Earth-atmosphere evolution based on new determination of Devonian atmosphere Ar isotopic composition

Finlay M. Stuart*, Darren F. Mark, Pierre Gandanger & Paul McConville

Isotope Geoscience Unit, Scottish Universities Environmental Research Centre, East Kilbride G75 0QF, United Kingdom

*Corresponding author e-mail: fin.stuart@glasgow.ac.uk

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Abstract

The isotopic composition of the noble gases, in particular Ar, in samples of ancient atmosphere trapped in rocks and minerals provide the strongest constraints on the timing and rate of Earth atmosphere formation by degassing of the Earth's interior. We have re-measured the isotopic composition of argon in the Rhynie chert from northeast Scotland using a high precision mass spectrometer in an effort to provide constraints on the composition of Devonian atmosphere. Irradiated chert samples yield $^{40}Ar/^{36}Ar$ ratios that are often below the modern atmosphere value. The data define a $^{40}Ar/^{36}Ar$ value of 289.5 ± 0.4 at $K/^{36}Ar = 0$. Similarly low $^{40}Ar/^{36}Ar$ are measured in un-irradiated chert samples. The simplest explanation for the low $^{40}Ar/^{36}Ar$ is the preservation of Devonian atmosphere-derived Ar in the chert, with the intercept value in ^{40}Ar-$^{39}Ar^{-36}Ar$ space representing an upper limit. In this case the Earth's atmosphere has accumulated only 3% ($5.1 \pm 0.4 \times 10^{16}$ mol) of the total ^{40}Ar inventory since the Devonian. The average accumulation rate of $1.27 \pm 0.09 \times 10^{8}$ mol ^{40}Ar/year overlaps the rate over the last 800 kyr. This implies that there has been no resolvable temporal change in the outgassing rate of the Earth since the mid-Palaeozoic despite the likely episodicity of Ar degassing from the continental crust. Incorporating the new Devonian atmosphere $^{40}Ar/^{36}Ar$ into the Earth degassing model of Pujol et al (2013) provides the most precise constraints on atmosphere formation so far. The atmosphere formed in the first ~100 Ma after initial accretion during a catastrophic degassing episode. A significant volume of ^{40}Ar did not start to accumulate in the atmosphere until after 4 Ga which implies that stable K-rich continental crust did not develop until this time.

1. Introduction

The concentration of the noble gases (He, Ne, Ar, Kr and Xe) in the main terrestrial reservoirs (mantle, crust and atmosphere) are not affected by the chemical and biological processes that govern the distribution of the reactive volatile elements. The presence of both stable and radiogenic noble gas isotopes can be used to provide temporal constraints on the outgassing history of the solid Earth and the age of the atmosphere. Consequently they have proved to be key tracers of the origin and evolution of the atmospheres of the terrestrial planets (e.g. Turcotte and Schubert, 1988).

The origin of the Earth's atmosphere has been critical in the understanding evolution of terrestrial planets. It has been recognised for many decades that the Earth's atmosphere is secondary in origin, a consequence of the outgassing of the planetary interior, rather than capture of solar nebula gases (Brown, 1949). Models of atmosphere growth are largely based on the noble gas isotope composition of the present day mantle, crust and atmosphere. The earliest models proposed that the atmosphere formed as a result of slow, continuous outgassing of the Earth's interior (Turekian, 1959). The low concentration of stable (primordial) noble gas isotopes in mantle rocks compared to primitive chondritic meteorites led to the conclusion that Earth must be strongly outgassed. Subsequent studies of Ar isotopes in Earth interior permitted the development of two-stage outgassing history; an extensive outgassing event soon after Earth accretion was followed by slow continuous degassing (Fanale, 1971; Hamano and Ozima, 1978). The early models were predicated on the assumption that the atmosphere formed by outgassing of only the crust and upper mantle where the deep mantle did not outgas significantly, and remained convectively isolated from the upper mantle (e.g. Allègre et al. 1986/87; 1996). Subsequent modelling demonstrated that the complete outgassing of an upper mantle down to the 670 km seismic discontinuity cannot

provide all the ^{40}Ar in the atmosphere (e.g. Davies, 1999). The measurement non-atmospheric Ne and Ar isotope compositions in basalts from intra-plate volcanoes (e.g. Honda et al., 1993; Burnard et al. 1994) led to the recognition that the lower mantle below 670 km cannot have remained convectively isolated for all of Earth history (e.g. Porcelli and Wasserburg, 1995; O'Nions and Tolstikhin, 1996). Recent Earth outgassing models incorporate some degree of volatile loss from the deep mantle (e.g. Gonnerman and Mukhopadyay, 2009), but the extent to which the deep Earth is degassed, and the source and location of primordial noble gases in Earth's interior remain unresolved (see discussion in Starkey et al. 2009).

While the isotopic composition of noble gases in modern terrestrial reservoirs is well established, the time-integrated rate of mass transfer between these reservoirs, as well as the rate of transfer of primordial and radiogenic volatiles, is much less well constrained (e.g. Farley et al. 1995; Stuart and Turner 1998). The determination of the isotopic composition of noble gases in ancient atmosphere provides a first order test of the degree and rate of gas and mass transfer processes. However, the ubiquity of contaminating modern atmosphere, and the ingrowth of radiogenic isotopes in minerals after crystalisation, severely hampers the precise determination of these signals. Despite this, a low $^{40}Ar/^{36}Ar$ component appears to have been incorporated in several ancient rocks and minerals (e.g. Cadogan, 1977; Hanes et al. 1985; Rice et al. 1994; Pujol et al. 2013). These values are consistent with the incorporation and retention of ancient atmospheric Ar, although it usually relies on a correction for radiogenic ^{40}Ar ingrowth after mineral or rock formation. The difficulty in explaining systematically low $^{40}Ar/^{36}Ar$ by any other mechanism, however, indicates that it is clearly a fruitful avenue for constraining the Earth outgassing history.

The Devonian hydrothermal Rhynie chert from northeast Scotland is probably the most thoroughly studied material that may preserve an ancient atmospheric Ar signal. The

first detailed study yielded an initial $^{40}Ar/^{36}Ar$ = 291.0 ± 1.6 which, it was argued, represented the value of Devonian atmosphere (Cadogan, 1977). Although this value was consistent with what would be expected for catastrophic early Earth degassing (e.g. Turner, 1989) the veracity of the measurements failed to convince some at the time (see Ozima and Podosek, 1983). Subsequent intensive study replicated the low $^{40}Ar/^{36}Ar$ (291.1 ± 0.6; Rice et al. 1994). However, as with the initial study, this work yielded no gas extraction steps with $^{40}Ar/^{36}Ar$ ratios that were unequivocally lower than the present day atmospheric value and the presence of palaeo-atmospheric Ar relied on the (not unreasonable) assumption that radiogenic ^{40}Ar was present to some degree in all gas extraction steps. High precision determinations have been made of the isotope composition of atmospheric argon trapped in samples of Antarctic ice dating back several hundred thousand years (Bender et al. 2008). These data require an average modern outgassing rate of 1.1 x 10^8 mol ^{40}Ar/year. This rate is broadly consistent with, and more precise than, the long-term average calculated from the measurements of Rhynie chert. Most recently a low $^{40}Ar/^{36}Ar$ trapped in Archaean hydrothermal quartz from 3.5 Ga Pilbara craton, Western Australia (Pujol et al. 2013) has been used to place constraints on the rate of atmosphere degassing early in Earth history, which has implications for the timescale of formation of continental crust.

Several factors warrant a re-assessment of the possibility that the Rhynie chert is a repository of ancient atmospheric noble gases. Recent improvements in multi-collector noble gas mass spectrometers allows for high precision Ar isotope measurements (Mark et al. 2010). The re-determination of the Ar isotope composition of the modern atmosphere (see Mark et al. 2011a for discussion) means that fractionation in the mass spectrometer can be correctly determined, and an appropriate correction for trapped modern air can be made. Finally, a better understanding of the petrology of the Rhynie chert (e.g. Baron et al. 2004) means that potentially problematic components of the rock,

120 e.g. detrital clay, can be avoided. Here we present new determinations of the $^{40}Ar/^{36}Ar$ of
121 the Rhynie chert in an effort to determine isotopic composition of the Devonian
122 atmosphere. The new value for Devonian air is incorporated into the Earth degassing
123 model developed by Pujol et al. (2013) and is used to place constraints on the
124 degassing history of the Earth.

125

126 **2. Samples and analytical methods**

127 Argon isotopes have been measured in mg-sized chips of irradiated and un-irradiated
128 pristine siliceous sinter from a single specimen of Rhynie chert. Samples were selected
129 specifically in order to avoid entrained fine-grained sediment, minimising potential issues
130 resulting from the recoil of K-derived ^{39}Ar. We specifically targeted the siliceous sinter
131 that developed on the surface and cooled in direct exposure to the Devonian
132 atmosphere. Detailed descriptions of the Rhynie chert are given elsewhere (e.g. Rice et
133 al. 1994; Baron et al. 2004). Nine samples were irradiated for 100 hours in the Cd-lined
134 nuclear reactor at McMaster, Canada. Eight of these samples were incrementally heated
135 in 5 steps using a 50 W CO_2 laser in an attempt to selectively remove absorbed modern
136 atmospheric Ar and release palaeo-atmospheric Ar. One sample was fused in a single
137 step. Biotite from the Mount Dromedary monzonite (GA1550, 98.8 ± 0.5 Ma, Renne et
138 al. 1998) was used as a neutron fluence monitor. Details of the irradiation parameters
139 are given in the Supplementary Information. Samples were outgassed at ~80°C in a Cu
140 laser pan for 10 days prior to analysis in order to remove adhering atmospheric Ar. The
141 extraction, purification and analysis procedures were similar to those described in Mark
142 et al. (2011b).

143 Argon isotopes were measured in 12 unirradiated chips of Rhynie chert. The gas
144 extraction procedure and purification was identical to that applied to the irradiated chips.

145 Five samples were incrementally heated in three steps, and seven were fused in a single
146 step.

147 Argon isotope abundances and ratios were determined using a GVI ARGUS multiple-
148 Faraday collector mass spectrometer using established laboratory procedures (Mark et
149 al. 2010). System blanks were measured after every two measurements of unknowns.
150 Average blank measurements for the entire run sequence were used to correct raw peak
151 intensities. Mass discrimination (1.0059 ± 0.0009/amu) was determined by repeated
152 measurement of air pipettes during the period of analysis (following every five analyses).

153

154 **3. Results**

155 The data from the irradiated and unirradiated samples are compiled in the
156 Supplementary Information. Argon in the samples likely derives from four sources;
157 modern air, Devonian air, ^{40}Ar generated from ^{40}K decay and "excess" ^{40}Ar in the
158 hydrothermal fluids (see Rice et al. 1994 for review). These components can best be
159 resolved using the analyses of irradiated samples. In ^{40}Ar-^{39}Ar-^{36}Ar space the data define
160 a triangular region that appears to have a well-defined lower bound (Figure 1). The data
161 that plot above the lower bound may be affected by a small contribution of excess ^{40}Ar
162 that originates in the trapped hydrothermal fluid. They are statistically insignificant. A
163 correlation between Ca-derived ^{37}Ar and K-derived ^{39}Ar (SI Table 1) indicates that a Ca-
164 and K-bearing mineral or fluid inclusion phase is present in the chert. While a trapped
165 fluid phase is present in the Rhynie chert (Rice et al. 1994), the presence of detrital clay
166 minerals cannot be ruled out. ^{39}Ar recoil from clays can perturb the Ar isotope
167 systematics but there is no clear evidence of the effect in this case (Figure 1).

168 Following the protocol established by earlier studies (Cadogan 1977; Rice et al. 1994;
169 Pujol et al. 2013) we use a conventional isochron to determine the palaeo-atmosphere

$^{40}Ar/^{36}Ar$. The majority of the data define a statistically robust isochron that has a slope consistent with a $^{40}Ar/^{39}Ar$ age of 380 ± 30 Ma (see Figure 1 for description). This overlaps the more precise $^{40}Ar/^{39}Ar$ age (408 ± 2 Ma) determined on adularian felspar from a feeder vein beneath the Rhynie chert body (Mark et al. 2011b; 2013). The intercept of the y-axis at $K/^{36}Ar = 0$ is consistent with the trapped argon having a $^{40}Ar/^{36}Ar$ of 289.5 ± 0.4. This is significantly lower than modern air value and is consistent with, though significantly lower than, previous studies (Cadogan 1977; Rice et al. 1994).

In contrast to these earlier studies, the $^{40}Ar/^{36}Ar$ of many individual measurements are lower than the modern air value, providing some confidence that the sub-atmospheric $^{40}Ar/^{36}Ar$ is trapped in the chert, and is not an artifact of disturbance to the K-^{40}Ar system. There is no systematic relationship between ^{40}Ar or K-derived ^{39}Ar with Cl-derived ^{37}Ar produced during the irradiation process that might be indicative of the low $^{40}Ar/^{36}Ar$ component residing in hydrothermal fluid inclusions. Further the analyses that appear to contain small excesses of ^{40}Ar (yellow data in Figure 1) do not have a clear relationship with Cl-derived ^{38}Ar that might indicate an origin in hydrothermal fluid inclusions (e.g. Turner, 1988).

It is tempting to invoke a palaeo-atmospheric source for the sub-atmospheric $^{40}Ar/^{36}Ar$ ratios in the chert. However, we must exclude alternative possibilities. The unirradiated samples reproduce the low $^{40}Ar/^{36}Ar$ measured in the irradiated samples while $^{38}Ar/^{36}Ar$ ratios are within analytical uncertainty of the atmospheric composition (Figure 2 and Table SI2). This provides no indication for the presence of fractionated modern air Ar in the chert, and rules out significant mass fractionation during analysis, or a significant contribution of isobaric interferences of $^{12}C_3^+$ or $H^{35}Cl^+$ at $^{36}Ar^+$. The samples are from boreholes several tens of meters underground. Along with the absence of excess ^{38}Ar (Figure 2), this rules out cosmogenic ^{36}Ar as an explanation for the low $^{40}Ar/^{36}Ar$.

Following the earlier studies (Cadogan, 1977; Rice et al. 1994) we conclude that the Rhynie chert has trapped Ar derived from ancient atmosphere. Assuming that it was incorporated at the time of chert formation, it reflects the signature of Devonian atmosphere. The likelihood that a small contribution of modern air-derived Ar is present in some of the analyses used to define the isochron implies that the $^{40}Ar/^{36}Ar$ intercept value (289.5 ± 0.4; Figure 1) is an upper limit of the Devonian atmosphere.

4. Discussion

4.1 Earth outgassing since Devonian

The $^{40}Ar/^{36}Ar$ of the Devonian atmosphere in this study (289.5 ± 0.4) is 3.1 ± 0.2 % lower than the best estimate of present day air (298.8 ± 0.5; Lee et al. 2008). Previous studies of Rhynie chert have reported trapped $^{40}Ar/^{36}Ar$ ratios of around 291 (Cadogan, 1977; Rice et al. 1994). These determinations were made on instruments that had been calibrated against atmospheric Ar assuming $^{40}Ar/^{36}Ar$ = 295.5 ± 0.5 determined by Nier (1956). In these cases the trapped palaeo-atmospheric $^{40}Ar/^{36}Ar$ is ~1.5% lower than the present day atmosphere value. If our new measurement represents atmosphere trapped at the time of chert formation, the post-Devonian degassing rate is approximately twice the rate determined previously, approximately 3% lower than modern air (Cadogan, 1977; Rice et al. 1994).

For a modern global atmospheric ^{40}Ar inventory of 1.65 x 10^{18} moles (Hamano and Ozima, 1978), our data imply that the atmosphere has accumulated 5.1 ± 0.4 x 10^{16} moles of ^{40}Ar in the last 404 million years. This equates to an average degassing rate of 1.27 ± 0.09 x 10^{8} mol ^{40}Ar/year. This is slightly in excess of, but overlaps within 1σ uncertainty, the Quaternary accumulation rate of ^{40}Ar in the atmosphere derived from

measurements of Greenland and Antarctic ice cores in the last 800,000 years (1.1 ± 0.1 x 10^8 mol ^{40}Ar/year; Bender et al. 2008).

The bulk of the atmosphere ^{40}Ar flux outgases from the continental crust as a result of mineral breakdown during chemical weathering and metamorphism, and diffusion from deep crustal rocks (Bender et al. 2008). The short-term outgassing rate of the crust is expected to vary according to the proportion of ancient (^{40}Ar-rich) basement rocks that is available for weathering, and the intensity of metamorphism. The apparent overlap of the short-term (<1 million years) and the long-term (400 million years) outgassing rates suggests that the time constant for Ar outgassing from the crust may be so long as to minimize the effect of large scale, episodic geological processes such as orogenesis.

4.2 Degassing of the early Earth

Recently Pujol et al. (2013) reported the Ar isotope composition of hydrothermal quartz in Archaean-aged metasedimentary rocks from the Pilbara craton, Western Australia. Although no individual incremental heating steps yielded a measured ^{40}Ar/^{36}Ar ratio below the modern atmosphere value, when corrected for ^{40}K-decay the individual steps extrapolated to a ^{40}Ar/^{36}Ar value of 143 ± 24 (1σ). They argued that this represents the best estimate of the isotopic composition of Ar in the Earth atmosphere at 3.5 Ga (Pujol et al. 2013). Using a first-order rate box model similar to the one developed by Hamano and Ozima (1978) they used this palaeo-atmospheric ^{40}Ar/^{36}Ar to constrain the evolution of the atmosphere ^{40}Ar/^{36}Ar and thus place limits on the timing of crust formation and degree of crust degassing. How this data constrains the evolution of atmosphere ^{40}Ar/^{36}Ar since 4.56 Ga and 500 Ma is shown in Figures 2a and 2b respectively, along with our new determination of Devonian atmosphere ^{40}Ar/^{36}Ar. The new data plots well

within the limits predicted by the Pujol et al (2013) degassing model (Figure 2b), confirming the veracity of their data and model.

Here we incorporate our new data into the atmospheric Ar isotope evolution model established by Pujol et al. (2013). The model parameters are similar to Pujol et al. (2013) (see Supplementary Information for description) with the exception that we fix the current ^{40}Ar degassing rate at 1.2 x 10^8 mol ^{40}Ar/year, in line with this work and Bender et al. (2008), rather than the lower degassing rate derived from the earlier measurement of palaeoatmospheric Ar in Rhynie chert (6.6 ± 3.3 x 10^7 mol ^{40}Ar/year; Cadogan, 1977). This makes no significant difference to the Ar outgassing curves that we derive, or to the conclusions of this work. The evolution of the atmospheric ^{40}Ar/^{36}Ar has been determined for a single crust growth model where only the degree of crustal degassing has been varied.

The Earth outgassing histories that predict the maximum and minimum Devonian atmosphere ^{40}Ar/^{36}Ar defined by our new measurements, and those of Pujol et al. (2013), are shown in Figure 2. The new model curves are within the envelope of degassing histories that describe the earlier data. However, the new model predicts a narrower range of atmospheric ^{40}Ar/^{36}Ar (120 to 130) at 3.5 Ga than extrapolated from the measurement of the Pilbara hydrothermal quartz (119 to 167; Pujol et al., 2013) (Figure 2b). This higher precision determination of early Earth atmosphere ^{40}Ar/^{36}Ar ratio provides a significantly improved constraint on the early degassing history. Our new model predicts atmospheric ^{40}Ar/^{36}Ar at 3.5 Ga that are at the lower end of the range measured by Pujol et al. (2013). The slightly higher ^{40}Ar/^{36}Ar of Pujol et al (2013) may reflect the presence of a small contribution of modern atmospheric Ar in their measurements.

The refined atmospheric Ar evolution model (Figure 2a and b) confirms the need for outgassing of a significant proportion of the Earth's primordial volatile inventory within 100 million years or so of accretion (e.g. Fanale, 1971; Hamano and Ozima, 1978; Turner, 1989). This is significantly earlier than the Late Heavy Bombardment (3.8 - 4.1 Ga) (Gomes et al. 2005) and rules out wholesale loss of the early atmosphere during this process. The catastrophic outgassing overlaps the time of formation of a magma ocean within the first few tens of million years after accretion (Abe, 1997) and it is tempting to invoke it as the cause. The availability of Xe isotopes produced by short half-life decays should make them suitable for more precisely constraining the timing of degassing (e.g. Staudacher and Allègre 1982). However, uncertainties in the U/Pu of early Earth and fission Xe isotope spectra need to be resolved before they can unequivocally identify early Earth degassing (Boehnke et al. 2015).

The similarity of the atmospheric $^{38}Ar/^{36}Ar$ ratio with the chondritic value (0.188) (e.g. Ott, 2002), and an inability of kinetic fractionation to explain atmosphere Ne-Ar isotope systematics (e.g. Marty, 2012), rules out significant loss of early Earth atmospheric noble gases by hydrodynamic escape. It is commonly argued that the contribution of primordial volatiles to Earth by comets until the Late Heavy Bombardment (LHB) at 3.8 Ga appears is limited (e.g. Dauphas et al. 2000), and mass balance calculations imply that the atmospheric noble gas inventory requires a trivial contribution (Marty and Meibom, 2007). However the concentration of noble gases in cometary material, and the proportion of the material involved in the LHB that was cometary in origin, are both poorly constrained.

The new degassing model requires that significant amounts of ^{40}Ar did not accumulate in the Earth's atmosphere until after 4 Ga. As the K-rich continental crust is the dominant source of degassing ^{40}Ar (e.g. Bender et al. 2008) the atmosphere accumulation history can be used to place constraints on the growth history of the continental crust. The new

atmosphere outgassing history is consistent with models of continental crust growth that requires initiation at around 4.0 Ga and slow continuous growth (e.g. Dhuime et al. 2012) rather than early and rapid crust growth (e.g. Armstrong 1981) or late and rapid growth (e.g. Taylor and MacLennan, 1985). This is not necessarily inconsistent with the earlier formation of small volumes of K-poor basaltic crust, but does, however, support evidence that large-scale differentiation of mantle and crust occurred several hundreds of million years after Earth accretion (e.g. Kemp et al. 2010).

5. Summary

We have made high precision determinations of Ar isotopes trapped in the Devonian-aged Rhynie chert from northeast Scotland. The $^{40}Ar/^{36}Ar$ intercept value (289.5 ± 0.4) is a minimum of 3% lower than the modern air value, and is consistent with earlier studies that demonstrates it has incorporated ancient atmospheric Ar. This new determination requires that the Earth's atmosphere has accumulated 5 ± 0.2 x 10^{16} moles of ^{40}Ar in the last 400 million years. The average rate (1.24 ± 0.06 x 10^{8} mol ^{40}Ar/year) overlaps the rate determined from ice cores for the last 800,000 years (Bender et al. 2008), and implies that there has been no resolvable temporal change in the rate of Earth outgassing since the mid-Palaeozoic. The new data have been incorporated into the Earth outgassing model of Pujol et al (2013) and offer precise constraints on the evolution of the atmosphere $^{40}Ar/^{36}Ar$ and the differentiation history of solid Earth. The model results require the degassing of the Earth's primordial volatiles in the first 100 Ma after accretion. The atmosphere $^{40}Ar/^{36}Ar$ only started to increase significantly after 4 Ga, suggesting that major Earth differentiation occurred 100s million years after accretion.

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Figure captions

Figure 1. $^{40}Ar/^{36}Ar$ vs. $^{39}Ar/^{36}Ar$ isochron plot for the new analyses of Rhynie chert. The data plot within a triangle identified by the grey dotted lines. The dashed line is the air $^{40}Ar/^{36}Ar$ (298.8 ± 0.5; Lee et al. 2008). The full black line is the isochron determined using the *Masspec* Ar isotope redaction software. The intercept at $^{39}Ar/^{36}Ar = 0$ defines a palaeo-atmospheric $^{40}Ar/^{36}Ar$ of 289.5 ± 0.4 (MSWD = 1.3). The isochron age (380 ± 30 Ma) is indistinguishable from the age of the hydrothermal feeder vein. The yellow data are excluded when they do not overlap the isochron at 2σ level; they can be most readily explained by the presence of excess ^{40}Ar derived from the hydrothermal fluids (e.g. Stuart and Turner, 1992). Uncertainties are 2σ.

Figure 2. Plot shows the deviation of Ar isotope composition of unirradiated Rhynie chert from modern atmosphere ($\delta^{38}Ar = 0$, $\delta^{40}Ar = 0$). The yellow circles are the total gas released by step-heating chert fragments, and the clear circles are the single-step fusions of small fragments (see SI Table 2). All uncertainties are 2σ. Delta values have been determined from:

$$\delta^{x}Ar = 1000 \times ({}^{x}Ar/{}^{36}Ar_{measured} - {}^{x}Ar/{}^{36}Ar_{air})/({}^{x}Ar/{}^{36}Ar_{air})$$

Figure 3. Plots showing the evolution of the atmosphere $^{40}Ar/^{36}Ar$ ratio versus time, constrained using the box model (see text and Supplementary Information). The blue curves represent modeled history derived from this work. The black curves represent the extremes of crustal degassing constrained from Pilbara quartz (Pujol et al., 2013). The upper panel shows atmosphere evolution over all of Earth history, and the lower panel shows the last 500 million years. The grey bars at 3.5 Ga and 404 Ma record the extrapolated atmospheric $^{40}Ar/^{36}Ar$ of Pujol et al. (2013) and this work respectively.

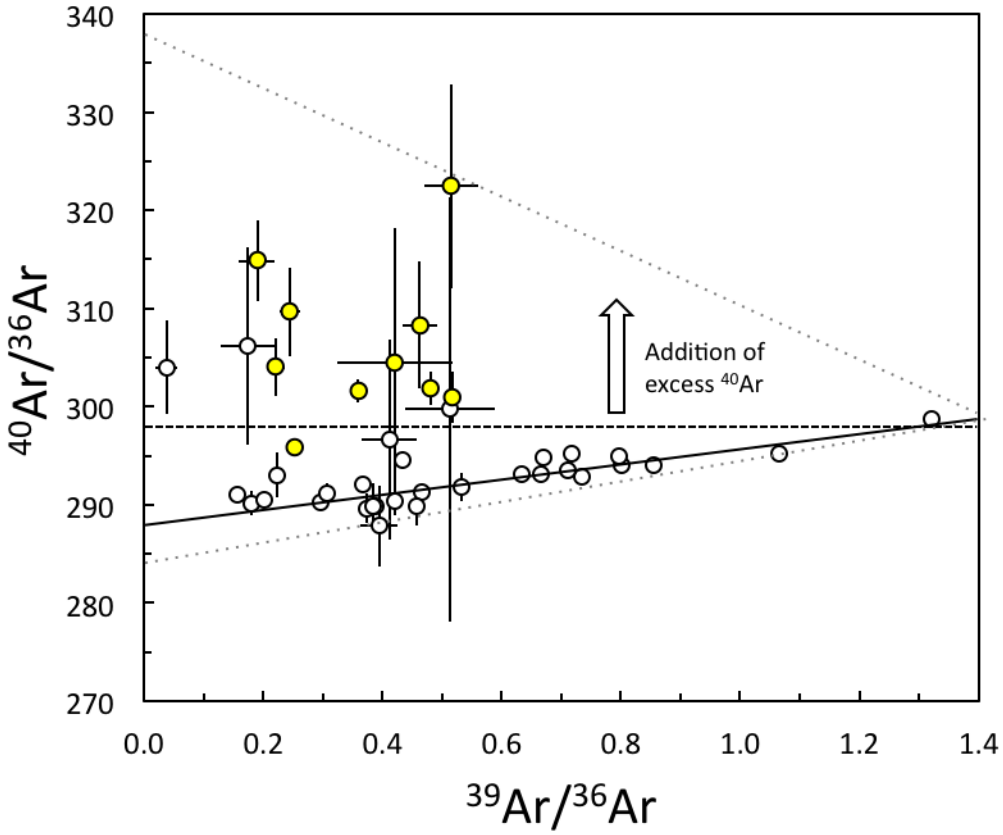
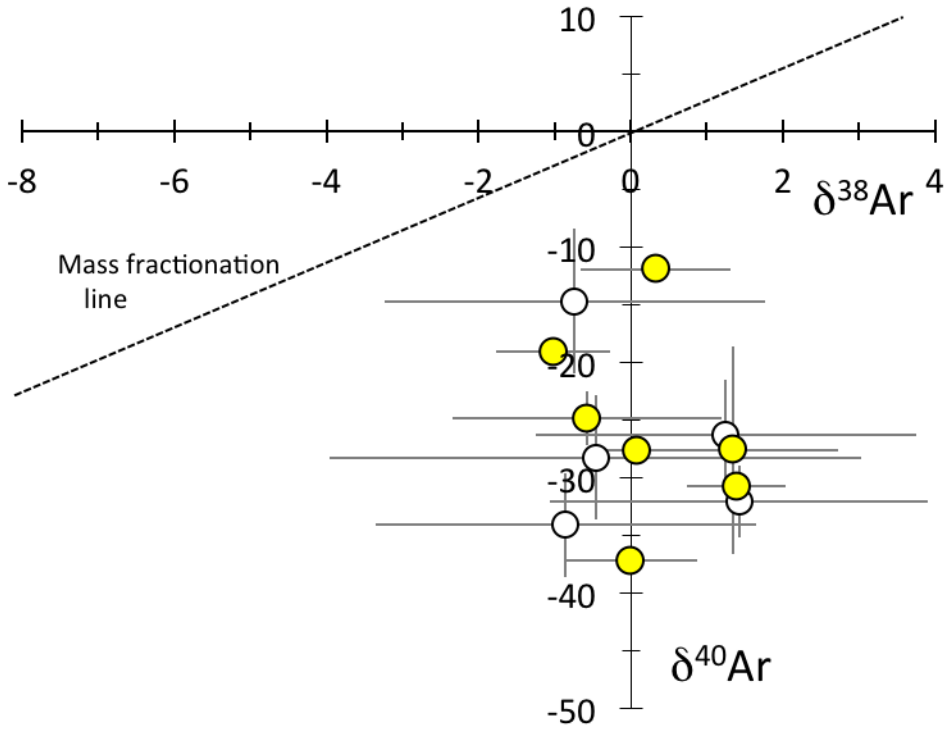


Figure 1: Stuart et al.



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471 Figure 2: Stuart et al.
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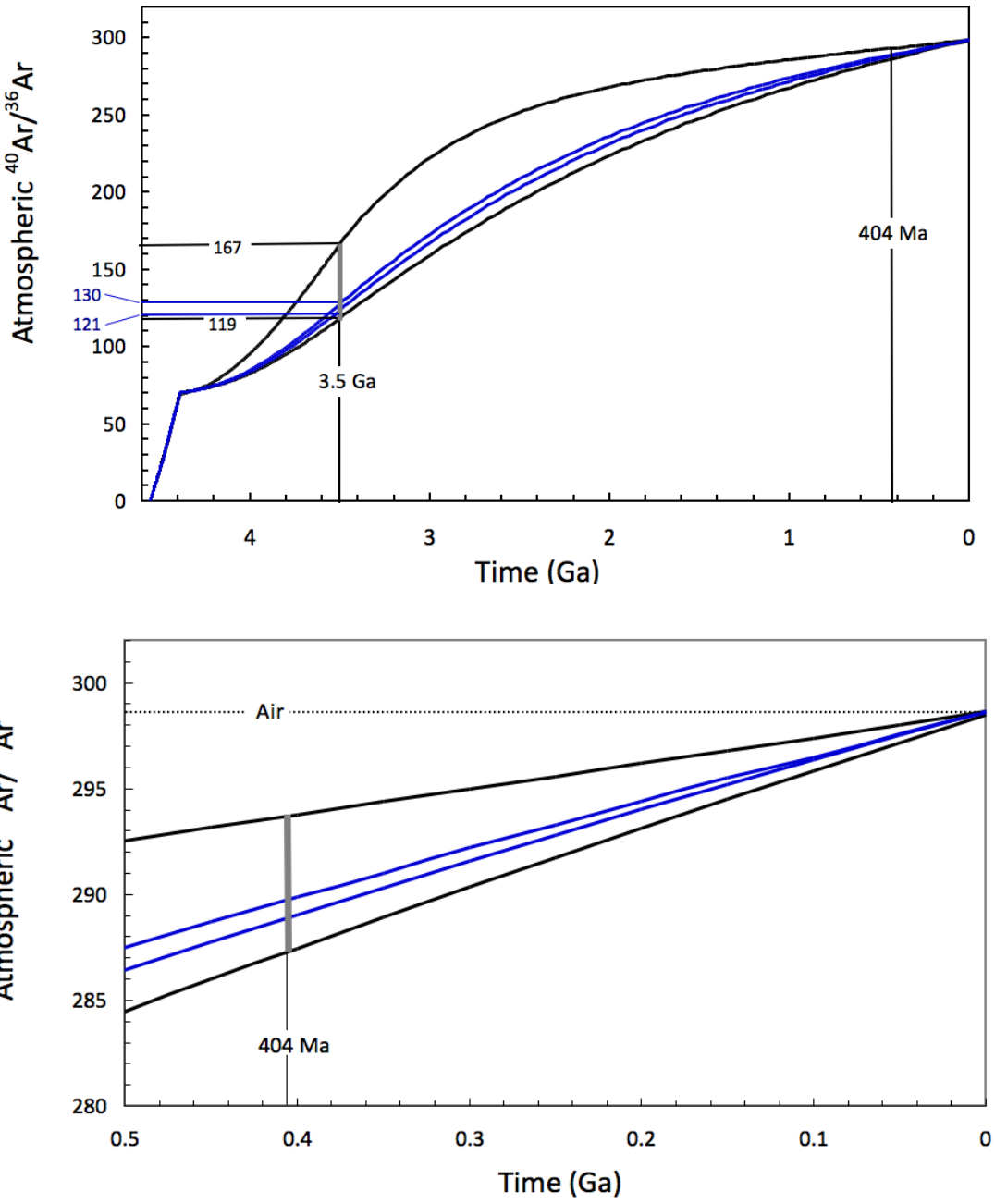

Figure 3 Stuart et al.