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1 **Argon isotopic composition of Archaean atmosphere probes early**
2 **Earth geodynamics**

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16 **Understanding the growth rate of the continental crust through time is a**
17 **fundamental issue in Earth sciences¹⁻⁸. The isotopic signatures of noble gases in the**
18 **silicate Earth (mantle, crust) and in the atmosphere permit exceptional insight into the**
19 **evolution through time of these reservoirs⁹. However, no data for such compositions**
20 **exists for the distant past, and temporal exchange rates between the Earth's interior and**
21 **its surface are severely under-constrained due to a lack of samples preserving the**
22 **original signature of the atmosphere at the time of their formation. Here, we report the**
23 **analysis of argon in 3.5 Ga-old hydrothermal quartz. Noble gases are hosted in primary**
24 **fluid inclusions containing a mixture of Archaean freshwater and hydrothermal fluid.**
25 **Our component analysis shows the occurrence of Archaean atmospheric argon having a**
26 **lower ⁴⁰Ar/³⁶Ar (143±24, 3.5 Ga ago) than the present-day value (where ⁴⁰Ar has been**
27 **produced by the radioactive decay of ⁴⁰K which has a half-life of 1.25 Ga, and ³⁶Ar is**
28 **primordial in origin). This ratio is consistent with an early development of the felsic**
29 **crust, which might have played an important role in climate variability during the first**
30 **half of the Earth's history.**

31 The continents formed by extraction of incompatible elements from the mantle such as
32 those producing radiogenic heat (U, Th, ⁴⁰K). The extracted elements have been stored at the
33 Earth's surface since the crust is buoyant, that is, less dense than the underlying mantle.
34 Consequently, the development of the continents impacted the composition of the mantle and
35 also shaped the thermal regime of the silicate Earth. Yet no consensus exists on the mode of
36 formation and on the growth rate of the crust. Geological units formed during the first Ga are
37 scarce, and geochemical methods available to model crustal evolution such as Sm-Nd of
38 shales⁷, U-Pb and Hf isotopes of zircons^{1,8} may have difficulties in distinguishing between
39 reworking of already existing crust and creation of juvenile crust (although a combination of
40 isotope tracers seems to provide better constraints¹).

41 The terrestrial atmosphere has evolved due to volatile exchange between the mantle
42 and the surface of our planet. The inert gases in the atmosphere have accumulated for eons
43 and have kept an integrated memory of the degassing of the mantle and the crust. Argon
44 isotopes are potentially useful tracers of these exchanges⁹: ³⁶Ar is primordial, and has been
45 thoroughly degassed from the mantle early in Earth history, whereas ⁴⁰Ar, in negligible
46 amount at the time of terrestrial accretion, has been produced by the decay of ⁴⁰K. Presently
47 ⁴⁰Ar is the most abundant argon isotope in the atmosphere (the atmospheric ⁴⁰Ar/³⁶Ar =
48 298.6¹⁰), a robust indication of terrestrial degassing through time. The atmosphere contains
49 1.65 x 10¹⁸ moles of ⁴⁰Ar¹¹, which corresponds to about **half** of the total ⁴⁰Ar produced in the
50 solid Earth (4.0 x 10¹⁸ mol ⁴⁰Ar for a silicate Earth K content of 280 ppm¹²). The mantle has
51 been evolving through convection and partial melting, during which argon was degassed from
52 mantle-derived magmas into the hydrosphere and atmosphere, while potassium was
53 concentrated into magmas due to its incompatible nature, and in-part stored in the continental
54 crust. As soon as the continental crust was formed, even partially, produced radiogenic ⁴⁰Ar
55 was less easily degassed into the atmosphere. Consequently, the atmospheric ⁴⁰Ar/³⁶Ar ratio
56 has the potential to trace not only mantle activity but also the growth of the continental
57 crust¹³, and to constrain the numerous models of mantle-atmosphere evolution that have been
58 proposed¹⁴⁻¹⁷. Unfortunately, the record of ancient atmospheric argon isotope ratios in
59 sedimentary rocks is severely compromised by subsequent *in situ* ⁴⁰Ar production as well as
60 by interaction with crustal fluids containing ⁴⁰Ar from fluid-rock interaction. Only two
61 attempts to measure ancient atmosphere in a single sedimentary rock appear to have been
62 unaffected by the presence of excess ⁴⁰Ar. Cadogan¹⁸ and Rice et al.¹⁹ proposed that the
63 ⁴⁰Ar/³⁶Ar ratio of the atmosphere in the 395 Ma Rhynie chert, NE Scotland, was 294.1 ± 1.5
64 (re-normalized to a present day value of 298.56±0.31¹⁰). This temporal change requires a ⁴⁰Ar
65 flux of 6.2±2.1 x 10⁷ mol/yr from the solid Earth (crust+mantle) to the atmosphere averaged

66 over the last 400 Ma, which is consistent with a contemporaneous ^{40}Ar flux of $11\pm 1 \times 10^7$
67 mol/yr estimated from measurements of atmospheric argon trapped in Antarctic ice over a
68 time period of 780 Ka²⁰.

69 Our sample comes from the 3.5 Ga-old Dresser Formation (Warrawoona Group,
70 Pilbara Craton) at North Pole, Western Australia. This formation comprises metabasalts and
71 metakomatiites interleaved with three beds of cherty metasediments that have experienced
72 low-grade metamorphism²¹. The lowermost unit is intercalated with several barite beds and is
73 overlain by silicified carbonate. Undeformed pillow basalts are found above the contact with
74 the chert-barite horizon. Some of the pillow basalts host isolated quartz-carbonate aggregates
75 forming pods. The studied sample is from one of these pods which resemble typical
76 mineralisation associated with passive hydrothermal circulation of water through shallow
77 crust. Intrapillow quartz crystals contain abundant, 1-25 μm , two phase (liquid and <5%
78 vapor) aqueous inclusions, [that have been extensively studied for their chemistry](#)²². Fluid
79 inclusions are randomly distributed throughout the host quartz, which argues for a primary
80 origin. The absence of crosscutting veins, metamorphic overprint, and deformation features
81 affecting basalt pillows and associated pods indicates negligible fluid remobilization and
82 circulation after deposition and crystallization.

83 The argon and xenon abundances and isotopic compositions, together with K and Cl
84 contents, were measured by vacuum stepwise crushing, followed by stepwise heating [of the](#)
85 [powder remaining after crushing](#), using the extended Ar-Ar method²³ ([Tables A1 & A2](#),
86 [Supplementary Information](#)). With this method, samples were irradiated [before analysis](#) with
87 neutrons to transform ^{35}Cl , ^{37}Cl and ^{39}K to ^{36}Ar , ^{38}Ar and ^{39}Ar , respectively, in order to
88 determine the Cl and K contents on the same extraction steps as ^{36}Ar and ^{40}Ar . Our crushing
89 step data (Table A1) confirm the presence of hydrothermal fluids that were previously
90 identified by X-ray microfluorescence²²: the Cl/K ratios from crushing experiments vary

91 between 3.6 and 9.4 (Figure A1, Supplementary Information), within the range of 2-48
92 previously observed²².

93 The $^{40}\text{Ar}/^{36}\text{Ar}$ and $\text{Cl}/^{36}\text{Ar}$ ratios clearly correlate (Fig. 1) between a component rich in
94 radiogenic ^{40}Ar and chlorine and having a near-constant $\text{Cl}/^{40}\text{Ar}$ ratio of 3245 ± 330
95 (Supplementary Information), and a second component with low $^{40}\text{Ar}/^{36}\text{Ar}$ and low $\text{Cl}/^{36}\text{Ar}$
96 values. Because potassium was also measured in these extractions, we compute how much
97 ^{40}Ar could have been produced in-situ ($^{40}\text{Ar}_{\text{IS}}$) by ^{40}K decay during 3.5 Ga (Table A1). This
98 accumulation can account for only 5% at best of total ^{40}Ar for the crushing steps, and 25-34%
99 for the heating steps. Thus the correlation of Fig. 1 indicates mixing between a low $^{40}\text{Ar}/^{36}\text{Ar}$,
100 low salinity component that we regard as water containing dissolved atmospheric gases, and
101 an hydrothermal fluid end-member containing excess ^{40}Ar ($^{40}\text{Ar}_{\text{HY}}$), in constant proportion
102 with respect to Cl. The component displaying low Cl contents and low $^{40}\text{Ar}/^{36}\text{Ar}$ ratios also
103 has low Cl/K ratios (<2 ; Fig. A1, Supplementary Information), and is most apparent in the
104 stepwise heating release of gases from the crushed samples, possibly preserved in micrometric
105 fluid inclusions (Fig. 1). The low Cl/K ratio cannot be explained by a simple dilution of the
106 hydrothermal fluids released during sample crushing, nor by the occurrence of a seawater
107 component ($\text{Cl}/\text{K} = 57$ for modern seawater). It is instead consistent with the occurrence of a
108 paleo-atmospheric end-member dissolved in freshwater.

109 An estimate of the atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio can be derived from the intercept of the
110 correlation shown in Fig. 1. However, the data must also be corrected for $^{40}\text{Ar}_{\text{IS}}$. Since K is
111 measured for all crushing and heating steps, the correction only requires knowledge of the
112 time of argon trapping in the sample. The Dresser formation is well dated at 3.52 Ga by the
113 U-Pb method²⁴, at 3.5 Ga by the Sm-Nd method²⁵, and at 3.49 Ga by the Pb-Pb method²⁶.
114 Massive barite from the Dresser formation has a U-Xe_f (Xe_f represent xenon isotopes
115 produced by the natural fission of ^{238}U) age of 3.7 ± 0.5 Ga²⁷ and contains excesses of ^{130}Xe

116 ($^{130}\text{Xe}^*$) from the double electron capture decay of ^{130}Ba ($T_{1/2} = 6 \times 10^{20}$ a) in both fluid
117 inclusions and in the matrix, that demonstrate the antiquity of trapped noble gases²⁷. Ar-Ar
118 dating of trapped fluids could not be directly determined for the present sample due to the
119 large contribution of inherited Ar, but we present in the Methods section an Ar isotope data
120 analysis that suggests strongly that fluids trapped in the samples are ≥ 2.7 Ga, probably as old
121 as the Dresser unit. Further evidence that hydrothermal quartz can store noble gases over Ga
122 timescales arises from the study of another hydrothermal quartz sample filling vacuoles in the
123 komatiitic basaltic unit in the Dresser formation. In that sample, in-situ radiogenic Ar
124 dominates over the hydrothermal and atmospheric components²⁸, and yields a Ar-Ar plateau
125 age of 3.0 ± 0.2 Ga²⁸. Both that sample²⁸ and the one studied here (Supplementary Information)
126 have radiogenic $^{130}\text{Xe}^*$ from the decay of very long-lived ^{130}Xe , and the stable isotope
127 composition of trapped xenon appears fractionated (that is, enriched in the light isotopes
128 compared to the modern atmospheric Xe, Table A2 and Fig. A3, Supplementary Information),
129 a signature of paleo-atmospheric xenon from the Archean eon²⁸. The last regional
130 metamorphic event took place 2.7 Ga ago, after which the terranes have been thermally and
131 tectonically stable up to the present²¹. These different lines of evidence, including the textural
132 ones presented above for a primary origin of fluid inclusions, indicate an Archean age for
133 fluids trapped in this sample, consistent with the formation age of 3.5 Ga, with a possible
134 lower limit of 2.7 Ga.

135 After correction for radiogenic ^{40}Ar , the intercept of the mixing correlation yields an
136 Archean atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 143 ± 24 (95 % conf. int., MSWD = 1.5) for $t = 3.5$ Ga,
137 obtained using an error-weighted York's regression²⁹. Assuming younger fluid ages of 3.0 Ga
138 and 2.7 Ga, the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are 189 ± 21 and 211 ± 21 , respectively. The first heating
139 step at 400°C released argon with $^{40}\text{Ar}/^{36}\text{Ar} = 305 \pm 13$, which is consistent with the modern
140 atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio (298.6 ± 0.3^{10}), and could indicate modern atmospheric

141 contamination. Although during this step ^{39}Ar from neutron irradiation of ^{39}K was also
142 released, suggesting that trapped argon was released at this temperature, we attempted
143 regressions without the 400°C data, which yielded Archean atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of
144 143 ± 29 (3.5 Ga), 190 ± 28 (3.0 Ga) and 212 ± 27 (2.7 Ga). These values are undistinguishable
145 from those obtained by including the 400°C step, demonstrating that the results do not depend
146 the low temperature step data.

147 We have developed a first order rate box model following Hamano & Ozima⁹, in
148 which the mantle degasses Ar isotopes into the atmosphere through geological time.
149 Potassium is extracted from the mantle during partial melting and is retained in majority in the
150 developing continental crust. The boxes are the mantle, the crust which accumulates K and
151 the atmosphere. The variables are the mantle extraction rate, the crustal degassing rate for
152 ^{40}Ar (characterized by a β parameter⁹ varying between 0.05, representing almost no crustal
153 degassing, and 0.37, corresponding to 50% crustal degassing, ref. 9 for justification) and the
154 fraction of early degassed ^{36}Ar . The constraints of the model applied to validate the possible
155 solutions are the present-day mantle $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (5,000 and 40,000 for mantle plume and
156 mid-ocean ridge basalt sources, respectively), the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the modern atmosphere of
157 298.6^{10} , the paleoatmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ values determined above, the fraction of bulk silicate
158 Earth K present in the present-day continental crust (between 20% and 50%¹²), and the mean
159 ^{40}Ar flux to the atmosphere in the last 400 Ma¹⁸, representing modern conditions. Hundreds of
160 tests run with this model gave all possible solutions matching modern conditions and the
161 range of Archaean atmosphere $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (Supplementary Information). The best
162 solutions indicate that: (i) catastrophic mantle degassing during the first 170 Ma (impact
163 degassing of accreting bodies cannot be differentiated here); (ii) between 170 Ma and 3.8 Ga,
164 less than 10 % stable felsic crust; (iii) between 3.8 Ga and 2.5 Ga, formation of a crustal
165 volume equivalent to 80 ± 10 % of the present-day one; (iv) between 2.5 Ga and present-day,

166 less than 30 % crustal generation, consistent with possible reworking of previously emplaced
167 felsic crust¹.

168 The extraction of a large reservoir of felsic crust during the Archaean eon modified
169 profoundly the thermal regime of the Earth by storing heat-producing radio-elements at the
170 surface. It might have been instrumental to decrease the partial pressure of atmospheric CO₂,
171 via alteration of this juvenile crust, from high contents of several percents necessary to
172 prevent Earth's surface from total freezing when the Sun was ~25 % less energetic (eg., ³⁰), to
173 a few hundreds of ppm that allowed snowball Earth episodes in the late Archaean.

174 **Methods Summary**

175 We selected quartz because of its generally low content of noble gas-producing
176 elements (e.g., K and U). The sample was first neutron-irradiated (to obtain, in addition to
177 natural Ar isotopes, the Cl and K contents), then progressively crushed, and the resulting
178 powder was heated in several temperature steps. ³⁶Ar is predominantly from the atmosphere,
179 but ⁴⁰Ar can be contributed by three sources, the atmosphere, "excess" ⁴⁰Ar from the
180 hydrothermal component (⁴⁰Ar_{HY}) and ⁴⁰Ar produced in-situ (⁴⁰Ar_{IS}) from the in-situ decay of
181 ⁴⁰K. To determine the atmospheric ⁴⁰Ar/³⁶Ar ratio, the measured ⁴⁰Ar content needs to be
182 corrected for contributions of ⁴⁰Ar_{HY} and ⁴⁰Ar_{IS}. Evaluating the latter requires only knowledge
183 of the age since K is also measured. In addition to geological and geochemical evidences
184 presented in the main text, we have applied a statistical approach that confirms the Archaean
185 age of the trapped fluids. We first correct for the hydrothermal contribution. The
186 hydrothermal Cl/⁴⁰Ar_{HY} ratio is obtained from the analysis of the crushing runs which are
187 dominated (≥95%) by this component (Table A3). The step-heating run data are corrected for
188 hydrothermal contribution by subtracting the step-heating Cl contents multiplied by the
189 Cl/⁴⁰Ar_{HY} ratio obtained above. The assumption that the Cl/⁴⁰Ar_{HY} ratio of the step-heating

190 and crushing runs are similar is justified by the unique slope of the Fig. 1 correlation.
191 Corrected step-heating data define several equations (one per temperature step) with two
192 unknowns, the amount of in-situ produced ^{40}Ar which depends on fluid age, and the initial
193 (atmospheric) $^{40}\text{Ar}/^{36}\text{Ar}$ ratio. We explored the sets of ages and initial $^{40}\text{Ar}/^{36}\text{Ar}$ values that fit
194 best the equations and found that they correspond to ages around 3.5 Ga (Methods, Table A3
195 and Fig. A2 in Supplementary Information). These ages were then used to correct for $^{40}\text{Ar}_{\text{IS}}$
196 the regression shown in Fig. 1. The initial, presumably paleo-atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio was
197 computed using the error-weighted regression method of York²⁹.

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267

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278 [improve the clarity of this ms.](#) CRPG contribution n° 2239.

279 **Authors' contributions**

280 MP and RB performed the experiments and analyzed the data. PP provided the sample
281 and characterized the fluid inclusions. MP and BM did the calculations, the modeling, and
282 wrote the paper. All of authors commented on the manuscript.

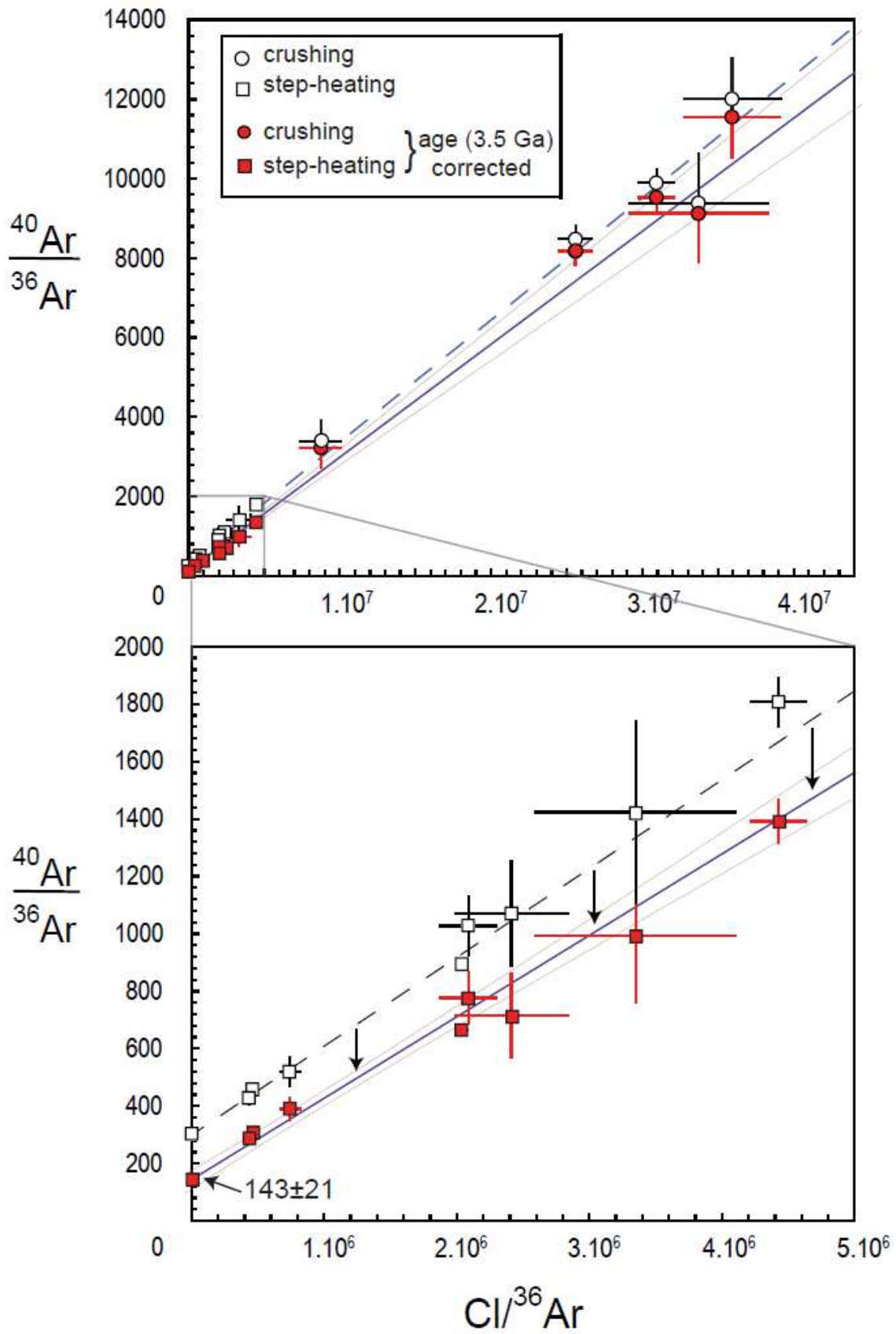
283

Figures

284 **Figure 1: $^{40}\text{Ar}/^{36}\text{Ar}$ vs. $\text{Cl}/^{36}\text{Ar}$ for step-heating and step-crushing data of the irradiated**
285 **sample (top : all data; bottom : enlargement on the stepwise heating data).** Data define a
286 two-component mixing trend between an hydrothermal end-member rich in chlorine and
287 inherited $^{40}\text{Ar}_{\text{HY}}$, and a low $^{40}\text{Ar}/^{36}\text{Ar}$, $\text{Cl}/^{36}\text{Ar}$ end-member representative of low salinity
288 water component containing dissolved atmospheric gases. The open symbols represent data
289 from Table A1, and the red symbols represent data corrected for in-situ production of
290 radiogenic ^{40}Ar since the time of fluid trapping (dotted line and solid line, error-weighted
291 regressions of uncorrected, and age-corrected data, respectively). Here an age of 3.5 Ga has
292 been taken, and the regression line²⁹ for age-corrected data yields $^{40}\text{Ar}/^{36}\text{Ar} = 143 \pm 24$ (95 %
293 conf. int.) for the Archaean atmosphere at 3.5 Ga. Taking other possible ages of 3.0 Ga and
294 2.7 Ga (see text and Methods for justification) will change the $^{40}\text{Ar}/^{36}\text{Ar}$ values to 189 ± 21 and
295 211 ± 21 , respectively. These different possible values are also used in the atmospheric
296 $^{40}\text{Ar}/^{36}\text{Ar}$ evolution and crustal growth model shown in Fig. 2.

297

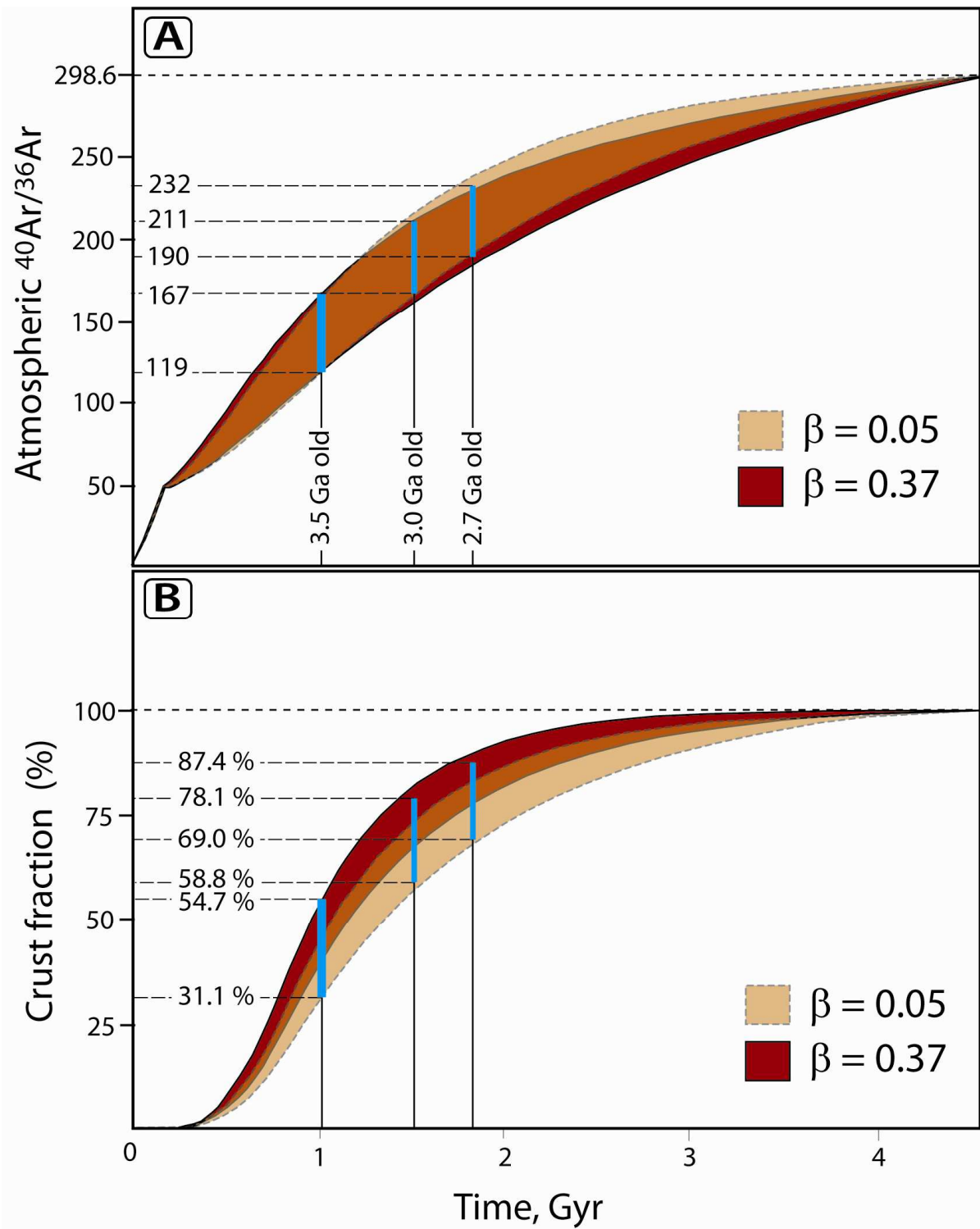
298 **Figure 2: Evolution of the atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio and of the volume of continental**
299 **crust relative to its present-day volume, as a function of time.** A- atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$
300 vs. time obtained with our box model described in the Supplementary Information. The
301 shadowed areas integrate the trajectories of atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio through time for the
302 two extreme rates of crustal degassing ($\beta=0.05$ corresponds to less than 1% crust degassing
303 rate and $\beta=0.37$ corresponds to 50% crust degassing rate⁹). Only the corresponding model
304 runs that match our inferred $^{40}\text{Ar}/^{36}\text{Ar}$ range of values for Archaean atmospheric argon and
305 ages (shown as vertical bars) on one hand, and the boundary conditions presented in Table A3
306 on another hand, are represented. B- Crust fraction vs. Time. Evolution of the volume of
307 continental crust through time, represented as a fraction of the present-day volume. The
308 shadowed areas integrate the model runs that fit the conditions defined above. Note that the
309 different boundary conditions we tested (ages of 3.5 Ga, 3.0 Ga and 2.7 Ga, corresponding
310 initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of 143 ± 24 , 189 ± 21 , and 211 ± 21 , respectively) yield essentially the
311 same evolution curve for crustal growth.



312

313

Figure 1



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317

318

Figure 2

319

320 **Methods**

321 **Neutron irradiation and Ar isotope analysis**

322 The argon isotopic analysis of neutron-irradiated quartz (0.09 g), performed at
323 Manchester University, United Kingdom, was used to determine Ar, K (via $^{39}\text{Ar}_\text{K}$), Cl
324 ($^{38}\text{Ar}_\text{Cl}$), Ca ($^{37}\text{Ar}_\text{Ca}$) concentrations. Neutron irradiation of samples was carried-out in position
325 B2W of the SAFARI-1 reactor, NESCA, Pelindaba (South Africa) with a fast neutron flux of
326 1×10^{18} n/cm² as determined from Hb3gr flux monitors included in the irradiation.
327 Experimental procedures were similar to those described previously³¹. Samples were
328 progressively crushed in vacuo using modified Nupro[®] valves. Liberated gases were purified
329 using hot (400°C) Al-Zr getters before being analyzed in the mass spectrometer. Samples of
330 crushed residue were stepped heated in a Ta-resistance furnace using several temperature
331 steps, each of 30 min duration. One low temperature step at 200 °C was used to remove
332 adsorbed atmospheric noble gases from the samples. Sequential temperature steps at 200°C
333 intervals between 400-1600°C were used to extract argon from the quartz. The argon is most
334 likely to be contained in microscopic fluid inclusions, because the siliceous matrix does not
335 contain appreciable amount of noble gases²³. For both crushing and stepped heating isotopic
336 measurements were made using the MS1 mass spectrometer using a Faraday detector for Ar
337 isotope measurements. Average furnace hot blanks (1800°C) were 4×10^{-13} mol of ^{40}Ar . Data
338 were corrected for mass discrimination, radioactive decay since irradiation and minor neutron
339 interference corrections obtained from irradiated salts. Concentrations of K, Ca and Cl were
340 determined from samples using Hb3gr monitor data²³.

341

342 **Fluid composition**

343 Gases released by step crushing reveal the composition of a hydrothermal component
344 having a Cl/K molar ratio between 3.7 and 9.4, with elevated $^{40}\text{Ar}/^{36}\text{Ar}$ ratio. The range of
345 Cl/K is within hydrothermal end-member values found for large fluid inclusions analyzed by
346 Foriel et al. (ref. 22) (Figure A1). Gases released by crushing have lower argon isotope and
347 Cl/K (<2) ratios. $^{40}\text{Ar}/^{36}\text{Ar}$ and Cl/K correlate, indicating that the low $^{40}\text{Ar}/^{36}\text{Ar}$ component (i)
348 cannot result from dilution of an hydrothermal component by air because of the correlated
349 variation of the Cl/K ratio; and (ii) cannot be mixing with seawater (Cl/K = 57 for modern

350 seawater) because the latter would result in an inverse correlation between $^{40}\text{Ar}/^{36}\text{Ar}$ and
351 Cl/K.

352 **Statistical constraints on the age of trapped fluids**

353 The correlations shown in Fig. 1 use the data given in Table A1 (Supplementary
354 Information). In order to derive the initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratio which we propose to be that of the
355 atmosphere at the time of fluid trapping, data need to be corrected for in situ production, and
356 the age of trapped fluids is critical. In the main text we have given several geological and
357 geochemical arguments that these fluids are Archaean in age, here we further analyze the
358 present data.

359 Argon-40 ($^{40}\text{Ar}_{\text{TOT}}$) trapped in fluid inclusions and in the matrix is a mixture of three
360 components : in-situ produced ^{40}Ar ($^{40}\text{Ar}_{\text{IS}}$) since closure of the sample, atmospheric ^{40}Ar
361 ($^{40}\text{Ar}_{\text{ATM}}$) trapped at the time of closure, and inherited argon from the hydrothermal fluid
362 ($^{40}\text{Ar}_{\text{HY}}$).

$$363 \quad ^{40}\text{Ar}_{\text{TOT}} = ^{40}\text{Ar}_{\text{HY}} + ^{40}\text{Ar}_{\text{IS}} + ^{40}\text{Ar}_{\text{ATM}}$$

364 In gases extracted by crushing, $^{40}\text{Ar}_{\text{TOT}}$ is dominated by hydrothermal $^{40}\text{Ar}_{\text{HY}}$ and
365 $^{40}\text{Ar}_{\text{ATM}}$ represent only a few percent of total ^{40}Ar . This is can be verified for the most
366 extreme conditions, by computing the maximum $^{40}\text{Ar}_{\text{IS}}$ contribution assuming a maximum
367 age of 3.5 Ga and a $^{40}\text{Ar}_{\text{ATM}}$ content obtained by multiplying the observed ^{36}Ar by the modern
368 value of $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{ATM}}$ (298.6). This is a non-realistic case because it is not possible for both
369 conditions to apply, however it demonstrates that even in the most extreme case $^{40}\text{Ar}_{\text{HY}}$ is ≥ 95
370 % of total ^{40}Ar .

371 The $\text{Cl}/^{40}\text{Ar}_{\text{TOT}}$ value of the crushing steps represents the ratio in the hydrothermal fluid
372 end-member at better than 95%. We assume that the $\text{Cl}/^{40}\text{Ar}$ ratio of the hydrothermal end-
373 member is the same for the crushing runs as for the step-heating runs. The assumption is
374 justified by the fact that the data identify a single hydrothermal end-member having a constant
375 $\text{Cl}/^{40}\text{Ar}$ ratio, e.g., in a $^{40}\text{Ar}/^{36}\text{Ar}$ vs. $\text{Cl}/^{36}\text{Ar}$ diagram. Thus we correct $^{40}\text{Ar}_{\text{TOT}}$ extracted by
376 step-heating for the $^{40}\text{Ar}_{\text{HY}}$ contribution, using the mean $(\text{Cl}/^{40}\text{Ar}_{\text{TOT}})$ value of the crushing
377 runs. In practice, we subtract from stepheating $^{40}\text{Ar}_{\text{TOT}}$ the measured stepheating Cl
378 $(\text{Cl}_{\text{stepheating}})$ multiplied by the mean $(\text{Cl}/^{40}\text{Ar})_{\text{crushing}}$ ratio:

$$379 \quad (^{40}\text{Ar}_{\text{TOT}})_{\text{stepheating}} = (^{40}\text{Ar}_{\text{HY}})_{\text{stepheating}} + (^{40}\text{Ar}_{\text{IS}})_{\text{stepheating}} + (^{40}\text{Ar}_{\text{ATM}})_{\text{stepheating}}$$

380 $\Leftrightarrow [(^{40}\text{Ar}_{\text{IS}})_{\text{stepheating}} + (^{40}\text{Ar}_{\text{ATM}})_{\text{stepheating}}] = (^{40}\text{Ar}_{\text{TOT}})_{\text{stepheating}} - \text{Cl}_{\text{stepheating}} / (\text{Cl}/^{40}\text{Ar}_{\text{TOT}})_{\text{crushing}}$

381 In order to be independent from the age and from the initial $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{ATM}}$ value, we
 382 calculated the $(\text{Cl}/^{40}\text{Ar}_{\text{HY}})$ ratios of the crushing steps by correcting $^{40}\text{Ar}_{\text{TOT}}$ from the (small)
 383 contributions of $^{40}\text{Ar}_{\text{ATM}}$ and $^{40}\text{Ar}_{\text{IS}}$ for ages varying between 0 and 3.5 Ga and $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{ATM}}$
 384 ratios varying between 100 and 298.6. For all these conditions, the $(\text{Cl}/^{40}\text{Ar}_{\text{HY}})$ ratio varies
 385 between 3100 and 3300, which is well within the standard deviation of 330 among the 4
 386 crushing data (computed with data from Table A1). We obtain $(\text{Cl}/^{40}\text{Ar})_{\text{HY}} = 3245$ (mean of
 387 all these conditions) ± 330 (standard deviation for the four crushing steps). ^{40}Ar from
 388 stepheating runs consists now of a mixture of in-situ produced $^{40}\text{Ar}_{\text{IS}}$ and atmospheric
 389 $^{40}\text{Ar}_{\text{ATM}}$. For each step, we computed the amount of $^{40}\text{Ar}_{\text{IS}}$ as :

390 $(^{40}\text{Ar}_{\text{IS}})_{\text{stepheating}} = [(^{40}\text{Ar}_{\text{IS}})_{\text{step heating}} + (^{40}\text{Ar}_{\text{ATM}})_{\text{stepheating}}] - (^{36}\text{Ar}_{\text{ATM}})_{\text{stepheating}} \times (^{40}\text{Ar}/^{36}\text{Ar})_{\text{ATM}}$

391 (where $[(^{40}\text{Ar}_{\text{IS}})_{\text{step heating}} + (^{40}\text{Ar}_{\text{ATM}})_{\text{stepheating}}]$ has been computed as above). Since we do not
 392 know a priori $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{ATM}}$, we consider this ratio as an input parameter for which we
 393 assume different values, in practice varying it between 100 and 298.6. With the obtained
 394 $(^{40}\text{Ar}_{\text{IS}})_{\text{stepheating}}$, we compute the corresponding ages as we also have K concentration for each
 395 step.

396 Thus for each $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{ATM}}$ input value, we obtain a set of stepheating data and we test
 397 statistically the homogeneity of ages between the different steps. For that, we computed the
 398 Ar-Ar plateau (using the Isoplot software developed by K. Ludwig,
 399 http://bgc.org/isoplot_etc/isoplot.html) corresponding to each $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{ATM}}$ value (Table
 400 A3). The best solutions are those for which ages have the lowest standard deviation and the
 401 mean square weighted deviation (MSWD) value closest to 1 (meaning that the errors can
 402 account for the spread of data), as given in Table A3 and illustrated in Fig. A2, and
 403 correspond to ages close to the formation age of 3.5 Ga. For ages lower than 3 Ga, the MSWD
 404 value becomes rapidly close to 0 and the standard deviations increase dramatically. This,
 405 together with an age of 3.0 Ga obtained for a previously analysed quartz sample (for which
 406 the in-situ produced ^{40}Ar was dominant and the hydrothermal contribution was constant for all
 407 steps, so that direct Ar-Ar plateau ages could be obtained²⁷) as well as with the geological and
 408 morphological evidence discussed earlier, points to a paleo-Archaean age for fluids trapped in
 409 quartz, probably the formation age, and excludes a young age for trapped fluids.

410

411 Xenon isotopic signature

412 Xenon isotope analysis was done at CRPG Nancy, France. Pure quartz grains (1-2 mm
413 in size) were selected and ultrasonically cleaned with acetone. After cleaning, 0.2-0.8 g of the
414 quartz sample was loaded into a stainless steel tube for crushing. The tube was then baked
415 overnight at 150°C under high vacuum to desorb atmospheric noble gases from the sample
416 surface before extraction. The sample was crushed at room temperature by activating a piston
417 1000 times. During crushing, condensable gases including xenon were trapped in a glass cold-
418 finger immersed in liquid nitrogen to separate them from lighter noble gases (He, Ne, Ar).
419 After cryogenic separation, the non-trapped fraction was rapidly pumped, condensable gases
420 were desorbed, and Xe was purified using five successive getters cycled between 700°C and
421 room temperature. Xe isotopes were then analyzed by static mass spectrometry.

422 The Xe isotope abundances (Figure A3, Table A2), normalized to ^{132}Xe and to the
423 isotopic composition of xenon in modern air, display excesses at masses 126 and 131 (Figure
424 A3-a), comparable to excesses reported by Srinivasan³³ for an Archaean barite sample, and
425 attributed by this author to cosmic ray spallation reactions forming ^{126}Xe , and production of
426 ^{130}Ba (n,γ) ^{131}Xe by epithermal neutrons^{27,33,34}. Interaction with cosmic rays is consistent with
427 the location of the present sample at the surface. Not only ^{126}Xe and ^{131}Xe isotopes are in
428 excess relative to ^{132}Xe , but also are other lighter Xe isotopes including ^{130}Xe and ^{129}Xe . ^{130}Xe
429 is itself in excess of ^{129}Xe , indicating the contribution of the natural radioactivity of ^{130}Ba
430 ($^{130}\text{Ba}(2\text{EC})^{130}\text{Xe}$, with a half life of $6.0 \pm 1.1 \times 10^{20} \text{ a}^{27}$) and therefore the presence of an old
431 xenon component. Thus the heavy isotopes of xenon ($^{132,134,136}\text{Xe}$) must also be contributed by
432 products of the natural fission of ^{238}U and the original Xe isotope composition has to be
433 corrected. The U content was measured in these samples (Service d'Analyse des Roches et
434 des Minéraux, CRPG Nancy, France) by two different methods (light leaching of powders to
435 obtain an average U content of fluid inclusions, and U measurement of quartz before any
436 crushing) which both gave a similar U concentration of 0.15 ppm. In Figure A3-b, the heavy
437 isotope abundances of Xe are corrected for contribution of fissiogenic Xe during 3.5 Ga
438 (using the younger fluid ages of 3.0 or 2.7 Ga results in a smaller but essentially comparable
439 corrections, Fig. A3-b). The corrected Xe abundance is clearly deficient in heavy Xe isotopes
440 ($\sim 1\%/amu$) compared to modern air. Such depletion, found previously in well dated samples
441 like 3.5 Ga barite and 3.0 Ga quartz^{33, 27, 28} is proposed to represent the Xe isotope
442 composition of Archaean air.

443 **Building of the model**

444 We used a 3 reservoir (mantle crust and atmosphere), first order rate, box model
445 similar to the one developed by Hamano & Ozima⁹ (Figure A4). In such a model, the mantle
446 contained initially primordial noble gases (here, ³⁶Ar) that were subsequently degassed into
447 the atmosphere. However, atmospheric noble gases might have been contributed by sources
448 other than mantle degassing, e.g., late accretion of volatile-rich bodies. In this case, the model,
449 although conceptually different, yields essentially the same results. Indeed it does not make a
450 mathematical difference between an early catastrophic event that injects mantle-derived ³⁶Ar
451 into the atmosphere before production of significant ⁴⁰Ar, and the occurrence of a ³⁶Ar-
452 bearing atmosphere, with later contribution of ⁴⁰Ar from the mantle. Note that the early
453 degassing event is required by all models based on Ar isotopes, to account for the large
454 ⁴⁰Ar/³⁶Ar contrast between the mantle and the atmosphere⁹. ⁴⁰Ar is only produced from the
455 radioactive decay of ⁴⁰K, with a half life of 1.25 Ga. Potassium, initially in the mantle, has
456 been extracted together with Ar, during mantle melting (we assume that both Ar and K are
457 highly incompatible during mantle melting, which is well established in the case of K, and
458 well supported by experimental data for Ar³¹). Ar degasses into the atmosphere and a fraction
459 of K is transferred in the crust (resulting in 20-50 % bulk silicate Earth potassium being stored
460 in the crust nowadays). ⁴⁰Ar produced in the crust partly degasses (see next paragraph). Thus,
461 ⁴⁰Ar originates from both the mantle and the crust, and its flux into the atmosphere will
462 depend on mantle convection/degassing and also on the volume of crust that stores K. The
463 computations were carried out with the Stella[®] code. Data used to build this model and
464 constrain its solutions are presented in Table A4.

465 The mantle convection rate impacts directly on the degassing of Ar and on the storage
466 of K in the crust through felsic crust production. In order to mimic the decrease of heat in
467 Earth, especially that due to radioactivity, an exponential decrease of mantle convection is
468 classically assumed⁹. However, such an exponential decrease is not sufficient to explain the
469 modern high ⁴⁰Ar/³⁶Ar difference between the present-day mantle and atmosphere, so that an
470 early catastrophic degassing event is required that occurred in the first ~100-200 Ma. Such an
471 early high convection rate is independently supported by extinct radionuclides⁴⁰⁻⁴². Different
472 durations of catastrophic degassing have been tested and a time interval of 170 Ma gives the
473 largest numbers of solutions. Thus degassing rates can be separated in two parts: before 170
474 Ma during the intense degassing with a constant rate, and after 170 Ma with the exponential
475 decrease of degassing. A fraction of radiogenic argon generated in the crust degasses into the

476 atmosphere, with a degassing coefficient taken as variable between 5% and 50 %, the last
477 number corresponding to a comparison between Rb-Sr and K-Ar ages for crustal rocks⁹. The
478 model is run with variable atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratios constrained by the present quartz data
479 at the different periods of time defined above: $t = 3.5$ Ga, $^{40}\text{Ar}/^{36}\text{Ar} = 119-167$; $t = 3.0$ Ga,
480 $^{40}\text{Ar}/^{36}\text{Ar} = 167-211$; and $t = 2.7$ Ga, $^{40}\text{Ar}/^{36}\text{Ar} = 190-232$. The crustal growth curves obtained
481 with these different closure ages are indistinguishable (Figure 2), which means that these
482 results are not model-dependent within the 2.7-3.5 Ga range.

483 The solutions of our Ar-based model evolution of the continental crust indicate that
484 about half of the present-day continental crust was already present 3.5 Ga ago (range : 31-55
485 %) and that at our lower age limit of 2.7 Ga, the crustal volume was 69-88 % of the present-
486 day felsic crust. Our continental crust growth curves (Fig. A5) are intermediate between those
487 representing early and intense growth in the Hadean^{1,3,43} and those representing late^{4,44} or
488 sigmoidal growths^{5,45}. They predict a larger crustal volume in the Hadean than the model
489 based on U-Pb or Hf isotope compositions of zircons. However, these geochemical proxies
490 integrate crustal reworking, which can be corrected for by combining these data with oxygen
491 isotopes¹. In such a case our model runs are consistent with those derived from U-Pb, Hf and
492 O isotopes of continental zircons, that is, high crustal production in the Archaean, followed by
493 a factor of ~2-4 reduction of the net growth rate beginning at ~ 3.0 Ga ago (same position of
494 the inflection, Fig. A5).

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