

SYNCHRONIZING THE ABSOLUTE AND RELATIVE CLOCKS: Pb-Pb AND Al-Mg SYSTEMATICS IN CAIs FROM THE ALLENDE AND NWA 2364 CV3 CHONDRITES. A. Bouvier¹ and M. Wadhwa¹, ¹Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA (audrey.bouvier@asu.edu).

Introduction: In recent years, several high-resolution chronometers have been applied towards addressing the important question of the age of the Solar System, which is best estimated from the formation age of the calcium-aluminum-rich inclusions (CAIs), recognized as the earliest-formed solids in the solar nebula. However, there are inconsistencies in the ages of CAIs as determined by different high-resolution absolute and relative chronometers. In particular, estimates of the Pb-Pb ages for CAIs range from 4567.1 ± 0.1 Ma [1] to 4568.5 ± 0.5 Ma [2] for inclusions from the CV3 chondrites Efremovka and Allende. This age range of ~1-2 Myr is significantly larger than the time interval for CAI formation estimated from ²⁶Al-²⁶Mg isotope systematics (i.e., less than a few tens of thousands of years [3, 4]. Analytical methodologies involved in Pb-Pb dating (particularly, differences in the types of mass spectrometers and in the chemical treatments) are unlikely to be the source of the apparent range in the Pb-Pb ages reported for CAIs since (i) Pb isotope analyses (using double-spike and Tl-doping methods) by MC-ICPMS are comparable in precision and accuracy to those obtained by TIMS [5] and (ii) we have previously tested various leaching protocols on different fractions of an Allende type-B CAI and have excluded the possibility of leaching-induced Pb isotope fractionations [6]. As such, the apparent discrepancy between the Pb-Pb and Al-Mg systematics in CAIs may be due to other causes such as isotopic heterogeneities in the analyzed samples or secondary alteration processes on the parent body. With the goal of resolving the possible cause of this discrepancy, we have investigated the Pb-Pb and Al-Mg isotope systematics in a CAI from the oxidized CV3 chondrite NWA 2364. We also present here additional Al-Mg data for an Allende CAI for which we have previously reported some preliminary Pb-Pb and Al-Mg data [6].

Samples and Analytical Techniques: We analyzed a ~500mg fragment of a large type-B inclusion from the CV3 chondrite NWA 2364 for Pb-Pb and ²⁶Al-²⁶Mg isotope systematics. The interior and rim portions of the NWA 2364 CAI were separated, and a fraction of the interior portion was subjected to mineral separation using heavy liquids, followed by hand picking to obtain melilite-rich and fassaite-rich separates. Also, in continuation of a previous study [6], we

determined Al-Mg systematics in four additional mineral separates of a type-B CAI from Allende.

For the Al-Mg isotope analyses, fragments and mineral separates of the NWA 2364 and Allende CAIs were processed without any prior leaching (so as not to fractionate Al/Mg ratios). Dissolution and chemical separation of Mg from these fractions, as well as measurements of Al/Mg ratios and Mg isotope compositions were performed using established protocols described in [7].

For the Pb isotope analyses, a bulk interior fraction (#1), two mineral separates (#2, fassaite-rich and #3, melilite-rich) from the interior, and a bulk fraction composed of the rim (#4) of the NWA 2364 CAI were all leached using the same leaching protocol. This leaching protocol included 7 steps (denoted as L₁, L₂,...L₇) using HBr, HNO₃, HCl and HF and involving different acid concentrations, temperatures, and durations. Residues (denoted as R) and leachates were fully dissolved in concentrated HF-HNO₃, and converted to the chloride form before Pb extraction using 50µl anionic columns. The total procedural blank for the Pb isotope analyses was decreased to ~0.7 pg during this study and the measured Pb isotopic composition of each sample was corrected accordingly. The Pb solutions were spiked with a Tl standard solution for correction of instrumental mass bias. Pb isotope measurements were made on a Thermo-Finnigan Neptune MC-ICPMS at Arizona State University. A secondary electron multiplier (SEM) was used to monitor the low ²⁰⁴Pb signal and Faradays cups were used for simultaneously measuring ²⁰⁰Hg, ²⁰²Hg, ²⁰³Tl, ²⁰⁵Tl, ²⁰⁶Pb, and ²⁰⁷Pb. Solutions were introduced into the mass spectrometer using an Apex desolvating nebulizer (with a 50 µl/min flow rate). Repeated analyses of two Pb isotope standards (2ppb Pb - 1ppb Tl) over the course of this investigation yielded the following compositions: ²⁰⁶Pb/²⁰⁴Pb = 16.958 (± 0.06%) and ²⁰⁷Pb/²⁰⁶Pb = 0.91450 (± 0.02%) for NBS 981, and ²⁰⁶Pb/²⁰⁴Pb = 2,796 (± 1.3%) and ²⁰⁷Pb/²⁰⁶Pb = 0.0712 ± (0.06%) for NBS 983 (errors are 2SE).

Results: The Pb isotopic compositions of the solutions of the 7 leaching steps (L₁-L₇) and final residues (R) of each of the two bulk (interior and rim) and two mineral fractions of the NWA 2364 type-B CAI were measured. The uncorrected ²⁰⁶Pb/²⁰⁴Pb ratios range from 48 to 10,171 for the leachates, and from 1,040 to

5,245 for the residues. The Pb isotopic compositions of the leachates and the residue from the rim fraction attest to the presence of a component with more common Pb (possibly the chondritic matrix). When only the residues and corresponding L7 leachates of the three interior (bulk and mineral separate) fractions (having corrected $^{206}\text{Pb}/^{204}\text{Pb}$ ratios >965) are considered, we obtain an internal Pb-Pb isochron age of 4568.67 ± 0.17 Ma (MSWD=1.4) (Fig. 1). This is 1.0 to 1.6 Ma older than the internal Pb-Pb isochron ages obtained for other CAIs from Allende and Efremovka [6, 8, 9] but is concordant with the age estimated by [2] for CV3 CAIs.

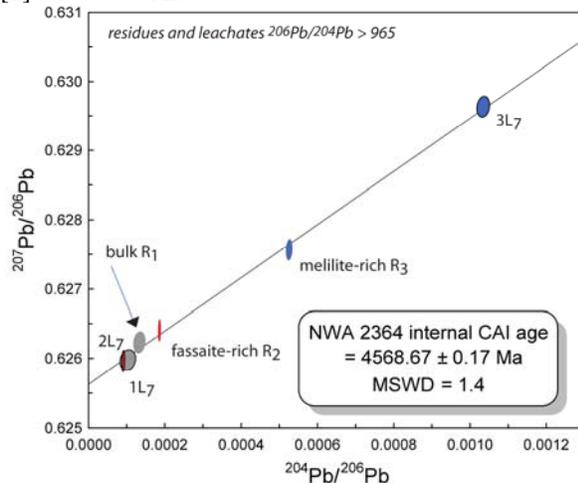


Figure 1: internal Pb-Pb isochron of a type-B CAI of NWA 2364. Age regression includes the 3 residues ($R_{1,3}$) and 3 last step leachates (L_7) of the bulk fraction (grey), fassaite-rich fraction (red), and melilite-rich fraction (blue) from the interior of the CAI. Error ellipses are $\pm 2\sigma$.

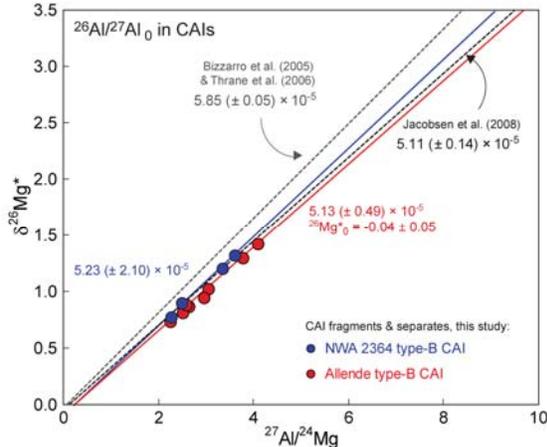


Figure 2: Al-Mg isotope systematics and initial $^{26}\text{Al}/^{27}\text{Al}$ values in CAIs of Allende and NWA 2364 (this study), and comparison with values from the literature [4, 9, 10].

The 4 unleached fractions of the NWA 2364 CAI analyzed for Al-Mg isotope systematics have a narrow range of $^{27}\text{Al}/^{24}\text{Mg}$ ratios (2.30-3.63) (Fig. 2). The radiogenic ^{26}Mg excesses ($\delta^{26}\text{Mg}^*$) in these fractions range from +0.76‰ to +1.31‰. The internal isochron

yields an initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of $5.23 (\pm 2.1) \times 10^{-5}$. The 9 unleached fractions of the Allende CAI have $^{27}\text{Al}/^{24}\text{Mg}$ ratios ranging from 2.26 to 4.11 and $\delta^{26}\text{Mg}^*$ ranging from +0.73‰ to 1.41‰; this corresponds to an initial $^{26}\text{Al}/^{27}\text{Al} = 5.13 (\pm 0.49) \times 10^{-5}$. The $^{26}\text{Al}/^{27}\text{Al}$ ratios inferred for these CAIs from NWA 2364 and Allende are consistent with the value inferred for Allende CAIs by [9] (Fig. 2).

Discussion: If the D'Orbigny angrite is used as an anchor [7, 11], Al-Mg ages of 4569.2 ± 0.6 Ma and 4569.2 ± 0.2 Ma are obtained for the NWA 2364 and Allende CAIs, respectively. While the Al-Mg age for the NWA 2364 CAI is marginally concordant with its Pb-Pb age, the Al-Mg age of the Allende CAI is discordant with its Pb-Pb age [6].

The Pb-Pb age of 4568.67 ± 0.17 Ma of the NWA 2364 type-B CAI is ~ 1 Ma older than for the Allende type-B CAI [6, 9], and ~ 1.5 Ma older than the Pb-Pb age of the E60 CAI [7]. As mentioned earlier, this range in Pb-Pb ages is inconsistent with the Al-Mg systematics which suggest a significantly narrower time interval for CAI formation [3, 4]. As such, this may reflect disturbance of the U-Pb isotope systematics in CAIs due to secondary alteration (e.g., shock or aqueous processing) on their meteorite parent bodies. An alternative explanation for the apparent range in the Pb-Pb ages of CAIs could be an early episode of U isotope fractionation [12].

Finally, we note that the Pb-Pb age reported here for the NWA 2364 CAI is concordant with the Pb-Pb age estimated by [2] for CV3 CAIs; this age also agrees with the Hf-W model age of CAIs from Allende and NWA 2364 (anchored to the Pb-Pb and Hf-W isotope systematics in the angrites) [13].

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References: [1] Amelin et al. (2006) 37th Lunar Planet. Sci. Conf., abstr. #1970. [2] Bouvier et al. (2007) Geochim. Cosmochim. Acta., 71, 1583-1604. [3] Young et al. (2005) Science, 308, 223-227. [4] Thrane et al. (2006) Astrophys. J., 646, L159-L162. [5] Amelin et al. (2008) Eos Trans. AGU 89(53), abstr. V13A-2088. [6] Bouvier et al. (2008) Meteorit. Planet. Sci. 41, abstr. #5299. [7] Spivak-Birndorf et al. (2009) Geochim. Cosmochim. Acta, in revision. [8] Amelin et al. (2006) 38th Lunar Planet. Sci. Conf., abstr. #1970. [9] Jacobsen et al. (2008) Earth Planet. Sci. Lett., 272, 353-364. [10] Bizzarro et al. (2004) Nature, 431 275-278. [11] Amelin (2008) Geochim. Cosmochim. Acta, 72, 221-232. [12] Brennecka et al. (2009) 40th Lunar Planet. Sci. Conf., submitted [13] Burkhardt et al. (2008) Geochim. Cosmochim. Acta, 72, 6177-6197.