Improved methods for high-precision Pb-Pb dating of extra-terrestrial materials

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Abstract

Dating meteoritic materials by the Pb-Pb isochron method depends on constructing linear arrays typically defined by mixtures of initial and radiogenic Pb after the removal of terrestrial contaminant Pb. The method also depends on minimizing the amount of laboratory Pb blank added to the sample during processing and analyses. With the aim to analyze smaller sample sizes and decrease processing times, we have devised a new method for the construction of isochrons using the stepwise dissolution of meteoritic materials that better defines reduced amounts of Pb blank, reduces the risk of random anomalous Pb contamination, and increases sample throughput. Samples are processed in a PFA Teflon™ pipette tip fitted with a frit inside a heated, sealed chamber that can be manually over-pressured to expel reagents directly into a PFA Teflon™ vial below. With four independent chambers, three samples can be processed simultaneously with a fourth position to assess the Pb contribution of the combined blank and spike for each step. The matched blank-spike Pb for each step provides a specific blank estimate for each step that ensures a more accurate correction for non-sample Pb and, therefore, reduces the uncertainty on each analysis. We assess the performance of this new method by reporting the results of dating a fragment of a chondrule from the well-characterized CBa chondrite Gujba and compare these results with previously published data for this meteorite. The improvements reduce the minimum sample sizes that can be successfully dated by the Pb-Pb method, an important development for size-limited materials such as small chondrules and samples returned from space missions.

Introduction

The successful dating of chondrules by the Pb-Pb method requires parsing Pb into different aliquots representing more and less radiogenic compositions to define an isochron, by either processing different mineral fractions or by progressive dissolution (Connelly and Bizzarro, 2009; Connelly et al., 2012; Connelly et al., 2017). A ubiquitous laboratory Pb blank that is necessarily subtracted from each aliquot must be small relative to the sample Pb and reproducible for an accurate correction of each aliquot.

The progressive dissolution method employs a range of acids and acid strengths that preferentially dissolves different phases to define an isochron (Connelly and Bizzarro, 2009). This has traditionally required transferring the supernate from each dissolution step by a pipette into a Teflon™ vial for further processing, with inherent risk that Pb blank may be added in this step and that some suspended solid material may be transferred with the acid and any subsequent rinses.

The amount of laboratory blank attributed to each aliquot is approximated by processing several blank samples with each chondrule processed. Without mimicking the pipette transfer step, this method typically evaluates blank added during chemical purification and mass spectrometry but this does not take into account the dissolution step and initial transfer of each aliquot. A set amount of Pb blank is assigned to this part of the procedure based on the initial development of the method (Connelly and Bizzarro, 2009). Inappropriate blank correction will have the effect of scattering points that should have plotted in a linear fashion along a true isochron. Randomly higher or lower than predicted blanks for a low number of fractions may still leave enough points to define the isochron but is inelegant in that points that may have helped define the isochron and reduce the final age uncertainty are rejected. Besides the concern for random blanks, different acids used in the progressive dissolution may have different Pb blanks or have the capacity to leach different amounts of Pb from Teflon™ vials.

We have devised a method that better quantifies the actual Pb blank for each aliquot while reducing the amount of sample handling and the potential for undissolved solid material to be included in the transfer (Connelly and Bizzarro, 2009). The reduced sample handling has lowered the Pb blank for each aliquot and made the amount of blank more consistent from aliquot to aliquot. The new method also increases sample throughput as three samples and one set of blanks can now be processed simultaneously through the stepwise dissolution process.

Uranium-Corrected Pb-Pb Dating

The U-Pb decay system: Lead has four naturally occurring isotopes, [204]Pb, [206]Pb, [207]Pb and [208]Pb, that were inherited from the molecular cloud parental to our Solar System in relative abundances that have been estimated using troilite from the Type IAB Canyon Diablo iron meteorite that contains negligible amounts of U (Tatsumoto et al., 1973). All Pb isotopes except [204]Pb have increased their abundances through the radioactive decay of [238]U, [235]U and [232]Th. Only [204]Pb preserves its primordial abundances such that the radiogenic ingrowth of Pb isotopes is most conveniently expressed as [206]Pb/[204]Pb, [207]Pb/[204]Pb and [208]Pb/[204]Pb ratios that evolved according to the general equation:

$$\left(\frac{^{20x}Pb}{^{204}Pb}\right)_{today} = \left(\frac{^{20x}Pb}{^{204}Pb}\right)_{t} + \left(\frac{^{23z}U, {}^{232}Th}{^{204}Pb}\right)_{today} \left(e^{\lambda t} - 1\right), \qquad Eq.\,1$$

where t represents the time before present and λ represents the decay constant of the parent isotope. In objects with only initial Pb (Pb$_i$) and radiogenic Pb (Pb$_r$) present, this permits the theoretical possibility of calculating three independent ages based on the [235]U-[207]Pb, [238]U-[206]Pb and [232]Th-[208]Pb. However, only the two U isotopes have decay constants large enough to provide ages for chondrules with errors of less than 1 Myr. Pre-cleaning of all chondrules is required to remove ubiquitous modern terrestrial Pb contamination, an action that may fractionate U/Pb ratios rendering Eq. 1 ineffective for determining ages. To circumvent the uncertainty of the U/Pb ratio, we employ the dual decay of the U-Pb system that results in unique radiogenic [207]Pb/[206]Pb ratios for different times in the past, by combining the two equations:

$$\left(\frac{^{207}Pb}{^{204}Pb}\right)_{today} = \left(\frac{^{207}Pb}{^{204}Pb}\right)_{t} + \left(\frac{^{235}U}{^{204}Pb}\right)_{today} \left(e^{\lambda_1 t} - 1\right), \qquad Eq.\,2$$

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)_{today} = \left(\frac{^{206}Pb}{^{204}Pb}\right)_{t} + \left(\frac{^{238}U}{^{204}Pb}\right)_{today} \left(e^{\lambda_2 t} - 1\right), \qquad Eq.\,3$$

to derive:

$$\left[\frac{\left(\frac{^{207}Pb}{^{204}Pb}\right)_{today} - \left(\frac{^{207}Pb}{^{204}Pb}\right)_{t}}{\left(\frac{^{206}Pb}{^{204}Pb}\right)_{today} - \left(\frac{^{206}Pb}{^{204}Pb}\right)_{t}}\right] = \left(\frac{^{235}U}{^{238}U}\right)_{today} \left(\frac{e^{\lambda_1 t} - 1}{e^{\lambda_2 t} - 1}\right), \qquad Eq.\,4$$

where the left side of the equation equals the radiogenic ($^{207}Pb/^{206}Pb$) ratio [$(^{207}Pb/^{206}Pb)_r$] so that Eq. 4 can be reduced to:

$$\left(\frac{^{207}Pb}{^{206}Pb}\right)_{r} = \left(\frac{^{235}U}{^{238}U}\right)_{today} \left(\frac{e^{\lambda_1 t} - 1}{e^{\lambda_2 t} - 1}\right) \qquad Eq.\,5$$

Equation 5 forms the basis for determining ages based on radiogenic $^{207}Pb/^{206}Pb$ ratios, including those based on the "inverse Pb-Pb diagram" that plots $^{207}Pb/^{206}Pb$ vs $^{204}Pb/^{206}Pb$ ratios. In this construct, the y-intercept of the array corresponds to the Pb isotope composition that lacks ^{204}Pb and must, therefore, equal the radiogenic $^{207}Pb/^{206}Pb$ ratio. This approach works most effectively for highly-radiogenic systems where at least some points fall close to the y-axis, thus minimizing the extrapolation to and uncertainties in the calculation of the y-intercept. All chondrules dated by the Pb-Pb method employ the inverse Pb-Pb method such that the discussion that follows concentrates on this approach.

Defining a Pb-Pb age based on the $(^{207}Pb/^{206}Pb)_r$ ratio requires that any initial Pb incorporated into different phases had a single Pb isotopic composition, that the system remained closed and that the $^{238}U/^{235}U$ ratio is known for each individual sample (but not the U/Pb ratio). It is important to note that these requirements are common to all chronometric methods based on radiogenic isotopes and are, therefore, not unique to the Pb-Pb method of dating. Whether an individual sample adheres to these requirements can be tested by evaluating the linearity of the

data used to calculate ages. In some rare cases, the sample may not contain any initial Pb such that a pure $(^{207}Pb/^{206}Pb)_r$ component is directly measured. The widespread addition of tetraethyl Pb to gasoline for over 50 years has contaminated the Earth's surface (Patterson, 1965) and contributed to the near ubiquitous inclusion of terrestrial Pb in meteorites. As such, this component of Pb in meteorites must be recognized and, in the most general cases, be removed from the sample for meteoritic Pb isotopic measurements to provide accurate age information. For samples lacking initial Pb, an array defined by a binary mix of radiogenic Pb and terrestrial contaminant Pb will still extrapolate to the correct radiogenic Pb composition on the y-axis of an inverse Pb-Pb diagram.

Calculating an age based on Equation 5 requires knowledge of the $^{238}U/^{235}U$ ratio of the sample being dated. Previous work on meteorites has determined that variations in the $^{238}U/^{235}U$ ratio only exist in high temperature calcium-aluminium inclusions and that all other objects, including chondrules and achondrites, have a fixed value of 137.786±0.015 (Brennecka, 2015; Connelly et al., 2012).

Limitations with Existing Methods

With ion-counting TIMS analyses capable of measuring picogram levels of Pb with adequate precision for Pb-Pb dating of meteoritic materials (Connelly et al., 2017), the main limitation of existing methods becomes the amount and reproducibility of the laboratory blank Pb added to samples. The effect of three different blank assessments of 0.10, 0.25 and 0.50 pg with uncertainties of ±50% on an arbitrarily chosen analysis containing 90 pg of Pb is shown in Fig. 1. Since the isotopic composition of the laboratory blank typically plots near the isochrons of samples formed within 10 Myr of t_0 as defined by CAIs, all three points plot within their respective uncertainties on a model isochron of 4562 Ma (where the isochron is constrained by the primordial Pb composition of Tatsumoto et al., 1973). However, the size of the ellipse increases with decreasing sample/blank Pb ratios to an extent that the point corresponding to the larger blank correction no longer adequately constrains the isochron. The traditional method of assessing Pb blank was to repeatedly run full or partial procedural blanks alongside samples and to assign uncertainties based on long term reproducibility of these measured blanks. The result of this approach led to blank assignments in the order 0.250±0.125 pg (e.g. Connelly et al., 2012; Bollard et al., 2015; Bollard et al., 2017; Connelly et al., 2019).

A new approach was sought to reduce the amount of Pb added to each analysis and to improve the reproducibility of the blank contribution to allow for the analyses of smaller amounts of Pb and, consequently, smaller sample sizes. A collateral benefit would include faster processing times to allow for higher sample throughput.

A New Approach to the Stepwise Dissolution Method

We recognized two of the highest risk steps in the processing of samples by our existing methods as: 1) the Pb purification using columns arranged in a linear rack that was placed within a full size vertical laminar flow HEPA-filtered work box, and 2) the manual transfer of acids/reagents by pipette from the dissolution vial to the vial used to carry the sample forward through the ion-exchange chemistry steps.

The first issue was addressed by placing the columns in a carousel that was placed inside a small HEPA-filtered box with laminar flow from back to front. This results in the operators gloved hand being downwind of the columns at all times, reducing the risk of random particles falling into the column or vial below.

To avoid the transfer of different acids by pipette, a device was constructed so that the acid could be added to the sample for a prescribed length of time before being drained from the sample through a filter by remote control. This has the dual benefit of eliminating the need for working above the sample with a pipette and to reduce or minimize the inclusion of solids in the transfer. By processing a blank analysis in parallel with samples, it has a third advantage of being able to assess the contribution of Pb from the blank for each dissolution step so that an accurate correction can be made for each reagent used in the progressive dissolution.

The device (Figs. 2 and 3) represents four isolated chambers within a single machined block of PTFE Teflon™ where the pressure of each chamber can be individually controlled by a syringe connected to a valve manifold (Fig. 2). The base of the device is heated by a Teflon™ coated aluminium block containing two barrel heater elements. A constant temperature is maintained by an external controller connected to a thermocouple that is also embedded

within the aluminium block. The actual temperature of the sample chambers can be measured by an infrared thermometer.

A Savillex Corporation® PFA Teflon™ pipette tip fitted with a polypropylene frit in the bottom serves as the digestion vessel with the pipette tip tightly fitted in a hole in the base of the chamber. The hole in the base of the chamber is threaded so that the PFA Teflon™ pipette tip wound with two turns of Teflon™ plumbers tape can be screwed into position so that it forms an adequate seal. After the pipette tip is inserted in the chamber but before the sample is added, the pipette tip and frit are exposed to all the reagents used during the cleaning and stepwise dissolution procedure to minimize Pb blank contribution from this step.

A lightly-crushed, pre-cleaned sample is loaded onto the frit in the pipette tip at the start of the procedure and cleaned by cycling distilled water, ethanol and weak HBr that may be kept for analyses or discarded. If the initial washes are discarded, the last pre-cleaning steps are normally collected and processed to help understand the nature and amount of contaminant Pb present just before the dissolution procedure formally starts.

Each step comprises adding approximately 0.2 ml of a reagent to the sample and letting it stand for a prescribed length of time, after which the reagent is pushed out of the pipette tip and into a pre-cleaned 3 ml Savillex Corporation® PFA Teflon™ vial placed below the pipette by over-pressuring the chamber. After the reagent is expelled, 0.2 ml of H_2O is added to the sample and then expelled into the same vial. By completely emptying the pipette tip including the pore space within the frit, the next reagent will not pass through the frit until the chamber is over pressured again.

As with previous descriptions of this basic method (Connelly and Bizzarro, 2009), early steps of weak HBr, HNO_3 and HCl are designed to remove any remaining labile contaminant Pb from the sample but also will dissolve carbonate, sulphide and phosphate minerals that may be present in the sample. Each acid is left on the sample for between 5 to 80 minutes (see Table 1) before it is pushed through the frit into the clean Teflon™ vial.

To assess the Pb blank contribution in each dissolution aliquot, all steps can be mimicked in an adjacent chamber containing an identical pipette tip fitted with a frit but without a sample so that any variation in the Pb blank contribution from different acids can be assessed.

Combining the Subtraction of Pb in the Blank and Spike

Standard procedures for isotope dilutions using the artificial equal atom ^{202}Pb-^{205}Pb double spike (with trace amounts of ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) involve determining the isotope compositions of both the spike and blank Pb independently, so that naturally-occurring isotopes in these components can be subtracted separately from the total amount of Pb to determine the residual sample Pb. While the amount of spike added can be volumetrically or gravimetrically measured for this purpose, this method requires that the estimated blank is well calibrated and consistent for all the dissolution steps.

Since the new method allows for a step-by-step assessment of the blank contribution, adding the same known amount of spike to each sample and blank step, the non-sample Pb correction scheme can be simplified by treating the spike and blank Pb as one component. We refer to this combined Pb as "blank-spike Pb". Measuring the composition of the blank-spike Pb for each dissolution step precludes the need to assume the blank amounts and their isotopic composition and requires only that the ^{202}Pb/^{205}Pb ratio is well characterized in the spike but not the relative abundances of naturally occurring isotopes. The disadvantage of this method is the faster rate of consumption of the ^{202}Pb/^{205}Pb double spike of which there is a limited supply available. However, after initial characterization of the reproducibility of the Pb blank, only 1 blank per step for every 3 samples will be processed, resulting in a modest 25% greater consumption of the spike. The benefit will be more reproducible and, therefore, more accurate blank-spike corrected Pb isotope data leading to a greater number of steps defining isochrons and increased confidence in the age.

Assessing the Reproducibility of the Blank-Spike Pb Contribution

We use the measured isotope ratios of naturally-occurring Pb isotopes relative to ^{205}Pb in the blanks to assess the total amount of non-sample Pb in each dissolution step. The measured uncertainties of the ^{205}Pb/^{206}Pb, ^{205}Pb/^{207}Pb, ^{205}Pb/^{208}Pb ratios are typically less than 0.25%

whereas the uncertainty of the ^{205}Pb/^{204}Pb is typically higher but below 1%. However, it would be unrealistic to use these measured uncertainties in the calculation of any single dissolution step to represent the variability of blank-spike Pb between the blank and sample. To assess this variability, we have processed 16 blank-spike analyses with a single acid (2M HCl) in four sets of four columns. All 16 blank-spike aliquots were passed through a full chemistry session and run in sequence on outgassed, zone-refined Re filaments on a single turret. Table 2 reports the isotope ratios of the 16 analyses as well as their coefficients of variability (see below). One analyses with a Pb content of 1.03 pg is a clear outlier and has been excluded in the calculation of the reproducibility of these ratios. This is justified as the occurrence of a significant outlier in the blank-spike determination for an analysis of an actual sample would result in that dissolution step falling off of the isochron and being excluded from the age calculation. As a result, the uncertainties of the remainder of the dissolution steps should not be inflated for the sake of an outlier that would not be used in the final age calculation.

To assess the variability of the spike-blank compositions, we subject the isotopic ratio measurements of the 15 blank-spike measurements to a logarithmic transformation. This removes the positive skewness of the frequency distributions and produces a multivariate normal distribution of logratios (Figure 4). The 15 sets of logratio measurements are strongly correlated ($\rho > 0.99$), except for ^{202}Pb/^{205}Pb, which is only weakly correlated ($\rho < 0.3$) with the other logratios. Taking the square root of the diagonal elements of the covariance matrix reveals that the ^{202}Pb/^{205}Pb, ^{204}Pb/^{205}Pb, ^{206}Pb/^{205}Pb, ^{207}Pb/^{205}Pb and ^{208}Pb/^{205}Pb-ratios exhibit coefficients of variation of 0.11%, 15.4%, 19.9%, 20.5% and 20.7%, respectively. All but the ^{202}Pb/^{205}Pb error are much greater than the $< 1\%$-level analytical precision of the mass spectrometer measurements. In other words, the spike-blank measurements are overdispersed with respect to the analytical uncertainties. To capture the reproducibility of the blanks, we use the full covariance matrix of the replicate blank measurements as the basis of the error propagation. The corresponding (geometric) mean spike-blank composition is as follows: ^{204}Pb=0.0052 pg, ^{206}Pb=0.069 pg, ^{207}Pb=0.059 pg and ^{208}Pb=0.144 pg, with coefficients of variation of 15.4, 19.9, 20.5 and 20.7%, respectively. This corresponds to an average total Pb amount in the spike-blank mixtures of 0.16 pg with a 20.3% coefficient of variation.

Assigning Uncertainties on Individual Analyses

Given the excellent fit of the blank data to a multivariate lognormal distribution (Figure 4), the rest of the data reduction and error propagation is also carried out in logratio space. In this respect, our data reduction software (which can be accessed from https://github.com/pvermees/PbPbRedux/) is similar to the algorithms of Vermeesch (2015). After taking logarithms, the data are free to range from $-\infty$ to $+\infty$, thereby fulfilling an important requirement for the application of standard error propagation techniques, which require Gaussian residuals. Mass-dependent fractionation is corrected using the kinetic fractionation factor of Young, Galy, and Nagahara (2002):

$$\frac{(^{x}Pb/^{z}Pb)_{corrected}}{(^{x}Pb/^{z}Pb)_{measured}} = \left[\frac{(^{y}Pb/^{z}Pb)_{true}}{(^{y}Pb/^{z}Pb)_{measured}}\right]^{\frac{\ln(x)-\ln(z)}{\ln(y)-\ln(z)}}$$

Note that this exponential expression becomes linear after taking logarithms. This is another advantage of the logratio approach (McLean 2014; Vermeesch 2015). Error propagation is done by conventional first order Taylor approximation, using the full covariance matrix of the sample and spike-blank measurements. For the spike-blanks, this matrix is obtained from replicate measurements as explained in the previous section. For the samples, it is assumed that the analytical uncertainties faithfully reflect the residuals. Any violation of this assumption would be reflected in the scatter around the best fit isochron.

The strong error correlations of the spike-blank (log)ratios carry forward through the data processing chain and cause the blank-corrected sample compositions to be correlated as well. These correlated uncertainties manifest themselves as inclined error ellipses in isochron space. Error correlations are the strongest for dissolution steps that are poor in Pb and, therefore, require relatively large blank corrections. For Pb-rich aliquots, where the blank correction is smaller, the error ellipses are less steeply inclined.

Assessing the New Procedure – Analyses of a Gujba Chondrule

To assess this new method, we have processed a 59.1 mg fragment of a chondrule from the CBa chondrite Gujba. This sample has the advantages of having been well studied using the Pb-Pb method (Krot et al. 2005; Bollard et al, 2015) and containing chondrules presumed to represent a single age, the latter attributed to their coeval formation after a planetesimal collision. Our previous study of this meteorite returned a combined Pb-Pb age for chondrule formation of 4562.49±0.21 Ma that is based on the pooled age of four individual chondrules. It was determined that these four chondrules lack initial Pb such that the array in [204]Pb/[206]Pb

vs ^{207}Pb/^{206}Pb space defining the radiogenic ^{207}Pb/^{206}Pb age regresses to a terrestrial contamination Pb composition that corresponds to the region of discovery in Nigeria (Bollard et al, 2015). We have processed a lightly-crushed fragment of a chondrule from Gujba to assess the efficiency of our revised step-wise dissolution procedure. The chemical separation of Pb from the matrix elements as well as the details of thermal ionization mass spectrometry are described in Appendix 1.

Using the new method that includes linked blank-spike analyses results in 10 of 13 dissolution steps (including the residue; Table 1) forming an isochron (MSWD = 2.0) corresponding to an age of 4562.64±0.13 Ma (95% confidence interval), consistent with ages for four chondrules reported by Bollard et al. (2015; Fig. 5 and 6). As predicted in the previous section, the ^{207}Pb/^{206}Pb and ^{204}Pb/^{206}Pb ratio uncertainties are strongly correlated. Some of this correlation is due to the fact that they share a common denominator, but most of it is caused by the blank-spike correction. Ignoring these error correlations in the isochron regression would result in a loss of precision and accuracy.

The isochron projects through a similar isotopic composition of terrestrial contamination Pb that corresponds to environmental Pb in Nigeria. As with previous reports of stepwise dissolution methods (Connelly and Bizzarro, 2009; Merle et al., 2020), the early steps of HF results in the highest or most-radiogenic ^{206}Pb/^{204}Pb ratios. In fact, the 2nd, 3rd and 4th steps using HF represent the highest measured raw ^{206}Pb/^{204}Pb ratios than any previous attempt to date Gujba chondrules using the traditional method (Bollard et al., 2015). This confirms that the new method successfully parses Pb from a meteoritic component at least as effectively as pre-existing methods while minimizing the manual manipulation of the sample during stepwise dissolution.

A solid residue left after the final dissolution step was subsequently removed and fully dissolved on a hotplate using a mixed HF-HNO3 solution (3:1 mixture) to assess the amount of Pb remaining (Fraction R, Table 2). Approximately 10% of the total Pb remained in the residue, with an Pb isotope composition that plots on the isochron defined by the former stepwise dissolution steps. This concordancy suggests that Pb isotopes are not being fractionated during the progressive dissolution.

The amount of Pb released in each dissolution step is commensurate with those reported in Bollard et al. (2015), when normalized to the sample size. The total amount of blank-spike Pb for each digestion step and the two stage chemistry ranged from 0.12 to 0.23 pg with two higher values at 0.60 (L4) and 0.68 pg (R), respectively. The (geometric) mean of the blank-spike Pb is 0.19 pg with a 52% coefficient of variation.

Discussion

The successful parsing of Pb into aliquots with a range $^{206}Pb/^{204}Pb$ ratios that define an isochron with an age that overlaps the previously published age demonstrates that the new method works in principle. This confirmation was required given that the new method operates at lower temperatures than established hotplate methods (80-90°C in the heating block compared to +100°C on a hotplate) and does not allow for any ultrasonication. Compared to the established methods, the new method has the potential benefits of: 1) reduced blanks, 2) more consistent blanks, 3) reduces the occurrences of random higher than background blanks, 4) specific step-by-step blank correction, and 5) higher sample through put, which we discuss below in more detail.

1. Reduced blanks: the reduced Pb blank reflects the fact that Eppendorf pipette tips are no longer used in the transfer of each reagent, only 20% of the acid volumes are used in each dissolution step and that the exchange columns are set up on a carousel that sits within a horizontal laminar HEPA-filter air flow box. For the latter point, the operator's gloved hand and the dispensing bottles are always downwind of the columns in the carousel.

2. More consistent blanks: The blanks are more consistent over the longer term given that the addition and removal of each reagent in the stepwise dissolution entails identical manoeuvres that minimize user interaction with the sample.

3) Reducing randomly high blanks: The remotely-controlled removal of reagents in each step of the dissolution avoids the need to manipulate an Eppendorf tip over the sample which, in turn, reduces the opportunity for particles falling randomly into either the dissolution vial or the transfer vial from the Eppendorf or the users glove.

4. Step specific blanks: Since the sample can be processed in parallel with a blank with identical actions, each step has a specific blank estimate that can reflect the blank level of different acids or acid combinations. However, our results show that the dispersion of the acid-specific spike-blank compositions far exceeds the analytical uncertainties. Therefore, it is important to combine several replicate spike-blank measurements to characterise the reproducibility of the blank correction, using the geometric mean and covariance matrix of these replicates.

5. Increased productivity: With four chambers, the device allows for the processing of three samples in concert with one blank, such that a single session will yield a total of 60 aliquots (4 x 15 steps) that will require anion exchange chemistry and TIMS mass spectrometry. With a limit of 20 columns on a single carousel, this requires that aliquots be processed through chemistry in 3 batches and that mass spectrometry will take ca. 142 hours (ca. 3 hours per sample and ca. 30 min per blank). The blank analyses can be run as an automated sequence overnight, leaving ca. 135 hours of supervised mass spectrometry.

The combined effect of the reduced blanks that are more reproducible allows for the analyses of smaller amounts of Pb per sample and, in turn, that the dating of smaller chondrules is theoretically possible.

Comparison of Uncertainties on a Single Analysis

The benefit of a reduced and more consistent blank is difficult to quantify as it depends on ratio of sample to blank for any given analyses. Here, we consider the difference in the sizes of error ellipse between the case considered above using the traditional method where the amount of Pb in the sample is 90 pg and Pb blank is assigned to be 0.1, 0.25 and 0.50 pg with ±50% uncertainties (Fig. 1). For the ellipse generated for the new method, we correct for non-sample Pb (blank-spike Pb) using the averaged values of the measured $^{205}Pb/^{204}Pb$, $^{205}Pb/^{206}Pb$, $^{205}Pb/^{207}Pb$, $^{205}Pb/^{208}Pb$ ratios derived from the 15 blank-spike measurements and their 2SD uncertainties of 36% (Table 2). The resulting error ellipse is larger than that derived for the 0.10 pg (±50%) correction of blank Pb but smaller than that derived for the 0.25 pg (±50%) pg correction of blank Pb (Fig. 1). More importantly, the position of an analyses is expected to be more accurate given that the combined blank-spike Pb contribution is measured for each step.

Conclusions

A method has been developed to lower and better constrain the amount of laboratory Pb blank that is unavoidably added to meteoritic samples processed for Pb-Pb dating with the immediate purpose of dating smaller chondrules. An internally-heated device with four isolated chambers allows for the stepwise dissolution of lightly-crushed chondrules using smaller amounts of acids that are extracted from the sample by a remotely-controlled method based on pressure. This obliviates the need to remove acid from the dissolution vial by an Eppendorf pipette, a step that is considered the highest risk in increasing the Pb blank and decreasing its reproducibility. To test the effectiveness of this method, we have processed a single fragment of a chondrule from the CBa chondrite Gujba, for which published ages exist for four chondrules (Bollard, et al., 2015). Ten of 13 fractions define an isochron corresponding to an age of 4562.64±0.13 Ma, an age that overlaps with the published average age of Gujba chondrules.

The method allows for the assessment of the Pb blank added in each dissolution step to more accurately correct for the amount of Pb added in each dissolution step. To assess the reproducibility of laboratory Pb blank added, 15 blank analyses indicated an average value of 0.10±0.07 pg (2SE) for the dissolution and full 2-stage chemistry. The addition of a constant amount of volumetrically added spike to both sample and blank measurements allows for a single correction scheme for Pb from the tracer and the blank. The appropriate uncertainties on the ratios (i.e. $^{205}Pb/^{206}Pb$, $^{205}Pb/^{207}Pb$, $^{205}Pb/^{204}Pb$ and $^{205}Pb/^{208}Pb$ ratios) used for the subtraction of sample-tracer Pb of the blank aliquot are here derived from 15 blank analyses of a single acid but they can be modified by the long term reproducibility of measured ratios for each acid in future digestions. We expect that the method will increase the productivity of our chondrule dating campaign, allow us to date smaller chondrules from a more diverse suite of chondrites than has been possible and minimize points falling off the isochron due to inaccurate blank correction.

While the impetus for improving the stepwise dissolution Pb-Pb method came from our desire to increase productivity in chondrule dating and to date smaller chondrules, the method is not specific or limited to chondrule dating. The method should work equally well on any lightly-crushed meteoritic material, including fragments of differentiated meteorites and

CAIs, provided that are amenable to the Pb-Pb method in principle. Finally, the new method will be useful for attempts to Pb-Pb date samples returned by space missions where sample sizes are likely to be extremely limited.

Appendix 1: Chemical Purification of Pb and Mass Spectrometry

With each dissolution step of the sample and corresponding blank-spike step collected in clean 3 ml Savillex Corporation® vials, a set amount of ^{202}Pb-^{205}Pb tracer is added to each vial volumetrically. After refluxing the dissolution acid on a Teflon™ -coated hotplate for approximately an hour with the cap on, the liquids are evapourated and each aliquot is re-dissolved in 0.3 mls of 1M HBr in preparation for the chemical separation. Our mixed HBr-HNO$_3$ chemical separation using Eichrom Industries® anion resin follows the procedures outlined in Connelly and Bizzarro (2009) with an estimated Pb blanks for two passes through chemistry and evaporation steps of less than 0.1 pg. The 0.055 ml Teflon™ columns are held in a carousel that is placed inside a small HEPA-filtered chamber that is itself standing inside a larger HEPA-filtered workstation.

After the second pass through chemistry, the samples were dried down with a 10 μl of 0.1M H$_3$PO$_4$. The samples were loaded onto outgassed zone-refined Re ribbon inside a HEPA-filtered loading chamber with silica gel made following the recipe of Gerstenberger and Haase (1997) but using four times more silicic acid than they recommended. The isotopic composition of Pb was determined using the ThermoScientific™ Triton™ thermal ionization mass spectrometer at the Centre for Star and Planet Formation (StarPlan), University of Copenhagen, Denmark. Given the low amounts of Pb present in the dissolution steps, all analyses were made using an axially-positioned secondary electron multiplier - ion counter (SEM-IC) where each Pb isotope was measured sequentially in peak jumping mode by switching the magnetic field. Instrumental mass fractionation was internally corrected for each run using the known ^{205}Pb/^{202}Pb ratio of the spike. NIST-982 was run at the start and end of all analytical sessions to ensure that the mass spectrometer was operating nominally. All data was reduced using an inhouse data reduction scheme with the final regression and age calculation using IsoplotR (Ludwig, 2003; Vermeesch, 2018).

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Figure Captions

Figure 1. Pb isotope composition of a single synthetic "analyses" of 90 pg of Pb with corrections of 0.10, 0.25 and 0.50 pg (±50%) of laboratory Pb blank shown as the three green ellipses (from smallest to largest, respectively). In red, the same "analyses" corrected for a combined blank-spike Pb with 36% uncertainties on the isotopic compositions for this component (representing the average of 15 measured blank-spike analyses).

Figure 2. Schematic drawing of the device used in the refined stepwise dissolution method presented here.

Figure 3. Photograph of the device used in the refined stepwise dissolution method presented here. Ruler is 30 cm long.

Figure 4. Logarithmic correlation plot of the replicate spike-blank measurements. Error ellipses cover 95% confidence. Errors on the individual analyses are smaller than the black markers.

Figure 5. Pb-Pb isochron plot representing the stepwise dissolution of a fragment of a chondrule from the chondrite Gujba.

Figure 6. Plot showing the new Pb-Pb aged derived here by the refined method (red bar) in comparison with published ages in Bollard et al. (2015). All errors are 2-sigma.

Figure 1

Digital Controller for Heating Element

PFA Teflon Tubing

Vent Port

Sample Chamber

TFE Valves

TFE Teflon Block

Syringe

TFE Teflon block with polycarbonate lid fitted with neoprene gasket

Front view

PFA pipette tip with frit

Al heating plate

3 ml Savillex vials
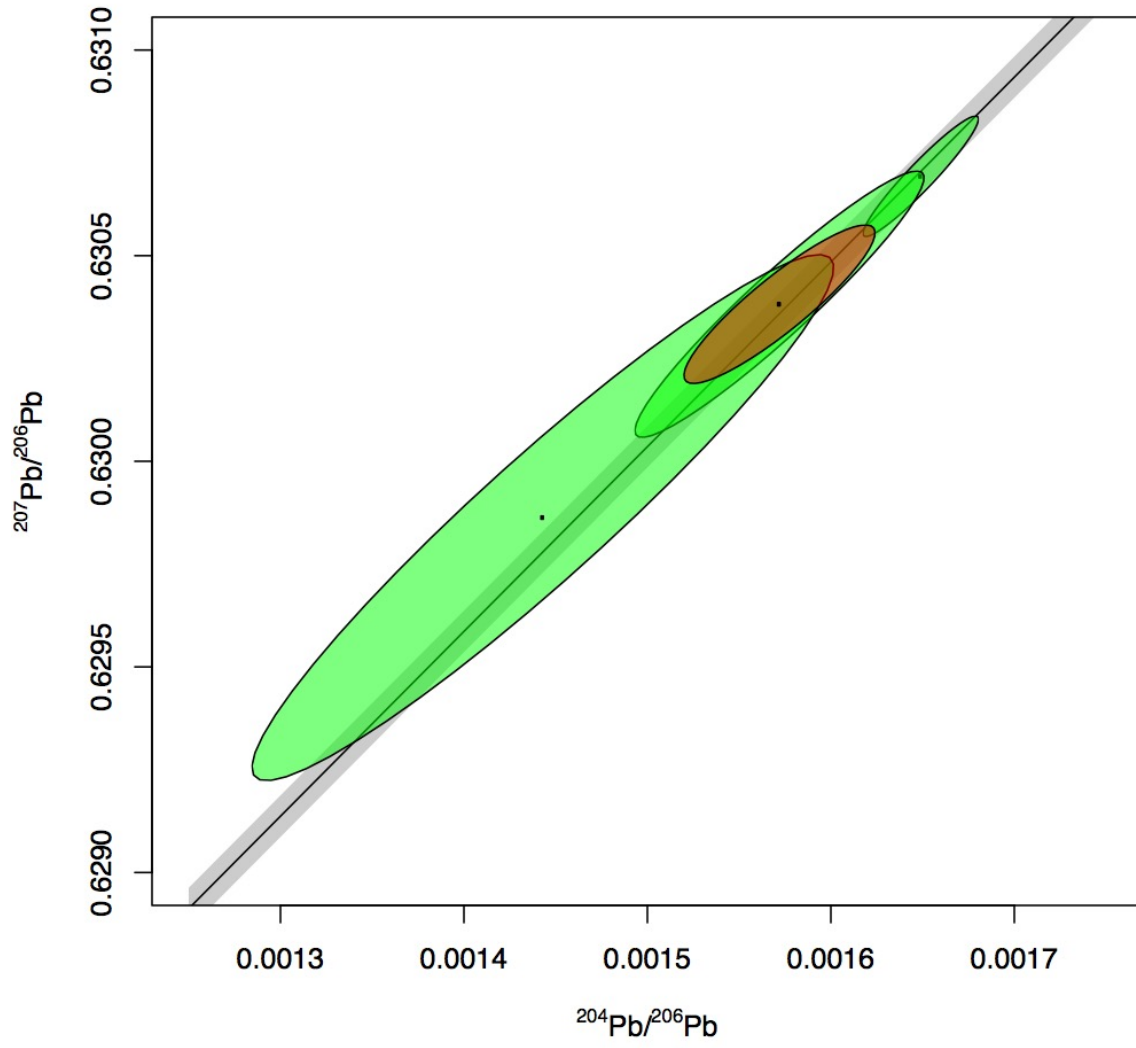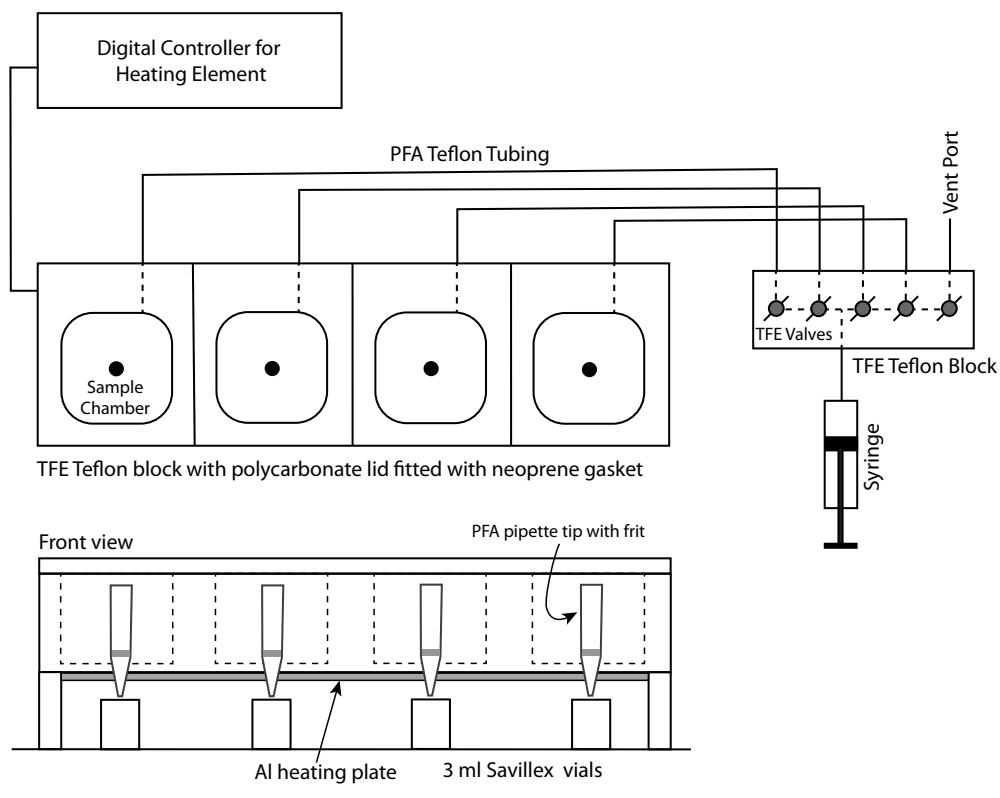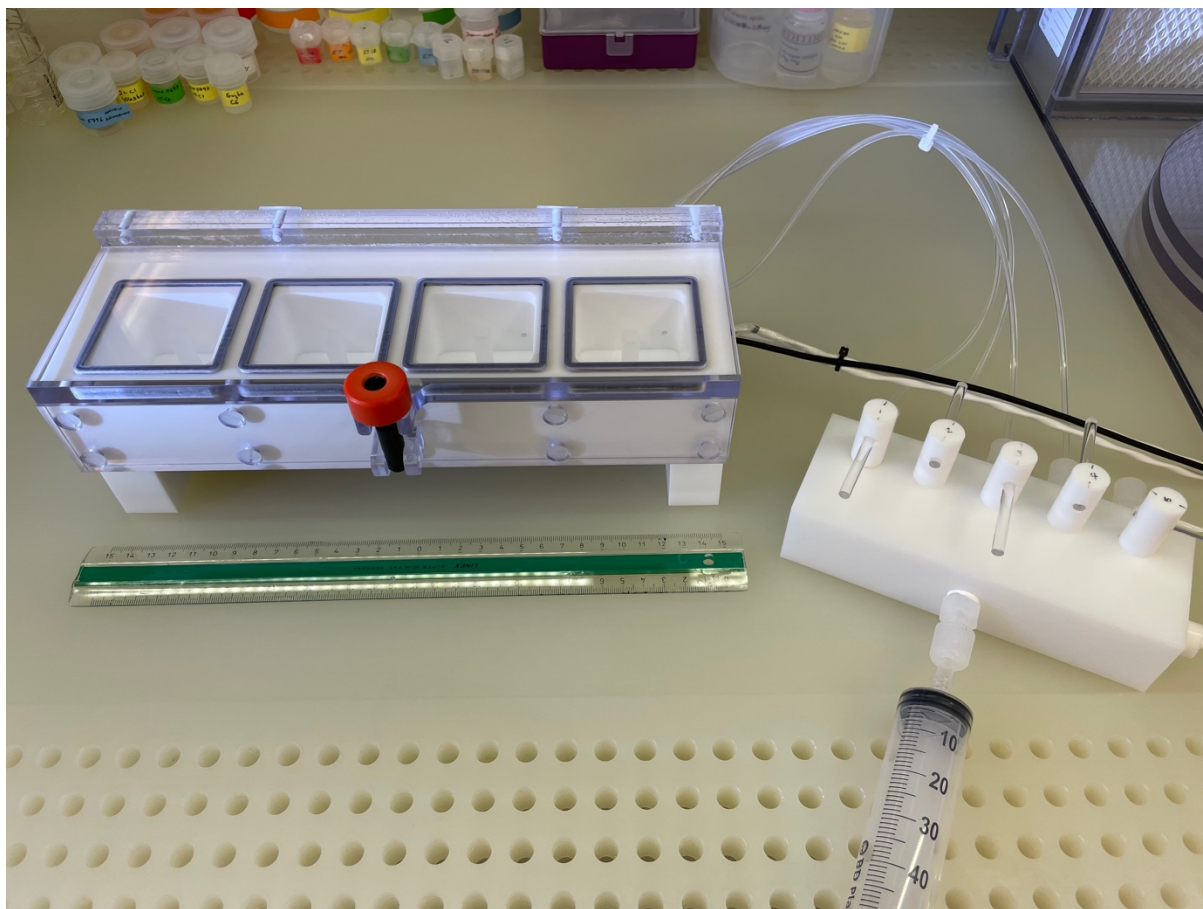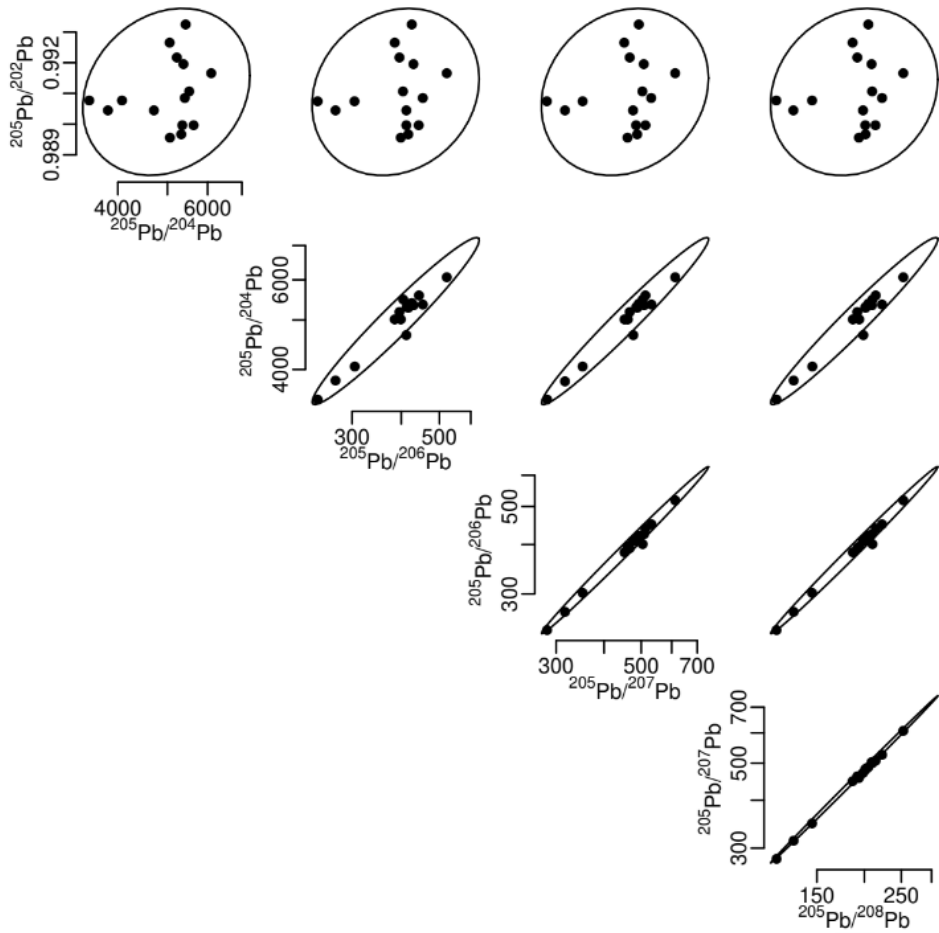
Figure 2

Figure 3

Figure 4

Gujba Chondrule

Age = 4562.64 ± 0.13 Ma
(n = 10)   MSWD = 2

$^{207}Pb/^{206}Pb$
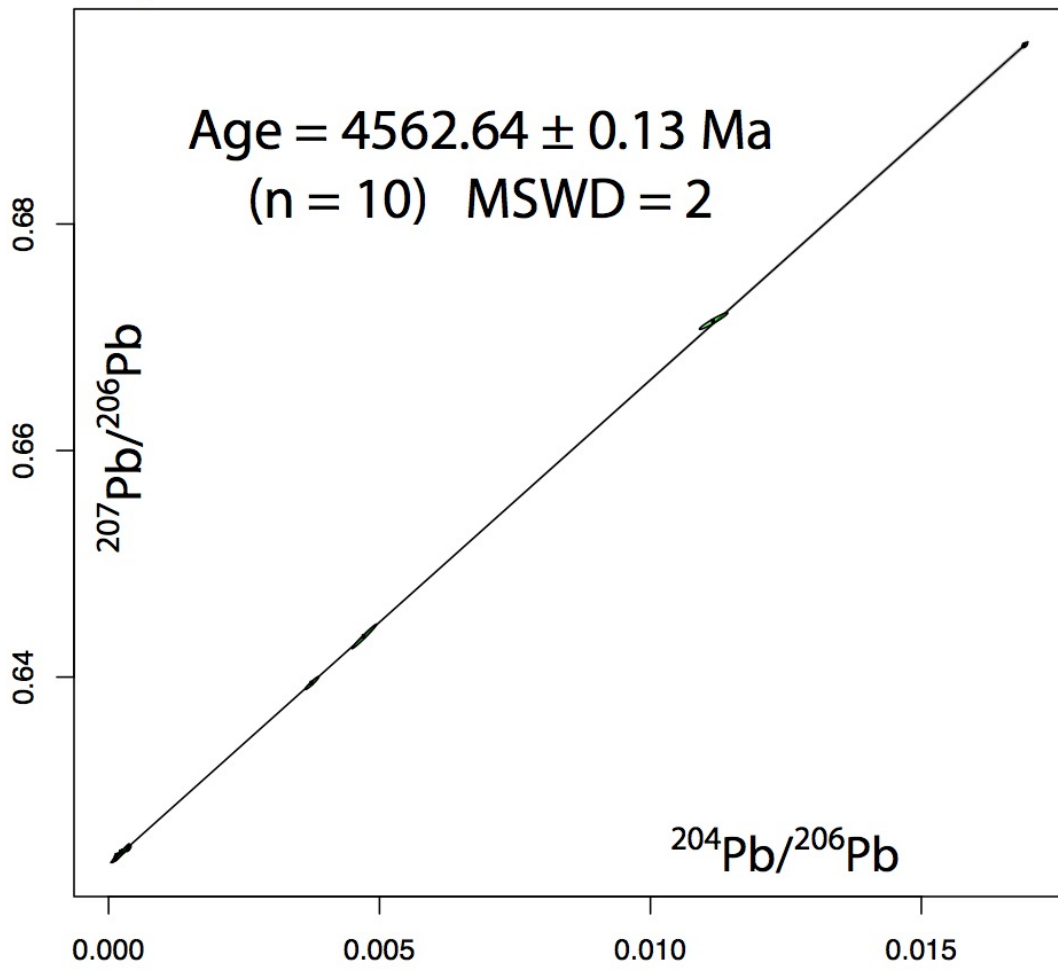
$^{204}Pb/^{206}Pb$
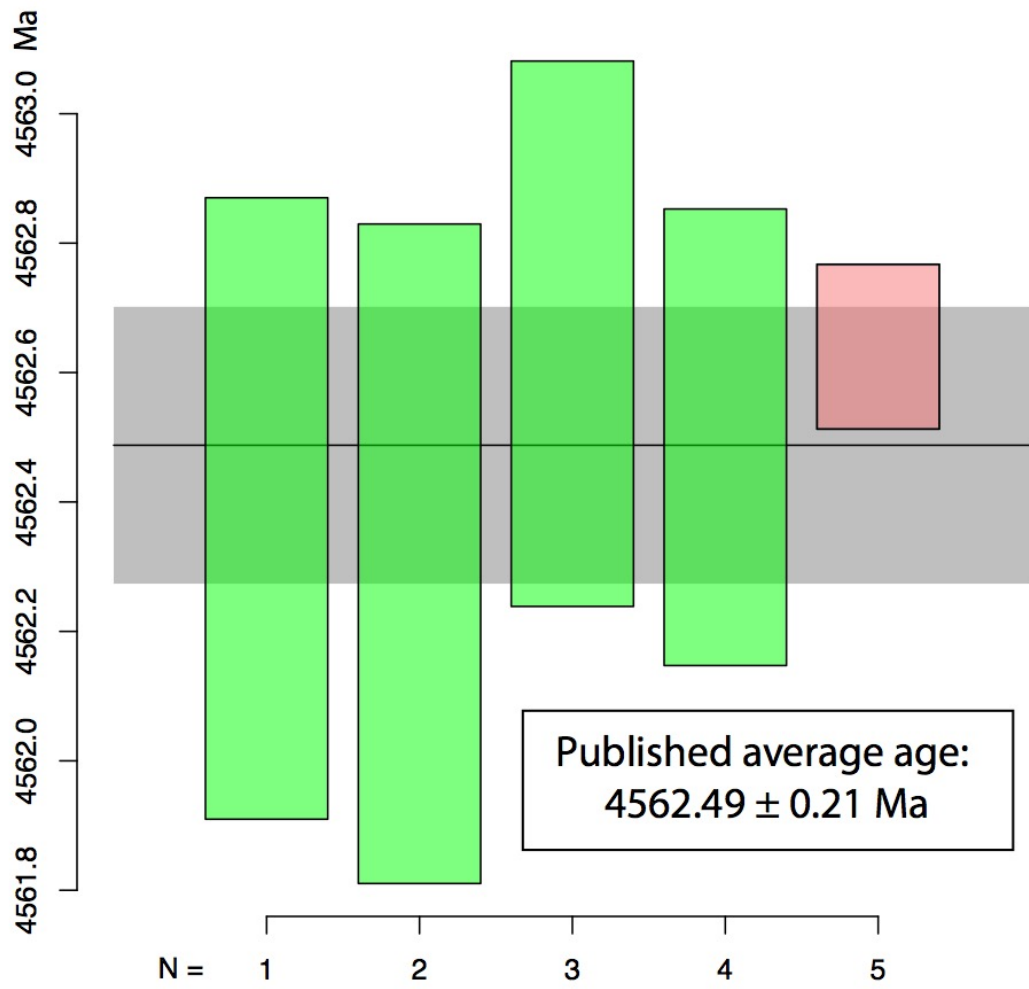
Figure 5

Figure 6

Table 1. Pb isotope date for Gujba chondrule

Fraction	Acid	Duration	Pb (pg)[a]	Pb blank (pg)[b]	$^{206}Pb/^{204}Pb$ (raw)[c]	$^{204}Pb/^{206}Pb$[d]	2SE(%)	$^{207}Pb/^{206}Pb$[d]	2SE(%)	Rho[e]	Nigerian Model Age[f]
W1	Dilute HBr	60 min	12.1	0.14	42	0.0233769	2.07	0.722605	0.253	0.986	4549.84
W2	Dilute HBr	60 min	5.6	0.16	42	0.0223685	7.01	0.718956	0.839	0.995	4551.04
L1	1M HBr	10 min	150.5	0.14	59	0.0169932	0.26	0.695515	0.032	0.650	4554.81
L2[g]	3M HCl	10 min	161.9	0.12	59	0.0169080	0.24	0.695801	0.027	0.528	4557.07
L3[g]	3M HNO$_3$	15 min	44.3	0.19	203	0.0047186	3.96	0.643592	0.137	0.984	4561.37
L4	3M HNO$_3$	10 min	17.8	0.61	244	0.0027172	49.70	0.636146	1.002	0.996	4564.69
L5[g]	3M HCl	15 min	36.3	0.14	88	0.0111656	1.91	0.671438	0.090	0.960	4560.07
L6	6M HCl	10 min	26.7	0.23	96	0.0099797	3.70	0.666623	0.264	0.992	4561.23
L7[g]	6M HCl	35 min	71.7	0.15	258	0.0037544	2.75	0.639472	0.073	0.953	4561.63
L8[g]	1M HF	10 min	222.4	0.17	2450	0.0003690	10.26	0.624854	0.034	0.786	4562.18
L9[g]	1M HF	20 min	134.0	0.18	4935	0.0001385	47.71	0.624043	0.055	0.911	4562.61
L10[g]	7M HF	10 min	357.8	0.18	5519	0.0001557	16.19	0.624260	0.028	0.626	4562.98
L11[g]	7M HF	30 min	410.9	0.22	3828	0.0002357	10.79	0.624569	0.029	0.652	4562.89
L12[g]	28M HF - 7M HNO$_3$	80 min	163.5	0.23	2914	0.0002789	22.56	0.624620	0.053	0.913	4562.56
R[g,h]	28M HF - 7M HNO$_3$	3 days	237.3	0.68	2757	0.0002499	43.39	0.624515	0.100	0.974	4562.61

Notes:

[a] Total amount of Pb in each fraction corrected for spike and blank.

[b] Measured amount of total Pb in associated blank-spike analysis.

[c] Measured isotope ratio.

[d] Isotope ratio corrected for mass fractionation, spike and blank.

[e] Rho value for the $^{207}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$ ratios.

[f] Model age (Myr) calculated with local Nigerian terrestrial Pb isotopic composition, estimated to accurately characterize the common Pb reservoir in Gujba chondrite (Bollard et al., 2015).

[g] Fractions used in the regression to define an age for Gujba chondrule.

[h] Residual grains were transfered to a 3 ml Savillex Corporation® vial and put on hotplate at 110°C until complete dissolution.

Table 2. Pb isotope data for 16 total procedurual blanks.

Fraction[a]	Pb[b] (pg)	$^{205}Pb/^{206}Pb$[c]	2SE(%)	$^{205}Pb/^{204}Pb$[c]	2SE(%)	$^{205}Pb/^{207}Pb$[c]	2SE(%)	$^{205}Pb/^{208}Pb$[c]	2SE(%)	$^{205}Pb/^{202}Pb$[c]	2SE(%)
Col-1-L1	0.15	415.80	0.23	5316.89	0.90	486.71	0.31	200.86	0.25	0.9897	0.03
Col-2-L1*	1.03	60.80	0.69	1035.91	0.77	69.61	0.70	28.81	0.62	0.9915	0.02
Col-3-L1	0.23	271.96	0.45	3818.04	0.69	315.59	0.44	129.93	0.45	0.9905	0.02
Col-4-L1	0.15	424.80	0.24	5422.75	0.49	491.59	0.35	204.11	0.24	0.9933	0.03
Col-1-L2	0.16	397.94	0.26	5046.88	1.09	459.95	0.45	193.10	0.25	0.9896	0.02
Col-2-L2	0.15	411.51	0.32	5339.25	1.16	483.84	0.22	200.70	0.29	0.9900	0.04
Col-3-L2	0.16	384.41	0.24	5043.86	0.86	450.88	0.21	185.84	0.14	0.9927	0.02
Col-4-L2	0.14	442.27	0.37	5618.09	0.92	511.80	0.45	213.46	0.28	0.9900	0.03
Col-1-L3	0.15	411.21	0.82	4698.02	2.13	475.19	0.81	197.93	0.43	0.9905	0.04
Col-2-L3	0.15	403.62	0.26	5510.30	1.08	502.73	0.30	209.26	0.15	0.9911	0.02
Col-3-L3	0.20	304.15	0.64	4068.68	0.84	350.76	0.56	145.41	0.62	0.9908	0.02
Col-4-L3	0.14	452.68	0.37	5399.20	1.39	530.25	0.54	221.89	0.31	0.9909	0.03
Col-1-L4	0.14	428.61	0.20	5365.10	0.63	507.19	0.34	208.49	0.17	0.9920	0.02
Col-2-L4	0.25	245.03	0.32	3508.91	0.95	283.34	0.32	117.18	0.22	0.9908	0.03
Col-3-L4	0.12	520.51	0.35	6089.87	1.37	611.70	0.51	252.30	0.32	0.9917	0.03
Col-4-L4	0.16	395.08	0.45	5207.08	0.56	465.49	0.61	191.07	0.56	0.9922	0.02
Average	**0.16**	**393.97**		**5030.20**		**461.80**		**191.44**		**0.9911**	
%Error[d]	**20.0**	**36.0**		**19.9**		**20.5**		**20.7**		**0.11**	

Notes:

[a] Blanks were measured as 4 consecutive sets of 4 blanks where all 4 chambers were used.

[b] Total Pb from blank + spike

[c] Measured isotope ratio.

[d] Coefficient of variation (%)

* Not included in the average or error calculation