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

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Abstract

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

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

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

2. The meteorites

Four ungrouped achondrites with similar mineralogy and composition unlike those of any previously known achondrites were recovered from the dry deserts of north-western Africa between 2010 and 2015. Northwest Africa 6693 is a 5.1 kg ungrouped achondrite purportedly found in Morocco in 2010 (Meteoritical Bulletin no.99 April 2012). Its mineralogy and composition are described by Warren et al. (2013) and Jambon et al. (2012). Northwest Africa 6704 is a 8.39 kg achondrite found in Algeria (Meteoritical Bulletin no.99 April 2012). Mineralogy and petrology of NWA 6704 have been studied by Irving et al. (2011) and Hibiya (2016), and are discussed in detail in the companion paper by Hibiya et al. (2018). Many
similarities between these two meteorites suggest that they are paired (Warren et al. 2013). A smaller (220 g) group of specimens classified as NWA 6926 is very similar to the other two meteorites, and is thought to be a part of the original stone of NWA 6704 that was broken by the original finders and later reconstructed (Hupé 2011).

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

These meteorites have broadly chondritic abundances of lithophile elements with 50% condensation temperatures ($T_c$, Lodders 2003) above 900 K and only weakly fractionated patterns of highly siderophile elements, suggesting that the parental melt and precursor did not undergo significant segregation of metals, sulphides, or silicate minerals (Hibiya et al. 2018). Variable degrees of depletion in the elements with $T_c$ below 900 K relative to chondrites suggest partial loss of volatile elements during magmatism. These medium grained achondrites are composed mainly of large orthopyroxene oikocrysts and sodic plagioclase with elevated potassium content (~$\text{Ab}_{92}\text{An}_4\text{Or}_{4}$), and also contain less abundant olivine grains, and minor Cr-spinel, awaruite, and merrillite (Warren et al., 2013, Hibiya et al. 2018). These rocks are also dissimilar to other known achondrites in a number of other features: ferroan mafic silicate minerals with elevated FeO/MnO ratios and anomalously high Ni contents, very Ni-rich (75-81 wt.%)) metal. The latter features were interpreted as reflecting highly oxidised nature of chondritic precursor material that was preserved during melting (Warren et al. 2013). Their oxygen isotopic composition (Hibiya et al. 2018) plots within the field for acapulcoites-lodranites.

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

3. Analytical procedures

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

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

4. Results

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

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

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

Concentrations of U, Th (whenever measured) and Pb in acid leachates are reported relative to the sample weights prior to leaching. For three pyroxene fractions from NWA 6693 measured in the batch A104, we have also estimated the composition that the residue fraction would have if the last HF washing step (W4) was not applied. These values are denoted “W4+R recombined”. All analyses were checked for possible quality problems including accidental processing contamination (indicated by anomalously high blank), persistent interferences in mass spectrometry, anomalous mass fractionation, and low total ion yield. All data reported in the table are free from these problems. Discordance between the 238U/206Pb* and 207Pb*/206Pb* isotopic dates (U-Pb discordance column BZ) is calculated as 100 × [(exp((λ238U × Age207Pb*/206Pb*) − 1) − 206Pb*/238U/[exp((λ238U × Age207Pb*/206Pb*) − 1].

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

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

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

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

To determine the crystallisation age with minimum uncertainty due to the presence of two non-radiogenic Pb components, we used only pyroxene data points with blank-corrected
$^{206}\text{Pb}/^{204}\text{Pb} > 700$ (which corresponds to $^{204}\text{Pb}/^{206}\text{Pb} < 0.0014$, Table 1). Fourteen acid-washed pyroxene residues satisfy this requirement. “Robust” regression of these data yielded the age of 4562.65 ± 0.31/−0.36 Ma (EA4 sheet 3). Exclusion of one point that plots distinctly above the main set improves precision, and yields the “robust” regression with the radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ratio (y-intercept of the isochron) of 0.62354 ± 0.00009/−0.00012, corresponding to the age 4562.76 ± 0.22/−0.30 Ma (Fig. 1, and EA4 sheet 4). We consider this value the best age estimate for NWA 6704. No “conventional” isochrons could be calculated from these data. One pyroxene residue with $^{206}\text{Pb}/^{204}\text{Pb} > 700$, A049 8R, plots above the isochron for the other thirteen fractions. Similar but more pronounced excess of radiogenic $^{207}\text{Pb}$ is observed in all four plagioclase residues that plot above the Pb-Pb isochron for pyroxene residues (EA4 sheet 16). Elevated $^{207}\text{Pb}/^{206}\text{Pb}$ in these fractions can be related to the capture of radiogenic Pb with high $^{207}\text{Pb}/^{206}\text{Pb}$ that accumulated in merrillite grains early in the history of the parent body. Radiogenic Pb could have been leaking out of phosphate grains during cooling while the temperature of the rock was higher than the closure temperature for diffusion. Loss of radiogenic Pb from merrillite in a secondary event (e.g. shock metamorphism) is also possible, considering the young $^{40}\text{Ar}/^{39}\text{Ar}$ age of NWA 6704 (section 4.6). However, this possibility remains speculative because, to the best of our knowledge, there are no firm experimental data on response of the U-Pb isotopic system in merrillite to shock metamorphism.

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

Pb-isotopic data for NWA 6693 (EA2 sheets 5,6) are also dispersed. The isochron regression through all data passes close to the isotopic composition of primordial Pb which suggests that the relative contribution of terrestrial contamination to the Pb-isotopic systematics is much smaller than in the case of NWA 6704. Some of the most radiogenic Pb in NWA 6693 pyroxenes with $^{206}\text{Pb}/^{204}\text{Pb} > 700$ are contained in the 0.5M HF washes (W4) and residues after HF leaching in batch A104. However, comparison of Pb-isotopic systematics of HF washes and residues shows that the former have systematically higher $^{207}\text{Pb}/^{206}\text{Pb}$ at the same $^{204}\text{Pb}/^{206}\text{Pb}$ and hence higher $^{207}\text{Pb}^* /^{206}\text{Pb}^*$ model dates (EA4 sheet 7; Fig. 2), consistent with fractionation of radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ during partial dissolution in dilute HF which was
observed in CAIs, and pyroxenes in some other achondrites (Amelin et al. 2016). The difference between the average value of model dates calculated from W4 (4563.7±0.7 Ma, 2SD) and residues (4562.3±0.4 Ma) is 1.4±0.8 Ma, significantly larger than the uncertainties of individual dates.

In order to mitigate the fractionation induced by HF leaching and calculate the accurate age of NWA 6693, we numerically re-combined the W4 and residue data for each fraction. The \(^{207}\text{Pb}*/^{206}\text{Pb}*\) model dates of the recombined fractions are close to the data for NWA 6693 pyroxenes that were analysed in the batch A123 after leaching in HNO\(_3\) and HCl but without HF exposure (Fig. 2). Regressing together these re-combined points, third (hot HCl) washes of A104, and three pyroxene fractions of the batch A123, produced a “conventional” isochron with slight excess scatter (MSWD=3.8) and a y-intercept of 0.62346±0.00010, corresponding to the age of 4562.57±0.21 Ma (Fig. 3). “Robust regression” of the same data yielded the age of 4562.63±0.29/-0.21 Ma. The “conventional” and “robust” regressions are practically identical and have similar uncertainties. For consistency of isochron regressions between the two meteorites, we chose the “robust” age value as our best estimate of the age of NWA 6693. Including third (hot HCl) washes of A104 in these regressions is justified because of the absence of detectable terrestrial non-radiogenic Pb. Regressions without third washes yield identical results with slightly larger uncertainties (EA2 sheet 8a).

4.4 U-Pb system

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

4.5 \(^{87}\text{Rb-87Sr}\) and \(^{84}\text{Sr/86Sr}\)

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

Acid leaching of the pyroxene from NWA 6693 in HNO\(_3\) and HCl (leaching steps W1 and W2) removes only a small part of Sr and almost no Rb, whereas HF leaching (step W4) brings ~20-30% of these elements into solution.

The isochron plot for acid leached pyroxenes analysed in the batch A104 (leaching procedures for the samples in different batches are described in the Electronic Annex EA3) shows wide dispersion of data, and very radiogenic \(^{87}\text{Sr}/^{86}\text{Sr}\) up to 0.99 in some fractions (electronic annex EA5 sheet 2). Removing HF washes from the regression significantly decreases dispersion, and brings the isochron apparent age of 4665±360 Ma (MSWD=19) into agreement, within its large uncertainty, with the Pb-isotopic age of NWA 6693. The data for unleached minerals and whole rocks (batch A116) from both meteorites, shown in EA5 sheet 3 and in Fig. 4, display much smaller dispersion than the leaching steps of the pyroxenes. An isochron using all mineral fractions only yields the best regression with only a small excess scattering (MSWD=3.5), corresponding to an age of 4543±46 Ma and initial \(^{87}\text{Sr}/^{86}\text{Sr}\) of 0.699013±0.000055.
The $^{84}\text{Sr}/^{86}\text{Sr}$ ratios were measured in all unspiked aliquots, but only fractions with sufficiently large Sr content yielded data with usable precision. The average value from three fractions that contained over 100 ng Sr (NWA 6704 whole rock, and plagioclase fractions from both meteorites) yielded $\varepsilon(^{84}\text{Sr})=0.22\pm0.37$, indistinguishable from the reference value for the SRM 987 standard (EA5 sheet 4).

4.6 $^{40}\text{Ar}-^{39}\text{Ar}$ ages

$^{40}\text{Ar}-^{39}\text{Ar}$ ages are summarized in Tables EA6-1 and EA6-2, and plotted as an apparent age spectrum in Fig. 5. Complementary normal and inverse isochrons are reported in Fig. EA7-1 to EA7-5. Although petrographic studies identified voids/vesicles in pyroxenes (Irving et al., 2011; Jambon et al. 2012; Warren et al., 2013, Hibiya et al. 2018), during the argon extraction experiments there was no obvious release of trapped Ar gas by vesicle decrepitation. In fact, the normal and inverse isochron plots (Figures EA7-1 to EA7-4) show that the trapped/excess (i.e., non-radiogenic) $^{40}\text{Ar}$ content is negligible for all step heating releases; hence there is no need for data correction for this component. The variation in the $^{40}\text{Ar}/^{36}\text{Ar}$ in low-temperature steps are mainly from variable amount of solar wind $^{36}\text{Ar}$, whereas the high-temperature $^{36}\text{Ar}$ is mainly of cosmogenic origin. No terrestrial contamination was observed during the Ar step heating release or during the EMP/SEM work. The two $^{40}\text{Ar}-^{39}\text{Ar}$ spectra obtained from the two bulk samples largely overlap. Both spectra indicate a loss of a small portion of $^{40}\text{Ar}$ during a thermal event at $\leq2.12 \text{ Ga}$, which is more obvious in the low-temperature data for Fragment #2. A well defined age plateau is obtained for Fragment #1 over the intermediate and high-temperature steps, however the data for Fragment #2 are more dispersed and do not define a plateau.

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

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

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

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

With these two problems taken care of, and the precision of isochron dates (including uncertainty of $^{238}$U/$^{235}$U ratios but excluding uncertainty of the U isotope half-lives) of about 0.3-0.5 Ma, such as reported in this study, Pb-isotope chronology can resolve fine details in the magmatic history of asteroids. Still, Pb-Pb isochrons are imperfect, and dating of NWA 6704 and NWA 6693 show sides of this imperfection that need to be dealt with. The Pb-isotopic system of NWA 6704 is complicated by the presence of initial Pb and terrestrial contamination Pb in comparable quantities. Passing of the preferred isochron defined by isotopic data for the residues between the points of primordial and modern terrestrial Pb (EA2 sheet 4) shows that the step leaching greatly reduced the total content of non-radiogenic Pb, but did not completely eliminate either of the two non-radiogenic Pb components. The age of 4562.76+0.22/-0.30 Ma (Fig. 1) can be considered reliable because it is solely based on highly radiogenic data and is therefore insensitive to the exact isotopic composition of residual non-radiogenic Pb. In NWA 6693, the content of terrestrial Pb is much lower and
does not pose a problem, but $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in highly radiogenic residues and W4 washes are fractionated by partial dissolution in HF. This fractionation was eliminated by numeric re-mixing of the W4 washes and residues at the data reduction stage (Amelin et al. 2016), that produces the data indistinguishable from those obtained without HF leaching (Fig. 2). The isochron date of 4562.63±0.29/−0.21 Ma based on re-combined HF washes and residues, regressed together with analyses of pyroxenes without HF washing is considered a reliable age. The ages of these meteorites are identical within uncertainty, and, assuming that they formed simultaneously, we could calculate their combined more “precise” age as the weight average of the two individual ages. However, we prefer a safer approach of treating them as different rocks with potentially different ages.

5.2 Open vs. closed isotopic systems

The question of open vs. closed system behaviour of the isotopic chronometers can be assessed by comparison between the readings of multiple chronometers applied to the same rocks and minerals. In response to secondary events that occurred long time after formation of the rocks, long-lived chronometers either yield younger isochron dates that reflect the timing of the secondary event (in case of complete resetting), or develop scattering or sometimes excess isochron slope (in case of partial resetting). Long-lived chronometer systems are insensitive to the secondary processes that occurred shortly after crystallisation. The $^{87}\text{Rb}-^{87}\text{Sr}$ age of 4543±46 Ma (section 4.5) and the $^{187}\text{Re}-^{187}\text{Os}$ age of 4576±250 Ma (Hibiya et al. 2018), are consistent, within their large uncertainties, with the U-Pb ages (section 4.6). Short-lived extinct radionuclide chronometers are, on the other hand, affected by both early and late disturbances. The extinct chronometer ages of NWA 6704: $^{26}\text{Al}-^{26}\text{Mg}$ age of 4563.13±0.27 Ma, and $^{53}\text{Mn}-^{53}\text{Cr}$ age 4562.17±0.76 Ma (Sanborn et al. 2018), calculated relative to the rapidly cooled angrite D’Orbigny, are indistinguishable from the Pb-isotopic age of NWA 6704. This consistency of ages is either an extremely unlikely coincidence, or evidence that the parent rocks of NWA 6693 and NWA 6704 remained closed to migration of both lithophile and siderophile elements since crystallisation and initial cooling of the parent rocks. The presence of a small excess of radiogenic $^{207}\text{Pb}$ in plagioclase and one pyroxene fraction is likely to be a result of early migration of radiogenic Pb that was lost from phosphate during post-magmatic cooling. No evidence of extensive migration of radiogenic Pb such as that recorded in Pb-isotopic systematics of eucrite minerals (Iizuka et al., 2016) have been found in NWA 6693 or NWA 6704.
On the other hand, the Ar-Ar system was reset at 4.20±0.03 Ga by an event that did not have any detectable impact on the other isotopic systems. The possible reasons of this open system behaviour are discussed in the following section in the context of post-magmatic cooling.

5.3 The rate of post-magmatic cooling

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

The Ar-Ar system can also be used for assessment of post-magmatic cooling, if it can be demonstrated that the age resetting was not caused by a impact-related shock. The ^40Ar^39Ar age of NWA 6704 suggests a possible thermal event at ~4.2 Ga when the K-Ar isotopic system was completely reset. This thermal event, which is not matched by any evidence of shock deformation (Hibiya et al. 2018), is also interpreted as the reason why the vesicles within this sample are empty. The K-Ar system in feldspars and orthopyroxenes closes below the temperature range of 573–873 K, respectively (Cassata et al., 2009, 2011), which is similar to, or lower than the closure of Pb diffusion in merrillite. The rates of Ar diffusion (and hence the temperature of the age resetting) in feldspars strongly depend on composition, structural state, and microstructural characteristics. Albitic plagioclase, such as the mineral that hosts most K in NWA 6704, can be particularly prone to low-temperature (down to 473K) loss of radiogenic argon due to low-temperature structural changes (Cassata and Renne 2013).
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 \(^{40}\text{Ar} - ^{39}\text{Ar}\) 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.
Isotopic clocks in meteorites can be affected by elemental and, in some cases, isotopic fractionation caused by natural processes that occur on the asteroids (e.g. metamorphism, alteration and impacts), by terrestrial weathering, or by cleaning procedures that are intended to remove the products of these natural secondary processes. Acid leaching / partial dissolution, in particular, is considered indispensable for removing non-radiogenic Pb, and it is indeed efficient in most cases except the most stubborn ones (e.g. Merle and Amelin 2016), but preferential dissolution of radiogenic Pb compared to U (or vice versa) that commonly occurs in step leaching rendering the U-Pb system discordant, although the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios from step leachates and residues, plotted in a concordia diagram, can still be used to test whether the minerals experienced multi-stage U-Pb evolution (Chen and Papanastassiou 2008, Amelin et al. 2009). Such tests, however, can be reasonably reliable only for analyses with small amount of non-radiogenic Pb.

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

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

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

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

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

To use a certain ESS material (e.g. achondrite) as an age reference, we require evidence that the initial abundances of short-lived radionuclides in its source are representative of the Solar System, or at least in the ESS domain that is being studied. Comparing multi-chronometer data from several well preserved achondrites derived from different parent asteroids would be useful in a search for possible heterogeneities in the distribution of short-lived radionuclides in the accreting solar protoplanetary disk (Yin et al. 2017). Since NWA 6704 and 6693 show “carbonaceous chondrite” type Ti-Cr-Sr isotope affinity and can be considered as derived from outer Solar System, they allow us to better understand the distribution of short-lived nuclides between the inner and outer Solar System.
High K/Ca and Rb/Sr ratios in NWA 6693/6704, particularly in pyroxene and olivine, together with well-preserved closed geochemical systems, and rapid formation and cooling confirmed by consistency of the short-lived $^{26}\text{Al}-^{26}\text{Mg}$ and $^{53}\text{Mn}-^{53}\text{Cr}$ chronometers suggest that these meteorites may be suitable for $^{40}\text{K}-^{40}\text{Ca}$ vs. $^{87}\text{Rb}-^{87}\text{Sr}$ vs. U-Pb half-life comparisons, subject to better understanding of behaviour of the Ar-Ar system at the mineral level, and a detailed study of the history of low-temperature secondary processes. NWA 6693 and NWA 6704 are among the samples included in our ongoing half-life determination study.

5.6 The prospect of measuring the timing of parent body accretion

U-Pb, $^{87}\text{Rb}-^{87}\text{Sr}$, $^{26}\text{Al}-^{26}\text{Mg}$ and $^{53}\text{Mn}-^{53}\text{Cr}$ dates reported here and by Sanborn et al. (2018) refer to the time readings between crystallisation of the parent rocks of NWA 6693/6704 and closure of the isotopic clocks to diffusion during cooling shortly after. The timing of the accretion of their source asteroid is a different matter: it can be anywhere between the time of formation of the Solar System's first solids, and the age of the parent body of the meteorites. Accretion can be dated only indirectly because it does not produce chemical fractionation that can be uniquely linked to this event (Amelin and Ireland 2013), but several indirect (and variably model dependent) approaches to dating accretion have been proposed. For example, the timing of accretion of the chondrite parent bodies is bracketed between the age of the youngest chondrules and the age of the oldest post-accretional secondary minerals (e.g. fayalite, Ca phosphates). For achondrites several other approaches, each with its own set of model assumptions, can be used to bracket the time of accretion. The timing of mantle differentiation, which can be interpreted as solidification of the primary magma ocean, can be determined from whole rock $^{26}\text{Al}-^{26}\text{Mg}$ and $^{53}\text{Mn}-^{53}\text{Cr}$ isochrons constructed with meteorites that are thought to be derived from the same parent body, and yields the younger limit of the timing of accretion. Using these mantle differentiation ages and(or) metal-silicate separation ages (e.g. from $^{182}\text{Hf}-^{182}\text{W}$ systematics), estimating the temperatures of mantle differentiation and core formation, and applying a suitable thermal model that involves $^{26}\text{Al}$ decay as a heat source (e.g. Bizzarro et al. 2005, Hevey and Sanders 2006), one can estimate the timing of accretion (Sugiura and Fujiya 2014). The time of accretion calculated with this approach depends on correct estimation of the size and thermal properties of asteroids, and on the assumptions about distribution of $^{26}\text{Al}$ (homogeneous vs. heterogeneous) in the ESS.
An alternative approach, pioneered by Papanastassiou and Wasserburg (1969), uses initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio to estimate the timing of separation of the low-Rb/Sr achondrite precursor material from high-Rb-Sr solar nebula (Halliday and Porcelli 2001). This approach, sometimes referred to as initial Sr chronometry, relies on the assumptions about the processes in which volatility-induced differentiation in the nebula took place (condensation or melting; chondrule-size, asteroid-size, or intermediate), but is free from assumptions involved in the accretion time estimates based on thermal evolution of asteroids described above. The estimates of the time of accretion based on consistent values from these two approaches should be considered the most reliable.

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

5.7 $^{84}\text{Sr}$ and cosmochemical affinity of NWA 6693 and NWA 6704

The average $^{84}\text{Sr}/^{86}\text{Sr}$ measured in NWA 6693 and NWA 6704 plagioclase and whole rock is identical, within uncertainty, to the value in the SRM 987 standard, and corresponds to $\varepsilon^{(84}\text{Sr})$ of 0.22±0.37 relative to SRM 987. However, SRM 987 has distinctly higher $^{84}\text{Sr}/^{86}\text{Sr}$ than terrestrial igneous rocks by ~ 0.25 $\varepsilon^{(84}\text{Sr})$ units (Moynier et al. 2012, Paton et al. 2013, Yokoyama et al. 2015). Considering this difference, NWA 6693 and NWA 6704 show a ~0.47±0.37 $\varepsilon^{(84}\text{Sr})$ units excess relative to terrestrial igneous rocks, similar to the slight excesses of $^{84}\text{Sr}$ reported for carbonaceous chondrites. This result is consistent with the carbonaceous chondrite affinity of NWA 6693 and NWA 6704 established from $\Delta^{17}\text{O}$, $^{54}\text{Cr}$ and $^{50}\text{Ti}$ isotope systematics (Sanborn et al. 2018, Hibiya et al. 2018). Possible use of the $^{84}\text{Sr}$ data
for NWA 6693 and NWA 6704 for more detailed identification of the meteorite sources and
the study of heterogeneity of the solar protoplanetary disk would require additional, more
precise, analyses of plagioclase fractions that can be done in conjunction with refinement of
the initial $^{87}\text{Sr}/^{86}\text{Sr}$ chronometry.

5.8 Petrogenetic implications of variable volatile depletion

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

This difference in Rb concentrations between NWA 6693 and NWA 6704 raises the question
about the nature of the event that is responsible for the loss of highly volatile elements from
their parent body. A combination of volatile loss with the absence of fractionation of
refractory and moderately volatile elements (both lithophile and siderophile) is interpreted
by Hibiya et al. (2018) as evidence that the melting was caused by intensive rapid collision-
induced heating in an already hot planetesimal. Taking this scenario one step further in order
to explain the compositional difference between NWA 6693 and NWA 6704, we suggest that
the volatile loss occurred during collision that broke down the target body into many partially
molten fragments of various sizes. Smaller fragments were losing highly volatile elements
more rapidly. Re-assembly of these fragments produced a body that has uniform abundance
of refractory elements, but significant variations in abundances of highly volatile elements.
The absence of post-crystallisation shock features (Hibiya et al. 2018, Irving et al. 2011)
suggests that the body was re-assembled while the fragments were still hot and possibly contained some melt. This scenario explains rapid cooling (of rock fragments) during early stage of crystallisation that produced dendritic orthopyroxene crystals, followed by much slower cooling (in the re-assembled body) below ~1373 K, as proposed by Hibiya et al. (2018).

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

**Conclusions**

Integrated data from this study and the companion papers by Hibiya et al. (2018) and Sanborn et al. (2018) show that paired ungrouped achondrites NWA 6693 and NWA 6704 are meteorites with broadly chondritic abundances of refractory and moderately volatile elements and variable abundance of more volatile elements with 50% condensation temperatures below 900 K. Their parent body formed under high oxygen fugacity from a precursor with carbonaceous chondrite-like $^{54}\text{Cr}$, $^{50}\text{Ti}$, and $^{84}\text{Sr}$ isotopic affinity. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ data suggest that the parent body accreted 1.5±2.1 Ma after CAI formation, and, while still hot, experienced collision that caused fragmentation and melting at 4562.5-4562.8 Ma. After re-assembly and cooling, the parent body remained closed to migration of lithophile and siderophile elements since then. Using U-Pb and Rb-Sr data obtained from the same mineral fractions from these meteorites, we discuss various aspects of methodology of achondrite studies including the ways of optimisation of sample preparation for the studies of
meteorites that involve multiple isotope chronometers with conflicting requirements regarding acid leaching, and show that the leaching steps performed for removal of terrestrial Pb for Pb-isotopic dating can be successfully recombined to undo the effects of elemental and isotopic fractionation. The U-Pb, $^{26}$Al-$^{26}$Mg, $^{53}$Mn-$^{53}$Cr, $^{87}$Rb-$^{87}$Sr and $^{187}$Re-$^{187}$Os isotopic systems show no evidence for post-crystallisation disturbance, whereas the $^{40}$K-$^{40}$Ar system was reset at ~4.2 Ga by a thermal e.g., impact event and, partially re-set by a minor disturbance at ~2.2 Ga. Owing to their geochemical closed system behaviour, and being suitable for dating with many isotopic extinct and extant isotopic chronometers, NWA 6693 and NWA 6704 can serve as reference samples in the early Solar System chronometry as an alternative or complement to rapidly crystallised angrites.

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**Figure captions**

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

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

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

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

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

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


Table 1. Pb-isotopic data.

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<th>207/206 (total)</th>
<th>%err</th>
<th>4/6-7/6</th>
<th>Age (Ma)</th>
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<td>A042_7R</td>
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<td>0.625036</td>
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<td>0.989</td>
<td>4562.56</td>
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<td>A049_6R</td>
<td>Px</td>
<td>Residue</td>
<td>0.001167</td>
<td>18.4</td>
<td>0.628490</td>
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<td>Px</td>
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<td>0.000460</td>
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<td>0.625417</td>
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<td>0.000221</td>
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<td>0.624613</td>
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<td>0.000852</td>
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<td>Residue</td>
<td>0.000141</td>
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<td>0.624158</td>
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<td>UCD NWA 6704 3R</td>
<td>Px</td>
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<td>0.000881</td>
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<td>UCD NWA 6704 7R</td>
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<td>0.001010</td>
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<td>0.627672</td>
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<td>4561.81</td>
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<td><strong>NWA 6693</strong></td>
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<tr>
<td>A104 1W3</td>
<td>Px</td>
<td>Wash 3</td>
<td>0.004312</td>
<td>51.4</td>
<td>0.641677</td>
<td>1.330</td>
<td>0.997</td>
<td>4559.79</td>
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<tr>
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<td>Px</td>
<td>Wash 3</td>
<td>0.010745</td>
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<td>Wash 3</td>
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<td>Recomb W4+R</td>
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<td>Recomb W4+R</td>
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<td>Recomb W4+R</td>
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<td>Residue</td>
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<td>Residue</td>
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<td>A123 8R</td>
<td>impure Px</td>
<td>Residue</td>
<td>0.000271</td>
<td>19.3</td>
<td>0.624703</td>
<td>0.033</td>
<td>0.993</td>
<td>4562.64</td>
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Table 2. Summary of $^{40}$Ar-$^{39}$Ar ages obtained for fragments #1 and #2 derived from age spectra, and normal and inverse isochrones show in figures EA7-1 to EA7-4

<table>
<thead>
<tr>
<th>NWA 6704 sub-fragment</th>
<th>Age Spectrum (Ga)</th>
<th>%$^{39}$Ar Release</th>
<th>Normal Isochron Age (Ga)</th>
<th>Inverse Isochron Age (Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>4.232±0.033</td>
<td>88</td>
<td>4.222±0.110</td>
<td>4.199±0.032</td>
</tr>
<tr>
<td>#2</td>
<td>2.121±0.329*</td>
<td>-</td>
<td>4.125±0.300</td>
<td>4.291±0.058</td>
</tr>
<tr>
<td>Total Average Age (Ga)</td>
<td>4.340±0.287</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Maximum age for a later partial re-setting event.
Figure 1

NWA 6704
Pyroxene residues
$^{206}\text{Pb}/^{204}\text{Pb}>700$,
one point excluded

Robust Regression (~95% conf.) n=13
Age = 4562.76 $\pm$0.22/-0.30 Ma
Slope = 4.21 $\pm$0.13/-0.17
Intercept = 0.62354 $\pm$0.000087/-0.00012
$^{238}\text{U}/^{235}\text{U}=137.778\pm0.0097$
NWA 6693 Pyroxene
A104 W3 and recombined W4+R
A123 R

Model 1 Solution (±95%-conf.) on 9 points
Age = 4562.57±0.26 Ma
w. decay-const errs: (±6.9 Ma)
Slope = 4.74±0.21 (95% conf)
Inter = 0.62346±0.00010
Xbar = 0.000355958, Ybar = 0.625147
MSWD = 3.8, Probability = 0.000
$^{238}\text{U}/^{235}\text{U}=137.7784±0.0097$

Robust regression (~95% conf.) 9 points
Age = 4562.63 ±0.29/-0.21 Ma
Slope = 4.34 ±0.73/-0.13
Intercept = 0.623485 ±0.00012/-0.000080
$^{238}\text{U}/^{235}\text{U}=137.7784±0.0097$
Batch A116: fractions of NWA 6693 and NWA 6704 analysed without acid leaching

Symbol coding:
White: NWA 6693 minerals
Grey: NWA 6704 minerals
Black: NWA 6693 and 6704 whole rocks

Minerals and whole rocks: 4501±71 Ma
Initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.69903±0.00010$
MSWD = 21

Minerals only: 4543±46 Ma
Initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.699013±0.000055$
MSWD = 3.5
Plateau age = 4.232 ± 0.033 Ga (2σ) incl. J-err. of 0.208239%
MSWD = 1.7, prob. = 0.13 incl. 88% of the 39Ar

≤ 2.121 Ga (maximum age for a later thermal event)
Figure 6

Symbol coding:
- White squares: A116 NWA 6693 minerals
- Grey squires: A116 NWA 6704 minerals
- Black circles: A104 NWA 6693 pyroxene recombined

A116 only: 4543±46 Ma
Initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.699013±0.000055$
MSWD = 3.5

A116+recombined A104: 4543±30 Ma
Initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.699013±0.000036$
MSWD = 2.2
Electronic Annex 4 _U-Pb
Click here to download Electronic Annex: EA4_UPb data+plots_v11.xls