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Excess Ar in Some Metamorphic and Plutonic Rocks and Reduction of Thermal Neutron-induced ^{40}Ar by Cd Shielding

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It is well known that, by the K-Ar dating, a reliable age cannot be obtained from a sample containing excess Ar. The ^{40}Ar-^{39}Ar method, on the other hand, has, potentially, ability to provive us geologically meaningful ages even for such samples with excess Ar. A Mowson charnockite from Antarctica shows a good example.

In the ^{40}Ar-^{39}Ar dating, thermal neutron induced ^{40}Ar from 40K is one of the major source of errors in age calculation. Wrapping a sample with Cd foil is very effective in reducing this disturbing ^{40}Ar.

KEYWORDS: ^{40}Ar-^{39}Ar dating, Excess Ar, Thermal Neutron-induced ^{40}Ar , Shielding with Cd foil

1. Advantages and limits of the K-Ar dating method
-------An introduction

The K-Ar dating method is one of the most powerful tools in studying geohistory. We can date samples either as old as 4.5 Ga, such as lunar rocks, or as young as 1 Ma or even younger, such as Quartenary volcanic rocks by this method. This excellent property of the method mainly comes from the following two reasons: first, potassium is one of the most abundant elements in the earth's crust and universally occurs in major rock forming minerals, such as biotite, hornblende, feldspar, and so on, and secondly, the half life of potassium-40 (^{40}K) being 1.25 Ga is just suitable for dating most range of the terrestrial history.

The method totally stands on a nuclear process in which ^{40}K decays into argon-40 (^{40}Ar) by an electron capture reaction and into calcium-40 (^{40}Ca) through a beta decay. This decay can be written by following differential equations;

$$d(^{40}K)/dt = -\lambda(^{40}K) \quad \text{--- (1)}$$

$$d(^{40}Ar)/dt = (\lambda_e/\lambda)(^{40}K) \quad \text{--- (2)}$$

where λ is the total decay constant of ^{40}K and λ_e is the decay constant for the electron capture reaction. By solving these equations, we obtain a following age equation

$$t = (1/\lambda)\ln((\lambda/\lambda_e)(^{40}Ar/^{40}K)+1) \quad \text{---(3)}$$

Since equation (2) shows a relation between ^{40}K in a rock and ^{40}Ar produced by the decay of the ^{40}K, we must know the amount of ^{40}K and total ^{40}Ar produced in the sample in calculating the age of the sample by using equation (3). It means that we must know the amount of ^{40}Ar in the sample immediately after its formation. Since Ar is noble gas, we usually assume that the amount of Ar is negligible in newly formed lavas. Hence, the method is mostly applied on volcanic rocks. It also often applicable on igneous rocks and sometimes on metamorphic rocks.

Even if the initial Ar is negligible, if a part of ^{40}Ar has been lost from the sample by some reasons, it gives an age younger than it should be. A closed system for K and Ar is the basic requirement in the K-Ar dating. Any addition or loss of K and Ar after the formation of the sample gives a false age. This means that chemically altered or weathered samples are not suitable for the K-Ar dating. An exception is addition of atmospheric Ar. Since the isotopic composition of the atmospheric Ar is well known, we can correct the amount of the atmospheric ^{40}Ar by measuring the amount of ^{36}Ar in the sample.

There are some samples in which initially trapped Ar is not negligible. If the source material of the sample had accumulated ^{40}Ar and the sample initially contained this inherited ^{40}Ar, estimation of the amount of ^{40}Ar accumulated since the formation becomes impossible. Submarine glass is a good example of such a sample containing excess Ar [ex. 1]. A large confining pressure and low temperature of the surrounding water has not allowed Ar in

the magma to outgas.

As far as we use the conventional K-Ar dating method, it is difficult to tell whether a sample has excess Ar or loses Ar, or has kept a closed system for Ar and K. We cannot evaluate the confidence of an obtained age by the datum itself. This weak point could be overcome by ^{40}Ar-^{39}Ar method, a variation of the K-Ar method.

2. ^{40}Ar-^{39}Ar method --methodology

Since the ^{40}Ar-^{39}Ar method is a variation of the K-Ar method, the principle is identical between these methods. The difference is that the former needs fast neutron irradiation. By the irradiation, the following nuclear reaction occurs in a sample.

$$^{39}K\,(n,p)\,^{39}Ar$$

Since the isotopic composition of K is a well-established universal constant,we can estimate the amount of K in a sample if a production rate of ^{39}Ar from ^{39}K in the irradiation can be known. In the other word, we can rewrite a quantity $^{40}Ar/^{40}K$ in the eq.(3) as follows;

$$^{40}Ar/^{40}K=(^{40}Ar/^{39}Ar)(^{39}Ar/^{39}K)(^{39}K/^{40}K) \quad \text{---- (4)}$$

In this equation, the fist term in the right hand formula is observable,the second term is a coefficient determined for each irradiation, and the third term is a universal constant. As mentioned above, estimation of the irradiation factor ($^{39}Ar/^{39}K$) allows us to calculate $^{40}Ar/^{40}K$, which, in turn, gives us a K-Ar age of a sample. Defining J-value, an irradiation coefficient, as

$$J=(1/\lambda_e)(^{39}Ar/^{39}K)(^{39}K/^{40}K)\text{---(5)}$$

we can write the age equation as follows;

$$t=(1/\lambda)\ln(1+J(40Ar/39Ar)) \text{ ---- (6)}$$

This equation can be rewritten in the following form;

$$J=(\exp(\lambda t)-1)/(^{40}Ar/^{39}Ar)\text{---- (7)}$$

This equation indicates that by irradiating a sample whose age is known, we can estimate a J-value on a mass-spectrometer analysis of Ar isotopes. A samples whose age has been well known is called a standard sample.

In the early stage of developing this method, following points were admitted as merits:

1) The method does not require a direct measurement of K. Since Ar isotopic ratio ($^{40}Ar/^{39}Ar$) can be determined more precisely than absolute concentration of K in a sample, an obtained age may have smaller uncertainty.

2) The K-Ar method requires separate fractions for the K and Ar analyses. This means that inhomogeniety of K in a sample could cause a significant error in age determination. The ^{40}Ar-^{39}Ar method, on the contrary, requires a single analysis of Ar isotopes for an age determination. Hence, this method, in principle, is free from sample inhomogeniety.

The biggest advantage of the method is recognized a little later. Application of an incremental heating technique has allowed us to evaluate the confidence of an obtained age by plotting on a three isotope diagram. When the data from individual temperature steps form a straight array, we call it an "internal isochron". A age of the sample can be calculated from the gradient of the array. In this calculation, assumption of a trapped Ar isotopic composition is not necessary. If a sample contains trapped Ar, whose $^{40}Ar/^{36}Ar$ ratio is different from the atmospheric ratio, data point may plot on an internal isochron whose intercept on the ordinate does not show the atmospheric Ar ratio any more. A well defined isochron is an index of reliability of the age.

Even if a sample has lost a part of ^{40}Ar, ^{40}Ar-^{39}Ar dating with incremental heating provides us some useful informations.

1) In a case in which loss of Ar is not significant, data from high temperature steps often provide us a true age.

2) If a sample does not define an isochron because of its significant Ar loss, we can confidently judge that the obtained "age" of the sample is geologically meaningless.

The method, of course, has some difficulties. One of them is production of various Ar isotopes by various nuclear reactions on K and Ca isotopes (Table 1). Contributions of these interfering isotopes can be estimated by measuring Ar isotopic composition in irradiated K and Ca salts. Various laboratories in the world have reported fairly constant isotopic composition of Ar in both irradiated K and Ca salts except for ^{40}Ar in K salt. A $^{40}Ar/^{39}Ar$ ratio in an irradiated K salts, on the contrary,

Table 1. Reactions producing argon isotopes in neutron irradiated samples [2]

Argon isotope produced	Calcium	Potassium
^{36}Ar	^{40}Ca(n,nα)^{36}Ar (−7.04, 96.94)	
^{37}Ar	^{40}Ca(n,α)^{37}Ar (+1.75, 96.94)	^{39}K(n,nd)^{37}Ar (−15.99, 93.26)
^{38}Ar	^{42}Ca(n,nα)^{38}Ar (−6.25, 0.65)	^{39}K(n,d)^{38}Ar (−4.16, 93.26) ^{41}K(n,α)^{38}Cl $\xrightarrow{\beta^-}$ ^{38}Ar (−0.12, 6.73)
^{39}Ar	^{42}Ca(n,α)^{39}Ar (+0.34, 0.65)	^{39}K(n,p)^{39}Ar (+0.22, 93.26)
	^{43}Ca(n,nα)^{39}Ar (−7.59, 0.14)	^{40}K(n,d)^{39}Ar (−5.36, 0.01167)
^{40}Ar	^{43}Ca(n,α)^{40}Ar (+2.28, 0.14)	^{40}K(n,p)^{40}Ar (+2.29, 0.01167)
	^{44}Ca(n,nα)^{40}Ar (−8.85, 2.09)	^{41}K(n,d)^{40}Ar (−5.58, 6.73)

shows a significant diversion from laboratory to laboratory. Table 2 shows some of such examples.

Contrasting to ^{39}Ar which, in a K salt, is produced only by irradiation with fast neutrons, contribution of thermal neutron irradiation to ^{40}K takes a significant role in producing ^{40}Ar. In dating young rocks, this neutron induced ^{40}Ar disturbs a precise measurement radiogenic ^{40}Ar in a sample. Shielding by Cd foil has been known effective to preventing thermal neutrons.

In this paper, I will show some recent results concerning samples with excess Ar and reduction of thermal neutron-induced ^{40}Ar by shielding with Cd foil.

Table 2. Correction factors for interfering Ar isotopes in various irradiation facilities [2]

Reactor (irradiation position)	Cadmium shielding	Slow/fast neutron flux	$(^{36}Ar/^{37}Ar)_{Ca}$ × 10^{-4}	$(^{38}Ar/^{37}Ar)_{Ca}$ × 10^{-5}	$(^{39}Ar/^{37}Ar)_{Ca}$ × 10^{-4}	$(^{37}Ar/^{39}Ar)_{K}$ × 10^{-4}	$(^{38}Ar/^{39}Ar)_{K}$ × 10^{-2}	$(^{40}Ar/^{39}Ar)_{K}$ × 10^{-4}	Reference
HFBR (core)	—	0.65	2.31 ± 0.01	6.2 ± 0.8	6.45 ± 0.29	<1	1.00 ± 0.01	<20	Husain (1974)
RRF (flux trap)	—	—	2.84 ± 0.02	—	7.69 ± 0.03	—	—	—	Bernatowicz et al. (1978)
BR-2 (core)	Yes	—	—	—	9.35 ± 0.17	—	—	—	Kirsten et al. (1973a)
Herald (core)	—	1.7	2.47 ± 0.09	13.9 ± 2.6	7.19 ± 0.24	—	1.14 ± 0.03	123 ± 24	Brereton (1970)
			2.46 ± 0.11	22.4 ± 3.7	7.12 ± 0.22	—	1.10 ± 0.01	164 ± 13	Brereton (1972)
			1.1 ± 0.2	8 ± 2	6.7 ± 0.3	—	—	—	Turner et al. (1973)
			2.0 ± 0.3	13 ± 3	—	—	—	—	
GETR (shuttle tube)	—	7.5	3.05 ± 0.06	—	7.32 ± 0.15	—	—	—	Turner et al. (1971)
	—	—	3.15 ± 0.09	47.7 ± 0.9	7.23 ± 0.09	—	1.46 ± 0.01	625 ± 9	Alexander and Davis (1974)
Melusine	—	—	2.39 ± 0.19	—	6.57 ± 1.11	—	—	261 ± 6	Féraud et al. (1982)
Herald (core edge)	—	3.3	2.51 ± 0.02	3.81 ± 0.21	6.44 ± 0.04	—	1.08 ± 0.02	160 ± 10	Roddick (1983)
GSTR (core)	—	0.9	2.64 ± 0.02	3.17 ± 0.02	6.73 ± 0.04	22.0 ± 0.7	1.34 ± 0.02	59 ± 7 101 ± 5 10 ± 10	Dalrymple et al. (1981)
49-2 (H4)	0.5 mm Cd	—	2.64	—	6.87	—	—	71.5	Wang et al. (1986)
49-2 (E7)	—	2.5	1.17 ± 0.05	—	7.56 ± 0.30	—	—	239 ± 12	Wang et al. (1985)
JMTR	—	—	5.5	390	7.0	—	6.7	700	Kaneoka et al. (1979)
	—	—	3.72 ± 0.06	206 ± 3	11.3 ± 0.4	—	3.47 ± 0.04	1960 ± 40	Kaneoka (1983)
McMaster	—	19	2.1 ± 0.3	—	6.6 ± 0.5	—	—	268 ± 2	Berger (1975)
			2.54 ± 0.09	—	6.51 ± 0.31	—	—	156 ± 4	Bottomley and York (1976)
Ford (H-5)	—	—	2.87	—	7.61	—	—	382	Foland (1983)
	—	—	2.21–2.26	—	8.00–8.25	—	—	250–470	Heizler and Harrison (1988)
FR-2	Yes	—	2.7 ± 0.2	6 ± 2	6.85 ± 0.20	—	1.8 ± 0.6	—	Stettler et al. (1973)
RRF (reflector pool)	—	13	2.5 ± 0.2	—	8.8 ± 0.1	—	1.7 ± 0.1	1300 ± 100	Hohenberg et al. (1981)
			2.13 ± 0.04	—	10.2 ± 0.3	—	1.71 ± 0.02	1340 ± 10	Honda et al. (1983)
HIFAR	No	~50?	3.06 ± 0.05	—	7.27 ± 0.08	—	—	3008 ± 138	
	0.2 mm Cd	—	—	—	—	0.15 ± 0.07	—	270 ± 20	Tetley et al. (1980); also this work
	0.5 mm Cd	—	—	—	—	—	—	30 ± 10	
	1.0 mm Cd	—	3.20 ± 0.02	—	7.9 ± 0.5	—	—	~20	

3. Excess Ar in some samples

3-1. Excess Ar in Mowson Charnockite from Antarctic

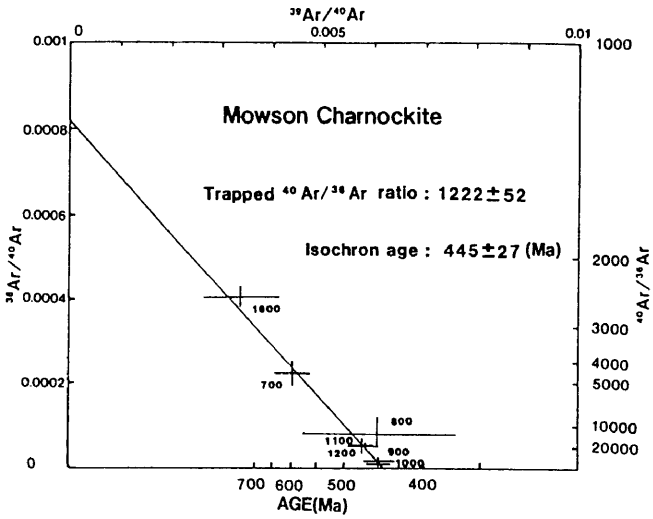

Fig. 1 The data for the Mowson charnockite fall on a straight line which indicates that the sample trapped the initial Ar with a ^{40}Ar/^{36}Ar ratio of 1222. The age of the sample is 445 Ma.

As mentioned previously, a K-Ar age is reliable only when a sample initially trapped Ar whose isotopic composition is identical to that of the atmospheric Ar. If a sample initially trapped Ar whose ^{40}Ar/^{36}Ar is higher than the atmospheric ratio, an age calculation on an assumption that the trapped Ar is atmospheric yields an age older then it should be. The ^{40}Ar-^{39}Ar dating, on the other hand, could provide a true age if a trapped Ar has a single

$^{40}Ar/^{36}Ar$ ratio. Such a situation can be realized when a reservoir of Ar for the sample had a uniform Ar isotopic composition which is different from the atmospheric one.
Mowson Charnockite [3] shows a good example.

A ^{40}Ar-^{39}Ar incremental heating analysis on this sample give a considerably well defined isochron whose trapped Ar ratio of 1222 +/- 52 is well above the atmospheric ratio (Fig. 1). An isochron age deduced from this plot is 445 +/- 27 Ma, which is younger than a K-Ar age of 475 +/- 15 Ma. (Errors cited are in 2 sigmas). This is the most textbookish result I have ever obtained on excess Ar.

3-2. Excess Ar in Tanzawa tonalite

The Tanzawa block is located in the South Fossa Magna and have recently been discussed that this block collided to the Honshu Arc about 6 Ma ago [ex. 4]. Dating Tanzawa tonalite is significant in the context of this collisional tectonics. Previously Sato et al.[5] with dating hornblende and biotite separated from a single specimens collected at two sites reported that hornblende from the two sites yielded an identical age of about 10 Ma, whereas the coexisting biotite showed an age of about 5 Ma. On these results, they proposed that the Tanzawa tonalite cooled with a cooling rate of 50°C/Ma.

On the contrary, dated more than 40 samples, Saito et al. [6] suggested the tonalite intruded later than 7 Ma, and 10 Ma ages of hornblende may be due to excess
Ar in the sample. Saito [7] conducted some ^{40}Ar-^{39}Ar analyses and showed that these old hornblende ages are really due to excess Ar (Fig. 2). In contrast to the Mowson Charnockite, Tanzawa tonalite did not allow to define an isochron. The samples have severely disturbed K-Ar systematics and, hence, we cannot deduce a formation age of the sample. It is safely concluded, however, that we cannot rely on these old hornblende ages.

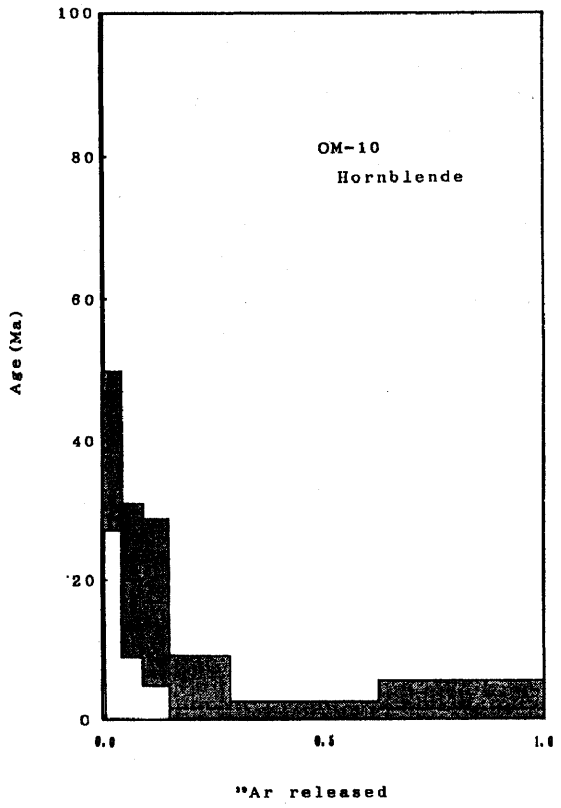

Fig. 2. A hornblende separated from a Tanzawa tonalite yields an age spectrum with low temperature fractions showing extraordinarily old apparent ages. Since a K-Ar systematics has been heavyly disturbed, any geologically meaningful age could be deduced from this sample.

4. Reduction of thermal neutron-induced ^{40}Ar by shielding with Cd foil

A thermal neutron to fast neutron ratio in a neutron dose in JMTR is considerably high as compared with those reported for the other foreign irradiation facilities. Sometimes the neutron induced ^{40}Ar to ^{39}Ar ratio in a K salt is as high as 0.2 [8] In some K rich young samples, measured $^{40}Ar/^{39}Ar$ ratio is nearly 1. Hence, insufficient correction of neutron induced ^{40}Ar in a sample brings a significant error in age. Hence, reduction of thermal neutron induced ^{40}Ar is desirable. Tetley et al. [9] reported that shielding with Cd foil is very effective in this reduction. Recently we tried to shield thermal neutrons with 0.5 mm Cd foil and obtained a good result (Table 3).

Table 3. Correction factors for interfering Ar isotopes for JMTR

$(^{36}Ar/^{37}Ar)_{Ca}$ x10-4	$(^{39}Ar/^{37}Ar)_{Ca}$ x10-4	$(^{40}Ar/^{39}Ar)_{K}$ x10-2	Ref.
	Without Cd Shielding		
2.6 +/- .1	17 +/- 1	4.3 +/-.1	[10]
2.3 +/- .1	-----	1.8 +/-.1	[11]
2.5 +/- .1	7. +/-.4	14 +/-.5	[11]
3.98 +/- .10	10.0 +/-1.8	18 +/- 2	[3]
4.05 +/- .14	9.65 +/-.25	8.37 +/-.26	[7]
	With Cd Shielding		
------	------	0.5 +/-.5	This work

5. Concluding remarks

The ^{40}Ar-^{39}Ar dating is a powerful tool in investigating geohistory. It allows to deduce a formation age of a sample even if the sample has a slightly disturbed K-Ar systematics by later heating or by not completely outgas its inheritant Ar at it formation. Even if a sample has experienced severe disturbance, we can evaluate reliability of the sample age.

The method also has its own disadvantages, such as disturbance with neutron induced "disturbing isotopes" on naturally occurring Ar isotopes. Among which thermal neutron induced ^{40}Ar potentially brings a large error in an age calculation. This kind of difficulty can, however, be overcome by a well designed experiment and by a careful treatment in sample irradiation.

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