Cosmogenic ^{39}Ar in extraterretrial materials: Application to ^{40}Ar/^{39}Ar dating

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Meteorites and other extraterrestrial materials have cosmogenic ^{39}Ar which may be propotional to their potassium contents. Assuming several conditions, direct in situ ^{40}Ar/^{39}Ar dating without neutron irradiation may be applicable on those naturally activated samples. We consider the condtions to obtain satisfactory results. The estimate of ^{39}Ar production rate from nuclear data shows disagreement with experimental data by several orders of magnitude, suggesting processes other than n-p transformation might be working.

Introduction

In meteorites and extraterrestrial materials, cosmogenic ^{39}Ar is normally found. The amount is small and limited because of their small sample sizes. Recent development of technology allows us to have an accurate determination of such argon isotopes even in underground (Xu, *et al.*, 2015). We have already reported a possibility of ^{40}Ar/^{39}Ar dating on meteorites without neutron irradiation in a reactor (Takeshima, 2001). Conditions for such determination is considered here.

Cosmogenic argon isotopes

We assume that the cosmogenic argon isotopes have the same process as that we observe in a nuclear reactor. The major isotope reactions in ^{40}Ar/^{39}Ar age determination are as follows.

$$^{35}\mathrm{Cl}(\mathrm{n},\gamma)^{36}\mathrm{Cl} \rightarrow {}^{36}\mathrm{Ar}\ (\beta\ \text{decay})$$
$$^{40}\mathrm{Ca}\ (\mathrm{n},\mathrm{n}\alpha)^{36}\mathrm{Ar}$$
$$^{40}\mathrm{Ca}\ (\mathrm{n},\alpha)^{37}\mathrm{Ar}$$
$$^{42}\mathrm{Ca}(\mathrm{n},\alpha)^{39}\mathrm{Ar} \rightarrow {}^{39}\mathrm{K}\ (\beta\ \text{decay})$$
$$^{39}\mathrm{K}(\mathrm{n},\mathrm{p})^{39}\mathrm{Ar} \rightarrow {}^{39}\mathrm{K}\ (\beta\ \text{decay})$$
$$^{40}\mathrm{K}(\mathrm{n},\mathrm{p})^{40}\mathrm{Ar}$$

Possible source of neutron are solar wind and galactic cosmic ray. Because the sun is the closest source, the flux is probably the strongest. Let us assume that the neutron flux mostly from solar wind is uniform over a long period (*e.g.* 10^4 years), and assume that the production rate R_{39} is constant. The differential equation for production and decay of ^{39}Ar which has a half life of 269 years, is written as

$$\frac{dN_{39Ar}}{dt} = -\lambda_{39}N_{39Ar} + N_{39K}R_{39} \qquad (1)$$

where λ_{39} is the decay constant of ^{39}Ar, and N_{39Ar} and N_{39K} represent number of atoms for ^{39}Ar and ^{39}K in a mineral, respectively. The beta decay of ^{39}Ar brings itself back to ^{39}K. Therefore, the total number of atoms during the production and dacay does not change. i.e.

$$N_0 = N_{39Ar}+N_{39K} \qquad (2)$$

From this relation, Eq. (1) is rewritten as

$$\frac{dN_{39Ar}}{dt} = -(\lambda_{39}+R_{39})\,N_{39Ar}+N_0R_{39} \qquad (3)$$

The solution of Eq.(3) is

$$N_{39Ar}(t) = N_{39Ar0}\exp[-(\lambda_{39}+R_{39})t] + \frac{R_{39}}{\lambda_{39}+R_{39}}N_0 \qquad (4)$$

N_{39Ar0} is determined by initial condition; $N_{39Ar}(0) = 0$. *i.e.*

$$N_{39Ar}(t) = -\frac{R_{39}}{\lambda_{39}+R_{39}}N_0\exp[-(\lambda_{39}+R_{39})t] + \frac{R_{39}}{\lambda_{39}+R_{39}}N_0 \qquad (5)$$

After a long period, N_{39Ar} reaches to an equilibrium of $N_0R_{39}/(\lambda_{39}+R_{39})$ (*e.g.* $t = 1.3\times10^3$ years for 99% of equilibrated value). This is actually the same result obtained from a equilibrium condition;

$$dN_{39Ar}/dt = 0 = -\lambda_{39} N_{39Ar} + N_{39K} R_{39} \qquad (6)$$

Thus, the equilibrated ^{39}Ar is proportional to initial potassium content N_0.

The decay constant for ^{39}Ar, λ_{39} is 2.58×10^{-3}/y , or $8.17\times10^{-11}/^{39}$K atom/sec. We do not exactly know the rate R_{39}. On lunar surface for an example, R_{39} could be the same everywhere (i.e. the neutron flux is the same) over a long time. An estimation of cosmogenic ^{39}Ar in atmosphere has been made at sea level (Saldanha *et al.* 2019), although the process is different from ^{39}K (n, p) ^{39}Ar, Their value for ^{39}Ar production is 759 atoms/kgAr/day which is 5.84×10^{-28} atoms/Ar atom/sec. This is significantly lower than the detection limit in a mass spectrometer. The incoming neutron flux above atmosphere is measured by Lockwood and Friling (1968). It is dependent on the earth's latitude, varying from 0.1 to 0.8 neutrons/cm^2/sec. On the lunar surface, neutron flux is estimated by Livengood *et al.* (2018). For fast neutron, it varies from 1.2 to 16 depending on the methods.

A simple estimate of ^{39}Ar production rate can be made using cross section of ^{39}K in the n-p reaction. Assuming uniform average fast neutron flux of F_n = 1 neutrons/ cm^2/sec and the maximum cross section of the reaction; σ = 0.38 barn = 3.8×10^{-25} cm^2 at 10-20 MeV (Shibata *et al.*, 2002), the production rate R_{39} is the number of reactions, *i.e.*;

$$R_{39} = F_n \sigma = 3.8\times10^{-25}/^{39}\text{K atom /sec .} \qquad (7)$$

Since this estimate is a lot smaller than the decay constant, the equilibrated value A for ^{39}Ar after reasonably long period is,

$$A = R_{39} / \lambda_{39} = 4.7\times10^{-15}/^{39}\text{K atom .} \qquad (8)$$

In other expression, cosmogenic ^{39}Ar in 1 gram of potassium of extraterrestrial material could be found as

$$A^* 1/39 = 4.7\times10^{-15}\times6.02\times10^{23}/39 = 7.3\times10^{7}\ {}^{39}\text{Ar atom/g ,}$$
$$\text{or } 1.2\times10^{-16} \text{ mole/g .}$$

This value may be compared with ^{39}Ar found in Allende meteorite. In an experiment (Takeshima, 2001), ^{39}Ar contained in a chondrule of about 10^{-7} gram was typically found to have ^{39}Ar of about 10^{-12} ccSTP, which is equivalent to 4.5×10^{-17} mole. Assuming high concetration of potassium about 7%, the estimation and the experimental data disagree. It may possibly be due to a wrong estimate of neutron flux and/or that other ^{39}Ar production process are involved, suggesting that 10^7 to 10^8 times greater production rate which Allende meteorite experienced.

The similar formulation can be applied on other interfering argon isotopes. ^{36}Ar and ^{39}Ar from calcium isotopes, ^{36}Ar from ^{35}Cl, and ^{40}Ar from ^{40}K affect on the ^{40}Ar/^{39}Ar age determination. Among them ^{40}Ar may not play an important role. Since neutron has relatively short life (14.8 minutes), thermal neutron which contributes to the majority of the ^{40}K (n, p)^{40}Ar reaction, seems to exist little and its penetration in silicate materials may be shallow compared to fast neutrons.

Contribution of interfering calcium isotopes are estimated from calcium derived ^{37}Ar. It is known that ^{36}Ar and ^{39}Ar have a lot smaller production rate which is represented by ^{36}Ar/^{37}Ar and ^{39}Ar/^{37}Ar ratios of 2 - 3×10^{-4} and 7×10^{-4}, respectively. ^{36}Ar is a stable isotope, and ^{37}Ar has a half life of 35 days. Therefore, ^{36}Ar can build up, and ^{39}K from ^{39}Ar decay also adds up after a long period of time. The theoretical and experimental cross sections for ^{40}Ca (n, nα)^{36}Ar reaction varies (Shibata *et al.*, 2002). In general, it is one order of magnitude less (c.a. 0.02 - 0.1 barns) compared to ^{39}K (n, p) ^{39}Ar reaction at 10-20MeV. For ^{42}Ca (n, α) ^{39}Ar reaction, the cross section ranges between 0.04 and 0.1 barns. Considering the small isotopic ratio of calcium (^{42}Ca is 0.65% of total calcium) and their small cross section compared to ^{39}Ar production in the reactions, the contribution from these interfering isotopes on ^{40}Ar/^{39}Ar age may not be significant as long as the K/Ca ratio is more than 100.

If extraterrestrial material has chlorine, it also contributes to the increase of ^{36}Ar and ^{38}Ar. We have made ^{40}Ar/^{39}Ar dating on Allende meteorite which has chlorine bearing sodalite (Takeshima, 2001; Takeshima et al., 2003). The amount of ^{36}Ar possibly from ^{35}Cl was so large compared to terrestrial material. However, it has so large amount of ^{40}Ar that ^{36}Ar does not affect the age results possibly due to the potassium content. If we assume atmospheric ratio of ^{40}Ar/^{36}Ar, the apparent "air" contamination was about 2%. Allowing some uncertainty of the age determination, the 2% error is tolerable.

Summary

The present estimate of ^{39}Ar production and experimental results disagree at least 7 orders of magnitude. Whatever processes are involved, samples from same environment would have the same production rate R_{39}.

Combination of pilot sampling with precise measurement in a laboratory and survey using in-situ measurement may be possible to carry out age mapping on extraterrestrial materials. assuming relatively low calcium content. Since in situ sampling by a laser apparatus is applicable, this method may particularly suitable for survey purpose on lunar surface and other inner planets like mars.

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