A TH/U PERSPECTIVE ON THE AGE OF THE SOLAR SYSTEM. J. Blichert-Toft[1], C. Göpel[2], M. Chaussidon[2], and F. Albarede[1], [1]Ecole Normale Supérieure de Lyon, UMR CNRS 5276, 46 Allée d'Italie, 69007 Lyon, France (jblicher@ens-lyon.fr; albarede@ens-lyon.fr), [2]Institut de Physique du Globe de Paris, Université Paris Diderot, UMR CNRS 7154, 1 rue Jussieu, 75005 Paris, France (gopel@ipgp.fr; chaussidon@ipgp.fr).

Introduction: Once the issue of the variable $^{238}U/^{235}U$ ratio of CAIs and chondrules had been resolved, it seemed that the absolute age of the Solar System, as defined by the U-Pb age of CAIs, had also been resolved [1-3]. Here we measured the Pb isotope abundances of 14 single Allende (CV3) chondrules and six samples of multiple Allende chondrules targeting their Th/U ratios. We also review literature data on Allende chondrules and CAIs and discuss how they affect our understanding of the Pb-Pb age of the Solar System.

Material and Methods: Allende chondrules were separated at IPGP under clean room conditions. The Allende material was crushed with a trimmer (hydraulic press) and a sapphire mortar until the size of the fragments was ~1.5 cm. Repeated sieving with nylon sieves during this procedure allowed eliminating the finest powder to collect free chondrules in the sieved fraction and then to isolate those chondrules that were still partially enclosed within the matrix with tweezers under a binocular microscope. The matrix was gently rubbed off prior to leaching. The chondrules were leached successively in hot 1M HBr, hot 6M HCl, and hot concentrated HNO_3, under clean room conditions at ENS de Lyon, then dissolved in a 3:1:0.5 mixture of concentrated $HF:HNO_3:HClO_4$. All residue and leachate fractions were individually put through 0.25 ml anion-exchange columns to separate the Pb, which was analyzed for its isotopic composition on a Neptune Plus MC-ICP-MS, also at ENS de Lyon.

Results: Since high-precision Pb isotope data on Allende chondrules with extremely small blanks have been published previously [1-4], the present study is not intended to propose a new high-precision, low-blank Pb-Pb age. Nevertheless, the isochron age of 13 out of the 14 analyzed individual single-chondrule residues (excluding 1-4R) is 4.564±4 Ga (Fig. 1), and the most radiogenic samples are consistent with the range of ages published so far. The error on the 13-point residue isochron is due to the small size of the single chondrules analyzed, which contained only very little Pb (of the order of ppt) after the severe leaching protocol.

Precision and blank levels are not critical to determining Th/U ratios, which are the main focus here. The residues and their leachates plot on a line going through Canyon Diablo initial Pb [5] in $^{208}Pb/^{206}Pb$–$^{204}Pb/^{206}Pb$ space (Fig. 2). A novel observation is made from this plot. The intercept of the line joining the point representative of primordial Pb and the fraction in question (residue or leachate) with the y-axis gives an estimate of the radiogenic $^{208}Pb^*/^{206}Pb^*$, and therefore of the Th/U ratio of each fraction. Most residues of individual chondrules have Th/U ranging from 3.0 to 5.2 (Fig. 2), consistent with the whole-rock Th/U value of 3.9±0.2 of [6] and the more recent, more precise planetary value of 3.876±0.016 of [5], but with outliers at 0.65 (10R) and 14.7 (16R) (Fig. 2). Likewise, the Th/U of the six combined (smaller multiple) chondrule fractions (not shown to avoid overloading the figure but plotting on the same isochron as the single chondrules) vary between 2.9 and 5.1. There is no correlation between $^{208}Pb^*/^{206}Pb^*$ and $^{207}Pb^*/^{206}Pb^*$, i.e. no correlation between model Th/U and Pb-Pb ages.

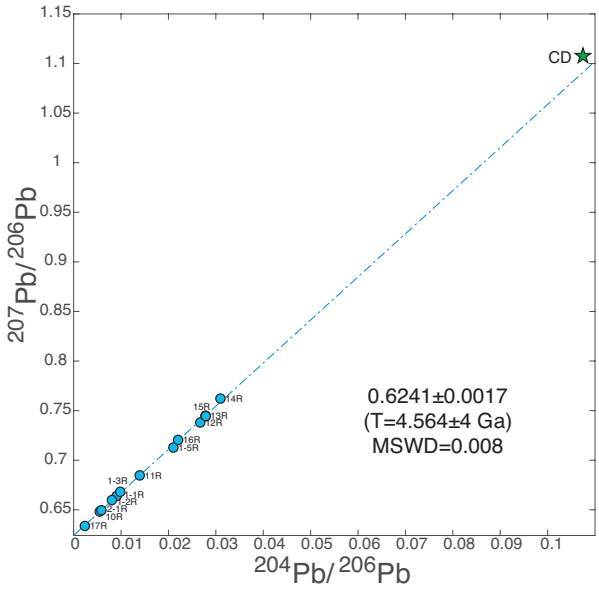

Figure 1: Isochron diagram for the residues of 13 individual chondrules from Allende. The small MSWD is due to the x5 error adopted for the blank. CD = Canyon Diablo.

Discussion: Beyond evidence for anomalous $^{238}U/^{235}U$ ratios, Brennecka et al. [7] identified a positive correlation between $^{235}U/^{238}U$ and $^{232}Th/^{238}U$ for CAIs. The range of Th/U observed by these authors (2.1-70) is even larger than that observed here for Allende chondrules (0.65-14.7). The only high-temperature phases significant in CAIs and chondrules

that could effectively enrich Th over U are hibonite and melilite [8,9]. The Th/U scatter widely around the planetary value of [5], but shows that residues are aligned with their own leachates. The slopes of the leachates and their corresponding residue define a negative correlation with the intercepts, which demonstrates that these alignments are also aligned with a point representing primordial Pb, not significantly different from the Canyon Diablo value. Two exceptions are samples #16 and #17, for which the alignment is rather poor. Inspection of literature data for which leaching procedures even more severe than those adopted here were used [1-4] confirms that Th/U may also be heterogeneous within a single chondrule. Th/U heterogeneities therefore show up both within and among chondrules. This observation also holds for CAIs [2,3]. As already mentioned above, a key complementary characteristic is that both sub- (<3.9) and supra- (>3.9) planetary Th/U ratios are observed.

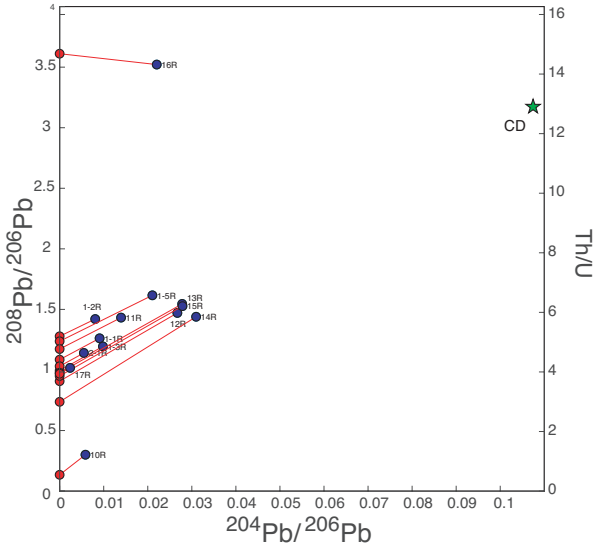

Figure 2: $^{208}Pb^*/^{206}Pb^*$ (in red) and Th/U calculated for the residues of 13 individual chondrules from Allende. CD = Canyon Diablo.

Brennecka et al. [7] interpreted the correlation between $^{235}U/^{238}U$ and both Th/U and Nd/U in CAIs by the decay of ^{247}Cu. Amelin et al. [1] argued against this interpretation by comparing Allende whole-rock and CAI values of $^{235}U/^{238}U$ and Nd/U. If the correlation is of universal relevance, sub-planetary Th/U ratios identified in the present Allende chondrules and the CAIs analyzed by [2] are difficult to account for by excess ^{247}Cm. Although the excess due to neutron capture is well documented in Allende by Sm isotopic measurements [10,11], the cross-section of ^{235}U for thermal neutron capture is too small to result in a significant effect on ^{232}Th. Preferential recoil of ^{238}U during decay from nanophases and low-temperature alteration are possible alternative interpretations.

Regardless of the final interpretation, the correlation between $^{235}U/^{238}U$ and both Th/U observed by [7] and the scatter of Th/U in chondrules reflects the presence of CAIs within chondrule precursors and thus, possibly, mixing between unrelated nucleosynthetic components. The consequences for the age of the Solar System and the age(s) of chondrules are therefore significant: the Pb-Pb alignments so far considered to be isochrons contain an undetermined contribution of mixing and, hence, the absolute age used to 'anchor' extinct radioactivities needs further clarification.

References: [1] Amelin Y. et al. (2010) *Earth Planet. Sci. Lett., 300,* 343–350. [2] Connelly J. N. et al. (2012) *Science, 338,* 651–655. [3] Connelly J. N. et al. (2017) *Geochim. Cosmochim. Acta, 201,* 345–363. [4] Bollard J. et al. (2017) *Science Advances, 3,* e1700407. [5] Blichert-Toft J. et al. (2010) *Earth Planet. Sci. Lett., 300,* 152–163. [6] Rocholl A. and Jochum K. P. (1993) *Earth Planet. Sci. Lett., 117,* 265–278. [7] Brennecka G. A. et al. (2010) *Science, 327,* 449–451. [8] Kennedy A. K. et al. (1994) *Chem. Geol., 117, 379*–390. [9] Loroch J. et al. (2018) *Data in Brief, 21,* 2447–2463. [10] Carlson R. W. et al. (2007) *Science, 316,* 1175–1178. [11] Bouvier A. and Boyet M. (2016) *Nature, 537,* 399–402.