Terrestrial cosmogenic argon

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Abstract

Cosmogenically enriched $^{38}Ar/^{36}Ar$ ratios are detectable in Ca-bearing terrestrial samples, and are resolvable from a uniform background value of 0.18826 ± 0.00018 for materials lacking nucleogenic or kinetic mass fractionation effects. Relationships between $^{38}Ar/^{36}Ar$ and cosmogenic ^{3}He in apatite and fluorite are systematic but difficult to reconcile with current estimates of terrestrial production rates for ^{38}Ar and ^{36}Ar from Ca, suggesting that production from Cl and/or other targets is significant, or that the estimates are inaccurate. In either case, the effects of time-varying production of ^{36}Ar from β^- decay of cosmogenic ^{36}Cl produced from Ca, K, or Cl on the $^{38}Ar/^{36}Ar$ ratio must be accounted for. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Cosmogenic nuclides such as ^{3}He, ^{10}Be, ^{26}Al, and ^{36}Cl produced in situ and accumulated in materials at or near Earth's surface have provided invaluable methods for determining exposure ages and related information such as erosion rates [1–5]. Another cosmogenic nuclide of possible interest is ^{38}Ar, produced mainly from Ca, for which Lal [6] estimated a terrestrial production rate of 200 atoms/g Ca/yr at sea-level and high latitude. Cosmogenic ^{38}Ar ($^{38}Ar_C$) has been measured rou-

tinely for decades in extraterrestrial materials [7], wherein much higher production rates and lower ambient concentrations (i.e. lower than in Earth's atmosphere) favor detection.

Lal's [6] estimated terrestrial production rate of ^{38}Ar from Ca ($P(^{38}Ar_{Ca})$) is comparable, in Ca-rich materials, to production rates of ^{3}He, ^{10}Be, ^{14}C, ^{20}Ne, ^{21}Ne, ^{22}Ne, or ^{26}Al from the important target elements O, Mg, Al, Si, Ca, and Fe. ^{38}Ar is stable, and cosmogenic accumulations should therefore be detectable in Ca-rich materials exposed near the surface of the Earth. Detection of $^{38}Ar_C$ is complicated, however, by two related factors.

The relatively high concentration (~ 6 ppm) of ^{38}Ar in the atmosphere ($^{38}Ar_A$) contributes to background both in terrestrial materials themselves and in analytical processes. $^{38}Ar_A$ occurs as a trapped component in many minerals and

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whole-rock samples in typical concentrations of 10^8–10^{10} atoms/g. An atmospheric correction based on $^{36}Ar_A$ is possible in principle, because the ratio $(^{38}Ar/^{36}Ar)_A$ of 0.18797 ± 0.00046 [8] is known to better than $\pm 0.5\%$. The terrestrial atmospheric ratio is indistinguishable from many other inferred planetary and solar components (e.g. [9]) although some data favor distinct values for certain extraterrestrial components (e.g. [10,11]). Our analysis of 50 air pipets yields $(^{38}Ar/^{36}Ar)_A = 0.18816 \pm 0.00023$, in good agreement with the results of Ozima and Podosek [8].

Our measurements (Fig. 1) of 34 mineral and rock samples from diverse environments known to lack significant surficial exposure indicate homogeneity of $^{38}Ar/^{36}Ar$ in atmospheric and other terrestrial reservoirs within the limits of measurement precision. The one statistically distinct value (0.19304 ± 0.00096) was determined from the glassy rind of a Hawaiian pillow lava, and we conclude that this may be a product of kinetic fractionation similar to that observed by Kaneoka [12]. We conclude tentatively that there are no sources or sinks of ^{38}Ar or ^{36}Ar capable of changing the $^{38}Ar/^{36}Ar$ ratio in large terrestrial crustal reservoirs at the detectable level over the history of the Earth except in the outermost few meters of the crust. The possibility of a primordial solar wind mantle component with subatmospheric $^{38}Ar/^{36}Ar$ [13] remains to be investigated more fully. For convenience we refer to the weighted average (0.18826 ± 0.00018) of $^{38}Ar/^{36}Ar$ values shown in Fig. 1 as the uniform non-cosmogenic terrestrial (UNCT) composition.

Resolving $^{38}Ar_C$ from UNCT in cosmic ray-exposed samples is complicated by the cosmogenic production of ^{36}Ar, whose terrestrial production rate from Ca $P(^{36}Ar_{Ca})$ was estimated by Lal [6] at 69 atoms/g Ca/yr. The basis of Lal's estimates of $P(^{36}Ar_{Ca})$ and $P(^{38}Ar_{Ca})$ is unclear, but presumably both reflect only direct neutron capture and spallation reactions.

$^{36}Ar_C$ is also produced indirectly from the β^- decay of cosmogenic ^{36}Cl ($t_{1/2} \sim 3 \times 10^5$ yr), introducing a time dependence into $P(^{36}Ar_C)$. For exposure ages significantly longer than the ^{36}Cl half-life, the production rate of ^{36}Ar in Ca-rich materials is effectively increased by $P(^{36}Cl_{Ca})$,

estimated at 67 atoms/g Ca/yr [14]. Thus based on these estimates the effective production ratio $P(^{38}Ar_{Ca})/P(^{36}Ar_{Ca})$ is expected to decrease from 2.9 (very recent exposure) to 1.4 ($> 1 \times 10^6$ yr exposure). Cosmogenic production from isotopes of Cl, K, Fe, and Ti, not considered by Lal [6], may also be significant.

Here we report measurements of $^{38}Ar/^{36}Ar$ in Ca-rich samples (four fluorapatites and one fluorite) from the Granite Harbor Intrusive suite of the Transantarctic Mountains [15] having significant cosmic radiation exposure as determined from ^3He concentrations. An additional apatite sample (96MR56) [16] from the rapidly eroding Coast Plutonic Complex of British Columbia was analyzed for both $^{38}Ar/^{36}Ar$ and ^3He for comparison. Also analyzed for $^{38}Ar/^{36}Ar$ were detrital garnet and epidote from the Eocene Montgomery Creek Formation (MC-1) of Northern California, known to have been derived from a rapidly eroding source and rapidly deposited [17], hence unlikely to have significant exposure. Sphene and plagioclase from a surface exposure of Cretaceous diorite (ET96-14) of the Okenyenya Complex [18] in Namibia were also analyzed; this complex is located in a tectonically quiescent and extremely arid region near the western margin of the Kalahari desert, and thus might be expected to exhibit $^{38}Ar_C$.

2. Analysis

Samples of 2–50 mg for argon measurement were baked overnight at 250–300°C in an ultra-high vacuum extraction line, then degassed by fusion with a 50 W Nd-YAG laser followed by gas purification for 180 s. Isotope abundances were measured with an MAP 215-50 noble gas mass spectrometer, using methods described previously [19] except for the use of 10 cycles of peak-hopping and eight integrations per cycle for ^{40}Ar, ^{39}Ar, and ^{37}Ar; 30 integrations/cycle for ^{36}Ar, and 40 integrations/cycle for ^{38}Ar. Mass discrimination (based on a power law) and spectrometer sensitivity were determined from analysis of air pipets interspersed with the samples. Air pipets of 7.5×10^{-14} mol ^{40}Ar were obtained by equili-

brating a 2 l reservoir of purified atmosphere with a 0.2 ml pipet volume, and then expanding the pipet contents into the extraction line. The pipet is isolated between the reservoir and extraction line by automated, pneumatically actuated valves. Initial filling of the reservoir is by expansion from the pipet after being evacuated to $< 10^{-5}$ Pa, followed by removal of reactive gases with an integral Ti foil getter activated at 800–850°C and then slowly cooled in equilibrium with the reservoir gas. The pipet volume is calibrated by reference to $^{40}Ar/^{39}Ar$ dating standards [19]. Spectrometer sensitivity calibration is subject to an estimated $\pm 5\%$ (2σ) error based on reproducibility of ^{40}Ar ion beam intensities between pipet measurements and uncertainties in pipet volume and absolute atmospheric abundance of ^{40}Ar. Procedural backgrounds (blanks) for ^{38}Ar were typically $4–7 \times 10^4$ atoms in the measurements reported here.

^3He data for three of the Antarctic apatite samples, and analytical methods for all ^3He analyses discussed here, are reported by Farley et al. [20] who inferred a sea-level, high latitude production rate of about 100 atoms $^3He/g/yr$ for apatite. Farley et al. [20] showed that other sources of ^3He, such as nucleogenic production from Li, are unlikely to be significant in these samples.

Fig. 1. $^{38}Ar/^{36}Ar$ measurements for 34 mineral and rock samples of diverse ages and geologic environments known to have minimal cosmic ray exposure, plus mean of 50 air pipets (AP) analyzed in the course of this study. Error bars show 95% confidence intervals. Gray bar shows weighted mean defining UNCT. Open symbol is a Hawaiian basalt (see text) excluded from the mean.

3. Results

Measured $^{38}Ar/^{36}Ar$ ratios vary from UNCT to values as high as 0.2894 ± 0.0029 (σ) for one of the Antarctic apatites (R22738; Table 1). Step-heating (Fig. 2) of this sample by incrementally increasing laser power yields progressive enrichment in $^{38}Ar/^{36}Ar$, from UNCT values up to 0.3640 ± 0.0136. This experiment suggests that $^{38}Ar_C$ is more tightly retained than the UNCT

Table 1
Summary of argon and helium data

Sample	Min	Mass (mg)	^{38}Ar (10^6 atoms)	$\pm \sigma$ (10^6 atoms)	$^{38}Ar/^{36}Ar$	$\pm \sigma$	^3He concentration (10^9 atoms/g)	^3He exposure age (Ma)
Transantarctic Mountains (granitoids)								
R22722	Ap	2.10	5.71	0.12	0.2248	0.0049	1.92	4.83
R22722	Ap	4.31	12.68	0.11	0.2193	0.0023	1.92	4.83
R22738	Ap	8.29	21.29	0.16	0.2894	0.0029	5.32	6.22
R22738	Ap	2.40	7.46	0.20	0.2966	0.0099	5.32	6.22
R22739	Ap	5.95	40.40	0.24	0.2005	0.0014	1.57	3.80
R22737	Fl	6.10	25.72	0.22	0.2296	0.0023	0.23	–
VN-1L	Ap	6.05	12.66	0.10	0.1919	0.0017	0.10	–
Coast Plutonic Complex (granitoid)								
96MR56	Ap	8.00	59.05	0.27	0.1879	0.0009	n.d.	n.d.
Montgomery Creek Formation (sand)								
MC-1	Gt	8.51	5.44	0.07	0.1880	0.0028	–	–
MC-1	Ep	6.71	21.69	0.13	0.1886	0.0013	–	–
Okenyenya Complex (diorite)								
ET96-14	Sp	4.90	9.03	0.13	0.1964	0.0033	–	–
ET96-14	Pl	13.67	67.74	0.53	0.1903	0.0018	–	–

Mass of sample refers to amount used for argon analysis. Helium data except VN-1L and R22737 are from Farley et al. [20]. n.d. = not detected, (–) = not measured.
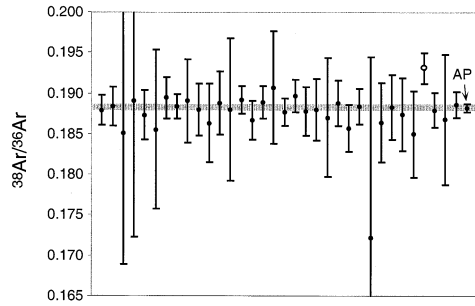
component, as expected if the latter is in part adsorbed or otherwise loosely bound in the apatite crystals. The integrated total $^{38}Ar/^{36}Ar$ (0.2966 ± 0.0099) from all six steps in this experiment agrees with that (0.2894 ± 0.0029) determined from total fusion of another (larger) aliquot of this sample. Reproducibility is further established by indistinguishable $^{38}Ar/^{36}Ar$ of 0.2248 ± 0.0049 and 0.2198 ± 0.0023 measured for two aliquots of R22722 apatite.

For the apatite samples, a reasonable correlation between $^{38}Ar/^{36}Ar$ and ^{3}He is evident (Fig. 3). However, it is difficult to reconcile these data with Lal's [6] estimates for $P(^{38}Ar_{Ca})$ and $P(^{36}Ar_{Ca})$ unless there are significant additional sources of ^{36}Ar beyond UNCT, as follows. If all ^{38}Ar and ^{36}Ar in the apatites are binary mixtures of UNCT and cosmogenic Ca-derived components, the concentration of either cosmogenic isotope can be calculated as:

$$^{38}Ar_{Ca} = \frac{^{38}Ar_T - {^{36}Ar_T} \cdot \left(\dfrac{^{38}Ar}{^{36}Ar}\right)_{UNCT}}{1 - \left(\dfrac{^{36}Ar}{^{38}Ar}\right)_{Ca} \cdot \left(\dfrac{^{38}Ar}{^{36}Ar}\right)_{UNCT}} \quad (1)$$

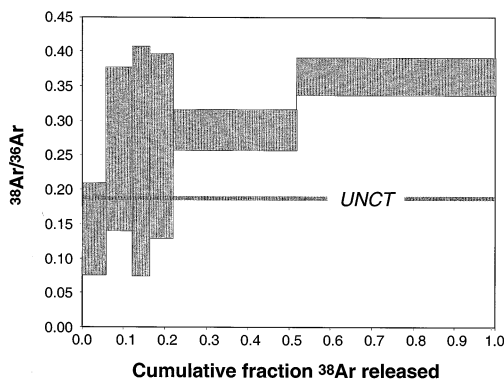where the subscript T denotes total abundance of either isotope. The time-dependent production ra-

Fig. 2. Incremental heating experiment for R22728 apatite showing progressive increase in $^{38}Ar/^{36}Ar$ with removal of surface-correlated atmospheric argon and proportional increase in cosmogenic component.
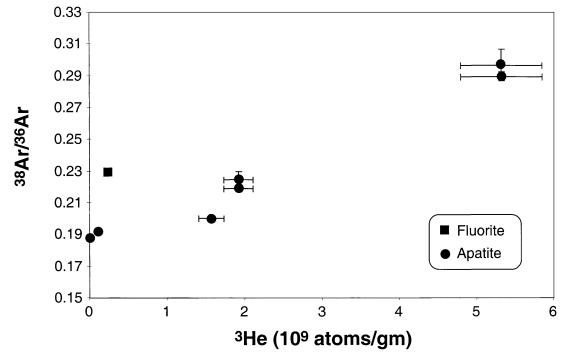

Fig. 3. Relationship between $^{38}Ar/^{36}Ar$ and ^{3}He for Antarctic apatite and fluorite samples.

tio is given by:

$$\left(\frac{^{36}Ar}{^{38}Ar}\right)_{Ca} = \frac{P(^{36}Ar_{Ca}) + P(^{36}Cl_{Ca}) \cdot (1 - e^{-\lambda t})}{P(^{38}Ar_{Ca})} \quad (2)$$

Applying Eqs. 1 and 2, using ^{3}He exposure ages to calculate time-dependent production from $^{36}Cl_{Ca}$, and estimating Ca contents from stoichiometry, model $^{38}Ar_{Ca}/Ca$ concentrations (i.e. based on $P(^{38}Ar_{Ca})/P(^{36}Ar_{Ca}) = 2.9$; [6]) for the apatite samples yield apparent $P(^{38}Ar_{Ca})$ values 0.5–0.9 times $P(^{3}He)$. In contrast, an apparent $P(^{38}Ar_{Ca})/P(^{3}He)$ value of ~ 9 is determined in similar fashion from the fluorite data. These discrepancies may be partly explained by additional production of ^{36}Cl via thermal neutron capture on ^{35}Cl followed by $^{36}Cl \rightarrow {^{36}Ar}$ β^- decay. Neutron capture on Cl is the most efficient mechanism for lowering $^{38}Ar/^{36}Ar$ due to a production ratio of ~ 0.003. $P(^{36}Cl_{Cl})$ in granite is estimated at 0.03 atoms/ppm Cl/g/yr [14], but taking this into account with an estimated 2000 ppm Cl in the apatites only raises the apparent $P(^{38}Ar_{Ca})$ values to 0.6–1.2 times $P(^{3}He)$, i.e. approximately two to three times lower than Lal's [6] estimate. The most discrepant result, for fluorite, has unknown significance because the ^{3}He production rate for this mineral is not known. The apparent (i.e. assuming $P(^{3}He)$ is similar to that in apatite) fluorite anomaly could result from partial loss of ^{3}He, although our diffusion measurements on other fluorite samples suggest that this mineral is He-re-

tentive under Earth surface conditions (Farley, unpublished).

4. Conclusions

Cosmogenically enriched $^{38}Ar/^{36}Ar$ ratios in terrestrial materials can be resolved from what appears to be a UNCT background of 0.18826 ± 0.00018. Detrital Ca-rich minerals (garnet and epidote) from a rapidly eroded (<2 Myr from erosion to deposition) source show no detectable enrichment in $^{38}Ar/^{36}Ar$, consistent with short residence time in the surficial environment. Sphene from an arid and tectonically quiescent environment shows enriched $^{38}Ar/^{36}Ar$, qualitatively consistent with an expected low erosion rate.

Apatite samples whose exposure history is constrained by cosmogenic ^{3}He measurements demonstrate an unambiguous correlation between ^{3}He and $^{38}Ar/^{36}Ar$. Considering ingrowth of Ca- and Cl-derived ^{36}Cl to ^{36}Ar, the production rate of ^{38}Ar from Ca estimated by Lal [6] appears to be several times too large, and/or the production rate of ^{36}Ar too small. The $P(^{38}Ar_{Ca})/P(^{36}Ar_{Ca})$ would have to be significantly lower than the value of ~ 1.7 inferred for lunar materials (e.g. [21]), and/or additional sources of cosmogenic ^{36}Ar must exist, to explain our data. On the other hand, the fluorite data suggest much higher $P(^{38}Ar_{Ca})$ than Lal's [6] estimates and, provided that cosmogenic ^{3}He is retained in the fluorite, this admits the possibility that we have underestimated the effects of Cl in producing ^{36}Ar. The complexity of environmental chemical factors governing nucleogenic ^{36}Cl production [14] leaves this question unresolved for the moment.

Further investigation of minerals with strategically selected compositions (i.e. Ca-rich minerals lacking Cl, and vice versa) and significant cosmic ray exposure should produce greater clarity as to the target isotope parentage of cosmogenic ^{38}Ar and ^{36}Ar. Similar strategies should also be employed to investigate ^{38}Ar and ^{36}Ar production from K, Ti, and Fe, although the contribution from these target elements is probably much lower than from Ca (e.g. [7,21]) except in K-rich materials.

Also potentially fruitful would be incremental heating analysis of neutron-irradiated samples using the method pioneered by Turner et al. [7]. This approach permits (1) direct measurement of $^{38}Ar_C/Ca$ and (2) thermal discrimination via incremental heating of adsorbed atmospheric from intra-lattice cosmogenic Ar for more sensitive detection of $^{38}Ar_C$.

Improved understanding of ^{38}Ar and ^{36}Ar production rates and mechanisms will be useful for several reasons. Stable cosmogenic isotopes are applicable to surface processes beyond the time range of relatively short-lived isotopes such as ^{10}Be, ^{26}Al, or ^{36}Cl. The generally lower diffusivity of argon than of helium or neon in minerals may offer advantages in terms of retentivity [8]. Analysis of $^{38}Ar_C/Ca$ to constrain erosion rates or exposure ages in carbonate rocks may be a particularly productive application. Cosmogenic argon may also play a useful role in models of atmospheric evolution, particularly since argon is heavy enough (cf. helium and neon) to be quantitatively retained in the atmosphere [8].

Finally, it should be noted that cosmogenic anomalies in $^{38}Ar/^{36}Ar$ could produce spurious K–Ar or $^{40}Ar/^{39}Ar$ dating results and sampling for such purposes should seek to avoid near-surface exposures, especially at high latitudes and/or elevations in regions of possibly low erosion rates.

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