BENCHMARKING THE Pb-Pb AGE OF UNGROUPED ACHONDRITE NWA 6704 FOR *PROJECT MILESTONES*.

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Introduction: The Pb-Pb chronometer is one of the most valuable tools for dating many Solar System materials. It is the only absolute chronometer providing a high enough precision to distinguish events within the first 10 Ma of the Solar System. Given a high enough radiogenic Pb content within a sample, it is possible to achieve a precision of a few 100 ka or less. At this precision level, differences in analytical protocols, laboratory and data reduction procedures can potentially cause resolvable interlaboratory discrepancies. One approach to address this issue are interlaboratory comparisons using solution standards (e.g. EARLYTIME [1]). While these standards ensure comparability of data collected from mass spectrometers and data reduction schemes, their analysis does not include all steps of sample handling prior to the acquisition of data on the mass spectrometer. In modern Pb-Pb chronology, the sample handling typically involves a series of acid leaching steps, followed by column chemistry. For these steps, it is crucial to separate non-radiogenic Pb (initial and terrestrial) from radiogenic Pb to obtain a precise date. It is also important to ensure low laboratory blank levels and determine its composition to obtain an accurate date. At UC Davis (UCD), the U-Pb dating capability was established only recently and comparability of our data with other well established laboratories is crucial. For this purpose, we set up an experiment on the ungrouped achondrite NWA 6704 to compare our results with those from the SPIDE^{2}R lab at the Australian National University (ANU).

Material: NWA 6704 is mainly composed of coarse grained orthopyroxene, plagioclase, some minor olivine and Cr-Spinel. A detailed description of this meteorite was presented by [2] and [3]. Pb-Pb chronology for this meteorite was previously reported by [4]. More extensive analyses were performed later by [5], to which we will compare our results.

Methods: The crushed sample was handpicked and separated into 4 fractions of 3 to 8 mg each (we note that these are substantially smaller sample sizes compared to those used in [5] by ~1/5). Three were pyroxene of different grain sizes (coarse, medium and fine) and one coarse plagioclase fraction. All fractions were subsequently treated in the same way in the following steps. 1. All fractions were rinsed in acetone, followed by an ultrasonic bath in ultrapure water. This step was not analysed. 2. The samples were then treat-ed with 0.5 M HNO_3 in an ultrasonic bath for 15 min multiple times (designated as W1). 3. The remainder samples were further leached with 6 M HNO_3 for ~ 2 h on a hotplate at 100°C (W2). 4. It was followed by the next leaching step in 6 M HCl for ~ 2 h on a hotplate at 100°C (W3). 5. The remaining solids were treated with 0.1 M HF in an ultrasonic bath for 30 min (W4). 6. Dissolution of the residue in conc. HF-HNO_3 mixture for two days. All leachates were spiked with a ^{202}Pb-^{205}Pb-^{233}U-^{236}U spike, evaporated and redissolved in 6 M HCl. Lead was separated from the matrix elements using anion exchange columns with an HCl-HBr based chemistry [6]. Samples were loaded onto zone refined Re filaments with a silica gel activator and phosphoric acid. The samples were analysed using a *Triton Plus* TIMS at UC Davis. This TIMS is equipped with 9 Faraday cups, which can be coupled with up to six 10^{13} Ohm resistors, and one secondary electron multiplier (SEM). For most fractions, an SEM in peak jumping mode was used and in rare cases Faraday cups coupled with 10^{13} ohm resistors, except for ^{204}Pb, which was always measured using SEM. For the gain calibration of the 10^{13} Ohm resistors, we used the Nd Standard La Jolla similar to the protocol described by [7]. The total procedural blanks for Pb are between 3 and 0.7 pg. Data was reduced using the algorithms of [8] and isochron regression dates were calculated using Isoplot [9]. All reported dates include the uncertainty of the U isotopic composition, as well as the Pb isotopic composition.

At the same time, a set of EARLYTIME standards was measured and yielded an age of 4559.45 ± 0.22 Ma, using the measured U isotopic composition [10]. In this case, all isotopes were determined in static mode using 10^{13} Ohm resistors, except for ^{204}Pb of the two most radiogenic samples, which was measured on the SEM. This is compared to 4559.53 ± 0.13 Ma and 4559.79 ± 0.32 Ma for the most radiogenic of the five EARLYTIME solutions at ANU using two different detector systems (Faraday and SEM, respectively). All these dates are the same within uncertainty. These are also consistent with our previously reported dates of these standards [10].

For NWA 6704 the U isotopic composition was determined as well, with two aliquots of samples being processed (crushed, dissolved and separated) at both UCD and ANU, while all were measured at UCD. At

both institutions similar procedures were used. A large sample size (>1g) was dissolved in both cases and U was separated using anion exchange chemistry followed by U-Teva chemistry. The U isotopic composition was determined using a *Neptune Plus* MC-ICPMS at UCD with analytical procedures described previously [10].

Results: The measured $^{238}U/^{235}U$ ratio is 137.784 ± 0.015 (UCD) and 137.775 ± 0.013 (ANU), respectively. Within the uncertainty, these results are identical. For age calculation, the weighted mean of 137.7784 ± 0.0097 (MSWD = 0.46) is used.

The first leachates (W1) yielded $^{206}Pb/^{204}Pb$ ratios between 30 and 50. The second leachates (W2) were much less radiogenic with $^{206}Pb/^{204}Pb$ ratios between 18 and 28. W3 and W4 (HCl and HF) for all fractions contain the smallest amount of Pb with $^{206}Pb/^{204}Pb$ ratios between 20 and 110, where W4 was typically more radiogenic than W3. Only one measurement of the final residue completed thus far (plagioclase) yielded $^{206}Pb/^{204}Pb$ ratio of 440. Out of all analysed leachates and the residue, only two fall off the isochron (W2 of the coarse px and W4 of the medium size px fraction). Based on the remaining analyses, an isochron an age of 4562.66 ± 0.81 Ma (MSWD = 1.3, n = 14) can be calculated using the measured $^{238}U/^{235}U$ ratio of 137.7784 ± 0.0097 (Fig. 1).
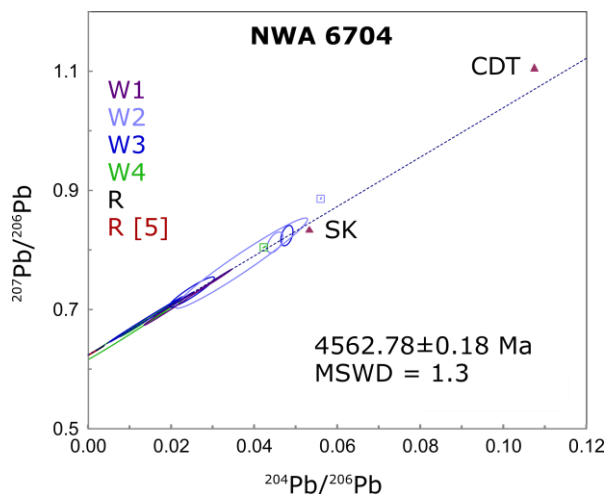

Fig. 1: Pb-Pb isochron for leachates and residues of pyroxene and plagioclase of NWA 6704. All leachates and one residue measured at UCD are shown; however, two are not considered in the isochron regression, these are marked by squares. For data from [5] only pyroxene residues included in the age calculation are shown. SK: modern terrestrial Pb; CDT: primordial Pb.

Discussion: For Pb isotopic determination for cosmochronology, the analytical protocols at ANU and UCD result in comparable dates at the sub-500 ka scale, which is shown with the use of EARLYTIME standards. This is consistent across two institutions, each with their own SEM and Faraday detector system and the respective calibrations.

For NWA 6704, the preliminary age determined at UC Davis is compared to 4562.46 ± 0.35 Ma reported by [5]. The difference between these dates is 0.20 ± 0.88 Ma. These ages determined at two different institutions are in agreement within the uncertainties. The larger uncertainty in this study can be related to a number of reasons. 1. Only one analysis of final residue sample is completed thus far with a radiogenic $^{206}Pb/^{204}Pb$ ratio of only 440, whereas the data obtained at ANU is up to 5000. 2. In this study, less material was used for each of the fractions (~1/5 of [5]), thus the total amount of Pb analysed was less and uncertainty from the blank correction is increased. We expect further improvement in precision is possible in the near future and anticipate the measurements for the remaining residue samples should be concluded by the time of the meeting.

Conclusion: This study shows the results for an interlaboratory comparison, which is needed for comparability of Pb-Pb dates generated by different laboratories especially when using different analytical procedures, different tracers, data reduction procedures, as well as different mass spectrometers and detector systems. Our results show that the laboratories at UC Davis and ANU yield consistent ages for solution standards, as well as a meteorite sample. Regressing through the obtained data from both institutions gives a composite age of 4562.78 ± 0.18 Ma (MSWD = 1.3) as shown in Fig. 1.

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