

Cosmic-ray produced radioisotopes in lunar samples from the Sea of Tranquillity (Apollo 11)

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Abstract— ^{10}Be , ^{14}C , ^{22}Na , ^{26}Al , ^{36}Cl , ^{37}Ar and ^{39}Ar have been measured in lunar fines (10084) and Type A rock (10057). The latter five isotopes have been studied using a selective dissolution technique to obtain activities (dpm/kg) for the bulk samples as well as their production rates from relevant target elements.

Our conclusions are: (1) During the past 400 years the mean flux of the high-energy component of the cosmic radiation ($E \geq 200$ MeV) has been roughly the same in the vicinity of the moon as that averaged over the orbits of meteorites; perhaps it was slightly less. (2) The lunar surface layers have been exposed to an intense flux of low-energy protons down to energies of at least 50 MeV. (3) Averaged over the last 400 years the flux of fast neutrons with $E > 1.5$ MeV has been $25 \text{ n/cm}^2 \text{ sec}$. Isotopes with different half-lives indicate either a peculiar energy spectrum, with an exceedingly large fraction of neutrons below 2 MeV, in which case the flux given is a lower limit, or a strong time-dependence of the neutron flux. (4) An attempt to measure the mean flux of thermal neutrons during the last 300,000 years gave inconclusive results, indicating the flux to have been less than $1 \text{ n/cm}^2 \text{ sec}$.

INTRODUCTION

THE EXTENSIVE study of cosmic-ray produced stable and radioactive isotopes in meteorites during the last decade has yielded a wealth of information on the intensity of the cosmic radiation in the past as well as on the history of the meteorites. While it appears to be generally agreed upon that on the average the high-energy component ($E > 200$ MeV) of the cosmic radiation has been constant within a factor of two during the past 10^9 yr (HEYMANN and SCHAEFFER, 1962; HONDA and ARNOLD, 1964; VOSHAGE, 1962, 1967), there are a number of cases where short-lived radioisotopes indicate short-term variations (FIREMAN, 1967; BEGEMANN *et al.*, 1969; FIREMAN and GOEBEL, 1969), especially of the low-energy component. Due to the fact, however, that the orbits of individual meteorites are not known there is always an inherent ambiguity as variations in time cannot be separated from variations in space.

In this respect, lunar surface material can be considered to be superior to meteoritic matter as, although the ideas on the origin of the moon are still as divergent as ever, the consensus is that it has been in its present orbit for a rather long period of time. Furthermore, while meteorites undergo ablation losses during their passage through the atmosphere, which to some extent destroy the record of the primary low-energy cosmic rays, material from the surface of the moon should contain such information as well.

It is for this reason and because of marked differences in the abundance of some important target elements in lunar samples and meteorites that the abundance *pattern* of the radioisotopes must be expected to differ from that found in meteorites. In order to facilitate a comparison with the numerous meteoritic data it is necessary

to know the production rates not only for the bulk samples but for individual target elements as well. Only then the difference in the chemical composition can be properly taken into account.

EXPERIMENTAL PROCEDURE

(A) General

Two samples of lunar material were available for the present investigation: 100.1 g of bulk fines, <1 mm size (10084-18), and 119.1 g of rock (Type A, 10057-40). No information was supplied regarding the original position of our rock specimen within the rock 10057.

Immediately upon receipt (September 18 and October 10, 1969, respectively) their γ -activity was determined by means of a large, high-resolution Ge(Li)-detector (13.8 per cent relative efficiency and 2.85 keV FWHM for the 1.332 MeV ^{60}Co line) and a 4000-channel analyser. The bulk fines were counted as received; the rock specimen was pulverized to pass a 60 μ sieve.

Next, after addition of a ^{37}Cl spike (20 mg NaCl) and 0.5 cm³ STP carrier Ar the fines were leached under vacuum for 3 hr with 500 cm³ of 10⁻⁴ N HNO₃, washed with acetone and dried overnight at 65°C. Subsequently, both samples were fractionally dissolved in order to fractionate as many relevant target elements as possible.

Preliminary experiments on small aliquots showed that about 20 per cent of *all* mineral components in the fines went into solution already with cold HNO₃ (1:3), that hot HNO₃ (1:3) preferentially dissolves feldspar, resulting in a fraction enriched in Ca and Al, and that NH₄HF₂ + H₂SO₄ (conc.) at 350°C completely decomposes the residue. Hence, these were the reagents chosen, the time of treatment was 3–4 hr. All steps were performed under vacuum, after addition of carriers (25 mg Be as BeSO₄, 25 mg Sc as Sc₂(SO₄)₃, 40 mg NaCl, 0.5 cm³ Ar). The Cl of the NaCl was enriched in ^{37}Cl (96 per cent), but was free of any detectable radioactivity.

(B) Chemistry

In order to minimize any contamination wherever possible we tried to apply procedures requiring only such reagents which can be purified via the gaseous phase.

1. *HNO₃-fractions.* The vacuum-system has been in use for work on meteorites for many years (WÄNKE and VILCSEK, 1959). The procedure to collect and purify the Ar is essentially unchanged.

After removal of the reaction vessel from the vacuum-system the undissolved residue was separated by centrifugation. The residues were washed repeatedly with water and finally acetone, dried at 65°C, and preserved for the next step.

An aliquot (5 per cent) of the supernatant was set aside for a determination of relevant elements. From the main solution the chlorine was precipitated as AgCl and centrifuged. After removal of the excess Ag⁺-ions silica was separated by dehydration. Iron was extracted with diethyl ether from 6 N HCl. Subsequently, to the aqueous solution the same volume of diethyl ether was added and the liquids saturated with gaseous HCl at 0°C (FISCHER and SEIDEL, 1941).

The precipitate containing Al and Na was purified by repeating the procedure, and Al separated by two successive precipitations with NH₄OH.

Mg was removed from the combined filtrates with an alcoholic solution of (NH₄)₂CO₃. After decomposition of the ammonium salts Na was precipitated again with gaseous HCl. The Al containing hydroxides were dissolved in HCl and the Al for further purification converted to aluminate with NaOH. The alkaline solution was acidified and Al (OH)₃ precipitated with NH₄OH.

The solution from the first gaseous HCl-precipitation step was extracted with tri-n-butyl phosphate for the separation of Sc (EBERLE and LERNER, 1955). The aqueous phase was evaporated to dryness, the solids taken up with HNO₃, and the rare earth elements extracted with tri-n-butyl phosphate, too (PEPPARD *et al.*, 1953).

In the further procedure Be was separated by precipitation with NH₄OH in the presence of ammonium salts, the hydroxides dissolved in H₂SO₄, ammonium-peroxy-disulphate added to oxidize chromium to chromate, and Be precipitated as hydroxide.

2. *Residue.* The residue after the hot HNO₃ step was mixed thoroughly with a four-fold amount of

HN_4HF_2 and put into a large Pt-beaker inside a glass vessel, which was then connected to the vacuum system mentioned above. After evacuating the system, carefully degassed concentrated H_2SO_4 (4 cm^3/g residue) was added slowly, and the temperature raised to 350°C . The evolved HCl and SiF_4 were condensed in a trap immersed in boiling nitrogen.

When the reaction was complete the decomposition vessel was taken off the vacuum-system, H_2SO_4 added to the cake, and heated to dryness to ensure the complete removal of fluorides. The cake was then elutriated with H_2O and insoluble sulfates brought into solution with HCl . From this solution the hydroxides of Fe, Ti, Cr, Al, Mn, Sc and Be were precipitated with NH_4OH , and redissolved in HCl . The further treatment was identical to that described for the HNO_3 -fraction after the removal of silica.

The filtrate of the hydroxide precipitation was further processed for the separation of Na as described above.

3. *Radiochemical purification.* Cl: AgCl was decomposed with Na_2CO_3 and the chlorine purified in form of HCl gas (VILCSEK and WÄNKE, 1963) and converted to NaCl for counting.

Be: Cu was added to the solution (1 N in HCl) and precipitated as CuS . This was followed by a purification step with $\text{Fe}(\text{OH})_3$ in NaOH and a BaSO_4 scavenge. The Be-acetylacetonate complex was extracted into CCl_4 (ALIMARIN and GIBALO, 1956). After addition of EDTA Be was precipitated with NH_4OH and ignited to BeO .

(C) Counting

Ar was counted in the Geiger-region after addition of Q-gas (98.5 per cent He, 1.5 per cent i-butane); the counter volume was 20 cm^3 , the total pressure 0.5 atm, the background 0.35 cpm, and the counting efficiency 80 per cent. The ^{37}Ar and ^{39}Ar contributions were separated by following the decay of ^{37}Ar for periods of time from 50 to 90 days. As a further check, the Ar from the different fractions of both samples was combined and the total ^{39}Ar -activity determined more than six half-lives of ^{37}Ar after the collection of the samples. As the rock specimen was received as late as 80 days after collection the ^{37}Ar could not be determined with any degree of accuracy. Hence, we prefer to give no value at all.

The ^{36}Cl - and ^{10}Be -activities were determined with two Sharp thin-window ($800\text{ }\mu\text{g}/\text{cm}^2$) gas-flow detectors, each shielded by a guard counter in anti-coincidence with the sample counter, again using Q-gas. The samples were mounted on shallow gold planchets to increase the counting efficiency by back-scattering. For both isotopes the efficiencies of the 1 in. and $\frac{1}{2}$ in. detector were around 40 and 20 per cent, respectively, depending slightly on the amount of sample counted. For the sample-weights in question the efficiencies for ^{10}Be were 10 per cent lower than those for ^{36}Cl . The background counting rates were 0.16 and 0.07 cpm, respectively, using dummies of a chemical composition the same as the samples.

^{22}Na was measured by placing the separated NaCl in plastic containers between two 3×2 in. $\text{NaJ}(\text{Ti})$ -crystals. The two 511-keV annihilation quanta were counted in coincidence, as well as the combined spectra from both crystals registered with a 512-channel analyser. The latter information was used only to check the absence of any interfering activities. The counting efficiency in the 511-keV coincidence mode was 5.0 per cent.

The ^{26}Al was counted as Al_2O_3 in plastic containers, utilizing the $\text{Ge}(\text{Li})$ -detector described above. Both the 511 keV and the 1.81 MeV γ -lines were used, the efficiencies were 2.3 and 0.45 per cent, respectively. The activities found via the two γ -lines always agreed within the statistical limits of error.

^{14}C was determined in a 10 g aliquot of the fines which was intended for determination of the Ar-activity in the bulk fines. This Ar, however, was unfortunately lost. The procedure used to produce CO_2 —after the addition of lamp black—was essentially that described by GOEL (1962) except that the conversion temperature was 1100°C . The CO_2 was converted to C_2H_2 with Li (BIEN, 1967); the activity determined by means of a thin-wall proportional counter (Oeschger-type) with a total volume of 2.5 l. and a central volume of 1.5 l., working at a pressure of 200 torr. The counting efficiency, with the lower and upper threshold chosen, was 49 per cent, the background 1.21 cpm.

RESULTS AND DISCUSSION

In Table 1, columns 5 and 9, are listed the concentrations in the bulk samples of those target elements which are most important for the production of the radioisotopes studied. (For a comparison with the results obtained in other laboratories see WÄNKE *et al.*, 1970b.) The amounts dissolved in each step of the fractional dissolution procedure are also given. They were determined by wet chemistry and/or neutron activation of aliquots of the various solutions as well as aliquots of the portions left

Table 1. Results of chemical and neutron activation analyses, and decay rates of the radioisotopes measured

	Lunar fines 10084-18					Lunar rock 10057-40			
	HNO ₃ (25°C)	HNO ₃ (70°C)	residue	sum	bulk	HNO ₃ (90°C)	residue	sum	bulk
Chem. analysis (% by weight)									
O	10.6	4.5	26.4	41.5		9.5	30.9	40.4	
Mg	1.9	0.14	2.8	4.8		0.4	3.8	4.2	
Al	3.9	1.8	1.2	6.9		3.4	1.2	4.6	
Si	3.9	1.8	14.0	19.7		4.0	14.9	18.9	
K	0.045	0.014	0.050	0.109		0.057	0.144	0.201	
Ca	3.6	1.6	3.6	8.8		2.3	5.6	7.9	
Ti	0.5	<0.2	3.8	4.3		0.33	5.35	5.7	
Fe	4.2	0.66	7.1	12.0		1.3	13.0	14.3	
Activity (dpm/kg)									
¹⁰ Be	5.9±1	—	5.8±1	14±3*	—	—	—	—	—
¹⁴ C	—	—	—	—	39±4	—	—	—	35±5
²² Na	32±5	10±2	19±3	61±6	61±15	9±2	24±6	33±7	24±6
²⁶ Al	57±13	37±15	27±14	121±25	86±12	25±10	32±16	57±20	70±10
³⁶ Cl	6.5±0.3	1.9±0.3	6.2±0.3	14.6±0.6	—	3.30±0.31	8.85±0.38	12.2±0.5	—
³⁷ Ar	14.4±0.9	4.7±4.3	14.1±0.9	33.2±4.5	—	—	—	—	—
³⁹ Ar	2.43±0.14	1.18±0.43	3.86±0.20	7.5±0.5	8.1±0.3	1.99±0.17	7.09±0.23	9.0±0.29	8.5±0.3

* The entry of ¹⁰Be under 'sum' contains a small contribution from the HNO₃ (70°C)-step, which was not measured but calculated via the amount of oxygen in this fraction. The ³⁹Ar-activities under 'bulk' are not based on measurements of bulk samples, proper, but on the combined Ar from the separate fractions.

undissolved after the individual steps. Oxygen was determined by fast neutron activation in the undissolved portions as well, but the entries in columns 2, 3 and 6 are calculated ones assuming all cations to have been present as oxides. The values obtained from the difference between the oxygen content of the initial samples and their respective residues are naturally rather uncertain ("Elephant method", HOUTERMANS, 1950).

The lower part of Table 1 shows the decay rates of the radioisotopes (in dpm/kg) for the individual fractions or the bulk samples, or both. With the exception of ²⁶Al in the 'fines', the agreement between the sum of the activities and that obtained on the bulk samples is good for a given isotope, showing the data to be internally consistent. Where comparable they, furthermore, agree fairly well with those obtained in other laboratories (LSPET, 1970; SHEDLOVSKY *et al.*, 1970; PERKINS *et al.*, 1970; STOENNER *et al.*, 1970; FIREMAN *et al.*, 1970).

Taking into account that the lunar surface has only a 2π -geometry for the exposure to the cosmic radiation, the decay rates for all isotopes and their abundance *pattern* are distinctly different from what is observed in meteorites (see e.g. HONDA and ARNOLD, 1964), reflecting the different chemical composition as well as the presence of low-energy solar primaries.

(A) *Production rates on individual target elements*

In order to separate the two effects as much as possible we shall now proceed to calculate the decay rates of ^{22}Na , ^{26}Al , ^{36}Cl , ^{37}Ar and ^{39}Ar on individual target elements from the data in Table 1.

^{39}Ar . Proton-induced spallation reactions on Ca can be neglected compared to the contribution from Ti, as only the rare isotopes of Ca with a combined abundance of 3 per cent can yield ^{39}Ar . This is reflected in the 600 MeV cross section data of STOENNER *et al.* (1970) who found the production on Ca to be eight times less than that on Ti.

Similarly, the contribution from the $^{41}\text{K}(\text{p}, 2\text{pn})^{39}\text{Ar}$ -reaction is insignificant. This can be seen when comparing the activities possibly produced by analogous reactions on other nuclides, e.g. $^{56}\text{Fe}(\text{p}, 2\text{pn})^{54}\text{Mn}$ and $^{48}\text{Ti}(\text{p}, 2\text{pn})^{46}\text{Sc}$, in lunar matter. The Q-values are -20.4 MeV and -22.1 MeV, respectively, compared to -17.7 MeV for the $^{41}\text{K}(\text{p}, 2\text{pn})^{39}\text{Ar}$ -reaction; the cross sections will thus be comparable. Allowing for the much lower abundance of ^{41}K we derive from the observed ^{54}Mn -activities of about 50 dpm/kg (SHEDLOVSKY *et al.*, 1970; PERKINS *et al.*, 1970; O'KELLEY *et al.*, 1970) a contribution of ^{39}Ar from ^{41}K of 0.04 dpm/kg; and from the ^{46}Sc -activities of about 10 dpm/kg (PERKINS *et al.*, 1970; O'KELLEY *et al.*, 1970) a value of 0.02 dpm/kg. These estimates are even upper limits, because both ^{54}Mn and ^{46}Sc are assumed to be solely produced by the (p, 2pn)-reaction. In both cases, however, (n, p)-reactions, on ^{54}Fe and ^{46}Ti , respectively, may very well contribute significantly to the activities observed.

With neutrons as bombarding particles the $^{40}\text{Ca}(\text{n}, 2\text{p})$ -, $^{42}\text{Ca}(\text{n}, \alpha)$ -, $^{43}\text{Ca}(\text{n}, \alpha\text{n})$ -reactions as well as similar ones on the heavier isotopes are possible. Of these, however, only the $^{42}\text{Ca}(\text{n}, \alpha)$ -reaction with a Q-value of $+0.34$ MeV is of any importance in spite of the low abundance of ^{42}Ca . For $^{40}\text{Ca}(\text{n}, 2\text{p})$ the Q-value is -8.1 MeV and the cross section on neighbouring nuclides at 14.7 MeV is smaller than 1 mb (BRAMLITT and FINK, 1963), while in case of the heavier isotopes the contribution will be negligible because of both the low abundance *and* the increasing Q-value.

Hence, the principal reactions responsible for the total ^{39}Ar -activity will be spallation reactions on Fe and Ti, and the $^{39}\text{K}(\text{n}, \text{p})$ - and $^{42}\text{Ca}(\text{n}, \alpha)$ -reactions induced by neutrons in the MeV energy range. Unfortunately, from the experimental data of Table 1 the latter two cannot be separated, and contrary to chondrites where the Ca/K-ratio is about an order of magnitude smaller the contribution from Ca cannot be neglected entirely.

In order to estimate its importance, however, one can compare the cross sections for the two competing reactions. Since no data are available for the $^{42}\text{Ca}(\text{n}, \alpha)^{39}\text{Ar}$ -reaction, we shall assume its cross section to be the same as that of the $^{40}\text{Ca}(\text{n}, \alpha)^{37}\text{Ar}$ -reaction, as both are exothermic (n, α)-reactions with similar Q-values. For energies

above 4 MeV the ratio $\sigma[^{40}\text{Ca}(n, \alpha)^{37}\text{Ar}]/\sigma[^{39}\text{K}(n, p)^{39}\text{Ar}]$ is about 0.6 while for lower energies it gradually decreases (JESSEN *et al.*, 1965; BASS, 1968). Hence, an upper limit for the contribution from Ca is obtained by adding to the amount of potassium in the samples 0.6 times the amount of ^{42}Ca .

The production rates $P(X)$ thus obtained are listed in Table 2. As the contributions from Fe and Ti cannot be calculated independently the yield from Ti was set to

Table 2. Production rates of various isotopes on the major target elements, given in dpm/kg target element

Isotope	Mg	Al	Target Si	K	Ca	Fe
^{22}Na (Fines)	300	550	50			
^{22}Na (Rock)	180	120	100			
^{26}Al (Fines)	—	1400	150			
^{26}Al (Rock)	—	540	170			
^{36}Cl (Fines)					175	
^{36}Cl (Rock)					152	
^{37}Ar (Fines)					400	
^{37}Ar (Rock)					—	
^{39}Ar (Fines)				3300	—	7.9
^{39}Ar (Rock)				2700	—	7.5

be four times that from Fe, corresponding to a hardness exponent of $n = 2.5$ in the semi-empirical spallation formula as given by GEISS *et al.* (1962). This formula has been found to fit the abundance pattern of cosmic ray produced stable and radioactive nuclides in meteorites over a wide mass range. We wish to emphasize that the production rates on potassium are essentially independent of the value of $P(\text{Ti})/P(\text{Fe})$. A change by a factor of two affects $P(\text{K})$ by less than 10 per cent. They, furthermore, are not very sensitive to the correction for the contribution from the $^{42}\text{Ca}(n, \alpha)$ -reaction. Neglecting it entirely, the production rates are 4400 and 3100 dpm/kg for the fines and rock, respectively (WÄNKE *et al.*, 1970a); assuming the (n, α) -cross section to be equal to the (n, p) -cross section for the whole range of neutron energies yields 2800 and 2500 dpm/kg, respectively.

^{37}Ar and ^{36}Cl . The important elements are Ca, Ti and Fe. From the data available at present, it is not possible to determine the contribution from Ti and Fe except to say that it is very minor: In the cold HNO_3 -fraction and the residue the same amounts of Ca were found as well as the same ^{37}Ar - and ^{36}Cl -activities, in spite of the fact that the Ca/Ti-ratio in the two fractions is different by a factor of 8 (Table 1). It should be remembered, however, that the entries in Table 2 are upper limits. For example, if the production of ^{36}Cl on Fe and Ti is set equal to that of ^{39}Ar on these elements, the production rate on Ca would be lower by about 20 per cent.

For ^{37}Ar we believe the predominance of Ca again to be due to fast neutrons, specifically to the $^{40}\text{Ca}(n, \alpha)^{37}\text{Ar}$ -reaction.

^{26}Al . At present, the large statistical errors in the decay rates do not allow to determine the contributions from Al and Si with the desired accuracy. Nevertheless, it is quite clear that in the fines as well as the rock Al is the more important target element. Especially in the fines, although the Si/Al-ratio is about 3, by far the largest percentage of the total ^{26}Al is produced on Al.

^{22}Na . The target elements to be considered are Mg, Al and Si. Here again, the entries in Table 2 are tentative only. What they do show, however, is a distinct difference in relative importance of the three target elements in the fines and in the rock. In the latter the production rates on Al and Si are about the same, while that on Mg is slightly higher. In the fines, on the other hand, the contribution from Si is very small and the yield from Al is distinctly *higher* than that from Mg.

(B) *Implications for the cosmic radiation*

Due to the peculiar chemical composition of the lunar material, especially the absence of major amounts of metallic iron and troilite, the only high-energy product which could be determined with sufficient accuracy is ^{39}Ar produced from iron. As mentioned above, the production rate in Table 2 has been calculated under the assumption that for this isotope $P(\text{Ti})/P(\text{Fe}) = 4$. If one uses a ratio of 2 instead—which appears to be the lowest reasonable choice— $P(\text{Fe})$ would be 11 dpm/kg. In small iron meteorites and the metal phase from stone and stony-iron meteorites, exposed in 4π -geometry, it ranges between 20 and 30 dpm/kg (VILCSEK and WÄNKE, 1963; BEGEMANN and VILCSEK, 1969). Hence, during the last 400 yr the intensity of the high-energy cosmic radiation ($E > 200$ MeV) in the vicinity of the moon has been roughly the same as that averaged over the orbits of the meteorites. If there is any difference at all the flux near the moon has been slightly less, in accordance with direct measurements during a solar minimum (O'GALLAGHER and SIMPSON, 1967), as well as conclusions drawn from measurements on meteorites (FIREMAN, 1967; BEGEMANN and VILCSEK, 1969).

For the low-energy component, there is much more information contained in the data. In the fines, e.g. ^{22}Na is more abundantly produced from Al than from Mg, and the yield from Si is much lower. As found in numerous target experiments with proton energies above 100 MeV (for a recent compilation see KIRSTEN and SCHAEFFER, 1969) that $\sigma(\text{Mg}):\sigma(\text{Al}):\sigma(\text{Si}) \approx 2:1.5:1$, we conclude that protons in this energy range cannot be responsible for most of the ^{22}Na in the fines. At lower energies, however, the $^{27}\text{Al}(p, x)^{22}\text{Na}$ cross section exhibits a pronounced maximum at about 50 MeV (RAYUDU, 1964; FURUKAWA *et al.*, 1965) which apparently does not exist for the $\text{Mg}(p, x)^{22}\text{Na}$ -reaction. It is true that older measurements show such a maximum for the latter reaction as well (MEADOWS and HOLT, 1957), but this appears to be an artifact introduced by the use of an erroneous excitation function for the $^{27}\text{Al}(n, x)^{24}\text{Na}$ monitor reaction. Using a more recent one (HICKS *et al.*, 1956) the maximum vanishes, in accordance with direct measurements by RAYUDU (1964). Hence, it is our contention that protons of around 50 MeV were the most important nuclear active particles for the production of ^{22}Na in the fines.

At the same time this accounts for the low yield on Si as well (Fig. 1). It, furthermore, explains the difference between fines and rock, if one assumes our specimen of the rock to have been partially shielded from these low energy protons. Not only will the bulk activity be lower in the rock, but the ratio $P(\text{Mg}):P(\text{Al}):P(\text{Si})$ will change towards a more equal production on the three target elements as well, in accordance with our observation.

The same conclusion is reached from the production rates of ^{26}Al on Al and Si.

Here, no cross section data are available, but one can compare the entries in Table 2 with those given by FUSE and ANDERS (1964) for stone meteorites. As these authors found $P(\text{Si}) = 310$ dpm/kg the agreement is excellent, because for the surface of a large body this has to be roughly reduced by a factor of two. Obviously, nuclear reactions on Si leading to ^{26}Al induced by low-energy protons are insignificant. This is supported, e.g. by the fact that ^{54}Mn , produced at least partly by the analogous reaction on ^{56}Fe , is found not to depend on depth in a single lunar rock (SHEDLOVSKY *et al.*, 1970). For the production on Al, on the other hand, the contribution from low-energy protons must play a major role, as is apparent from the continuous decrease of $P(\text{Al})$ in lunar fines [$P(\text{Al}) = 1400$ dpm/kg], lunar rock (540 dpm/kg) and

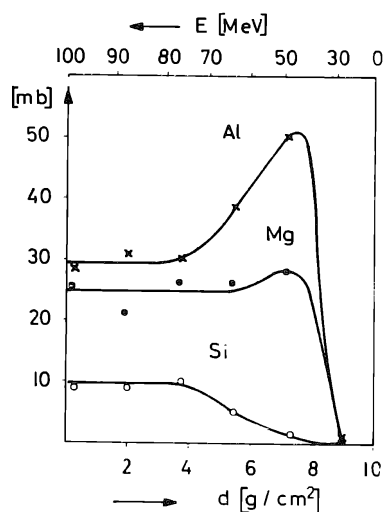


Fig. 1. Cross sections for the production of ^{22}Na from Mg, Al and Si upon bombardment of a thick target with 100 MeV protons (RAYUDU, 1964). The curves drawn through the data points as well as the energy scale were added by us.

meteorites ($480/2 = 240$ dpm/kg) (FUSE and ANDERS, 1969). Again, this is strikingly confirmed indirectly by the results of SHEDLOVSKY *et al.* (1970), who found a very steep decrease with depth of the activity of ^{55}Fe , an isotope whose position relative to the main target isotope is the same as that of ^{26}Al to Al.

In order to deduce the fast-neutron flux from the $^{39}\text{K}(n, p)$ -produced ^{39}Ar we shall follow the procedure described in detail by BEGEMANN *et al.* (1967). There, it has been shown that for energies above 1.5 MeV the effective cross section for the (n, p) -reaction is 140 mb, rather independent of the shape of the neutron energy spectrum assumed. (The limit of $E = 1.5$ MeV is solely due to the lack of cross section data for lower neutron energies.) This value combined with a production rate of 3000 dpm/kg potassium, found in both the fines and our rock specimen, yields for the mean flux of fast neutrons ($E > 1.5$ MeV), averaged over the last 400 yr, $\phi = 25$ n/cm² sec.

However, the high ratio of the production rates of ^{39}Ar from potassium via the (n, p) -reaction to that of ^{37}Ar from Ca via the (n, α) -reaction indicates that either the neutron energy spectrum contains an extremely large fraction of neutrons below

2 MeV, or the neutron flux is strongly time dependent (WÄNKE *et al.*, 1970b). (We want to point out that this conclusion is true even when ascribing all the ^{37}Ar to the $^{40}\text{Ca}(n, \alpha)$ -reaction. If in addition to the contributions from Ti and Fe (see above) any other reactions on Ca and K should be important as well, the argument would be even stronger.) In case there are indeed a large number of neutrons with energies < 2 MeV the flux of $25 \text{ n/cm}^2 \text{ sec}$ is a *lower* limit.

Finally, as was mentioned above, the first treatment of the fines consisted of a leach with 10^{-4} N HNO_3 at room temperature. The aim was to leach possibly some chlorine and to deduce the flux of thermal neutrons from the $^{35}\text{Cl}(n, \gamma)$ -produced ^{36}Cl -activity. The results, however, are not very conclusive. The ^{36}Cl -activity found was $(1.2 \pm 1.5) \times 10^{-2} \text{ dpm}$, the isotope dilution measurement showed an excess of 1.7 mg of chlorine after treatment of the sample, assuming normal isotopic composition for the excess. On the 3σ -significance level this corresponds to a specific activity of less than 3 dpm/kg for a normalized Cl-content of 100 ppm (EBERHARDT *et al.*, 1963), or a slow neutron flux of less than $1 \text{ n/cm}^2 \text{ sec}$, *provided* all the excess chlorine was actually leached from the sample. If part of it was introduced from other sources the specific activity and the neutron flux would be correspondingly higher. For this and other reasons the apparent agreement of this neutron flux with that derived by ALBEE *et al.* (1970) from measurements of the Gd isotopes is certainly fortuitous.

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REFERENCES

- ALBEE A. L., BURNETT D. S., CHODOS A. A., EUGSTER O. J., HUNEKE J. C., PAPANASTASSIOU D. A., PODOSEK F. A., RUSS G. PRICE II, SANZ H. G., TERA F. and WASSERBURG G. J. (1970) Ages, irradiation history, and chemical composition of lunar rocks from the Sea of Tranquility. *Science* **167**, 463–466.
- ALIMARIN I. P. and GIBALO I. M. (1956) Die Trennung des Be von Al und anderen Elementen. *Z. anal. Chem.* **156**, 435 (1957). (*Z. Anal. Chim.* **11**, 389–392.)
- BASS R. (1968) Private communication.
- BEGEMANN F., VILCSEK E. and WÄNKE H. (1967) The origin of the “excess” argon-39 in stone meteorites. *Earth Planet. Sci. Lett.* **3**, 207–212.
- BEGEMANN F., RIEDER R., VILCSEK E. and WÄNKE H. (1969) Cosmic ray produced radionuclides in the Barwell and St. Severin meteorites. In *Meteorite Research*, (editor P. Millman), pp. 267–274. D. Reidel.
- BEGEMANN F. and VILCSEK E. (1969) Chlorine-36 and argon-39 production rates in the metal of stone and stony-iron meteorites. In *Meteorite Research*, (editor P. Millman), pp. 355–362. D. Reidel.
- BIEN G. (1967) Personal communication.
- BRAMLITT E. T. and FINK R. W. (1963) Rare nuclear reactions induced by 14.7 MeV neutrons. *Phys. Rev.* **131**, 2649–2663.
- EBERHARDT P., GEISS J. and LUTZ H. (1963) Neutrons in meteorites. In *Earth Science and Meteoritics*, (editors J. Geiss and E. D. Goldberg), pp. 143–168, North-Holland.

- EBERLE A. R. and LERNER M. W. (1955) Separation and determination of Sc. *Anal. Chem.* **27**, 1551–1554.
- FIREMAN E. L. (1967) Radioactivities in meteorites and cosmic-ray variations. *Geochim. Cosmochim. Acta* **31**, 1691–1700.
- FIREMAN E. L. and GOEBEL R. (1969) Argon-37 and argon-39 in recently fallen meteorites and cosmic-ray variations. S.A.O. Reprint 906–164.
- FIREMAN E. L., D'AMICO J. C. and DEFELICE J. C. (1970) Tritium and argon radioactivities in lunar material. *Science* **167**, 566–568.
- FISCHER W. and SEIDEL W. (1941) Die Fällung von $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ aus ätherisch-wässriger Salzsäure und ihre Bedeutung als Trennungsoption. *Z. Anorg. Chem.* **247**, 333–366.
- FURUKAWA M., KUME S. and OGAWA M. (1965) Excitation functions for the formation of ^7Be and ^{22}Na in proton induced reaction on ^{27}Al . *Nucl. Phys.* **69**, 362–368.
- FUSE K. and ANDERS E. (1969) Aluminum-26 in meteorites—VI. Achondrites. *Geochim. Cosmochim. Acta* **33**, 653–670.
- GEISS J., OESCHGER H. and SCHWARZ U. (1962) The history of cosmic radiation as revealed by isotopic changes in the meteorites and the earth. *Space Sci. Rev.* **1**, 197–223.
- GOEL P. S. (1962) Cosmogenic carbon-14 and chlorine-36 in meteorites. Thesis, Carnegie Inst. Techn.
- HEYMANN D. and SCHAEFFER O. A. (1962) Constancy of cosmic rays in time. *Physica* **28**, 1318–1323.
- HICKS H. G., STEVENSON P. C. and NERVIK W. E. (1956) Reaction $^{27}\text{Al} (p, 3pn)^{24}\text{Na}$. *Phys. Rev.* **102**, 1390–1392.
- HONDA M. and ARNOLD J. R. (1964) Effects of cosmic rays on meteorites. *Science* **143**, 203–212.
- HOUSERMANS F. G. (1950) Personal communication.
- JESSEN P., BORMANN M., DREYER F. and NEUERT H. (1965) Compilation of experimental excitation functions of some fast neutron reactions up to 20 MeV. I. Inst. f. Experimentalphysik, Universität Hamburg, January 1965.
- KIRSTEN T. A. and SCHAEFFER O. A. (1969) High energy interactions in space. In *Interactions of Elementary Particle Research in Science and Technology*, (editor L. C. L. Yuan), Academic Press.
- LSPET (LUNAR SAMPLE PRELIMINARY EXAMINATION TEAM) (1969) Preliminary examination of lunar samples from Apollo 11. *Science* **165**, 1211–1227.
- MEADOWS J. W. and HOLT R. B. (1951) Some excitation functions for protons on magnesium. *Phys. Rev.* **83**, 1257.
- O'GALLAGHER J. J. and SIMPSON J. A. (1967) The heliocentric intensity gradients of cosmic-ray protons and helium during minimum solar modulation. *Astrophys. J.* **147**, 819–827.
- O'KELLEY G. D., ELDRIDGE J. S., SCHONFELD E. and BELL P. R. (1970) Elemental compositions and ages of lunar samples by non-destructive gamma-ray spectrometry. *Science* **167**, 580–582.
- PEPPARD D. F., FARIS J. P., GRAY P. R. and MASON G. W. (1953) Studies of the solvent extraction behaviour of the transition elements I. Order and degree of fractionation of the trivalent rare earths. *J. Phys. Chem.* **57**, 294–301.
- PERKINS R. W., RANCITELLI L. A., COOPER J. A., KAYE J. H. and WOGMAN N. A. (1970) Cosmogenic and primordial radionuclides in lunar samples by non-destructive gamma-ray spectrometry. *Science* **167**, 577–580.
- RAYUDU G. S. V. (1964) Nuclear reactions for the study of solar flare protons. Nuclear Chem. and Geochem. Res. at Carnegie Inst. Techn. 1963–64, Progress Report.
- SHEDLOVSKY J. P., HONDA M., REEDY R. C., EVANS J. C., LAL D., LINDSTROM R. M., DELANY A. C., ARNOLD J. R., LOOSLI H.-H., FRUCHTER J. S. and FINKEL R. C. (1970) Pattern of bombardment-produced radionuclides in rock 10017 and in lunar soil. *Science* **167**, 574–576.
- STOENNER R. W., LYMAN W. J. and DAVIS R., JR. (1970) Cosmic ray production of rare gas radioactivities and tritium in lunar material. *Science* **167**, 553–555.
- VILCSEK E. and WÄNKE H. (1963) Cosmic ray exposure ages and terrestrial ages of stone and iron meteorites derived from ^{36}Cl and ^{39}Ar measurements. In *Radioactive Dating*, pp. 381–393. IAEA Vienna.
- VOSHAGE H. (1962) Eisenmeteorite als Raumsonden für die Untersuchung des Intensitätsverlaufs der kosmischen Strahlung während der letzten Milliarden Jahre. *Z. Naturforsch.* **17a**, 422–432.

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- VOSHAGE H. (1967) Bestrahlungsalter und Herkunft der Eisenmeteorite. *Z. Naturforsch.* **22a**, 477–506.
- WÄNKE H. and VILCSEK E. (1959) Argon-39 als Reaktionsprodukt der Höhenstrahlung in Eisenmeteoriten. *Z. Naturforsch.* **14a**, 929–934.
- WÄNKE H., BEGEMANN F., VILCSEK E., RIEDER R., TESCHKE F., BORN W., QUIJANO-RICO M., VOSHAGE H. and WLOTZKA F. (1970a) Major and trace elements and cosmic-ray produced radioisotopes in lunar samples. *Science* **167**, 523–525.
- WÄNKE H., RIEDER R., BADDENHAUSEN H., SPETTEL B., TESCHKE F., QUIJANO-RICO M. and BALACESCU A. (1970b) Major and trace elements in lunar material. *Geochim. Cosmochim. Acta*, Supplement I.