmospheric in terms of the $^{38}\text{Ar}/^{36}\text{Ar}$ ratio, since no terrestrial reservoirs are known with a different composition, and nuclear processes other than those caused by cosmic ray irradiation can only change this ratio markedly in minerals that are very rich in U and Th [17]. However, isotopic mass fractionation, either related to the gas trapping process or as an unresolved instrumental artifact, might constitute a potential problem in assigning the atmospheric value to the $^{38}\text{Ar}/^{36}\text{Ar}$ ratio of the non-cosmogenic Ar fraction. Figure 2 shows a compilation of $^{38}\text{Ar}/^{36}\text{Ar}$ ratios in samples expected to be free of cosmogenic Ar, as determined during the relevant period in 2005 with either of the two noble gas lines at the GFZ Potsdam. The compilation shows both crushing and pyrolysis extractions of various minerals. Despite some variation in detail, the data are generally consistent with the atmospheric value within uncertainties. In particular, the pyrolysis data for olivines, pyroxenes and one amphibole obtained in the same line as for most of the Dry Valleys pyroxenes (line B was used for sample NXP and the crushing extraction of 444 only) yield an error-weighted mean of 0.18779 ± 0.00027 . Therefore, it seems justified to us to use the uncorrected atmospheric value of 0.1880 as a reference for the non-cosmogenic Ar composition. To assess the concentrations of

cosmogenic ^{38}Ar , however, the $^{38}\text{Ar}/^{36}\text{Ar}$ production ratio must be known also. This issue is discussed in the next section.

4. Discussion

4.1. Production systematics of cosmogenic argon

Cosmogenic Ar in terrestrial surface rocks is mainly produced by neutron-induced spallation of K and Ca nuclei and, to a minor extent, of Ti and Fe. The relative production rates from these elements have been extensively studied in meteorites and lunar material [e.g. 18,19,20]; those estimated by Hohenberg et al. [19] for 500 g cm^{-2} shielding depth beneath the lunar surface are shown in Table 4. At that depth, cosmogenic nuclide production on the moon is dominated by neutrons similar to the conditions on the terrestrial surface. In comparison, the atmospheric shielding depths of the samples used in this study vary between ~ 720 and 900 g cm^{-2} . More recent model calculations on relative production rates of Ar isotopes from different target elements, in particular adapted to terrestrial surface conditions, are not available to our knowledge. According to Table 4, cosmogenic production of ^{40}Ar is negligible. Production of ^{36}Ar and ^{38}Ar from Ti and Fe is small as well, $<1\%$ of that from Ca for a pyroxene separate with $\sim 10\%$ Ca, $\sim 10\%$ Fe, and $\sim 0.2\%$ Ti (cf. Table 2). Since the relative contributions of ^{36}Ar and ^{38}Ar from K and Ca vary by less than 5% below 40 g cm^{-2} on the moon, while those from Ti and Fe decrease steadily with depth [19], it is reasonable to assume that the production ratios on earth will be similar.

Among spallation reactions, only the production of ^{36}Ar and ^{38}Ar from K and Ca may thus be relevant for our samples. K concentrations are $<0.02\%$ in the five pure pyroxene separates studied here, at least a factor of 400 lower than Ca concentrations (Table 2). Therefore, spallation production from K can safely be neglected given that normalized ^{38}Ar production

rates from K are similar to those from Ca. Thermal and epithermal neutron capture of Cl is, however, another mechanism eventually leading to the production of Ar isotopes. In particular, ^{35}Cl has a rather high cross section of 44 barn for thermal neutron capture, producing ^{36}Cl which decays to ^{36}Ar with a half life of 3×10^5 a. The cross section of the corresponding reaction with ^{37}Cl is only 0.4 barn, making thermal neutron capture production of ^{38}Ar (by decay of ^{38}Cl with a half life of 37 min) insignificant. According to Phillips et al. [8], the upper limit of ~ 100 ppm Cl in our samples (section 3.1) corresponds to a sea level – high latitude production rate of roughly $3 \text{ at g}^{-1} \text{ a}^{-1}$ of ^{36}Cl in a basalt-like matrix, and therefore (allowing enough time for ^{36}Cl decay) $\sim 3 \text{ at g}^{-1} \text{ a}^{-1}$ of ^{36}Ar .

4.2. Cosmogenic ^{38}Ar concentrations

The cosmogenic ^{38}Ar concentrations ($^{38}\text{Ar}_c$) were calculated according to the equation

$$^{38}\text{Ar}_c = \frac{(^{38}\text{Ar}/^{36}\text{Ar})_{\text{sp}} \{ ^{36}\text{Ar}_{\text{tot}} [(^{38}\text{Ar}/^{36}\text{Ar})_{\text{tot}} - (^{38}\text{Ar}/^{36}\text{Ar})_{\text{air}}] + ^{36}\text{Ar}_{\text{Cl}} (^{38}\text{Ar}/^{36}\text{Ar})_{\text{air}} \}}{(^{38}\text{Ar}/^{36}\text{Ar})_{\text{sp}} - (^{38}\text{Ar}/^{36}\text{Ar})_{\text{air}}} \quad (1)$$

where indices tot and sp mean total and spallation, respectively, and $^{36}\text{Ar}_{\text{Cl}}$ is the ^{36}Ar concentration produced by thermal and epithermal neutron capture of ^{35}Cl and subsequent β^- decay of ^{36}Cl . This equation involves the assumption that the contribution of ^{38}Ar produced from Cl is negligible.

For the spallation production ratio $(^{38}\text{Ar}/^{36}\text{Ar})_{\text{sp}}$, we used a value of 1.5 ± 0.2 as derived for the target element Ca in well-shielded lunar material [19] (cf. Table 4). The error limit is a conservative assumption including other estimates of that ratio (1.4 [5] and 1.7 [18]); in any case the influence of the $(^{38}\text{Ar}/^{36}\text{Ar})_{\text{sp}}$ uncertainty on the overall accuracy of $^{38}\text{Ar}_c$ is minor compared to those of $^{36}\text{Ar}_{\text{tot}}$ and $(^{38}\text{Ar}/^{36}\text{Ar})_{\text{tot}}$. The $(^{38}\text{Ar}/^{36}\text{Ar})_{\text{sp}}$ ratio of 1.5 is only applicable if equilibrium between production and decay of ^{36}Cl has been attained, i.e. for rocks with a surface exposure age of at least ~ 1 Ma (~ 3 half lives of ^{36}Cl). This condition is fulfilled for all of our samples, and more recent burial which could change the equilibrium between ^{36}Cl

production and decay is not indicated either [4]. For younger samples, however, a correction factor containing the branching ratio $P(^{36}\text{Cl})/P(^{36}\text{Ar})$ from Ca spallation (estimated at around 1:1 [5]) and depending on the exposure time would have to be applied (cf. equation (2) in [5]). To assess the contributions of $^{36}\text{Ar}_{\text{Cl}}$, we used a sea level production rate of $(2 \pm 2) \text{ at g}^{-1} \text{ a}^{-1}$, which is a conservative estimate based on the Cl concentrations of $<100 \text{ ppm}$ in our samples and the production rate value reported in [8] (see section 4.1). The sea level value was scaled to the sampling site elevations and multiplied by the exposure ages of the samples (see next section for details of scaling and exposure age calculation), yielding $^{36}\text{Ar}_{\text{Cl}}$ concentrations which are at most 0.3% of total ^{36}Ar . The resulting $^{38}\text{Ar}_c$ concentrations are shown in Table 3. If we had neglected the contributions from $^{36}\text{Ar}_{\text{Cl}}$, they would be lower by less than 5%, i.e. well within error limits.

In Fig. 3, $^{38}\text{Ar}_c$ concentrations normalized to the Ca content are plotted versus $^3\text{He}_{\text{tot}}$ (A) and versus $^{21}\text{Ne}_c$ normalized to Mg (B), respectively. The normalizations have been chosen because $^{38}\text{Ar}_c$ is produced exclusively from Ca in these samples, as argued above, while ^3He production depends only weakly on the chemical composition. For ^{21}Ne , the production from Si is important also, but that from Mg is dominant [e.g. 9], and Mg concentrations vary significantly more between samples (Table 2). Na and Al do not contribute much due to their low concentrations (Table 2). The normalization to Mg is thus a suitable way to take account of the variations in chemical composition.

The correlation is very good in both panels of Fig. 3, indicating that the assumptions made above are valid and the determination of $^{38}\text{Ar}_c$ concentrations is reliable. The three impure pyroxene separates (open circles) deviate from the correlation line defined by the other five samples in the Ar-He plot (although the He and Ne data of [9] were used for 403 and 446 because of clear He and Ne deficiencies in our data), but not in the Ar-Ne plot. Assuming that the separates of [9] were purer than those used here but contained some feldspar as well, this

can be explained by the retentivity characteristics of feldspar from Ferrar Dolerite, which loses basically all cosmogenic ^3He but retains about half of cosmogenic ^{21}Ne on exposure time-scales discussed here.

4.3. ^3He and ^{21}Ne exposure ages

^3He and ^{21}Ne exposure ages of the samples used in this study were initially reported by Schäfer et al. [9]. However, those ages did not take into account the influence of persistent low air pressure over the Antarctic continent on production rates, which was published one year later [21]. Moreover, new production rate calculation methods for He and Ne based on elemental composition have become available in the meantime [22,23]. Therefore, we have recalculated all exposure ages using the ^3He and ^{21}Ne concentrations and the target element compositions determined in this work, except for the impure pyroxene separates 403 and 446 with obvious He and Ne loss, for which noble gas and target element data of [9] were used. ^3He and ^{21}Ne production rates (P_3 and P_{21}) at sea level (standard pressure) and high latitude were calculated based on the chemical composition (Table 2) using the methods of [22,23,24] (for He and Ne) and [9] (Ne only). The resulting values vary between 102 and 158 atoms $\text{g}^{-1} \text{a}^{-1}$ for P_3 and between 19 and 43 atoms $\text{g}^{-1} \text{a}^{-1}$ for P_{21} , respectively, depending to some extent on the chemical composition of the samples but mainly on the method used to determine the production rate. For ^3He , it is also possible to assume a production rate independent of the chemical composition, such as 115 at $\text{g}^{-1} \text{a}^{-1}$. There are numerous experimental determinations of the ^3He production rate which cluster around this value [e.g. 25,26,27], although most of them were performed with olivines where it is probably a few percent higher than in the chemically distinct pyroxenes [13,28]. All production rate values were scaled to the sampling location altitudes using the procedure of Stone [21] for the Antarctic pressure regime. The term for muogenic production was neglected since its fraction is not known for noble gases, but is probably small [7] and should affect the results in the low percent range at

most. Exposure ages were then computed for each method of production rate calculation and are presented in Table 5. The error limits only represent the analytical uncertainties of the ^3He and ^{21}Ne concentrations, but do not include any uncertainties of the production rate calculation or scaling procedures.

Table 5 shows a large scatter in exposure ages for any given sample. For the five cross-calibration samples He ages are generally higher than Ne ages, implying that incomplete gas retention is not an issue here. We emphasize that the cosmogenic ^3He and ^{21}Ne concentrations obtained in three different labs agree very well (Table 3) and are thus reliable. The scatter in exposure age values for a single sample up to a factor of 1.57 must therefore reflect problems in some of the production rate systematics applied. Roughly, the exposure age values can be grouped in two sets which are internally consistent: set “A” comprising the constant P_3 value, P_3 according to Masarik [22], and P_3 and P_{21} according to Masarik and Reedy [24], and set “B” consisting of P_3 and P_{21} according to Kober et al. [23] as well as P_{21} according to Schäfer et al [9] and Masarik [22].

Set A is quite well supported by experimental production rate determinations, with P_3 close to $115 \text{ atoms g}^{-1} \text{ a}^{-1}$ or somewhat lower and P_{21} yielding $41.0 \text{ atoms g}^{-1} \text{ a}^{-1}$ for Fo_{81} olivine (41.9% O, 25.8% Mg, 18.4% Si, 13.9% Fe), similar to the experimental determination of Poreda and Cerling [29] when calculated according to Masarik and Reedy [24]. On the other hand, Blard et al. [30] have recently reported a distinctly higher ^3He production rate in olivine, $128 \pm 5 \text{ atoms g}^{-1} \text{ a}^{-1}$, and explained the low values obtained in earlier work by unrecognized grain size-dependent loss of cosmogenic ^3He in samples crushed before pyrolysis. Moreover, the elemental production rates modeled in [9,22,23] have likewise been fitted to experimental data. As it is beyond the scope of this paper to assess the reliability of He and Ne production rate values, we are going to present $^{38}\text{Ar}/^3\text{He}$ and $^{38}\text{Ar}/^{21}\text{Ne}$ production rate ratios accompanied by a range of possible ^{38}Ar production rates depending on the choice for ^3He and ^{21}Ne production rates.

4.4. The ^{38}Ar production rate from Ca

The ^{38}Ar production rate from Ca can be directly related to ^3He and ^{21}Ne production rates using the correlations shown in Fig. 3, i.e., it is a factor of 1.70 higher than the total ^3He production rate or 0.876 times the total ^{21}Ne production rate normalized to Mg content (due to the influence of other target elements on ^{21}Ne production, the latter relation is only valid for pyroxenes with similar chemical composition to those used here). For example, assuming a ^3He production rate of $115 \text{ atoms g}^{-1} \text{ a}^{-1}$ would result in an ^{38}Ar production rate of $196 \text{ atoms (g Ca)}^{-1} \text{ a}^{-1}$.

To assess the absolute range of ^{38}Ar production rate values consistent with the current knowledge on ^3He and ^{21}Ne production rates, P_{38} values were calculated individually from the $^{38}\text{Ar}_c$ concentrations (Table 3), the Ca contents (Table 2), and the ^3He and ^{21}Ne exposure ages (Table 5), and were scaled to sea level at standard atmospheric pressure again using the Stone [21] scaling without muon contribution. Results for the five cross-calibration samples and the different production rate calculation methods are shown in Table 6. For each method, the values from different samples agree within error limits, and in particular the three most accurate determinations (from NXP, 464, and 318) are in excellent agreement.

For each production rate method, weighted means were calculated from the results of the five samples (Table 6). They agree within error limits for either of the two sets defined above, while there is a clear gap between values belonging to different sets. Therefore we define two “global means” from the four values for each set, and obtain an ^{38}Ar production rate of $(191 \pm 21) \text{ at (g Ca)}^{-1} \text{ a}^{-1}$ at sea level (with standard atmospheric pressure) and high latitude if set A production rates are used, or $(254 \pm 28) \text{ at (g Ca)}^{-1} \text{ a}^{-1}$ for set B production rates. The cited 2σ errors include the scatter induced by different production rate calculation methods within the same set.

The reason for the clustering of exposure ages and, consequently, ^{38}Ar production rate values in two sets is not clear. This clustering might imply that one of the sets of methods describes the He and Ne production rates adequately while the other one does not, but it is also possible that the clustering is fortuitous or due to some biasing, so that the true ^{38}Ar production rate may indeed be somewhere between the values defined by the sets. An ultimate assessment must await a better understanding of the ^3He and ^{21}Ne production systematics in pyroxene. Related investigations are currently underway in several labs.

Irrespective of the exact value, the ^{38}Ar production rate reported here is independent of the scaling method because the scaling factor cancels out provided that it is the same for ^3He , ^{21}Ne and ^{38}Ar . Likewise, any variations of the geomagnetic field in the past do not affect the ^{38}Ar production rate value, because such variations do not influence the cosmic ray intensity at high latitudes [e.g. 31]. Our range for the ^{38}Ar production rate between (192 ± 21) and (254 ± 28) at $(\text{g Ca})^{-1} \text{ a}^{-1}$ is in agreement with Lal's [7] theoretical estimate of ~ 200 at $(\text{g Ca})^{-1} \text{ a}^{-1}$ but a factor of 2-2.5 higher than the preliminary experimental determination of Knight et al. [6]. The ^{38}Ar production rate from Ca is about a factor of 4-5 higher than the ^{21}Ne production rate from Si. Therefore, cosmogenic Ar may become a viable dating tool in suitable Ca-rich minerals.

5. Conclusions

We have determined the terrestrial production rate of cosmogenic ^{38}Ar from Ca in pyroxene minerals separated from Antarctic Ferrar dolerite. Owing to their long surface exposure of up to 6-8 Ma and to low concentrations of other target elements for Ar production (K, Ti, Cl), five out of eight pyroxene separates are ideally suited for such a production rate determination. The high exposure ages do not only provide abundant cosmogenic ^{38}Ar , but

moreover they make sure that equilibrium between production of radioactive ^{36}Cl and decay to stable ^{36}Ar has been reached.

Due to the lack of consistency between different methods to calculate the ^3He and ^{21}Ne production rate in pyroxene, we cannot give a definite number for the ^{38}Ar production rate even though the analytical uncertainties of our determination are as small as $\sim 5\%$. Instead, we report a range between (191 ± 21) and (254 ± 28) atoms $(\text{g Ca})^{-1} \text{a}^{-1}$, which is defined by the two means obtained from two sets of He and Ne production rates. Once the He and Ne production rates are better known, it will be possible to specify the ^{38}Ar production rate with corresponding accuracy.

Even though the potential applications of cosmogenic Ar to studies of terrestrial surface processes may remain limited to relatively high exposure ages (i.e., low erosion rates) and/or to high elevation sites due to the substantial atmospheric Ar background in many rocks, it may provide a possibility to use minerals in which no other cosmogenic nuclide can be used today, e.g. because they do not retain the lighter noble gases and ^{36}Cl has reached secular equilibrium between production and decay. In particular, feldspar is a very abundant group of minerals which may eventually be accessible to surface exposure studies once the ^{38}Ar production rate from K has been determined in addition to that from Ca.

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References

- [1] J.C. Gosse, F.M. Phillips, Terrestrial in situ cosmogenic nuclides: theory and application, *Quat. Sci. Rev.* 20 (2001) 1475-1560.
- [2] S. Niedermann, Cosmic-ray-produced noble gases in terrestrial rocks: Dating tools for surface processes, *Rev. Mineral. Geochem.* 47 (2002) 731-784.
- [3] N.A. Lifton, A.J.T. Jull, J. Quade, A new extraction technique and production rate estimate for in situ cosmogenic ^{14}C in quartz, *Geochim. Cosmochim. Acta* 65 (2001) 1953-1969.
- [4] J.M. Schaefer, T. Faestermann, G.F. Herzog, K. Knie, G. Korschinek, J. Masarik, A. Meier, M. Poutivtsev, G. Rugel, C. Schlüchter, F. Serifiddin, G. Winckler, Terrestrial manganese-53 – A new monitor of Earth surface processes, *Earth Planet. Sci. Lett.* 251 (2006) 334-345.
- [5] P.R. Renne, K.A. Farley, T.A. Becker, W.D. Sharp, Terrestrial cosmogenic argon, *Earth Planet. Sci. Lett.* 188 (2001) 435-440.
- [6] K.B. Knight, P.R. Renne, K.A. Farley, Preliminary estimate of production rates for terrestrial cosmogenic ^{38}Ar from calcium, *Eos Trans. AGU* 84 (2003), Fall Meet. Suppl., Abstract V22G-08.
- [7] D. Lal, Cosmic ray labeling of erosion surfaces: in situ nuclide production rates and erosion models, *Earth Planet. Sci. Lett.* 104 (1991) 424-439.
- [8] F.M. Phillips, W.D. Stone, J.T. Fabryka-Martin, An improved approach to calculating low-energy cosmic-ray neutron fluxes near the land/atmosphere interface, *Chem. Geol.* 175 (2001) 689-701.
- [9] J.M. Schäfer, S. Ivy-Ochs, R. Wieler, I. Leya, H. Baur, G.H. Denton, C. Schlüchter, Cosmogenic noble gas studies in the oldest landscape on earth: surface exposure ages of the Dry Valleys, Antarctica, *Earth Planet. Sci. Lett.* 167 (1999) 215-226.

- [10] S. Niedermann, W. Bach, J. Erzinger, Noble gas evidence for a lower mantle component in MORBs from the southern East Pacific Rise: Decoupling of helium and neon isotope systematics, *Geochim. Cosmochim. Acta* 61 (1997) 2697-2715.
- [11] J.-Y. Lee, K. Marti, J.P. Severinghaus, K. Kawamura, H.-S. Yoo, J.B. Lee, J.S. Kim, A redetermination of the isotopic abundances of atmospheric Ar, *Geochim. Cosmochim. Acta* 70 (2006) 4507-4512.
- [12] A.O. Nier, A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium, *Phys. Rev.* 77 (1950) 789-793.
- [13] H.R. Margerison, W.M. Phillips, F.M. Stuart, D.E. Sugden, Cosmogenic ^3He concentrations in ancient flood deposits from the Coombs Hills, northern Dry Valleys, East Antarctica: interpreting exposure ages and erosion rates, *Earth Planet. Sci. Lett.* 230 (2005) 163-175.
- [14] P. Oberholzer, C. Baroni, M.C. Salvatore, H. Baur, R. Wieler, Dating late-Cenozoic erosional surfaces in Victoria Land, Antarctica, with cosmogenic neon in pyroxene, *Antarctic Science*, in revision (2007).
- [15] J.M. Schäfer, H. Baur, G.H. Denton, S. Ivy-Ochs, D.R. Marchant, C. Schlüchter, R. Wieler, The oldest ice on Earth in Beacon Valley, Antarctica: new evidence from surface exposure dating, *Earth Planet. Sci. Lett.* 179 (2000) 91-99.
- [16] R. Yokochi, B. Marty, R. Pik, P. Burnard, High $^3\text{He}/^4\text{He}$ ratios in peridotite xenoliths from SW Japan revisited: Evidence for cosmogenic ^3He released by vacuum crushing, *Geochem. Geophys. Geosyst.* 6 (2005) Q01004, doi: 10.1029/2004GC000836.
- [17] J. Eikenberg, P. Signer, R. Wieler, U-Xe, U-Kr, and U-Pb systematics for dating uranium minerals and investigations of the production of nucleogenic neon and argon, *Geochim. Cosmochim. Acta* 57 (1993) 1053-1069.

- [18] E.K. Jessberger, J.C. Huneke, F.A. Podosek, G.J. Wasserburg, High-resolution argon analysis of neutron-irradiated Apollo 16 rocks and separated minerals, *Proc. Lunar Conf. 5th* (1974) 1419-1449.
- [19] C.M. Hohenberg, K. Marti, F.A. Podosek, R.C. Reedy, J.R. Shirk, Comparisons between observed and predicted cosmogenic noble gases in lunar samples, *Proc. Lunar Planet. Sci. Conf 9th* (1978) 2311-2344.
- [20] I. Leya, S. Neumann, R. Wieler, R. Michel, The production of cosmogenic nuclides by galactic cosmic-ray particles for 2π exposure geometries, *Meteoritics Planet. Sci.* 36 (2001) 1547-1561.
- [21] J.O. Stone, Air pressure and cosmogenic isotope production, *J. Geophys. Res.* 105 (2000) 23,753-23,759.
- [22] J. Masarik, Numerical simulation of in-situ production of cosmogenic nuclides, *Geochim. Cosmochim. Acta* 66 (2002) A491.
- [23] F. Kober, S. Ivy-Ochs, I. Leya, H. Baur, T. Magna, R. Wieler, P.W. Kubik, In situ cosmogenic ^{10}Be and ^{21}Ne in sanidine and in situ cosmogenic ^3He in Fe-Ti-oxide minerals, *Earth Planet. Sci. Lett.* 236 (2005) 404-418.
- [24] J. Masarik, R.C. Reedy, Monte Carlo simulation of in-situ-produced cosmogenic nuclides, *Radiocarbon* 38 (1996) 163.
- [25] J.M. Licciardi, M.D. Kurz, P.U. Clark, E.J. Brook, Calibration of cosmogenic ^3He production rates from Holocene lava flows in Oregon, USA, and effects of the Earth's magnetic field, *Earth Planet. Sci. Lett.* 172 (1999) 261-271.
- [26] T.J. Dunai, J.R. Wijbrans, Long-term cosmogenic ^3He production rates (152 ka – 1.35 Ma) from $^{40}\text{Ar}/^{39}\text{Ar}$ dated basalt flows at 29°N latitude, *Earth Planet. Sci. Lett.* 176 (2000) 147-156.
- [27] T.E. Cerling, H. Craig, Cosmogenic ^3He production rates from 39°N to 46°N latitude, western USA and France, *Geochim. Cosmochim. Acta* 58 (1994) 249-255.

- [28] R.P. Ackert Jr., B.S. Singer, H. Guillou, M.R. Kaplan, M.D. Kurz, Long-term cosmogenic ^3He production rates from $^{40}\text{Ar}/^{39}\text{Ar}$ and K-Ar dated Patagonian lava flows at 47°S, *Earth Planet. Sci. Lett.* 210 (2003) 119-136.
- [29] R.J. Poreda, T.E. Cerling, Cosmogenic neon in recent lavas from the western United States, *Geophys. Res. Lett.* 19 (1992) 1863-1866.
- [30] P.-H. Blard, R. Pik, J. Lavé, D. Bourlès, P.G. Burnard, R. Yokochi, B. Marty, F. Trusdell, Cosmogenic ^3He production rates revisited from evidences of grain size dependent release of matrix-sited helium, *Earth Planet. Sci. Lett.* 247 (2006) 222-234.
- [31] J. Masarik, M. Frank, J.M. Schäfer, R. Wieler, Correction of in situ cosmogenic nuclide production rates for geomagnetic field intensity variations during the past 800,000 years, *Geochim. Cosmochim. Acta* 65 (2001) 2995-3003.

Figure Captions

Fig. 1. Ne three-isotope diagrams for stepwise heating data of eight pyroxene separates from the Antarctic Dry Valleys. 600°C data are shown by white symbols, 900°C data by gray, and $\geq 1700^\circ\text{C}$ data by black symbols. A larger range than in the main panels is displayed in the insets; note different scale for insets in A and B. The spallation line is the mixing line between atmospheric and cosmogenic Ne and was plotted according to [9]. For reference, mfl is the mass fractionation line.

Fig. 2. Compilation of $^{38}\text{Ar}/^{36}\text{Ar}$ ratios as determined in the two noble gas lines of GFZ Potsdam in various rock samples not expected to contain cosmogenic Ar. Pyrolysis data are shown by filled symbols, crushing data (line B only) by open symbols. The

dotted line denotes the atmospheric $^{38}\text{Ar}/^{36}\text{Ar}$ ratio of 0.1880 [12], which was assumed for calibration of our mass spectrometers.

Fig. 3. Concentrations of cosmogenic ^{38}Ar (normalized to Ca content) in Dry Valleys pyroxene separates versus total ^3He (A) and versus cosmogenic ^{21}Ne normalized to Mg content (B), respectively. Open circles denote impure pyroxene separates, for which ^3He loss is indicated in A. Regression lines have been forced through the origin.

Table 1. Results of He, Ne and Ar analyses in pyroxene separates from dolerites sampled in the Antarctic Dry Valleys [9]. Error limits are 2σ .

Sample Weight	T °C	⁴ He $10^{-8} \text{ cm}^3/\text{g}$	²⁰ Ne $10^{-12} \text{ cm}^3/\text{g}$	⁴⁰ Ar $10^{-8} \text{ cm}^3/\text{g}$	³ He/ ⁴ He 10^{-6}	²² Ne/ ²⁰ Ne 10^{-2}	²¹ Ne/ ²⁰ Ne 10^{-2}	⁴⁰ Ar/ ³⁶ Ar	³⁸ Ar/ ³⁶ Ar
403 0.70014 g	900	1090 ±120	459 ±38	223 ±21	3.65 ±0.17	11.557 ±0.069	1.443 ±0.019	1194.0 ±7.9	0.18917 ±0.00076
	1700	50.7 ±2.5	55.0 ±4.7	98.0 ±8.3	2.472 ±0.088	21.33 ±0.40	11.28 ±0.31	2055 ±38	0.2027 ±0.0019
	Total	1140 ±120	514 ±38	321 ±23	3.60 ±0.16	12.60 ±0.13	2.50 ±0.12	1369 ±20	0.19192 ±0.00077
444 0.60061 g	600	545 ±71	123 ±10	19.3 ±1.6	2.83 ±0.11	10.67 ±0.11	0.713 ±0.023	354.5 ±2.0	0.18939 ±0.00069
	900	188 ±25	50.0 ±5.2	25.1 ±1.8	1.441 ±0.059	11.22 ±0.10	1.325 ±0.072	1274 ±35	0.19090 ±0.00083
	1700	167 ±22	198 ±16	47.0 ±4.3	1.165 ±0.089	12.059 ±0.085	2.097 ±0.052	750 ±14	0.19258 ±0.00090
	Total	900 ±78	371 ±20	91.4 ±4.9	2.231 ±0.091	11.485 ±0.068	1.534 ±0.045	668 ±15	0.19107 ±0.00052
0.8753 g	crushed	29.0 ±1.4	39.8 ±2.1	3.92 ±0.20	0.112 ±0.010	10.20 ±0.15	0.325 ±0.022	314.7 ±1.8	0.1886 ±0.0013
446 0.70087 g	600	384 ±33	373 ±32	73.4 ±6.2	8.81 ±0.35	12.664 ±0.054	2.167 ±0.039	2372 ±54	0.1943 ±0.0015
	900	39.8 ±2.8	27.5 ±4.0	207 ±17	5.00 ±0.20	20.3 ±1.1	10.0 ±1.1	22900 ±1800	0.2151 ±0.0032
	1700	11.94 ±0.97	60.1 ±6.0	407 ±47	3.69 ±0.21	18.22 ±0.47	8.20 ±0.44	5370 ±260	0.2032 ±0.0026
	Total	436 ±33	461 ±33	687 ±50	8.32 ±0.31	13.84 ±0.15	3.42 ±0.15	5940 ±260	0.2018 ±0.0018

Table 1 (cont.)

Sample Weight	T °C	^4He $10^{-8} \text{ cm}^3/\text{g}$	^{20}Ne $10^{-12} \text{ cm}^3/\text{g}$	^{40}Ar $10^{-8} \text{ cm}^3/\text{g}$	$^3\text{He}/^4\text{He}$ 10^{-6}	$^{22}\text{Ne}/^{20}\text{Ne}$ 10^{-2}	$^{21}\text{Ne}/^{20}\text{Ne}$ 10^{-2}	$^{40}\text{Ar}/^{36}\text{Ar}$	$^{38}\text{Ar}/^{36}\text{Ar}$
NXP 93*52 1.0019 g	900	132.2	21.0	14.8	142.7	57.1	44.0	970	0.1948
		±6.6	±1.3	±1.4	±2.1	±1.6	±1.4	±24	±0.0013
	1800	1.337	54.7	19.9	128.8	95.1	80.1	342.7	0.2036
		±0.070	±3.7	±1.0	±3.4	±3.3	±3.1	±1.7	±0.0012
	Total	133.5	75.7	34.7	142.6	84.6	70.1	473	0.2018
		±6.6	±3.9	±1.7	±2.1	±2.5	±2.4	±12	±0.0010
435 1.00225 g	600	389	111.1	339	17.87	10.72	0.532	298.5	0.18764
		±28	±6.2	±35	±0.31	±0.11	±0.022	±2.8	±0.00062
	900	481	15.4	13.39	0.893	46.6	34.1	514.0	0.1890
		±34	±1.3	±0.94	±0.026	±1.4	±1.0	±2.8	±0.0011
	1750	930	18.0	24.7	0.92	68.4	53.2	344.4	0.20148
		±100	±2.1	±2.3	±0.11	±4.9	±4.5	±2.0	±0.00082
	Total	1800	144.5	377	4.58	21.7	10.67	305.7	0.18847
		±110	±6.7	±35	±0.30	±1.1	±0.97	±2.7	±0.00058
439 1.02773 g	600	1070	206	179	3.472	10.431	0.4426	298.5	0.18807
		±120	±15	±15	±0.085	±0.082	±0.0070	±1.7	±0.00066
	900	715	42.3	18.4	0.979	17.60	7.35	334.5	0.18849
		±51	±3.2	±1.3	±0.027	±0.12	±0.11	±1.8	±0.00064
	1750	134.4	29.9	11.79	0.859	33.64	22.33	409.3	0.21638
		±9.5	±2.5	±0.84	±0.036	±0.84	±0.78	±2.9	±0.00083
	Total	1920	278	209	2.360	14.02	3.85	306.1	0.18930
		±130	±16	±15	±0.093	±0.29	±0.26	±1.6	±0.00059

Table 1 (cont.)

Sample Weight	T °C	⁴ He <i>10⁻⁸ cm³/g</i>	²⁰ Ne <i>10⁻¹² cm³/g</i>	⁴⁰ Ar <i>10⁻⁸ cm³/g</i>	³ He/ ⁴ He <i>10⁻⁶</i>	²² Ne/ ²⁰ Ne <i>10⁻²</i>	²¹ Ne/ ²⁰ Ne <i>10⁻²</i>	⁴⁰ Ar/ ³⁶ Ar	³⁸ Ar/ ³⁶ Ar
464 1.06179 g	600	332	47.3	14.6	26.52	11.599	1.448	317.3	0.18777
		±24	±3.6	±1.0	±0.43	±0.091	±0.031	±1.9	±0.00076
	900	251	25.5	9.12	4.156	41.72	28.89	780.4	0.1890
		±17	±2.0	±0.65	±0.081	±0.56	±0.55	±6.7	±0.0012
	1750	21.6	27.5	16.6	6.42	57.9	43.3	393.4	0.22833
		±1.1	±2.6	±1.2	±0.15	±2.5	±2.3	±2.8	±0.00082
Total	605	100.3	40.3	16.52	32.0	19.9	403.6	0.2050	
	±29	±4.9	±1.7	±0.58	±1.2	±1.1	±4.5	±0.0010	
318 0.56816 g	600	146.7	91.7	24.3	145.0	12.21	1.900	335.6	0.18892
		±7.3	±6.0	±1.5	±1.7	±0.14	±0.031	±2.5	±0.00087
	900	16.02	28.8	10.76	330.9	56.0	43.34	1253	0.1981
		±0.80	±2.0	±0.65	±4.0	±1.3	±0.92	±23	±0.0016
	1750	2.37	133.1	15.43	203.8	43.45	31.40	352.7	0.2887
		±0.12	±8.8	±0.95	±5.7	±0.48	±0.39	±3.3	±0.0018
Total	165.1	254	50.5	163.9	33.58	22.09	404.8	0.2245	
	±7.3	±11	±1.9	±1.9	±0.70	±0.64	±5.1	±0.0021	
<i>For reference:</i>	<i>Atmosphere</i>				<i>1.39</i>	<i>10.20</i>	<i>0.2959</i>	<i>295.5</i>	<i>0.1880</i>

Table 2. Mineralogical composition and concentrations of major elements and Cl of the investigated pyroxene separates.

Sample	Pyroxene	Feldspar	Quartz	O	Na	Mg <i>wt. %</i>	Al	Si	K	Ca	Ti	Fe	Cl <i>ppm</i>
403	69	21	7	44.0	0.49	6.96	2.9	24.8	0.32	7.68	0.48	11.27	<100
444	78	20	2	43.7	0.24	8.58	1.8	24.4	0.04	8.00	0.41	11.76	<100
446	23	58	19	45.7	1.11	3.43	6.5	27.5	0.93	6.38	0.62	5.98	<100
NXP	n.d.	n.d.	n.d.	45.6	<0.10	15.6	1.2	25.6	0.01	3.71	0.09	8.4	n.d.
435	97	-	-	43.3	0.10	8.49	0.8	23.7	0.01	9.86	0.24	13.36	<100
439	92	-	3	43.5	0.09	9.26	0.8	24.2	<0.01	10.82	0.18	10.71	<100
464	97	-	-	43.5	0.10	8.79	0.9	24.2	0.01	11.15	0.20	10.78	<100
318	>99	-	-	43.8	0.10	10.33	1.2	25.4	<0.02	11.51	0.15	7.43	n.d.

n.d.: not determined

Table 3. Concentrations of total ^3He (as a close approximation to cosmogenic ^3He), cosmogenic ^{21}Ne , and cosmogenic ^{38}Ar in the investigated pyroxene separates, in units of 10^6 atoms g^{-1} . The data for ^3He and ^{21}Ne as obtained at ETH Zurich [9] and Lamont-Doherty Earth Observatory [4] are given for reference; all error limits are 2σ . The asymmetric error limits for $^{38}\text{Ar}_c$ in two cases (435 and 439) result from $^{38}\text{Ar}/^{36}\text{Ar}$ ratios overlapping with the atmospheric value in the 600°C and 900°C steps (Table 1) and the fact that an uncertainty range corresponding to negative ^{38}Ar excesses is physically unreasonable.

Sample	Elevation [m]	$^3\text{He}_{\text{tot}}$	This study		<i>Earlier work</i>		
			$^{21}\text{Ne}_c$	$^{38}\text{Ar}_c$	$^3\text{He}_{\text{tot}}$ [9]	$^3\text{He}_{\text{tot}}$ [4]	$^{21}\text{Ne}_c$ [9]
403	1750	1100 $\pm$ 130	304 $\pm$ 17	289 $\pm$ 56	1489 $\pm$ 38	1340 $\pm$ 120	340 $\pm$ 6
444	1145	539 $\pm$ 58	123.4 $\pm$ 7.9	131 $\pm$ 23	525 $\pm$ 18	520 $\pm$ 40	124 $\pm$ 11
446	1530	973 $\pm$ 86	387 $\pm$ 20	501 $\pm$ 76	2785 $\pm$ 71	3080 $\pm$ 160	712 $\pm$ 28
NXP	2555	5110 $\pm$ 260	1417 $\pm$ 66	326 $\pm$ 32	5210 $\pm$ 77	5210 $\pm$ 500	1590 $\pm$ 68
435	1595	2220 $\pm$ 150	402 $\pm$ 22	312 $^{+9}_-3$	1846 $\pm$ 46	2280 $\pm$ 120	391 $\pm$ 9
439	869	1220 $\pm$ 110	265 $\pm$ 15	276 $^{+12}_-2$	998 $\pm$ 18	920 $\pm$ 40	263 $\pm$ 7
464	1515	2680 $\pm$ 180	529 $\pm$ 28	535 $\pm$ 41	2361 $\pm$ 60	2780 $\pm$ 140	522 $\pm$ 23
318	2140	7260 $\pm$ 300	1485 $\pm$ 76	1420 $\pm$ 93	6900 $\pm$ 170	6090 $\pm$ 300	1623 $\pm$ 39

Table 4. Production rates of the stable Ar isotopes from target elements K, Ca, Ti, and Fe, relative to that of ^{36}Ar from Ca, as reported in [19] for 500 g/cm² shielding depth beneath the lunar surface.

Product	K	Ca	Ti	Fe
^{36}Ar	1.52	$\equiv 1$	0.066	0.003
^{38}Ar	1.51	1.48	0.052	0.006
^{40}Ar	0.030	0.012	0.015	0.002

Table 5. ^3He and ^{21}Ne exposure ages (T_3 and T_{21}) for the pyroxene separates studied in this work, as determined using different methods for production rate calculation according to references given in the column heads. “const.” denotes a ^3He production rate of 115 atoms g⁻¹ a⁻¹ at sea level and high latitude, independent of chemical composition. For 403 and 446, the ^3He and ^{21}Ne concentrations reported in [9] were used to calculate exposure ages. Error limits of the exposure ages (2σ) reflect only the analytical uncertainty of the noble gas analysis.

Sample	T_3 [Ma]				T_{21} [Ma]			
	const.	[24]	[22]	[23]	[24]	[9]	[22]	[23]
403	2.16	2.26	2.37	1.66	3.07	2.35	2.57	2.27
	± 0.06	± 0.06	± 0.06	± 0.04	± 0.05	± 0.04	± 0.05	± 0.04
444	1.27	1.35	1.42	1.01	1.49	1.16	1.25	1.11
	± 0.14	± 0.15	± 0.15	± 0.11	± 0.10	± 0.07	± 0.08	± 0.07
446	4.79	4.87	5.10	3.65	6.55	5.10	5.52	4.94
	± 0.12	± 0.12	± 0.13	± 0.09	± 0.26	± 0.20	± 0.22	± 0.19
NXP	4.22	4.22	4.41	3.07	4.28	3.15	3.47	3.19
	± 0.21	± 0.21	± 0.22	± 0.16	± 0.20	± 0.15	± 0.16	± 0.15
435	3.63	3.90	4.09	2.92	3.53	2.73	2.96	2.61
	± 0.25	± 0.26	± 0.28	± 0.20	± 0.19	± 0.15	± 0.16	± 0.14
439	3.65	3.89	4.07	2.93	4.03	3.09	3.36	2.97
	± 0.33	± 0.35	± 0.37	± 0.26	± 0.23	± 0.17	± 0.19	± 0.17
464	4.66	4.96	5.21	3.78	4.79	3.70	4.02	3.53
	± 0.31	± 0.33	± 0.35	± 0.25	± 0.25	± 0.20	± 0.21	± 0.19
318	7.93	8.21	8.68	6.33	7.52	5.77	6.26	5.53
	± 0.33	± 0.34	± 0.36	± 0.26	± 0.38	± 0.30	± 0.32	± 0.28

Table 6. ^{38}Ar production rate (P_{38}) values as calculated from ^3He and ^{21}Ne exposure ages (based on different production rate calculation methods; see Table 5) of five pure pyroxene separates from the Antarctic Dry Valleys. Units are atoms $(\text{g Ca})^{-1} \text{a}^{-1}$. The two sets A and B have been defined based on clustering of exposure ages in two distinct groups according to production rate calculation methods (see section 4.3 and Table 5). The individual 2σ error limits reflect only the uncertainties of the $^3\text{He}_{\text{tot}}$, $^{21}\text{Ne}_c$ and $^{38}\text{Ar}_c$ determinations. The error limits of the “global means” include the variations imposed by different production rate calculation methods among each set in addition.

Sample <i>Set</i>	P ₃₈ based on P ₃ according to:				P ₃₈ based on P ₂₁ according to:			
	const. <i>A</i>	[24] <i>A</i>	[22] <i>A</i>	[23] <i>B</i>	[24] <i>A</i>	[9] <i>B</i>	[22] <i>B</i>	[23] <i>B</i>
NXP	198±22	198±22	189±21	272±30	195±21	265±29	240±26	261±28
435	164 ⁺⁵³ ₋₂₁	152 ⁺⁴⁹ ₋₂₀	145 ⁺⁴⁶ ₋₁₉	203 ⁺⁶⁵ ₋₂₆	168 ⁺⁵³ ₋₂₁	218 ⁺⁶⁹ ₋₂₇	201 ⁺⁶⁴ ₋₂₅	228 ⁺⁷² ₋₂₈
439	240 ⁺¹¹⁰ ₋₃₁	225 ⁺¹⁰³ ₋₂₉	216 ⁺⁹⁹ ₋₂₈	299 ⁺¹³⁷ ₋₃₈	218 ⁺⁹⁹ ₋₂₃	284 ⁺¹²⁹ ₋₃₀	261 ⁺¹¹⁹ ₋₂₈	295 ⁺¹³⁴ ₋₃₂
464	206±21	194±20	184±19	254±26	200±19	260±24	239±22	272±25
318	195±15	189±15	178±14	245±19	206±17	269±23	247±21	280±23
<i>Mean</i>	197 ⁺¹¹ ₋₁₀	190±11	180 ⁺¹¹ ₋₁₀	249 ⁺¹⁵ ₋₁₄	199 ⁺¹² ₋₁₀	261 ⁺¹⁶ ₋₁₄	239 ⁺¹⁵ ₋₁₃	268 ⁺¹⁴ ₋₁₃
<i>Global Mean Set A</i>				191±21				
<i>Global Mean Set B</i>				254±28

Fig. 1

Fig. 2

Fig. 3

Table A1. Results of Kr analyses in pyroxene separates from dolerites sampled in the Antarctic Dry Valleys [9]. Error limits are 2σ .

Sample Weight	T °C	^{84}Kr $10^{-12} \text{ cm}^3 \text{ STP/g}$	$^{78}\text{Kr}/^{84}\text{Kr}$	$^{80}\text{Kr}/^{84}\text{Kr}$	$^{82}\text{Kr}/^{84}\text{Kr}$	$^{83}\text{Kr}/^{84}\text{Kr}$	$^{86}\text{Kr}/^{84}\text{Kr}$
403 0.70014 g	900	168 ± 15	0.006022 ± 0.000077	-	0.20141 ± 0.00096	0.20058 ± 0.00084	0.3067 ± 0.0015
	1700	28.2 ± 2.1	0.00593 ± 0.00022	-	0.1999 ± 0.0025	0.1999 ± 0.0028	0.3074 ± 0.0030
	Total	196 ± 15	0.006009 ± 0.000073	-	0.20119 ± 0.00090	0.20048 ± 0.00082	0.3068 ± 0.0014
444 0.60061 g	600	87.0 ± 7.4	0.00616 ± 0.00030	-	0.2019 ± 0.0015	0.2008 ± 0.0016	0.3046 ± 0.0023
	900	15.2 ± 1.2	0.00620 ± 0.00047	-	0.2018 ± 0.0041	0.2014 ± 0.0042	0.3050 ± 0.0070
	1700	25.3 ± 1.9	0.00618 ± 0.00020	-	0.2007 ± 0.0028	0.2011 ± 0.0033	0.3045 ± 0.0035
	Total	127.5 ± 7.7	0.00617 ± 0.00022	-	0.2017 ± 0.0013	0.2009 ± 0.0014	0.3046 ± 0.0019
0.8753 g	crushed	4.59 ± 0.24	-	-	0.2067 ± 0.0069	0.2041 ± 0.0086	0.3073 ± 0.0091
446 Pyroxen 0.70087 g	600	52.2 ± 8.9	0.00593 ± 0.00023	-	0.1998 ± 0.0027	0.2000 ± 0.0017	0.3042 ± 0.0020
	900	6.1 ± 1.6	0.00619 ± 0.00048	-	0.1980 ± 0.0031	0.1992 ± 0.0032	0.3054 ± 0.0051
	1700	26.7 ± 2.6	0.00602 ± 0.00022	-	0.2014 ± 0.0036	0.2011 ± 0.0018	0.3057 ± 0.0036
	Total	85.0 ± 9.4	0.00598 ± 0.00016	-	0.2002 ± 0.0020	0.2003 ± 0.0012	0.3048 ± 0.0017

Table A1 (cont.)

Sample Weight	T °C	^{84}Kr $10^{-12} \text{ cm}^3 \text{ STP/g}$	$^{78}\text{Kr}/^{84}\text{Kr}$	$^{80}\text{Kr}/^{84}\text{Kr}$	$^{82}\text{Kr}/^{84}\text{Kr}$	$^{83}\text{Kr}/^{84}\text{Kr}$	$^{86}\text{Kr}/^{84}\text{Kr}$
NXP93*52 1.0019 g	900	46.4 ±3.3	-	-	0.2017 ±0.0024	0.2010 ±0.0019	0.3046 ±0.0046
	1800	5.46 ±0.38	0.00601 ±0.00061	-	0.2013 ±0.0072	0.202 ±0.011	0.3047 ±0.0091
	Total	51.9 ±3.3	-	-	0.2017 ±0.0023	0.2011 ±0.0021	0.3046 ±0.0042
435 1.00225 g	600	495 ±31	0.006024 ±0.000074	-	0.20097 ±0.00074	0.20062 ±0.00052	0.3074 ±0.0019
	900	17.6 ±1.1	0.00608 ±0.00022	0.03971 ±0.00093	0.2025 ±0.0020	0.2019 ±0.0021	0.3074 ±0.0025
	1750	8.87 ±0.92	0.00622 ±0.00036	-	0.2016 ±0.0044	0.2017 ±0.0027	0.3086 ±0.0041
	Total	521 ±31	0.006029 ±0.000071	-	0.20103 ±0.00071	0.20068 ±0.00050	0.3074 ±0.0018
439 1.02773 g	600	209 ±13	0.005944 ±0.000076	-	0.20026 ±0.00084	0.20058 ±0.00089	0.3071 ±0.0013
	900	34.8 ±2.2	0.00610 ±0.00013	-	0.2016 ±0.0020	0.2012 ±0.0018	0.3070 ±0.0017
	1750	16.5 ±1.0	0.00611 ±0.00020	-	0.2017 ±0.0030	0.2005 ±0.0024	0.3063 ±0.0024
	Total	260 ±13	0.005975 ±0.000065	-	0.20053 ±0.00075	0.20066 ±0.00077	0.3070 ±0.0011

Table A1 (cont.)

Sample Weight	T °C	^{84}Kr $10^{-12} \text{ cm}^3 \text{ STP/g}$	$^{78}\text{Kr}/^{84}\text{Kr}$	$^{80}\text{Kr}/^{84}\text{Kr}$	$^{82}\text{Kr}/^{84}\text{Kr}$	$^{83}\text{Kr}/^{84}\text{Kr}$	$^{86}\text{Kr}/^{84}\text{Kr}$
464 1.06179 g	600	36.2 ±2.4	0.00610 ±0.00015	-	0.20122 ±0.00082	0.2006 ±0.0015	0.3072 ±0.0019
	900	8.53 ±0.53	0.00616 ±0.00040	-	0.2019 ±0.0040	0.2015 ±0.0046	0.3083 ±0.0052
	1750	19.5 ±1.2	0.00607 ±0.00018	-	0.2018 ±0.0024	0.2015 ±0.0019	0.3057 ±0.0028
	Total	64.2 ±2.7	0.00610 ±0.00011	-	0.2015 ±0.0010	0.2010 ±0.0012	0.3069 ±0.0015
	600	197 ±14	0.00613 ±0.00010	0.03974 ±0.00039	0.2022 ±0.0011	0.2014 ±0.0020	0.3061 ±0.0015
	900	8.49 ±0.81	0.00636 ±0.00034	0.0408 ±0.0031	0.2016 ±0.0062	0.2018 ±0.0091	0.3053 ±0.0079
318 0.56816 g	1750	18.5 ±1.3	0.00622 ±0.00053	0.04046 ±0.00087	0.2034 ±0.0049	0.2020 ±0.0033	0.3050 ±0.0050
	Total	224 ±14	0.00615 ±0.00010	0.03984 ±0.00037	0.2023 ±0.0011	0.2015 ±0.0018	0.3060 ±0.0014
<i>For reference: Atmosphere</i>			0.006087	0.03960	0.20217	0.20136	0.30524

Table A2. Results of Xe analyses in pyroxene separates from dolerites sampled in the Antarctic Dry Valleys [9]. Error limits are 2σ .

Sample Weight	T °C	¹³² Xe	¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³⁴ Xe	¹³⁶ Xe
		10 ⁻¹² cm ³ STP/g	¹³² Xe = 100							
403 0.70014 g	900	23.1	0.356	0.328	7.13	98.23	15.15	78.87	38.92	33.04
		±2.1	±0.019	±0.015	±0.10	±0.35	±0.16	±0.27	±0.21	±0.30
	1700	17.4	0.350	0.328	7.058	97.81	15.06	78.56	39.01	33.28
		±1.3	±0.019	±0.011	±0.077	±0.80	±0.23	±0.69	±0.38	±0.32
	Total	40.5	0.353	0.328	7.099	98.05	15.11	78.74	38.96	33.14
±2.5		±0.014	±0.010	±0.066	±0.40	±0.13	±0.33	±0.20	±0.22	
444 0.60061 g	600	23.5	0.358	0.334	7.12	98.64	15.16	78.86	38.71	32.96
		±2.7	±0.011	±0.022	±0.11	±0.84	±0.12	±0.74	±0.24	±0.27
	900	4.06	0.376	0.335	7.12	98.3	15.22	78.9	39.0	32.75
		^{+0.51} _{-0.48}	±0.050	±0.058	±0.34	±1.0	±0.59	±1.1	±1.1	±0.86
	1700	10.08	0.360	0.328	7.11	97.78	15.10	78.47	39.03	33.19
		^{+0.93} _{-0.80}	±0.019	±0.031	±0.17	±0.62	±0.35	±0.31	±0.57	±0.48
Total	37.6	0.360	0.333	7.12	98.37	15.15	78.76	38.83	33.00	
	±2.9	±0.010	±0.017	±0.09	±0.56	±0.14	±0.48	±0.24	±0.23	
0.8753 g	crushed	0.490	-	-	-	96.6	-	-	39.5	33.0
		±0.036				±4.9			±5.0	±3.2
446 0.70087 g	600	21.0	0.349	0.329	7.20	98.63	14.98	78.79	38.73	32.90
		±3.2	±0.035	±0.028	±0.26	±0.94	±0.42	±0.39	±0.45	±0.32
	900	2.37	0.348	0.329	7.04	95.5	14.77	77.4	39.4	33.15
		^{+0.70} _{-0.39}	±0.084	±0.082	±0.48	±2.6	±0.60	±2.2	±1.1	±0.46
	1700	3.11	0.3936	0.438	7.05	95.1	14.70	77.3	41.69	35.90
		^{+0.97} _{-0.65}	±0.0061	±0.019	±0.18	±1.4	±0.43	±1.5	±0.51	±0.56
Total	26.5	0.354	0.342	7.17	97.94	14.93	78.49	39.14	33.27	
	±3.4	±0.029	±0.024	±0.21	±0.81	±0.34	±0.41	±0.39	±0.29	

Table A2 (cont.)

Sample Weight	T °C	¹³² Xe <i>10⁻¹² cm³ STP/g</i>	¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³⁴ Xe	¹³⁶ Xe
<i>¹³²Xe = 100</i>										
NXP93*52 1.0019 g	900	29.6	-	-	-	98.03	-	-	38.89	33.04
		±2.8				±0.87			±0.33	±0.38
	1800	3.06	0.352	0.343	7.12	98.1	14.96	78.3	38.6	32.8
		±0.17	±0.070	±0.070	±0.36	±1.9	±0.75	±2.6	±1.2	±1.4
	Total	32.7	-	-	-	98.04	-	-	38.86	33.02
		±2.8				±0.81			±0.32	±0.37
435 1.00225 g	600	36.4	0.3563	0.3360	7.092	98.11	15.132	78.72	38.94	33.16
		±2.2	±0.0097	±0.0090	±0.048	±0.48	±0.064	±0.26	±0.22	±0.16
	900	2.84	0.358	0.339	7.05	97.4	15.13	78.61	38.87	32.84
		±0.15	±0.036	±0.029	±0.15	±1.1	±0.31	±0.96	±0.50	±0.41
	1750	3.11	0.354	0.328	7.00	96.0	14.97	77.7	40.26	34.56
		±0.21	±0.035	±0.028	±0.24	±1.3	±0.36	±1.0	±0.43	±0.57
	Total	42.4	0.3562	0.3356	7.082	97.91	15.120	78.64	39.03	33.24
		±2.2	±0.0091	±0.0082	±0.046	±0.43	±0.064	±0.24	±0.19	±0.15
439 1.02773 g	600	15.59	0.358	0.333	7.084	97.97	15.14	78.65	38.92	33.01
		±0.81	±0.016	±0.016	±0.075	±0.46	±0.14	±0.37	±0.27	±0.20
	900	5.95	0.352	0.332	7.13	98.03	15.10	78.97	38.85	32.97
		±0.79	±0.028	±0.011	±0.12	±0.79	±0.24	±0.58	±0.47	±0.42
	1750	5.58	0.358	0.331	7.119	97.86	15.10	78.57	39.02	33.27
		±0.30	±0.026	±0.034	±0.094	±0.99	±0.24	±0.85	±0.31	±0.50
	Total	27.1	0.357	0.332	7.101	97.96	15.12	78.70	38.93	33.05
		±1.2	±0.012	±0.012	±0.054	±0.38	±0.11	±0.30	±0.20	±0.18

Table A2 (cont.)

Sample Weight	T °C	¹³² Xe	¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³⁴ Xe	¹³⁶ Xe
		$10^{-12} \text{ cm}^3 \text{ STP/g}$	$^{132}\text{Xe} = 100$							
464 1.06179 g	600	8.7	0.357	0.328	7.11	98.0	15.16	78.89	38.91	33.00
		±1.3	±0.020	±0.013	±0.14	±1.3	±0.23	±0.79	±0.38	±0.35
	900	2.78	0.351	0.338	7.10	97.8	15.17	78.8	38.77	32.93
		±0.46	±0.030	±0.034	±0.31	±1.3	±0.30	±1.5	±0.66	±0.73
	1750	7.87	0.360	0.334	7.12	98.50	15.19	79.12	39.05	33.13
		±0.41	±0.017	±0.026	±0.15	±0.84	±0.17	±0.49	±0.29	±0.26
	Total	19.4	0.357	0.332	7.11	98.17	15.17	78.97	38.95	33.04
		±1.4	±0.012	±0.013	±0.10	±0.70	±0.13	±0.46	±0.23	±0.22
318 0.56816 g	600	129.3	0.3578	0.3334	7.124	98.25	15.151	78.85	38.79	32.87
		±8.5	±0.0071	±0.0092	±0.065	±0.55	±0.079	±0.24	±0.21	±0.21
	900	9.32	0.357	0.322	7.10	97.9	15.15	78.62	38.58	32.90
		±0.74	±0.031	±0.040	±0.23	±1.3	±0.17	±0.93	±0.40	±0.53
	1750	4.22	0.359	0.332	7.13	97.3	15.28	78.9	39.03	32.63
		±0.30	±0.066	±0.065	±0.24	±1.4	±0.25	±1.7	±0.60	±0.61
	Total	142.8	0.3578	0.3326	7.123	98.20	15.155	78.84	38.78	32.86
		±8.5	±0.0070	±0.0089	±0.061	±0.51	±0.073	±0.23	±0.19	±0.19
<i>For reference:</i>		<i>Atmosphere</i>	0.3537	0.3300	7.136	98.32	15.14	78.90	38.79	32.93