NITROGEN AND ARGON IN ALH 84001 REVISITED: UNRAVELLING A MARTIAN ATMOSPHERIC COMPONENT; Monica M. Grady[1,2], I. P. Wright[2] and C. T. Pillinger[2], [1]Dept. of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, UK, [2]Planetary Sciences Unit, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK.

Abstract: We have measured nitrogen and argon released simultaneously upon combustion of two samples of ALH 84001 (A84). Both nitrogen and argon appeared to be heterogeneously distributed in the rock: one sample liberated very little gas above blank levels, whereas the second sample, selected because it contained abundant material from the "crush zones", was rich in both species. Using the $^{40}Ar/^{14}N$ ratio and $\delta^{15}N$ of the gas liberated above 700°C from this second sample, an attempt has been made to calculate the relative quantities of adsorbed terrestrial gases and trapped martian atmospheric species. Following from this, excess ^{40}Ar attributed to radiogenic production from potassium decay can be used to determine a K-Ar age of the sample. We calculate that ~17.5% of the total ^{40}Ar is indigenous to the sample. Assuming that the trapped component would have a $^{40}Ar/^{14}N$ ratio equivalent to that in the present-day martian atmosphere (~0.33), then there is a small excess of ^{40}Ar (amounting to about 1.5% of the total ^{40}Ar). Taking a reasonable estimate of the potassium abundance (100-200 ppm) implies that A84 has a K-Ar age of ~0.76-1.28 Gyr, which is much younger than ages determined in previous studies and using other methods.

Age-dating studies have suggested that A84 is the oldest of all the martian meteorites, with a crystallisation age of ~4.56 Gyr [1,2]. K-Ar ages (dating a major shock event which might be the time when ALH 84001 was excavated from depth to the surface of Mars) are also high, and range from 2.4 to > 5 Gyr [3-5], depending on the assumed potassium abundance. Note, though, that the greatest ages (> 5 Gyr) were calculated using an incorrect potassium abundance [6,7]; when correct values are used, no ages greater than 4.5 Gyr are obtained. In contrast to K-Ar dating, which requires independent measurements of potassium and argon and is thus susceptible, in complex samples, to various uncertainties, an age determined by the ^{40}Ar-^{39}Ar method (4.17 Gyr; ref. 8) appears more reliable. Indeed, it has been considered that this age coincides with the late episode of heavy bombardment that is also observed on the Moon [9].

The authors of the K-Ar studies [3-5] make the point that if the meteorite contains trapped martian atmospheric argon, the measured K-Ar ages would be in error (i.e. too old). Argon is present in A84 from several sources: radiogenic ^{40}Ar from potassium decay, plus ^{40}Ar, ^{38}Ar and ^{36}Ar produced by spallation, and also trapped from both the martian and terrestrial atmospheres. Using the abundance and isotopic composition of nitrogen released simultaneously with argon from A84, we have attempted to deconvolute the atmospheric and cosmogenic components from the radiogenic argon, in order to assess, more accurately, the K-Ar age of this meteorite. On combustion of A84, ^{15}N-enriched nitrogen is released across two temperature ranges. Above 1200°C, this is influenced by a small amount of cosmogenic nitrogen. Abundant trapped gas was also released across a narrow temperature range (700-850°C). The species were characterised by elevated $\delta^{13}C$ (~+19‰; ref. 10), $\delta^{15}N$ (~+143‰) and enhanced levels of ^{40}Ar. Correction for cosmogenic components does not affect these values. On the basis of its enrichment in ^{15}N, $^{40}Ar/^{14}N$ = ~0.05-0.07 and $^{40}Ar/^{36}Ar$ = ~2000, the gas is inferred to be a mixture of terrestrial and martian atmospheric species, with additional ^{40}Ar from radiogenic decay of potassium.

The composition of trapped atmospheric species can be related to mixing between Earth and Mars atmosphere end-members on a plot of $\delta^{15}N$ versus $^{40}Ar/^{14}N$ [11,12]. Any excess ^{40}Ar is thus shown by points falling off the Earth-Mars atmospheric mixing line, in the direction of increasing $^{40}Ar/^{14}N$. When data from this study are plotted on such a diagram, there is very little deviation from the line, suggesting that any radiogenic component is only relatively minor. Such a result can be interpreted in a number of ways. Firstly, that there is actually no radiogenic argon present in the samples (similar to the glasses from EET A79001 and Zagami; refs. 11,12), in which case the apparent deviation of points from the Earth-Mars mixing line would be due to an inaccurate assessment of our errors. A second explanation is that there is no potassium present, thus the sample is of indeterminate age. Alternatively, and much more likely, some potassium is present, therefore the sample has to be relatively young, i.e. the glass was formed late in the history of the sample, presumably when it was ejected from the martian surface. Accepting the experimental evidence, that there really is only a small excess of ^{40}Ar, allows speculation about what this means in terms of the age of the sample.

Assuming end-member compositions of $\delta^{15}N$ ~0‰ (Earth) and $\delta^{15}N$ ~+600‰ (Mars), then it is possible to calculate the relative proportions of terrestrial and martian atmospheric species in the nitrogen liberated from A84. On this basis, approximately 17.5% of the nitrogen (15 ppb) is martian, the balance terrestrial. Taking the present-day martian atmospheric ratio of $^{40}Ar/^{14}N$ as 0.33, then 14.1 ppb ^{40}Ar is trapped from the martian atmosphere. However, the total amount of ^{40}Ar liberated with the nitrogen between 700 - 850°C is 15.4 ppb, i.e. there is an excess of 1.3 ppb ^{40}Ar. Assuming potassium contents of between 100-200 ppm, the calculated K-Ar age of A84 appears to be between 0.8 and 1.3 Gyr, much younger than previously reported, but closer to K-Ar ages reported for other martian meteorites. Our result is in conflict with those reported from other studies and especially that from the ^{40}Ar-^{39}Ar data [8,9]. However it is possible to reconcile a young K-Ar age with the ancient chronology of A84 outlined by Treiman [13]. Thus A84 crystallised soon after differentiation of the planet, was shocked and thermally metamorphosed in an early period of bombardment (possibly that recognised by ^{40}Ar-^{39}Ar chronology), then subjected to a second shock event at between 0.8 and 1.3 Gyr. This later event might mark the excavation of the A84 parent to the surface of Mars. What is difficult to rationalise is why the second shock event does not re-set the ^{40}Ar-^{39}Ar system (indeed, the same problem exists if we propose that there is no excess ^{40}Ar in the sample and that the gases were trapped in the recent history of A84). Perhaps the logic used in our interpretation is in some way erroneous, or maybe the assumption of present day values for $\delta^{15}N$ and $^{40}Ar/^{14}N$ is wrong. If in fact the gases trapped in A84 represent an earlier atmosphere of different composition then these values may have been different at the time of incorporation. The latter explanation would have to mean that we have uncovered a valuable new insight into the historical development of the martian atmosphere.

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