# $^{40}$AR/$^{39}$AR SYSTEMATICS OF SHERGOTTITE NWA 4468.

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**Introduction:** $^{40}$Ar/$^{39}$Ar ages obtained from Shergottites are often significantly older than ages obtained by other radioisotopic methods (e.g., Sm-Nd and Rb-Sr; [1]). Excess $^{40}$Ar ($^{40}$Ar$_e$) is generally cited as the cause of old apparent ages (e.g., [1, 2]), although 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; [3]). Anomalously old isochron ages can also be obtained if inaccurate corrections for cosmogenic $^{36}$Ar ($^{36}$Ar$_{cos}$) are applied. Here Ar isotope data from NWA 4468 are reported and used to illustrate the sensitivity of some Shergottite $^{40}$Ar/$^{39}$Ar isochron ages to the $^{36}$Ar$_{cos}$ correction. In this instance, applying corrections based on the minimum $^{36}$Ar/$^{37}$Ar ratio or the average $^{38}$Ar$_{cos}$/$^{37}$Ar ratio of the irradiated sample yields an erroneous crystallization age, which is due to the concomitant degassing of chlorine-derived $^{38}$Ar ($^{38}$Ar$_{Cl}$) produced during sample irradiation. Applying $^{36}$Ar$_{cos}$ corrections based on the exposure age determined from an un-irradiated aliquot of NWA 4468 (1.8 ± 0.1 Ma) yields an isochron age (188 ± 8 Ma) that is indistinguishable from Lu-Hf, Rb-Sr, and Sm-Nd ages (179 ± 27 Ma [4], 187 ± 6 Ma [5], and 150 ± 29 Ma [6], respectively). The trapped $^{40}$Ar/$^{36}$Ar ratio inferred from the NWA 4468 inverse isochron is significantly lower than the Martian atmospheric value.

**Analytical Procedures:** Individual fragments of NWA 4468 weighing 3-5 mg were co-irradiated with fluence monitors for 50 hours at the Oregon State University TRIGA reactor in the Cadmium-Lined In-Core Irradiation Tube (CLICIT). Noble gas extractions on irradiated and un-irradiated aliquots were conducted in the Livermore Noble Gas Lab using temperature-controlled diode laser-heating following procedures similar to those described in [7]. Released gases were analyzed using a Nu Instruments *Noblesse* mass spectrometer equipped with six Faraday cup detectors and four ion-counting, discrete dynode multiplier detectors. Total $^{36}$Ar signals were corrected for cosmogenic contributions using the following equation:

$$^{36}Ar_{cos} = T_{38}\left(\frac{P_{38}}{[Ca]}\right)\left(\frac{^{37}Ar}{\gamma}\right)\left(\frac{^{36}Ar}{^{38}Ar}\right)_{cos}, \qquad \text{Eq. (1)}$$

where $T_{38}$ is the $^{38}$Ar exposure age, $P_{38}$/[Ca] is the production rate of $^{38}$Ar$_{cos}$ relative to the Ca concentration [8], $\gamma$ is the irradiation parameter relating $^{37}$Ar$_{Ca}$ to Ca content [9], and ($^{36}$Ar/$^{38}$Ar)$_{cos}$ is 0.65 [10]. $P_{38}$/[Ca] was calculated on a step-wise basis using the measured Ca/K ratio and $^{38}$Ar$_{cos}$ production rates from Ca and K of [11].

**Results:** Figure 1 illustrates $^{40}$Ar/$^{39}$Ar isochron ages and reduced chi-squared fit statistics calculated for a range in assumed exposure ages. The inferred crystallization age of NWA 4468 varies by 100% over a 1 Ma range in assumed exposure age. To obtain an isochron age that is concordant with the crystallization age determined by the Rb-Sr, Sm-Nd, and Lu-Hf systems, an exposure age of ~1.6-1.9 Ma is required. This is considerably younger than the exposure age inferred from both the minimum $^{36}$Ar/$^{37}$Ar ratio (~2.3 Ma) and the average $^{38}$Ar$_{cos}$/$^{37}$Ar ratio (~4.5 Ma) obtained from step-wise degassing of NWA 4468. Applying $^{36}$Ar$_{cos}$ corrections based on these exposures ages yields

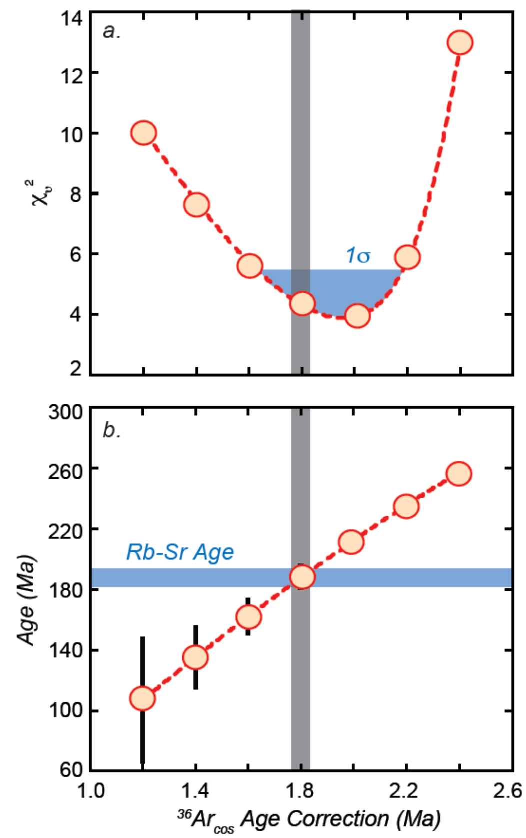


**Figure 1:** Plot of $^{40}$Ar/$^{39}$Ar inverse isochron ages for NWA 4468 as function of the exposure age used to correct total $^{36}$Ar abundances. The reduced chi-squared statistic reflects the goodness of fit. The 1σ error on the best-fit exposure age is estimated from values +1.2 units above the minimum in $\chi_v^2$. Using the exposure age obtained from an un-irradiated aliquot of NWA 4468 (~1.8 Ma; solid gray line) to correct for $^{36}$Ar$_{cos}$ reproduces the Rb-Sr age (187 Ma; solid blue line; [5]) and lies within the 1σ error envelope of the best-fit model solution.

anomalously old crystallization ages and excessively scattered isochrons (Fig. 1). The exposure age spectrum calculated based on apparent $^{38}Ar_{cos}/^{37}Ar$ ratios (no chlorine corrections; not shown) is highly variable, which indicates that $^{38}Ar_{Cl}$ produced during sample irradiation is released throughout the degassing experiment. This $^{38}Ar_{Cl}$ is likely associated with apatite present in NWA 4468 and possibly melt inclusions or alteration minerals. Although the individual step $^{38}Ar/^{36}Ar$ ratios generally do not exceed the nominal cosmogenic ratio of 1.54 [10], the exposure age inferred from the irradiated aliquot is meaningless. The $^{38}Ar_{cos}$ exposure age calculated from an un-irradiated aliquot of NWA 4468 is 1.8 ± 0.1 Ma. Applying corrections to $^{36}Ar_{cos}$ using this exposure age yields a $^{40}Ar/^{39}Ar$ inverse isochron age of 188 ± 8 Ma, which is indistinguishable from the Rb-Sr age of 187 ± 6 Ma [5].

**Discussion:** The $^{40}Ar/^{39}Ar$ age of NWA 4468, and other Shergottites, is highly dependent on corrections applied for $^{36}Ar_{cos}$ (Fig. 1). Nakhlite $^{40}Ar/^{39}Ar$ ages are also susceptible to isochron rotation due to erroneous $^{36}Ar_{cos}$ corrections, although the relative magnitude of the effect is generally less significant given their antiquity. It is not possible to calculate an exposure for NWA 4468 from irradiated fragments due to pervasive contamination by $^{38}Ar_{Cl}$. On-going analyses of He, Ne, Ar, Kr, and Xe in un-irradiated aliquots will be used to further refine the $^{40}Ar/^{39}Ar$ age and $^{38}Ar_{cos}$ exposure age of NWA 4468.

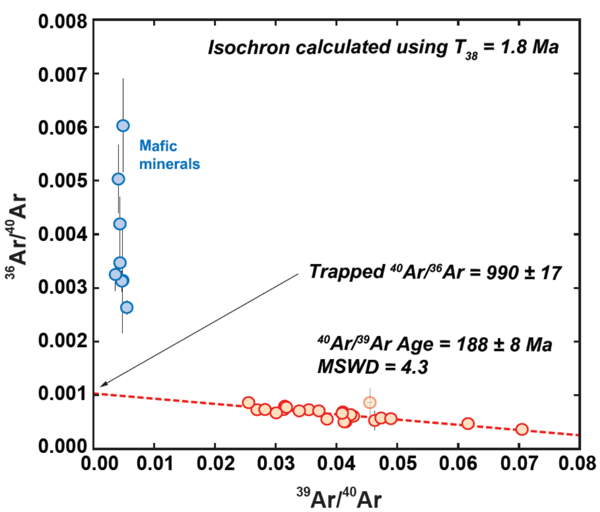


**Figure 2:** Inverse isochron diagram for NWA 4468 calculated using an exposure age of 1.8 Ma to correct total $^{36}Ar$ abundances. The felsic (red) and mafic (blue) derived gas extractions, distinguished by their K/Ca ratios and outgassing temperature, appear to have equilibrated with different noble gas reservoirs.

Figure 2 depicts an inverse isochron diagram for NWA 4468 calculated using an exposure age of 1.8 Ma to correct for $^{36}Ar_{cos}$. The trapped component defined primarily by maskelynite-derived gas (red data points in Figure 2) has a $^{40}Ar/^{36}Ar$ ratio of 990 ± 17. This ratio is relatively insensitive to the exposure age of the sample, varying by only ± 50 over the range in exposure ages shown in Figure 1. The $^{40}Ar/^{36}Ar$ ratio of the trapped component is significantly lower than the Martian atmospheric value, and likely represents an upper mantle or crustal component. On-going analyses of Xe isotopes will provide further insight into the nature of the trapped component in NWA 4468. High temperature extractions associated with Ar released from mafic minerals (blue data points in Figure 2) define an isochron with an age of 1515 ± 386 Ma (MSWD = 3.9; trapped $^{40}Ar/^{36}Ar$ = 159 ± 22). This age may reflect an excess Ar component or may be indicative of a xenocrystic origin of some mafic minerals. Future work will focus on applying the step-wise cosmogenic correction approach described above to other Shergottites in an effort to resolves age discrepancies and obtain high-precision constraints on trapped components.

**References:** [1] Bogard D. et al. (2009) *Meteoritics & Planetary Science, 44,* 905-923. [2] Bogard D. and Park J. (2008) *Meteoritics & Planetary Science, 43,* 1113-1126. [3] Lindsay F.N. et al. (2013) LPSC XXXXIV, Abstract #2911. [4] Lapen T.J. et al. (2009) LPSC XXXX, Abstract #2376. [5] Marks N.E. et al. (2010) LPSC XXXXI, Abstract #2064. [6] Borg L.E. et al., (2008) LPSC XXXIX, Abstract #1851. [7] Cassata W.S. et al. (2010) *Geochimica et Cosmochimica Acta, 74,* 6900–6920. [8] Turner G. et al. (1997) *Geochimica et Cosmochimica Acta, 61,* 3835-3850. [9] Levine J. et al. (2007) *Geochimica et Cosmochimica Acta, 71,* 1624-1635. [10] Wieler R. (2002) *Reviews in Mineralogy and Geochemistry, 47,* 125-170. [11] Eugster O. and Michel (1995) *Geochimica et Cosmochimica Acta, 59,* 177-199.

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