The fundamentally different origins of $^{40}\text{Ar}$ and $^{36}\text{Ar}$ (radiogenic and primordial respectively) make the ($^{40}\text{Ar}/^{36}\text{Ar}$) ratio in planetary atmospheres a sensitive parameter for studying the evolution of planetary interiors. Unlike argon from the mantle, atmospheric argon is always well mixed isotopically and represents the time-integrated product of chemical fractionation, radioactive decay and degassing processes within the planet. A theoretical value of $2 \times 10^{-4}$ has been calculated for the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in the primordial argon component (1) and an experimentally determined upper limit of $(1.4 \pm 0.6) \times 10^{-3}$ has been deduced from analyses of meteorites (2). The present day value for the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in the earth's atmosphere is 295.5, whereas Viking measurements have indicated ratios as high as 3,000 in the atmosphere of Mars.

The total quantity of $^{40}\text{Ar}$ in the atmosphere of the Earth establishes a firm lower limit for the earth's potassium content (80 ppm), based on the assumption that argon degassing is a first order process with a rate constant which is large compared to the mean life of $^{40}\text{K}$. Any model for the temporal evolution of the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio must consider not only the validity of this extreme assumption, but also the possibility that outgassing of $^{36}\text{Ar}$ may have been catastrophic rather than continuous. As it is reasonable to assume that $^{36}\text{Ar}$ must have been concentrated in the earth's crust/atmosphere more readily than K, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in the atmosphere must have increased monotonically with time. A number of models have been proposed for the shape of this evolution curve, and therefore its experimental determination should enable chemical fractionation processes and argon degassing rates to be critically investigated (3). The experimental determination of terrestrial palaeoatmospheric argon isotope ratios requires the existence of geologic samples which (a) are authigenic, (b) incorporated atmospheric argon during formation, (c) are low in potassium, (d) are very old, (e) are retentive, and (f) have had a simple geologic history. Non-marine cherts are among the most suitable samples for analysis. Previous attempts to detect palaeoatmospheric argon in Pre-Cambrian cherts were unsuccessful, possibly due to their marine origin and complex geologic history (3).

The samples selected for this work were chips of Rhynie chert from the Devonian of Aberdeenshire, Scotland. The Rhynie chert is very low in potassium (100 - 150 ppm), contains abundant silicified fossils of some of the oldest known land plants (ca 380 my) and is extremely well preserved. The samples (50 - 200 mg) were analysed by the $^{40}\text{Ar}/^{39}\text{Ar}$ method so that corrections for "in situ" decay of $^{40}\text{K}$ could be applied. Unirradiated samples were also analysed to investigate isotopic fractionation during gas extraction. No corrections for the production of $^{36}\text{Ar}$ and $^{39}\text{Ar}$ from calcium during irradiation could be applied (based on the $^{37}\text{Ar}$) because of the long elapsed time prior to analysis, but the total amounts of trapped $^{36}\text{Ar}$ were remarkably high $(2 - 3 \times 10^{-5}\text{ cc/g})$ and the total ($^{40}\text{Ar}/^{36}\text{Ar}$) ratios from the unirradiated samples $(297.2 \pm 1.5, 295.7 \pm 1.1)$ were in fact less than from the irradiated samples.
The thermal release patterns for $^{36}\text{Ar}$ from the irradiated samples (5, 6) were bimodal. The major gas fractions were released above 1200°C, with maxima between 1350°C and 1420°C (Figure 1). The $^{38}\text{Ar}$ was primarily a product of neutron capture by chlorine and its high temperature release exhibited maxima at similar temperatures. The $^{39}\text{Ar}$ thermal release patterns were broader with maxima at slightly lower temperatures (1220°C - 1350°C). These very high extraction temperatures suggest that the high temperature $^{36}\text{Ar}$ is very strongly trapped palaeoatmospheric argon, possibly situated in chlorine-rich rather than potassium-rich sites within the sample. The low temperature (< 850°C) $^{36}\text{Ar}$ component may be more recently adsorbed atmospheric argon.

Figure 2 is a 3 isotope correlation plot of $^{36}\text{Ar}/^{40}\text{Ar}$ vs. $^{39}\text{Ar}/^{40}\text{Ar}$. Mixtures of atmospheric and potassium-derived argon should define a mixing line on this plot between pure atmospheric argon ($^{36}\text{Ar}/^{40}\text{Ar} = 0$) and pure potassium-derived argon ($^{36}\text{Ar}/^{40}\text{Ar} = 0$). The small spread in $^{39}\text{Ar}/^{40}\text{Ar}$ ratios precludes the determination of a precise gas retention age, but a weighted least squares fit to all extractions yields an atmospheric $^{36}\text{Ar}/^{39}\text{Ar}$ ratio of (292.8 ± 2.1) assuming a gas retention age of 380 My. The $^{36}\text{Ar}$ thermal release patterns, however, indicate that the palaeoatmospheric argon is released only above 1220°C and if the $^{36}\text{Ar}/^{39}\text{Ar}$ ratios from only these extractions are similarly corrected for "in situ" decay, weighted palaeoatmospheric ($^{36}\text{Ar}/^{39}\text{Ar}$) ratios of (291.2 ± 2.8), (290.9 ± 3.2) and (290.0 ± 1.9) are calculated for samples 5, 6, and 5 + 6 respectively.

It should be noted that the two largest gas fractions (sample 6, 1350°C and 1420°C) do not fall on the best fit line within their very small analytical uncertainties. This is most likely due to diffusive isotopic fractionation during thermal extraction. For both samples 5 and 6 the $^{36}\text{Ar}/^{39}\text{Ar}$ ratios increase with extraction temperature: 1220 < 1350 < 1420, although this is only readily apparent from sample 6 when the analytical uncertainties are small. If diffusive isotopic fractionation occurs, $^{36}\text{Ar}$ would be expected to be released more readily than $^{39}\text{Ar}$, giving rise to low $^{36}\text{Ar}/^{39}\text{Ar}$ ratios at low temperature. The concordance of the total high temperature ($^{36}\text{Ar}/^{39}\text{Ar}$) ratios from the two samples argues against geological diffusion, but further analyses are required to confirm this concordance and to apply corrections for neutron-produced $^{36}\text{Ar}$ and $^{39}\text{Ar}$. The analyses of larger, un-irradiated samples would allow laboratory and geological diffusion to be investigated from the $^{36}\text{Ar}/^{39}\text{Ar}$ ratios.

If the calculated value for the $^{36}\text{Ar}/^{39}\text{Ar}$ ratio of the palaeoatmospheric argon trapped in the Rhynie chert (290.9 ± 1.9) is confirmed by further analyses, this is the first time that terrestrial atmospheric argon with a $^{36}\text{Ar}/^{39}\text{Ar}$ ratio significantly less than 295.5 has been detected. But even the most extreme first order degassing model ($\alpha > \lambda$, K$_p$ = 80 ppm), predicts a $^{36}\text{Ar}/^{39}\text{Ar}$ ratio of only 289.0, 380 My ago, and this value could only be raised further by postulating preferential (relative to K) retention of $^{36}\text{Ar}$ within the mantle. An alternative, and more reasonable, model which would be compatible with the experimental value, would be a degassing rate constant which has decreased with time, and a correspondingly higher K content for the earth. This would imply a gradual decrease in volcanic activity with time,
which would be consistent with the decrease in quantity of heat-producing radio nuclides within the earth. One model which satisfies the constraints is a potassium content for the earth of 230 ppm, catastrophic degassing 4,000 My ago followed by first order degassing of $^{40}\text{Ar} (\alpha = 2 \times 10^{-11} \text{ g}^{-1})$. It would clearly be desirable to sample Pre-Cambrian atmospheric argon to investigate this further but Pre-Cambrian fossils are wholly marine and any argon which they may have trapped would have been dissolved in sea water, where it would not have been exchanged directly with the atmosphere and could conceivably contain excess $^{40}\text{Ar}$ rising from the sea floor.