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U-Pb, Rb-Sr and Ar-Ar systematics of the ungrouped achondrites Northwest Africa 6704 and Northwest Africa 6693

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23 Abstract

24

25 We report U-Pb, ^{87}Rb - ^{87}Sr , ^{40}Ar - ^{39}Ar , and $^{238}\text{U}/^{235}\text{U}$ isotopic data for paired ungrouped
26 achondrites NWA 6704 and NWA 6693 that were derived from a highly oxidised parent body
27 with broadly chondritic composition (Warren et al. 2013, Hibiya et al. 2018). Pb-isotopic ages
28 derived from isochrons for multiple acid-leached pyroxene fractions are $4562.76 \pm 0.22 / -0.30$
29 Ma for NWA 6704 and $4562.63 \pm 0.29 / -0.21$ Ma for NWA 6693, calculated using $^{238}\text{U}/^{235}\text{U}$ ratio
30 of 137.7784 ± 0.0097 measured in NWA 6704. The Rb-Sr mineral isochron age of 4543 ± 46 Ma
31 (initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.699013 \pm 0.000055$) is consistent with the Pb-isotopic age. Together with
32 ^{187}Re - ^{187}Os isochron age of 4576 ± 250 Ma for NWA 6704 (Hibiya et al. 2018), and ^{26}Al - ^{26}Mg
33 and ^{53}Mn - ^{53}Cr ages calculated using the rapidly crystallized angrite D'Orbigny as a time
34 anchor are also consistent with the Pb-isotopic age (Sanborn et al. 2018), these data indicate
35 that the parent rocks of NWA 6693 and NWA 6704 remained closed to migration of both
36 lithophile and siderophile elements since crystallisation and initial cooling. The whole rock
37 ^{40}Ar - ^{39}Ar age of 4199 ± 32 Ma suggests a complete resetting of the K-Ar system approximately
38 360 Ma after crystallisation. A later event at ≤ 2.12 Ga partially reset the K-Ar system as shown
39 by the low temperature heating steps. Both meteorites have high $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (up to 7.0 in
40 NWA 6693 pyroxene) and very radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ up to 1.15. Together with the absence of
41 secondary disturbance in the Rb-Sr and U-Pb systems, this makes them suitable for cross-
42 calibration of the isotopic chronometers. These meteorites are also promising candidates to
43 serve as age reference samples for the early Solar System chronology, as an alternative or
44 complement to angrites of the early generation (D'Orbigny, Sahara 99555) that are currently
45 used for this purpose. Plagioclase in NWA 6704 has a sufficiently low Rb/Sr ratio to define
46 precise initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.698997 ± 0.000027 , which corresponds to the time of separation of
47 the parent body precursor material from the solar nebula of 1.5 ± 2.1 Ma. This value suggests
48 that the parent asteroid accreted within 3.6 Ma after CAI formation, or before 4563.7 Ma using
49 the CAI age of 4567.3 Ma (Connelly et al. 2012).

50

51 **1. Introduction**

52 Our understanding of the earliest magmatism in the Solar System is based on the studies of
53 achondrites – stony meteorites derived from asteroids that underwent melting and in some
54 cases differentiation. Most achondrites are classified into groups on the basis of similarities in
55 mineralogy and elemental and isotopic abundances, and these similarities have been
56 interpreted as an indication of common origin (Clayton and Mayeda 1996, Mittlefehldt et al.
57 1998, Greenwood et al. 2017). The studies of several achondrites from the same group and
58 inferred common parent body (e.g. HED meteorites, or angrites) that formed at different time
59 allow us to reconstruct the evolution of their parent asteroid, in a similar way as we study the
60 evolution of the Earth, Moon, and Mars. Several achondrites found in the recent years have
61 unique chemical and isotopic characteristics, and do not fit in the established groups. Studies
62 of these meteorites provide rare insights into the diversity of asteroids that formed and
63 partially melted in different domains in the accreting protosolar nebula, at different times,
64 from different source materials, and under different conditions.

65 Here we present U-Pb, $^{238}\text{U}/^{235}\text{U}$, ^{87}Rb - ^{87}Sr and ^{40}Ar - ^{39}Ar isotopic data for paired ungrouped
66 achondrites NWA 6704 and NWA 6693. The goals of this study are to determine the time of
67 igneous crystallization of these meteorites, to evaluate the nature of the source material and
68 the time of its separation from the solar nebula, and to estimate the timing and extent of the
69 later processes that could have disrupted their parent asteroid. This paper, together with the
70 studies by Hibiya et al. (2018) and Sanborn et al. (2018), is a part of small informal
71 consortium work by a group of researchers who started their investigations of these
72 meteorites independently, and decided to join their efforts.

73

74 **2. The meteorites**

75 Four ungrouped achondrites with similar mineralogy and composition unlike those of any
76 previously known achondrites were recovered from the dry deserts of north-western Africa
77 between 2010 and 2015. Northwest Africa 6693 is a 5.1 kg ungrouped achondrite
78 purportedly found in Morocco in 2010 (Meteoritical Bulletin no.99 April 2012). Its mineralogy
79 and composition are described by Warren et al. (2013) and Jambon et al. (2012). Northwest
80 Africa 6704 is a 8.39 kg achondrite found in Algeria (Meteoritical Bulletin no.99 April 2012).
81 Mineralogy and petrology of NWA 6704 have been studied by Irving et al. (2011) and Hibiya
82 (2016), and are discussed in detail in the companion paper by Hibiya et al. (2018). Many

83 similarities between these two meteorites suggest that they are paired (Warren et al. 2013). A
84 smaller (220 g) group of specimens classified as NWA 6926 is very similar to the other two
85 meteorites, and is thought to be a part of the original stone of NWA 6704 that was broken by
86 the original finders and later reconstructed (Hupé 2011).

87 A 940g achondrite NWA 10132 was found in Morocco in 2015. It is nearly identical in
88 mineralogy and oxygen isotopic composition to NWA 6693 and NWA 6704, but has a distinct
89 texture, most notably lacking the trapped microscopic 2-30 μm vesicles within orthopyroxene
90 grains that are common in NWA 6693 and NWA 6704 (Irving et al. 2011), and is thought to
91 represent another sample derived from the same parent body, but not a part of the same
92 meteoroid (Irving et al. 2015).

93 These meteorites have broadly chondritic abundances of lithophile elements with 50%
94 condensation temperatures (T_c , Lodders 2003) above 900 K and only weakly fractionated
95 patterns of highly siderophile elements, suggesting that the parental melt and precursor did
96 not undergo significant segregation of metals, sulphides, or silicate minerals (Hibiya et al.
97 2018). Variable degrees of depletion in the elements with T_c below 900 K relative to
98 chondrites suggest partial loss of volatile elements during magmatism. These medium grained
99 achondrites are composed mainly of large orthopyroxene oikocrysts and sodic plagioclase
100 with elevated potassium content ($\sim\text{Ab}_{92}\text{An}_4\text{Or}_4$), and also contain less abundant olivine
101 grains, and minor Cr-spinel, awaruite, and merrillite (Warren et al., 2013, Hibiya et al. 2018).
102 These rocks are also dissimilar to other known achondrites in a number of other features:
103 ferroan mafic silicate minerals with elevated FeO/MnO ratios and anomalously high Ni
104 contents, very Ni-rich (75-81 wt.%) metal. The latter features were interpreted as reflecting
105 highly oxidised nature of chondritic precursor material that was preserved during melting
106 (Warren et al. 2013). Their oxygen isotopic composition (Hibiya et al. 2018) plots within the
107 field for acapulcoites-lodranites.

108 The specimens are remarkably fresh, with only minor coatings of pale orange desert dust on
109 broken surfaces. Shock effects in NWA 6693 are described as “very minor brecciation, and
110 pervasively mobilized linear-arcuate trails of microinclusions and bubbles” (Warren et al.
111 2013), while shock effects in NWA 6704 are reported to be undetectable (Irving et al. 2011,
112 Hibiya et al. 2018). This combination of features makes these meteorites attractive targets for
113 a comprehensive isotopic and geochemical study. These rocks from a previously unsampled
114 asteroid can be dated with multiple methods, and the absence of evidence for significant

115 secondary processing suggests that the majority of the original chemical and isotopic
116 characteristics are likely to be well preserved.

117

118 **3. Analytical procedures**

119 Sample preparation and procedures for U-Pb, $^{238}\text{U}/^{235}\text{U}$, ^{87}Rb - ^{87}Sr and ^{40}Ar - ^{39}Ar analyses are
120 described in Electronic Annex EA-1. The uncertainties are reported at 2σ or 95% confidence
121 level.

122 In this study, we used two isochron regression procedures from Isoplot v. 3.75 (Ludwig
123 2012): “conventional” isochron that uses Model 1 of York (1969), and non-parametric “robust
124 regression” (Ludwig 2012, p.25) that calculates the isochron slope as the median of all
125 pairwise slopes. Both isochron regression procedures are described in more detail in the
126 electronic annex EA-1. In the following text, isochrons that are mentioned without specifying
127 the regression procedure are “conventional” ones. “Robust” isochrons are designated as such
128 in all cases. Uncertainties for both “conventional” and “robust” isochrons are reported as 95%
129 confidence intervals. The asymmetric uncertainties that are usually produced by the “robust
130 regression” procedure are reported as calculated, however in the final age evaluation we
131 assume more traditional symmetric uncertainty reporting, conservatively accepting the larger
132 of the lower and upper values as the measure of uncertainty.

133

134 **4. Results**

135 4.1 $^{238}\text{U}/^{235}\text{U}$

136 The individual results for the $^{238}\text{U}/^{235}\text{U}$ ratio in NWA 6704 and the standards for each
137 analytical session are shown in Table EA2. The isotopic ratios measured in three analytical
138 sessions in the samples processed at two different institutions (UC Davis and ANU) are
139 consistent within uncertainty. All standards agree with published values. For NWA 6704, the
140 weighted average $^{238}\text{U}/^{235}\text{U}$ ratio is 137.7784 ± 0.0097 ($n=3$, $\text{MSWD}=0.46$). This value is used
141 in all U-Pb age calculations and isochron regressions for both NWA 6704 and NWA 6693
142 unless indicated otherwise.

143

144 4.2 U and Pb concentrations

145 Lead, U and Th concentrations, U/Pb and Pb isotopic ratios obtained in six analytical sessions
146 at the ANU and one analytical session at UC Davis (Electronic Annex EA3), and model dates
147 calculated relative to primordial Pb (Tatsumoto et al. 1973, Blichert-Toft et al. 2010), are
148 presented in Electronic Annex EA4. All data are tabulated in the sheet #18, $^{207}\text{Pb}/^{206}\text{Pb}$ -
149 $^{204}\text{Pb}/^{206}\text{Pb}$ isochron plots and concordia diagrams are shown in the sheets 1-16. Colour
150 coding of data points in the isochron plots matches the colours in the table (sheet #17). Model
151 dates in the columns AK and BC-BG are calculated with the measured $^{238}\text{U}/^{235}\text{U}=137.7784$. All
152 isochron ages and model dates shown in the plots and reported in the text are calculated
153 using the same measured $^{238}\text{U}/^{235}\text{U}$ value and its uncertainty.

154 Concentrations of U, Th (whenever measured) and Pb in acid leachates are reported relative
155 to the sample weights prior to leaching. For three pyroxene fractions from NWA 6693
156 measured in the batch A104, we have also estimated the composition that the residue fraction
157 would have if the last HF washing step (W4) was not applied. These values are denoted
158 “W4+R recombined”. All analyses were checked for possible quality problems including
159 accidental processing contamination (indicated by anomalously high blank), persistent
160 interferences in mass spectrometry, anomalous mass fractionation, and low total ion yield. All
161 data reported in the table are free from these problems. Discordance between the $^{238}\text{U}/^{206}\text{Pb}^*$
162 and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ isotopic dates (U-Pb discordance column BZ) is calculated as $100 \times$
163 $[(\exp((\lambda^{238}\text{U}) \times \text{Age}^{207}\text{Pb}^*/^{206}\text{Pb}^*) - 1) - ^{206}\text{Pb}^*/^{238}\text{U})/(\exp((\lambda^{238}\text{U}) \times \text{Age}^{207}\text{Pb}^*/^{206}\text{Pb}^*) - 1)]$.

164 Concentrations of U, Th and Pb in the minerals and whole rocks are determined in two ways:
165 by analysis of fractions without acid leaching (batches A77 and A116), and by summing the
166 concentrations in all leaching steps. Uranium is distributed relatively evenly between the
167 minerals: multiple pyroxene fractions from both meteorites contain 5-13 ppb U, plagioclase –
168 6-10 ppb U, olivine has slightly lower U concentrations of 3-3.5 ppb. The whole rock
169 concentrations of 8-12 ppb are similar to the concentrations in pyroxene and plagioclase, and
170 are within the range of chondritic U abundances. The Th/U ratios in the minerals and whole
171 rock, both directly measured and calculated from radiogenic $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratios are lower
172 than the typical chondritic values of ~ 3.8 , suggesting possible Th-U fractionation during
173 accretion or melting in the parent body. Total concentrations of Pb in both meteorites and
174 their minerals are between 10-35 ppb.

175

176 4.3 Pb isotope systematics

177 Lead isotopic compositions in unleached minerals and whole rocks of both meteorites are
178 moderately radiogenic with $^{206}\text{Pb}/^{204}\text{Pb}$ from 37 to 107. Acid leaching effectively separates
179 radiogenic and non-radiogenic Pb (EA4, sheets 1 and 5): for example, measured $^{206}\text{Pb}/^{204}\text{Pb}$ in
180 pyroxene fractions from NWA 6704 vary between 18-80 in the first and second washes, and
181 between 130-2400 in the residues. Plagioclase residues in NWA 6704 also contain relatively
182 radiogenic Pb with $^{206}\text{Pb}/^{204}\text{Pb}$ of 160 to 470, but, in contrast to pyroxene, the Pb in the first
183 washes is more radiogenic ($^{206}\text{Pb}/^{204}\text{Pb}=42-61$) than in the second washes ($^{206}\text{Pb}/^{204}\text{Pb}=18-$
184 35). Furthermore, Pb in the first plagioclase washes has elevated $^{208}\text{Pb}/^{204}\text{Pb}$, corresponding
185 to higher model $^{232}\text{Th}/^{238}\text{U}$ of 3.5-3.6 compared to the values in the plagioclase residues (1.8-
186 1.9) and pyroxene residues (0.84-1.07). This suggests that the first wash dissolved a U-Th rich
187 mineral, most likely merrillite, which is closest to plagioclase in crystallisation sequence
188 (Hibiya et al. 2018) and has similar magnetic susceptibility, so it can be expected that trace
189 amounts of merrillite are present in the plagioclase fraction.

190 $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ isochron regressions (Pb-Pb isochrons hereafter) for all data from
191 NWA 6704 (EA2, sheets 1, 2) show significant dispersion (MSWD=4221), which suggests the
192 presence of both initial Pb (approximated by primordial Pb, Tatsumoto et al. 1973, Blichert-
193 Toft et al. 2010) and terrestrial contamination Pb (approximated by the modern crustal Pb in
194 the model of Stacey and Kramers 1975), in comparable quantities.

195 In order to better understand the U-Pb system in NWA 6704 and determine a reliable age, we
196 examine the data for plagioclase and pyroxene separately. An isochron for all leachates and
197 residues of four plagioclase fractions yields the date of 4560.5 ± 4.8 Ma, MSWD=24 (EA4 sheet
198 12), and passes through the point of primordial Pb. We think, however, that this isochron has
199 no age significance, because it effectively combines data from two, or possibly three minerals:
200 Pb in the first washes (model Th/U=1.8-2.0, EA4 sheet 17) is mostly from dissolved small
201 merrillite attached to plagioclase grains, Pb in the residues (model Th/U=1.1-1.6), is from
202 plagioclase itself, and the origin of Pb in the second washes is unclear (model Th/U=0.36-0.44
203 is quite distinct from both first washes and residues). Three out of four first washes yield an
204 isochron (MSWD=0.27) corresponding to the age of 4559.8 ± 2.8 Ma, which we consider a
205 preliminary estimate of the age of merrillite.

206 To determine the crystallisation age with minimum uncertainty due to the presence of two
207 non-radiogenic Pb components, we used only pyroxene data points with blank-corrected

208 $^{206}\text{Pb}/^{204}\text{Pb} > 700$ (which corresponds to $^{204}\text{Pb}/^{206}\text{Pb} < 0.0014$, Table 1). Fourteen acid-washed
209 pyroxene residues satisfy this requirement. “Robust” regression of these data yielded the age
210 of $4562.65 \pm 0.31/-0.36$ Ma (EA4 sheet 3). Exclusion of one point that plots distinctly above
211 the main set improves precision, and yields the “robust” regression with the radiogenic
212 $^{207}\text{Pb}/^{206}\text{Pb}$ ratio (y-intercept of the isochron) of $0.62354 \pm 0.00009/-0.00012$, corresponding
213 to the age $4562.76 \pm 0.22/-0.30$ Ma (Fig. 1, and EA4 sheet 4). We consider this value the best
214 age estimate for NWA 6704. No “conventional” isochrons could be calculated from these data.

215 One pyroxene residue with $^{206}\text{Pb}/^{204}\text{Pb} > 700$, A049 8R, plots above the isochron for the other
216 thirteen fractions. Similar but more pronounced excess of radiogenic ^{207}Pb is observed in all
217 four plagioclase residues that plot above the Pb-Pb isochron for pyroxene residues (EA4 sheet
218 16). Elevated $^{207}\text{Pb}/^{206}\text{Pb}$ in these fractions can be related to the capture of radiogenic Pb with
219 high $^{207}\text{Pb}/^{206}\text{Pb}$ that accumulated in merrillite grains early in the history of the parent body.
220 Radiogenic Pb could have been leaking out of phosphate grains during cooling while the
221 temperature of the rock was higher than the closure temperature for diffusion. Loss of
222 radiogenic Pb from merrillite in a secondary event (e.g. shock metamorphism) is also possible,
223 considering the young ^{40}Ar - ^{39}Ar age of NWA 6704 (section 4.6). However, this possibility
224 remains speculative because, to the best of our knowledge, there are no firm experimental
225 data on response of the U-Pb isotopic system in merrillite to shock metamorphism.

226 Projection of the pyroxene residue Pb-Pb isochron for NWA 6704 to the non-radiogenic
227 reservoir compositions (EA4 sheet 4) shows that the residual non-radiogenic Pb is a mixture
228 of primordial composition and terrestrial contamination. This observation reinforces the
229 choice of only the most radiogenic data points for age determination, thereby minimising the
230 effect of uncertainty in the isotopic composition of residual non-radiogenic Pb on the age
231 calculation.

232 Pb-isotopic data for NWA 6693 (EA2 sheets 5,6) are also dispersed. The isochron regression
233 through all data passes close to the isotopic composition of primordial Pb which suggests that
234 the relative contribution of terrestrial contamination to the Pb-isotopic systematics is much
235 smaller than in the case of NWA 6704. Some of the most radiogenic Pb in NWA 6693
236 pyroxenes with $^{206}\text{Pb}/^{204}\text{Pb} > 700$ are contained in the 0.5M HF washes (W4) and residues
237 after HF leaching in batch A104. However, comparison of Pb-isotopic systematics of HF
238 washes and residues shows that the former have systematically higher $^{207}\text{Pb}/^{206}\text{Pb}$ at the
239 same $^{204}\text{Pb}/^{206}\text{Pb}$ and hence higher $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ model dates (EA4 sheet 7; Fig. 2), consistent
240 with fractionation of radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ during partial dissolution in dilute HF which was

241 observed in CAIs, and pyroxenes in some other achondrites (Amelin et al. 2016). The
242 difference between the average value of model dates calculated from W4 (4563.7 ± 0.7 Ma,
243 2SD) and residues (4562.3 ± 0.4 Ma) is 1.4 ± 0.8 Ma, significantly larger than the uncertainties of
244 individual dates.

245 In order to mitigate the fractionation induced by HF leaching and calculate the accurate age of
246 NWA 6693, we numerically re-combined the W4 and residue data for each fraction. The
247 $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ model dates of the recombined fractions are close to the data for NWA 6693
248 pyroxenes that were analysed in the batch A123 after leaching in HNO_3 and HCl but without
249 HF exposure (Fig. 2). Regressing together these re-combined points, third (hot HCl) washes of
250 A104, and three pyroxene fractions of the batch A123, produced a “conventional” isochron
251 with slight excess scatter ($\text{MSWD}=3.8$) and a y-intercept of 0.62346 ± 0.00010 , corresponding
252 to the age of 4562.57 ± 0.21 Ma (Fig. 3). “Robust regression” of the same data yielded the age of
253 $4562.63 \pm 0.29 / -0.21$ Ma. The “conventional” and “robust” regressions are practically identical
254 and have similar uncertainties. For consistency of isochron regressions between the two
255 meteorites, we chose the “robust” age value as our best estimate of the age of NWA 6693.
256 Including third (hot HCl) washes of A104 in these regressions is justified because of the
257 absence of detectable terrestrial non-radiogenic Pb. Regressions without third washes yield
258 identical results with slightly larger uncertainties (EA2 sheet 8a).

259

260 4.4 U-Pb system

261 Interpretation of Pb-Pb isochron dates as the ages of rocks relies on single-stage evolution of
262 the U-Pb system, i.e. on the absence of migration of U and radiogenic Pb after formation of the
263 rock (Tera and Carlson 1999, Chen and Papanastassiou 2008). Extensive acid leaching such as
264 that used in this study, which is necessary to remove terrestrial Pb and U induced by
265 weathering, also fractionates radiogenic Pb from U. We tested behaviour of the U-Pb systems
266 by plotting U-Pb data for the same fractions that were used to construct our preferred Pb-Pb
267 isochrons. The U-Pb data for NWA 6704 pyroxene residues are 3-5% reversely discordant
268 (suggesting preferential loss of U relative to radiogenic Pb), and define a discordia with upper
269 intercept of 4564.1 ± 1.5 Ma (EA4 sheet 9). The U-Pb data for NWA 6693 pyroxene residues
270 and re-combined R+W4 show similar reverse discordance, and define a discordia with upper
271 intercept of 4562.50 ± 0.58 Ma (EA4 sheet 10). The upper intercepts of both of these discordia
272 lines are consistent with the Pb-Pb isochron ages, and the lower intercepts are equal to zero

273 within uncertainty. These results confirm that the dominant U-Pb fractionation is caused by
274 recent processes, most likely a combination of weathering and laboratory treatment, and
275 suggest that interpretation of Pb-Pb isochron dates as ages is valid.

276

277 4.5 ^{87}Rb - ^{87}Sr and $^{84}\text{Sr}/^{86}\text{Sr}$

278 The Rb-Sr data for NWA 6693 and NWA 6704 are summarised in the Electronic Annex EA5.
279 The whole rock fraction of NWA 6693 contains 6.2 ppm Sr and 3.2 ppm Rb. These values are
280 close to the abundances of these elements in CI chondrites of 7.8 and 2.3 ppm, respectively
281 (Palme et al. 2014), and translate into $^{87}\text{Rb}/^{86}\text{Sr}=1.50$. This value is higher than observed in
282 most chondrites, and is uncommon for achondrites. Pyroxene and olivine have lower Rb and
283 Sr contents of 0.15-1.0 ppm, but even higher $^{87}\text{Rb}/^{86}\text{Sr}$ of 6.1-7.0. Plagioclase has much higher
284 Rb and Sr concentrations of 14 and 33 ppm, and lower (but still high) $^{87}\text{Rb}/^{86}\text{Sr}$ of 1.28. NWA
285 6704 shows less extreme Rb enrichment and Sr depletion, but the distribution of these
286 elements between the minerals are similar. Whole rock and plagioclase of NWA 6704 have
287 $^{87}\text{Rb}/^{86}\text{Sr}$ of 0.054-0.101, sufficiently low to attempt calculation of the $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio
288 with only moderate correction for radiogenic ingrowth and therefore reasonable precision.

289 Acid leaching of the pyroxene from NWA 6693 in HNO_3 and HCl (leaching steps W1 and W2)
290 removes only a small part of Sr and almost no Rb, whereas HF leaching (step W4) brings ~20-
291 30% of these elements into solution.

292 The isochron plot for acid leached pyroxenes analysed in the batch A104 (leaching
293 procedures for the samples in different batches are described in the Electronic Annex EA3)
294 shows wide dispersion of data, and very radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ up to 0.99 in some fractions
295 (electronic annex EA5 sheet 2). Removing HF washes from the regression significantly
296 decreases dispersion, and brings the isochron apparent age of 4665 ± 360 Ma (MSWD=19) into
297 agreement, within its large uncertainty, with the Pb-isotopic age of NWA 6693. The data for
298 unleached minerals and whole rocks (batch A116) from both meteorites, shown in EA5 sheet
299 3 and in Fig. 4, display much smaller dispersion than the leaching steps of the pyroxenes. An
300 isochron using all mineral fractions only yields the best regression with only a small excess
301 scattering (MSWD=3.5), corresponding to an age of 4543 ± 46 Ma and initial $^{87}\text{Sr}/^{86}\text{Sr}$ of
302 0.699013 ± 0.000055 .

303 The $^{84}\text{Sr}/^{86}\text{Sr}$ ratios were measured in all unspiked aliquots, but only fractions with
304 sufficiently large Sr content yielded data with usable precision. The average value from three
305 fractions that contained over 100 ng Sr (NWA 6704 whole rock, and plagioclase fractions from
306 both meteorites) yielded $\epsilon(^{84}\text{Sr})=0.22\pm0.37$, indistinguishable from the reference value for the
307 SRM 987 standard (EA5 sheet 4).

308

309 4.6 ^{40}Ar - ^{39}Ar ages

310 ^{40}Ar - ^{39}Ar ages are summarized in Tables EA6-1 and EA6-2, and plotted as an apparent
311 age spectrum in Fig. 5. Complementary normal and inverse isochrons are reported in Fig.
312 EA7-1 to EA7-5. Although petrographic studies identified voids/vesicles in pyroxenes (Irving
313 et al., 2011; Jambon et al. 2012; Warren et al., 2013, Hibiya et al. 2018), during the argon
314 extraction experiments there was no obvious release of trapped Ar gas by vesicle
315 decrepitation. In fact, the normal and inverse isochron plots (Figures EA7-1 to EA7-4) show
316 that the trapped/excess (i.e., non-radiogenic) ^{40}Ar content is negligible for all step heating
317 releases; hence there is no need for data correction for this component. The variation in the
318 $^{40}\text{Ar}/^{36}\text{Ar}$ in low-temperature steps are mainly from variable amount of solar wind ^{36}Ar ,
319 whereas the high-temperature ^{36}Ar is mainly of cosmogenic origin. No terrestrial
320 contamination was observed during the Ar step heating release or during the EMP/SEM work.
321 The two ^{40}Ar - ^{39}Ar spectra obtained from the two bulk samples largely overlap. Both spectra
322 indicate a loss of a small portion of ^{40}Ar during a thermal event at ≤ 2.12 Ga, which is more
323 obvious in the low-temperature data for Fragment #2. A well defined age plateau is obtained
324 for Fragment #1 over the intermediate and high-temperature steps, however the data for
325 Fragment #2 are more dispersed and do not define a plateau.

326 Age spectrum for the fragment #1 shows that 89% of the ^{39}Ar release over the intermediate
327 and high temperature heating steps (700-1100°C) form an age plateau corresponding to an
328 age of 4232 ± 33 Ma (2σ). The ages obtained for the two fragments either by correlation or
329 calculated from 3-isotope plots (Figures EA7-1 and EA7-4) are indistinguishable within
330 uncertainty and range between 4291 ± 58 Ma and 4125 ± 3000 Ma. We consider the age of
331 4199 ± 32 Ma (Table 2) that is yielded by an inverse isochron for the fragment #1 our
332 preferred ^{40}Ar - ^{39}Ar age of NWA 6704 .

333

334 5. Discussion

335 5.1 Pb-isotopic systematics and the ages of NWA 6693 and NWA 6704

336 Pb-Pb isochrons yield the most precise “absolute” (i.e. time before present) ages of
337 achondrites. Modern protocols of acid leaching/partial dissolution permit efficient, and in
338 favourable cases, nearly complete, separation of radiogenic and non-radiogenic Pb from U-
339 bearing minerals for achondrites of various chemical composition and mineralogy. Zero lower
340 intercept ages from U-Pb discordia lines are consistent with closed system behaviour until
341 geologically recent exposure to the elements, and laboratory treatment. Small data dispersion
342 that is seen in Pb-Pb isochron diagrams and in concordia diagrams most likely reflects
343 variable proportion of initial and terrestrial components in residual non-radiogenic Pb.
344 Although we cannot completely rule out multi-stage evolution that could compromise
345 straightforward interpretation of Pb-Pb isochron ages, we see no evidence for it, hence our
346 preferred interpretation is that it does not exist at a detectable level.

347 A significant uncertainty (from today’s standpoint) in the Pb-isotopic ages reported in pre-
348 2010 studies, was caused by unrecognised variability of the $^{238}\text{U}/^{235}\text{U}$ ratios. This uncertainty
349 is now managed by directly measuring this ratio in the studied meteorites or their
350 components, or, if such measurements are impossible or unfeasible due to the limited sample
351 availability and/or very low U concentration (e.g. Koefoed et al. 2016), by using the $^{238}\text{U}/^{235}\text{U}$
352 ratios for other meteorites from the same group.

353 With these two problems taken care of, and the precision of isochron dates (including
354 uncertainty of $^{238}\text{U}/^{235}\text{U}$ ratios but excluding uncertainty of the U isotope half-lives) of about
355 0.3-0.5 Ma, such as reported in this study, Pb-isotope chronology can resolve fine details in
356 the magmatic history of asteroids. Still, Pb-Pb isochrons are imperfect, and dating of NWA
357 6704 and NWA 6693 show sides of this imperfection that need to be dealt with. The Pb-
358 isotopic system of NWA 6704 is complicated by the presence of initial Pb and terrestrial
359 contamination Pb in comparable quantities. Passing of the preferred isochron defined by
360 isotopic data for the residues between the points of primordial and modern terrestrial Pb
361 (EA2 sheet 4) shows that the step leaching greatly reduced the total content of non-radiogenic
362 Pb, but did not completely eliminate either of the two non-radiogenic Pb components. The age
363 of $4562.76 \pm 0.22 / -0.30$ Ma (Fig. 1) can be considered reliable because it is solely based on
364 highly radiogenic data and is therefore insensitive to the exact isotopic composition of
365 residual non-radiogenic Pb. In NWA 6693, the content of terrestrial Pb is much lower and

366 does not pose a problem, but $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in highly radiogenic residues and W4 washes
367 are fractionated by partial dissolution in HF. This fractionation was eliminated by numeric re-
368 mixing of the W4 washes and residues at the data reduction stage (Amelin et al. 2016), that
369 produces the data indistinguishable from those obtained without HF leaching (Fig. 2). The
370 isochron date of $4562.63 \pm 0.29/-0.21$ Ma based on re-combined HF washes and residues,
371 regressed together with analyses of pyroxenes without HF washing is considered a reliable
372 age. The ages of these meteorites are identical within uncertainty, and, assuming that they
373 formed simultaneously, we could calculate their combined more “precise” age as the weight
374 average of the two individual ages. However, we prefer a safer approach of treating them as
375 different rocks with potentially different ages.

376

377 5.2 Open vs. closed isotopic systems

378 The question of open vs. closed system behaviour of the isotopic chronometers can be
379 assessed by comparison between the readings of multiple chronometers applied to the same
380 rocks and minerals. In response to secondary events that occurred long time after formation
381 of the rocks, long-lived chronometers either yield younger isochron dates that reflect the
382 timing of the secondary event (in case of complete resetting), or develop scattering or
383 sometimes excess isochron slope (in case of partial resetting). Long-lived chronometer
384 systems are insensitive to the secondary processes that occurred shortly after crystallisation.
385 The ^{87}Rb - ^{87}Sr age of 4543 ± 46 Ma (section 4.5) and the ^{187}Re - ^{187}Os age of 4576 ± 250 Ma
386 (Hibiya et al. 2018), are consistent, within their large uncertainties, with the U-Pb ages
387 (section 4.6). Short-lived extinct radionuclide chronometers are, on the other hand, affected
388 by both early and late disturbances. The extinct chronometer ages of NWA 6704: ^{26}Al - ^{26}Mg
389 age of 4563.13 ± 0.27 Ma, and ^{53}Mn - ^{53}Cr age 4562.17 ± 0.76 Ma (Sanborn et al. 2018),
390 calculated relative to the rapidly cooled angrite D’Orbigny, are indistinguishable from the Pb-
391 isotopic age of NWA 6704. This consistency of ages is either an extremely unlikely
392 coincidence, or evidence that the parent rocks of NWA 6693 and NWA 6704 remained closed
393 to migration of both lithophile and siderophile elements since crystallisation and initial
394 cooling of the parent rocks. The presence of a small excess of radiogenic ^{207}Pb in plagioclase
395 and one pyroxene fraction is likely to be a result of early migration of radiogenic Pb that was
396 lost from phosphate during post-magmatic cooling. No evidence of extensive migration of
397 radiogenic Pb such as that recorded in Pb-isotopic systematics of eucrite minerals (Iizuka et
398 al., 2016) have been found in NWA 6693 or NWA 6704.

399 On the other hand, the Ar-Ar system was reset at 4.20 ± 0.03 Ga by an event that did not have
400 any detectable impact on the other isotopic systems. The possible reasons of this open system
401 behaviour are discussed in the following section in the context of post-magmatic cooling.

402

403 5.3 The rate of post-magmatic cooling

404 If the Pb-Pb age of plagioclase first washes in NWA 6704 is interpreted as the age of merrillite,
405 we can use the difference between this age, and the Pb-Pb age of pyroxene, to estimate the
406 cooling rate of this meteorite. Using the diffusion coefficients for Pb published by Cherniak
407 (2001) for enstatite, applying the diffusion coefficients of Cherniak et al. (1991) for apatite to
408 merrillite (to the best of our knowledge, there are no experimental diffusion data for
409 merrillite), and the range of crystal radii of 1-10 mm for pyroxene and 0.02-0.04 mm for
410 merrillite (Hibiya et al. 2018), we can estimate the closure temperature at 856 ± 39 K for
411 merrillite, and 1449 ± 109 K for pyroxene using the diffusion formalism of Dodson (1973).
412 Combining these closure temperatures with the age of merrillite of 4559.8 ± 2.8 and the age of
413 pyroxene of $4562.76 +0.22/-0.30$ Ma following the same approach as Amelin et al. (2005), we
414 estimate the minimum cooling rate at 98 K/Ma, and the probable cooling rate at 201 K/Ma
415 (details are in the electronic annex EA8). These estimates are much slower than the estimate
416 of the cooling rate from the olivine-spinel geospeedometer in Hibiya et al. (2018) that
417 corresponds to ca. 10^6 K/Ma. It is therefore likely that these values correspond to different
418 stages of cooling.

419 The Ar-Ar system can also be used for assessment of post-magmatic cooling, if it can be
420 demonstrated that the age resetting was not caused by a impact-related shock. The ^{40}Ar - ^{39}Ar
421 age of NWA 6704 suggests a possible thermal event at ~ 4.2 Ga when the K-Ar isotopic system
422 was completely reset. This thermal event, which is not matched by any evidence of shock
423 deformation (Hibiya et al. 2018), is also interpreted as the reason why the vesicles within this
424 sample are empty. The K-Ar system in feldspars and orthopyroxenes closes below the
425 temperature range of 573–873 K, respectively (Cassata et al., 2009, 2011), which is similar to,
426 or lower than the closure of Pb diffusion in merrillite. The rates of Ar diffusion (and hence the
427 temperature of the age resetting) in feldspars strongly depend on composition, structural
428 state, and microstructural characteristics. Albitic plagioclase, such as the mineral that hosts
429 most K in NWA 6704, can be particularly prone to low-temperature (down to 473K) loss of
430 radiogenic argon due to low-temperature structural changes (Cassata and Renne 2013). This

possibility can be checked by a detailed mineralogical and K-Ar isotopic study of individual minerals on NWA 6704 and NWA 6693, with particular emphasis on plagioclase, and by a (U, Th, Sm)/He chronological study that detects the processes that occur at even lower temperatures.

The Ar data also suggest a minor event at ≤ 2.2 Ga that is recorded by the low-temperature steps of fragment #2. Warren et al. (2013) suggested that NWA 6693 was shocked probably while the rock was still hot from its igneous petrogenesis, and this may be the reason why shock features are subdued and the vesicles are devoid of fluid. It should be noted, however, that Irving et al. (2011) and Hibiya et al. (2018) did not find shock features in NWA 6704, so apart from the hint on the Ar-system having potentially stayed at temperatures above closure temperature, the question about the origin of empty vesicles remains open.

In the context of other meteorite and planetary studies, the K-Ar data for NWA 6704 show that it was affected by an event at ~ 4.2 Ga, and age similar to that also observed in lunar rocks (Fernandes et al., 2013 and references therein), and in other planetary materials such as GRA 06128/06129 (Shearer et al., 2010) with a Ar age of ~ 4.3 Ga and a later one at ≤ 2.7 Ga, brachinite EET99402 (Garrison and Bogard, 2003) where the high-temperature heating steps suggest an age > 4265 Ma and a later partial loss at < 2400 Ma. Moreover, a compilation of the ^{40}Ar - ^{39}Ar literature data for different parent bodies presented in Fritz et al. (2014, Fig. 4; and references therein) suggest that parent bodies of various meteorites (IAB irons, IIE irons, L chondrites, enstatite chondrites, and Rumuruti chondrites) were continuously exposed to thermal events.

5.4 Optimal strategy for multi-chronometer studies of meteorites

If multiple isotopic and geochemical systems are studied in the same meteorite, there are several benefits in analysing some of them, or ideally all of them, in the same volume of the rock. This approach cancels the effects of sample heterogeneity on comparison between the isotopic systems, reduces the amount of work in mineral separation, picking and chemical procedures, and provides the most efficient way of using the samples that are available in limited quantities. Different requirements of the different isotopic systems to the sample pre-treatment, however, complicate the application of this approach. Here we discuss the strategy of sample preparation and handling in multi-chronometer studies of meteorites using examples from this study.

463 Isotopic clocks in meteorites can be affected by elemental and, in some cases, isotopic
464 fractionation caused by natural processes that occur on the asteroids (e.g. metamorphism,
465 alteration and impacts), by terrestrial weathering, or by cleaning procedures that are
466 intended to remove the products of these natural secondary processes. Acid leaching / partial
467 dissolution, in particular, is considered indispensable for removing non-radiogenic Pb, and it
468 is indeed efficient in most cases except the most stubborn ones (e.g. Merle and Amelin 2016),
469 but preferential dissolution of radiogenic Pb compared to U (or vice versa) that commonly
470 occurs in step leaching rendering the U-Pb system discordant, although the $^{206}\text{Pb}/^{238}\text{U}$ and
471 $^{207}\text{Pb}/^{235}\text{U}$ ratios from step leachates and residues, plotted in a concordia diagram, can still be
472 used to test whether the minerals experienced multi-stage U-Pb evolution (Chen and
473 Papanastassiou 2008, Amelin et al. 2009). Such tests, however, can be reasonably reliable only
474 for analyses with small amount of non-radiogenic Pb.

475 Reliability of other isotopic tracers, such as oxygen three-isotope systematics, can also be
476 improved by removal of weathering products. Leaching meteorites in acids and/or in non-
477 acidic agents such as ethanolamine thioglycollate is a common practice for removing
478 weathering products and improving consistency of the data (e.g. Greenwood et al. 2012).

479 One possible detrimental effect of acid leaching on Pb-isotopic system that can directly impact
480 the accuracy of the age is the relatively small (but in some cases significant) fractionation of
481 radiogenic Pb isotopes. It is demonstrated by the analyses of HF washes and residues from
482 NWA 6693 pyroxenes, and was also observed in some other meteorite materials (Amelin et al.
483 2016).

484 In contrast, in the dating schemes based on both extinct (short-lived) and extant (long-lived)
485 nuclides, where the elemental ratios are used directly in the age calculations, any decoupling
486 between the parent-daughter ratio and the radiogenic ingrowth compromises age accuracy.
487 Such decoupling is likely to occur in the case of incongruent dissolution of minerals, where
488 different fractions of parent and daughter elements go into solution during certain leaching
489 steps. Rb-Sr systematics of acid leaching of pyroxene from NWA 6693 (batch A104) is a clear
490 example of disturbance of the isotopic chronometer system by an incongruent dissolution of
491 the mineral (EA5 sheet 2) that, without leaching, behaves as a closed system (EA5 sheet 3).
492 This means that the meteoritic minerals leached using procedures optimised for the Pb-
493 isotopic system can yield unreliable Rb-Sr data and, by implication, initial $^{87}\text{Sr}/^{86}\text{Sr}$, Sm-Nd,
494 ^{26}Al - ^{26}Mg , ^{53}Mn - ^{53}Cr etc. data, and that such isotopic data have to be obtained on separate
495 sample aliquots cleaned by the physical means only (mechanical abrasion, ultrasonic agitation

etc.). However, there is a possibility of undoing the effects of leaching-induced fractionation and reconstructing the chemical and isotopic composition of an unleached sample by numeric recombination of elemental and isotopic ratios for all leaching steps and the residue. The recombined Rb-Sr data for the leached NWA 6693 pyroxenes are shown in the Rb-Sr data table (EA5 sheet 6) and in Fig. 6. The recombined pyroxene data are completely consistent with the isochron for untreated minerals. Furthermore, including these data in regression increases precision of the age and the initial $^{87}\text{Sr}/^{86}\text{Sr}$ value. This example shows that numeric recombination of the leaching steps can work very well, and that the mineral fractions prepared using the methods optimised for U-Pb can be also used in multi-chronometer studies. Similar approach was successfully used in Sm-Nd dating of the Martian meteorite NWA 7635 (Lapen et al. 2017).

The recombination procedure is not infallible, of course, and can give less than perfect results if there is a loss (unaccounted for) of the parent or daughter elements somewhere in the leaching procedure, or if the blank correction is not completely accurate. Recombination of leaching steps is an approach that should be reserved for meteorites, their components, and other extraterrestrial materials that are available in extremely limited quantities, and the most efficient usage of samples is a high priority. For studies of meteorites where sufficient material is available for separate analyses for U-Pb and other isotopic systems, separate sample processing with and without acid leaching is a more reliable approach.

515

516 5.5 NWA 6693 and NWA 6704 – potential reference samples for age comparison studies

Meteorites with well-behaved isotopic chronometer systems can serve as reference samples in two kinds of studies: for linking the timescales built using extinct radionuclide systems to each other and to the absolute time as determined from the extant nuclide chronometry (Nyquist et al. 2009, Amelin and Ireland 2013), and for determination of the half-lives of the long-lived radionuclides by geological age comparison (Begemann et al. 2001). To be suitable for either or both of these applications, meteorites must satisfy a number of strict requirements: 1) Form in a practically instantaneous, or “point-like” (Begemann et al. 2001) event; 2) Cooled after crystallisation very rapidly, to make any differences in the time of closure of isotopic clocks with different diffusion rates of parent and daughter elements insignificant; 3) Remain closed to migration of parent and daughter elements after formation; 4) Contain minerals that can be precisely dated with all the methods of interest. An additional

528 requirement for the Early Solar System (ESS) age references is an old enough age to contain
529 sufficiently high abundance of the shortest lived parent nuclide of interest (e.g. ^{26}Al) to
530 construct a precise fossil isochron. NWA 6693 and NWA 6704 satisfy these requirements
531 reasonably well, and can potentially be used in both ESS chronology and half-life studies.

532 Rapidly crystallized angrites of the older generation, in particular D'Orbigny, are currently the
533 most widely used anchor meteorites for the ESS chronology. Compared to such angrites, NWA
534 6693/6704 have some advantages and some disadvantages as the ESS age reference. An
535 advantage of angrites is higher content of uranium in pyroxene (a result of overall enrichment
536 in refractory elements in angrites, e.g. Keil 2012), which makes it easier to achieve high
537 precision of the Pb-isotopic age. Nevertheless, precision of the Pb-isotopic ages of NWA 6693
538 and NWA 6704 can be improved, if necessary, by performing additional analyses. Angrites
539 have a longer history of ^{26}Al - ^{26}Mg and ^{53}Mn - ^{53}Cr studies and hence more data are available,
540 but the NWA 6693/6704 proved to be well datable as well (Sanborn et al. 2018). Angrites
541 have a slight advantage with the ^{53}Mn - ^{53}Cr system due to variable Mn/Cr ratios reaching
542 exceptionally high values (McKibbin et al. 2013), which helps to construct very precise ^{53}Mn -
543 ^{53}Cr isochrons (Glavin et al. 2004, Yamashita et al. 2016). NWA 6693/6704 and all rapidly
544 crystallized angrites are finds and are thus not completely free from interaction with soil, dust
545 and rain, but the weathering in all these meteorites is minor and does not pose a serious
546 problem in isotopic studies. One advantage of NWA 6704 is that many pieces of this meteorite
547 are currently available from the owner of the original mass. This would facilitate independent
548 studies of these meteorites by several research groups that are highly desirable for age
549 anchors or any other reference samples. D'Orbigny and other angrites, on the other hand, are
550 much less accessible. To summarise, both rapidly crystallized angrites and NWA 6693/6704
551 make suitable age reference samples for ESS studies.

552 To use a certain ESS material (e.g. achondrite) as an age reference, we require evidence that
553 the initial abundances of short-lived radionuclides in its source are representative of the Solar
554 System, or at least in the ESS domain that is being studied. Comparing multi-chronometer
555 data from several well preserved achondrites derived from different parent asteroids would
556 be useful in a search for possible heterogeneities in the distribution of short-lived
557 radionuclides in the accreting solar protoplanetary disk (Yin et al. 2017). Since NWA 6704
558 and 6693 show "carbonaceous chondrite" type Ti-Cr-Sr isotope affinity and can be considered
559 as derived from outer Solar System, they allow us to better understand the distribution of
560 short-lived nuclides between the inner and outer Solar System.

561 High K/Ca and Rb/Sr ratios in NWA 6693/6704, particularly in pyroxene and olivine, together
562 with well-preserved closed geochemical systems, and rapid formation and cooling confirmed
563 by consistency of the short-lived ^{26}Al - ^{26}Mg and ^{53}Mn - ^{53}Cr chronometers suggest that these
564 meteorites may be suitable for ^{40}K - ^{40}Ca - ^{40}Ar vs. ^{87}Rb - ^{87}Sr vs. U-Pb half-life comparisons,
565 subject to better understanding of behaviour of the Ar-Ar system at the mineral level, and a
566 detailed study of the history of low-temperature secondary processes. NWA 6693 and NWA
567 6704 are among the samples included in our ongoing half-life determination study.

568

569 5.6 The prospect of measuring the timing of parent body accretion

570 U-Pb, ^{87}Rb - ^{87}Sr , ^{26}Al - ^{26}Mg and ^{53}Mn - ^{53}Cr dates reported here and by Sanborn et al. (2018)
571 refer to the time readings between crystallisation of the parent rocks of NWA 6693/6704 and
572 closure of the isotopic clocks to diffusion during cooling shortly after. The timing of the
573 accretion of their source asteroid is a different matter: it can be anywhere between the time of
574 formation of the Solar System's first solids, and the age of the parent body of the meteorites.
575 Accretion can be dated only indirectly because it does not produce chemical fractionation that
576 can be uniquely linked to this event (Amelin and Ireland 2013), but several indirect (and
577 variably model dependent) approaches to dating accretion have been proposed. For example,
578 the timing of accretion of the chondrite parent bodies is bracketed between the age of the
579 youngest chondrules and the age of the oldest post-accretional secondary minerals (e.g.
580 fayalite, Ca phosphates). For achondrites several other approaches, each with its own set of
581 model assumptions, can be used to bracket the time of accretion. The timing of mantle
582 differentiation, which can be interpreted as solidification of the primary magma ocean, can be
583 determined from whole rock ^{26}Al - ^{26}Mg and ^{53}Mn - ^{53}Cr isochrons constructed with meteorites
584 that are thought to be derived from the same parent body, and yields the younger limit of the
585 timing of accretion. Using these mantle differentiation ages and(or) metal-silicate separation
586 ages (e.g. from ^{182}Hf - ^{182}W systematics), estimating the temperatures of mantle differentiation
587 and core formation, and applying a suitable thermal model that involves ^{26}Al decay as a heat
588 source (e.g. Bizzarro et al. 2005, Hevey and Sanders 2006), one can estimate the timing of
589 accretion (Sugiura and Fujiya 2014). The time of accretion calculated with this approach
590 depends on correct estimation of the size and thermal properties of asteroids, and on the
591 assumptions about distribution of ^{26}Al (homogeneous vs. heterogeneous) in the ESS.

592 An alternative approach, pioneered by Papanastassiou and Wasserburg (1969), uses initial
593 $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio to estimate the timing of separation of the low-Rb/Sr achondrite
594 precursor material from high-Rb-Sr solar nebula (Halliday and Porcelli 2001). This approach,
595 sometimes referred to as initial Sr chronometry, relies on the assumptions about the
596 processes in which volatility-induced differentiation in the nebula took place (condensation
597 or melting; chondrule-size, asteroid-size, or intermediate), but is free from assumptions
598 involved in the accretion time estimates based on thermal evolution of asteroids described
599 above. The estimates of the time of accretion based on consistent values from these two
600 approaches should be considered the most reliable.

601 The initial Sr chronometry works best for achondrites such as eucrites and angrites having
602 whole rock Rb/Sr ratios of about 100-1000 times lower than NWA 6693/6704. However, the
603 plagioclase in NWA 6704 have sufficiently low Rb/Sr to yield precise initial $^{87}\text{Sr}/^{86}\text{Sr}$ of
604 0.698997 ± 0.000027 calculated using Pb-isotopic age (EA5 sheet 6). The initial $^{87}\text{Sr}/^{86}\text{Sr}$ from
605 the isochron y-intercept of 0.699013 ± 0.000036 is similar within error but less precise. Using
606 the CAI initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.698978 ± 0.000004 (Hans et al. 2013), and the model of Halliday
607 and Porcelli (2001) with the nebular $^{87}\text{Rb}/^{86}\text{Sr}=0.92$, we can calculate the time of nebular
608 separation of 1.5 ± 2.1 Ma, for the precursor of the NWA 6693/6704 parent asteroid. This value
609 suggests that the parent asteroid accreted within 3.6 Ma after CAI formation, or before 4563.7
610 Ma using the CAI age of 4567.3 Ma (Connelly et al. 2012). The igneous event that produced the
611 parent rocks of NWA 6693/6704 occurred at least 1 Ma after accretion, but more likely 2.5 Ma
612 after accretion.

613

614 5.7 ^{84}Sr and cosmochemical affinity of NWA 6693 and NWA 6704

615 The average $^{84}\text{Sr}/^{86}\text{Sr}$ measured in NWA 6693 and NWA 6704 plagioclase and whole rock is
616 identical, within uncertainty, to the value in the SRM 987 standard, and corresponds to $\epsilon(^{84}\text{Sr})$
617 of 0.22 ± 0.37 relative to SRM 987. However, SRM 987 has distinctly higher $^{84}\text{Sr}/^{86}\text{Sr}$ than
618 terrestrial igneous rocks by $\sim 0.25 \epsilon(^{84}\text{Sr})$ units (Moynier et al. 2012, Paton et al. 2013,
619 Yokoyama et al. 2015). Considering this difference, NWA 6693 and NWA 6704 show a
620 $\sim 0.47 \pm 0.37 \epsilon(^{84}\text{Sr})$ units excess relative to terrestrial igneous rocks, similar to the slight
621 excesses of ^{84}Sr reported for carbonaceous chondrites. This result is consistent with the
622 carbonaceous chondrite affinity of NWA 6693 and NWA 6704 established from $\Delta^{17}\text{O}$, ^{54}Cr and
623 ^{50}Ti isotope systematics (Sanborn et al. 2018, Hibiya et al. 2018). Possible use of the ^{84}Sr data

624 for NWA 6693 and NWA 6704 for more detailed identification of the meteorite sources and
625 the study of heterogeneity of the solar protoplanetary disk would require additional, more
626 precise, analyses of plagioclase fractions that can be done in conjunction with refinement of
627 the initial $^{87}\text{Sr}/^{86}\text{Sr}$ chronometry.

628

629 5.8 Petrogenetic implications of variable volatile depletion

630 The concentrations of Rb and Sr in NWA 6693 and 6704 can be used to infer mechanisms that
631 caused volatile element fractionation in these meteorites. Rb-Sr isochrons that are consistent
632 with Pb-Pb and extinct radionuclide dates confirm that Rb and Sr in these meteorites are
633 indigenous, and therefore can be used for petrogenetic reconstructions. Analyses of aliquots
634 from >1g samples ground for mineral separation in this study (section 4.5) show consistent Sr
635 concentration of ~6 ppm in both meteorites, and analyses of 30-50 mg rock fragments by
636 Hibiya et al. 2018 (their Table 4) yielded similar values (with exception of NWA 6704 analysis
637 that yielded 14 ppm Sr, but also 2.5 times higher concentration of Al than other fragments,
638 suggesting higher than average abundance of plagioclase). The concentrations of Rb are,
639 however, 16 times higher in NWA 6693 (3.18 ppm) than in NWA 6704 (0.193 ppm).
640 Concentrations of Rb in pyroxene and plagioclase in both meteorites are approximately
641 proportional to the whole rock values, suggesting that the Rb concentrations were established
642 before crystallisation and are controlled by volatile loss before or during melting, rather than
643 by igneous crystal fractionation.

644 This difference in Rb concentrations between NWA 6693 and NWA 6704 raises the question
645 about the nature of the event that is responsible for the loss of highly volatile elements from
646 their parent body. A combination of volatile loss with the absence of fractionation of
647 refractory and moderately volatile elements (both lithophile and siderophile) is interpreted
648 by Hibiya et al. (2018) as evidence that the melting was caused by intensive rapid collision-
649 induced heating in an already hot planetesimal. Taking this scenario one step further in order
650 to explain the compositional difference between NWA 6693 and NWA 6704, we suggest that
651 the volatile loss occurred during collision that broke down the target body into many partially
652 molten fragments of various sizes. Smaller fragments were losing highly volatile elements
653 more rapidly. Re-assembly of these fragments produced a body that has uniform abundance
654 of refractory elements, but significant variations in abundances of highly volatile elements.
655 The absence of post-crystallisation shock features (Hibiya et al. 2018, Irving et al. 2011)

656 suggests that the body was re-assembled while the fragments were still hot and possibly
657 contained some melt. This scenario explains rapid cooling (of rock fragments) during early
658 stage of crystallisation that produced dendritic orthopyroxene crystals, followed by much
659 slower cooling (in the re-assembled body) below ~ 1373 K, as proposed by Hibiya et al.
660 (2018).

661 This scenario needs to be reconciled with the evidence from initial $^{87}\text{Sr}/^{86}\text{Sr}$ chronometry that
662 the parent body of NWA 6693/6704 accreted 1.0-2.5 Ma before the melting event that
663 produced the rocks. If the parent body had chondritic Rb/Sr ratio, or even supra-chondritic
664 Rb/Sr ratio such as measured in NWA 6693, then the loss of Rb (and other moderately volatile
665 elements) that is dated by the initial $^{87}\text{Sr}/^{86}\text{Sr}$ chronometer, and formation of the rocks that is
666 dated by Pb-isotopic system in pyroxene and ^{26}Al - ^{26}Mg and ^{53}Mn - ^{53}Cr mineral isochrons, were
667 caused by the same collision and occurred very close in time, so the readings of these
668 chronometers should be identical. The controversy is resolved if the parent body had lower
669 than chondritic Rb/Sr ratio due to initial volatile loss during accretion, and during collision
670 the volatiles were re-distributed rather than completely lost, causing high Rb/Sr in some of
671 the fragments including the parent rock of NWA 6693. In this case, the initial Sr chronometer
672 date is intermediate between the time of accretion and the time of the melting-inducing
673 collision.

674

675 **Conclusions**

676 Integrated data from this study and the companion papers by Hibiya et al. (2018) and
677 Sanborn et al. (2018) show that paired ungrouped achondrites NWA 6693 and NWA 6704 are
678 meteorites with broadly chondritic abundances of refractory and moderately volatile
679 elements and variable abundance of more volatile elements with 50% condensation
680 temperatures below 900 K. Their parent body formed under high oxygen fugacity from a
681 precursor with carbonaceous chondrite-like ^{54}Cr , ^{50}Ti , and ^{84}Sr isotopic affinity. Initial
682 $^{87}\text{Sr}/^{86}\text{Sr}$ data suggest that the parent body accreted 1.5 ± 2.1 Ma after CAI formation, and,
683 while still hot, experienced collision that caused fragmentation and melting at 4562.5-4562.8
684 Ma. After re-assembly and cooling, the parent body remained closed to migration of lithophile
685 and siderophile elements since then. Using U-Pb and Rb-Sr data obtained from the same
686 mineral fractions from these meteorites, we discuss various aspects of methodology of
687 achondrite studies including the ways of optimisation of sample preparation for the studies of

688 meteorites that involve multiple isotope chronometers with conflicting requirements
689 regarding acid leaching, and show that the leaching steps performed for removal of terrestrial
690 Pb for Pb-isotopic dating can be successfully recombined to undo the effects of elemental and
691 isotopic fractionation. The U-Pb, ^{26}Al - ^{26}Mg , ^{53}Mn - ^{53}Cr , ^{87}Rb - ^{87}Sr and ^{187}Re - ^{187}Os isotopic
692 systems show no evidence for post-crystallisation disturbance, whereas the ^{40}K - ^{40}Ar system
693 was reset at ~ 4.2 Ga by a thermal e.g., impact event and, partially re-set by a minor
694 disturbance at ~ 2.2 Ga. Owing to their geochemical closed system behaviour, and being
695 suitable for dating with many isotopic extinct and extant isotopic chronometers, NWA 6693
696 and NWA 6704 can serve as reference samples in the early Solar System chronometry as an
697 alternative or complement to rapidly crystallised angrites.

698

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705

706

707 **Figure captions**

708 Fig. 1. Pb-Pb isochron for acid-washed pyroxene fractions (residues after partial dissolution)
709 from NWA 6704. Fraction A049 8R, marked with black square, is excluded from regression.

710 Fig. 2. Effect of leaching in 0.5M HF on Pb-isotopic system in pyroxene fractions from NWA
711 6693. Batch A104 involved leaching in 0.5M HF (A104 W4) as a final washing step before
712 residue dissolution (A104 Residues). The pyroxenes in the batch A123 are analysed without
713 HF leaching.

714 Fig. 3. Pb-Pb isochron for third washes (A104 W3), re-combined fourth washes and residues
715 (A104 W4+R), and HNO₃, HCl cleaned (A123 R) pyroxene fractions from NWA 6693.

716 Fig. 4. Rb-Sr isochron for NWA 6693 and NWA 6704. Uncertainty bars of all analyses except
717 one (NWA 6693 olivine) are smaller than plotting symbols.

718 Figure 5. Apparent age (Ga) versus fraction of ³⁹Ar released for fragments #1 (black and grey
719 blocks) and #2 (dashed blocks). The plateau obtained for NWA 6704 #1 encompasses 100%
720 of the ³⁹Ar released corresponding to an age of 4.225±0.061 Ga. A later minor thermal event at
721 ≤2.121 Ma.

722 Fig. 6. Rb-Sr data for the NWA 6693 and NWA 6704 analysed without acid leaching, and
723 recombined data for acid leached NWA 6693 pyroxene.

724

725

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Table 1. Pb-isotopic data.

Analysis #	Mineral	Washing step	204/206 (total)	204/206 %err	207/206 (total)	207/206 %err	Error corr. 4/6-7/6	207*/206* Age (Ma)
NWA 6704								
A041_7R	Px	Residue	0.000487	66.9	0.625457	0.202	0.997	4562.13
A041_8R	Px	Residue	0.001075	27.3	0.628127	0.181	0.996	4562.20
A042_5R	Px	Residue	0.001375	23.5	0.629353	0.202	0.978	4561.91
A042_6R	Px	Residue	0.000182	90.8	0.624227	0.104	0.980	4562.46
A042_7R	Px	Residue	0.000352	124.0	0.625036	0.271	0.989	4562.56
A049_6R	Px	Residue	0.001167	18.4	0.628490	0.134	0.977	4562.08
A049_7R	Px	Residue	0.000460	62.9	0.625417	0.185	0.963	4562.32
A123 1R	Px	Residue	0.000221	43.4	0.624613	0.060	0.994	4562.95
A123 2R	Px	Residue	0.000852	11.3	0.627439	0.059	0.992	4562.94
A123 3R	Px	Residue	0.000141	71.2	0.624158	0.063	0.981	4562.73
UCD NWA 6704 3R	Px	Residue	0.000881	27.6	0.627172	0.168	0.998	4562.00
UCD NWA6704 6R	Px	Residue	0.000730	25.4	0.626553	0.128	0.998	4562.15
UCD NWA 6704 7R	Px	Residue	0.001010	32.4	0.627672	0.226	0.998	4561.81
NWA 6693								
A104 1W3	Px	Wash 3	0.004312	51.4	0.641677	1.330	0.997	4559.79
A104 2W3	Px	Wash 3	0.010745	48.4	0.669435	2.930	0.997	4556.66
A104 3W3	Px	Wash 3	0.001376	275.0	0.630893	2.300	0.998	4565.52
A104 1 W4+R recombined	Px	Recomb W4+R	0.000259	24.5	0.624842	0.041	0.968	4563.09
A104 2 W4+R recombined	Px	Recomb W4+R	0.001228	5.8	0.629274	0.045	0.974	4563.28
A104 3 W4+R recombined	Px	Recomb W4+R	0.000061	125.0	0.623745	0.049	0.975	4562.60
A123 6R	Px	Residue	0.000210	43.9	0.624397	0.057	0.995	4562.56
A123 7R	Px	Residue	0.000191	66.1	0.624402	0.078	0.995	4562.78
A123 8R	impure Px	Residue	0.000271	19.3	0.624703	0.033	0.993	4562.64

Table 2

Table 2. Summary of ⁴⁰Ar-³⁹Ar ages obtained for fragments #1 and #2 derived from age spectra, and normal and inverse isochrones show in in figures EA7-1 to EA7-4

NWA 6704 sub-fragment	Age Spectrum (Ga)	% ³⁹ Ar Release	Normal Isochron Age (Ga)	Inverse Isochron Age (Ga)
#1	4.232±0.033	88	4.222±0.110	4.199±0.032
#2	2.121±0.329*	-	4.125±0.300	4.291±0.058
Total Average Age (Ga)	4.340±0.287			

*Maximum age for a later partial re-setting event.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Electronic Annex 1_Methods

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Electronic Annex 2_Uranium 238_235
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