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A new approach to cosmogenic corrections in $^{40}Ar/^{39}Ar$ chronometry: Implications for the ages of Martian meteorites

W.S. Cassata *, L.E. Borg

Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA

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Abstract

Anomalously old $^{40}Ar/^{39}Ar$ ages are commonly obtained from Shergottites and are generally attributed to uncertainties regarding the isotopic composition of the trapped component and/or the presence of excess ^{40}Ar. Old ages can also be obtained if inaccurate corrections for cosmogenic ^{36}Ar are applied. Current methods for making the cosmogenic correction require simplifying assumptions regarding the spatial homogeneity of target elements for cosmogenic production and the distribution of cosmogenic nuclides relative to trapped and reactor-derived Ar isotopes. To mitigate uncertainties arising from these assumptions, a new cosmogenic correction approach utilizing the exposure age determined on an un-irradiated aliquot and step-wise production rate estimates that account for spatial variations in Ca and K is described. Data obtained from NWA 4468 and an unofficial pairing of NWA 2975, which yield anomalously old ages when corrected for cosmogenic ^{36}Ar using conventional techniques, are used to illustrate the efficacy of this new approach. For these samples, anomalous age determinations are rectified solely by the improved cosmogenic correction technique described herein. Ages of 188 ± 17 and 184 ± 17 Ma are obtained for NWA 4468 and NWA 2975, respectively, both of which are indistinguishable from ages obtained by other radioisotopic systems. For other Shergottites that have multiple trapped components, have experienced diffusive loss of Ar, or contain excess Ar, more accurate cosmogenic corrections may aid in the interpretation of anomalous ages. The trapped $^{40}Ar/^{36}Ar$ ratios inferred from inverse isochron diagrams obtained from NWA 4468 and NWA 2975 are significantly lower than the Martian atmospheric value, and may represent upper mantle or crustal components.

Keywords: Mars; Shergottite; $^{40}Ar/^{39}Ar$; Chronology; Cosmogenic

1. INTRODUCTION

Apparent $^{40}Ar/^{39}Ar$ ages obtained from Shergottites are often significantly older than ages obtained by other radioisotopic methods (e.g., Bogard and Garrison, 1999; Bogard and Park, 2008; Bogard et al., 2009; Korochantseva et al., 2009; Lindsay et al., 2012, 2013). The magnitude of this effect is variable, but often exceeds 100%. For example, Bogard et al. (2009) obtained a $^{40}Ar/^{39}Ar$ isochron age of 366 ± 3 Ma from maskelynite in NWA 2975, which is a factor of two older than the Sm–Nd age of 177 ± 11 Ma reported therein. The problem is especially disconcerting as anomalously old $^{40}Ar/^{39}Ar$ ages are often inferred from seemingly robust isochron regressions (e.g., Bogard et al., 2009; Lindsay et al., 2012, 2013), which, in the absence other chronometric data, would be taken as reliable age determinations. The cause of such anomalously old ages is poorly understood, and as a result the $^{40}Ar/^{39}Ar$ method has contributed less to our knowledge of Shergottite chronology than it has to many other meteorites, lunar samples, and terrestrial rocks.

* Corresponding author.
E-mail address: cassata2@llnl.gov (W.S. Cassata).

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Argon that is observed in Martian meteorites is derived from a combination of sources including: (1) radioactive decay of ^{40}K (radiogenic ^{40}Ar: $^{40}Ar^*$), (2) cosmic ray spallation reactions (cosmogenic Ar: $^{38}Ar_{cos}$ and $^{36}Ar_{cos}$), and (3) trapped or inherited atmosphere, crustal, and/or mantle gas ($^{40}Ar_{trap}$, $^{38}Ar_{trap}$, and $^{36}Ar_{trap}$). Excess $^{40}Ar_{trap}$ (denoted $^{40}Ar_e$),[1] or $^{40}Ar_{trap}$ that is not present in fixed proportion to $^{36}Ar_{trap}$ and $^{38}Ar_{trap}$, is generally cited as the cause of old apparent ages obtained from Shergottites (e.g., Bogard and Park, 2008; Bogard et al., 2009). Such Ar may be incorporated as a result of in-diffusion of grain boundary ^{40}Ar (e.g., near contact metamorphic aureoles; Harrison and McDougall, 1981) or interaction with magmas and/or fluids characterized by spatially or temporally variable Ar isotopic compositions (e.g., Esser et al., 1997). When observed in terrestrial samples, $^{40}Ar_e$ contamination of this nature is typically heterogeneously distributed, giving rise to discordant age spectra (e.g., Lanphere and Dalrymple, 1976; Boven et al., 2001). While some Shergottites yield erratic age spectra consistent with heterogeneously distributed $^{40}Ar_e$, in some instances samples yield well-defined isochrons requiring $^{40}Ar_e$ and ^{40}K to be approximately co-located such that a uniform $(^{40}Ar^*+^{40}Ar_e)/^{39}Ar$ ratio is obtained during step-wise degassing (e.g., NWA 2975; Lindsay et al., 2013). Such a situation might arise when $^{40}Ar_e$ is uniformly distributed within a compositionally homogeneous phase (Lindsay et al., 2013).

Anomalously old ages can also be obtained if inaccurate corrections for cosmogenic ^{36}Ar are applied (as discussed by, e.g., Bogard and Garrison, 1999; Korochantseva et al., 2009; Park et al., 2013, 2014). In $^{40}Ar/^{39}Ar$ dating experiments, samples are irradiated in a nuclear reactor to generate ^{39}Ar from K ($^{39}Ar_K$) and ages are inferred from $^{40}Ar^*/^{39}Ar_K$. The presence of $^{40}Ar_{trap}$ in samples requires the use of isochron diagrams (see McDougall and Harrison, 1999) to deconvolve $^{40}Ar^*$ and $^{40}Ar_{trap}$ from the total abundance of measured ^{40}Ar ($^{40}Ar_{tot}$). Linear mixing arrays are obtained on plots of $^{40}Ar_{tot}/^{36}Ar_{trap}$ vs. $^{39}Ar_K/^{36}Ar_{trap}$ (a "normal" isochron) or $^{36}Ar_{trap}/^{40}Ar_{tot}$ vs. $^{39}Ar_K/^{40}Ar_{tot}$ (an "inverse" isochron) when ^{40}Ar is present in fixed proportions relative to both the non-radiogenic trapped component ($^{36}Ar_{trap}$) and the reactor-produced proxy for its parent ^{40}K ($^{39}Ar_K$). The amount of $^{36}Ar_{trap}$ in a given extraction is determined by subtracting from the total abundance of ^{36}Ar ($^{36}Ar_{tot}$) the cosmogenic component ($^{36}Ar_{cos}$). Thus, the cosmogenic correction directly affects inferred ages as well as the isotopic compositions of trapped components by virtue of its incorporation in the denominator of a normal isochron ($^{40}Ar_{tot}/^{36}Ar_{(tot\text{-}cos)}$ vs. $^{39}Ar_K/^{36}Ar_{(tot\text{-}cos)}$) or numerator of an inverse isochron ($^{36}Ar_{(tot\text{-}cos)}/^{40}Ar_{tot}$ vs. $^{39}Ar_K/^{40}Ar_{tot}$).

The cosmogenic correction is particularly important for Shergottites compared to other extraterrestrial materials containing cosmogenic Ar because (1) they are relatively young and K-poor, and therefore contain a greater proportion of $^{40}Ar_{trap}$ relative to $^{40}Ar^*$, and (2) have elevated $(^{40}Ar/^{36}Ar)_{trap}$ ratios, such that inaccuracies in the inferred abundance of $^{36}Ar_{trap}$ have a more significant effect on the inferred age. Despite the importance of accurately applying the cosmogenic correction, current methods are inherently flawed. Three different approaches are generally used to correct for $^{36}Ar_{cos}$, the strengths and weaknesses of which are discussed below (see also discussions by Bogard and Garrison, 1999; Korochantseva et al., 2009; Park et al., 2013, 2014).

(1) Method 1: Perhaps the most widely adopted methodology used to correct for $^{36}Ar_{cos}$ assumes that the total ^{38}Ar and ^{36}Ar measured in a given extraction reflects a two-component mixture of cosmogenic Ar (with a $^{38}Ar/^{36}Ar$ ratio of 1.54; Wieler, 2002) and trapped Ar (with, e.g., a $^{38}Ar/^{36}Ar$ ratio of 0.244; Wiens et al., 1986). The advantage of this approach is that spatial variations in the cosmogenic production rate resulting from intra-grain zonation in Ca, K, and other target elements (Fe, Ti, Ni, Mn, Cr) or the concomitant degassing of multiple mineral phases are *a priori* accounted for by the mixing model, insofar as $(^{38}Ar/^{36}Ar)_{cos}$ is approximately equivalent over the range of compositions present in a given sample. Two problems with the deconvolution method are (1) it assumes that reactor-derived ^{38}Ar from neutron capture on ^{37}Cl ($^{38}Ar_{Cl}$) is not a significant contributor to the total ^{38}Ar measured in a given extraction, and (2) the isotopic composition of the trapped component is known. For Shergottites, $^{38}Ar_{Cl}$ is present in non-trivial quantities (e.g., Bogard et al., 2010) and the $^{38}Ar/^{36}Ar$ ratio of the trapped component varies between ~0.19 and 0.25 (see reviews by Bogard et al., 2001; Swindle, 2002). As such, the method is liable to yield spurious corrections, particularly for samples with young exposure ages, high concentrations of trapped Ar, or high concentrations of chlorine.

(2) Method 2: Another commonly employed approach to correct for $^{36}Ar_{cos}$ is to multiply the measured abundance of ^{37}Ar in each extraction by the minimum $^{36}Ar/^{37}Ar$ ratio observed during the incremental heating experiment (Bogard and Garrison, 1999). ^{37}Ar is produced during sample irradiation via the reaction $^{40}Ca(n,\alpha)^{37}Ar$ and therefore serves as a proxy for Ca. Because Ca is a dominant target element for $^{36}Ar_{cos}$ production in feldspathic phases, ^{37}Ar is generally correlated with $^{36}Ar_{cos}$. This correction method is thus based on the assumptions that ^{37}Ar is a proxy $^{36}Ar_{cos}$. Additionally, it is assumed that $^{36}Ar_{trap}$ is exhausted at lower temperatures than $^{36}Ar_{cos}$ (e.g., because it is surface correlated) such that the step with the minimum $^{36}Ar/^{37}Ar$ ratio contains only cosmogenic ^{36}Ar. The advantages of this approach are that it does not require assumptions regarding the isotopic composition of the trapped component (Bogard and Garrison, 1999) and results are insensitive to the presence of $^{38}Ar_{Cl}$ produced during irradiation. Two

[1] The definition of excess Ar adopted here differs from that traditionally used in $^{40}Ar/^{39}Ar$ dating of terrestrial samples, wherein any supra-atmospheric trapped $^{40}Ar/^{36}Ar$ ratio is considered excess.