Step leaching Pb-Pb isochron age of unradiogenic single chondrule from CV Allende chondrite.

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Introduction: The U-Pb system is suitable for precise single chondrule dating, but its successful application via ID-TIMS analysis requires analysing picogram quantities of radiogenic Pb, and separation of radiogenic Pb from terrestrial contamination and other non-radiogenic (initial) Pb components. The latter requirement can be potentially fulfilled by a multi-step dissolution procedure able to reduce a multi-component mixture to a two components mixture of initial and radiogenic Pb suitable for a meaningful isochron regression [1-5]. Here we explore the potential of multi-step dissolution for Pb-isotopic dating of individual chondrules and its effects on the U-Pb isotopic system and Pb-Pb isochron calculation through analysis of multiple fractions from a large Allende chondrule [6] that contains abundant non-radiogenic Pb that is notoriously difficult to remove.

Sample and analytical methods: A very large chondrule (>10 mm) referred to as megachondrule hereafter was extracted and split into nine fractions ranging between 2 and 12 mg analysed in three batches. These batches included between 2 to 4 fractions with increasing grain size. They were processed using three different step dissolution protocols involving 4, 9 and 12 step of HBr, HCl, HNO3, HF leaching with varying concentration, temperature, and duration of treatment followed by final dissolution in concentrated HF. Pb isotopic analyses were performed on a Triton Plus TIMS using a secondary electron multiplier in a peak jumping mode. Total procedure blanks varied between 0.5-1.6 pg Pb between the leaching steps and sample batches. The preliminary data [6] together with new analyses have been processed and filtered for analytically unreliable data. The Pb-Pb have been calculated using with the new $^{238}U/^{235}U = 137.764 \pm 0.016$ of [7].

Results and discussion: The total Pb contents range from 110 to 452 ppb for the nine fractions and are independent of the grain size and fraction weight. The blank corrected $^{206}Pb/^{204}Pb$ ratios range from 15.6 to 61.7. In the $^{204}Pb/^{207}Pb$ vs $^{207}Pb/^{206}Pb$ plot, the entire dataset fills a triangular field revealing the presence of present radiogenic Pb, initial Pb close to primordial composition, and contamination terrestrial Pb. Excepting two data points, the proportion of unradiogenic Pb (initial and contamination) represents between 43 to 70% of the total Pb content measured in the different fractions. In all leaching protocols, the $^{206}Pb/^{204}Pb$ ratios tend to increase through the entire leaching procedure suggesting that radiogenic Pb is progressively extracted showing that the step-leaching process does separate Pb components. For a given protocol, slight differences can be observed between the fractions in the values of $^{206}Pb/^{204}Pb$ ratio and proportion of total Pb content removed during a given step. For instance, the first step of HBr leaching tends to remove contamination Pb more efficiently if the grain size is smaller. Other differences might be related to the mineralogical variations between the fractions. The two first steps (water+acetone and HBr) release between 16 to 85% of the total Pb content with corresponding $^{206}Pb/^{204}Pb$ ratios close to modern terrestrial crust suggesting that (1) contamination Pb is preferentially removed during these steps and (2) for the majority of the analysed fractions of the megachondrule, contamination Pb represents a significant part of the total Pb content. The early HCl step tends to leach preferentially radiogenic Pb, and large fractions of both total Pb and U are released at this step, suggesting dissolution of U-bearing minerals. The final dissolution tends to yield less Pb with lower $^{206}Pb/^{204}Pb$ ratios than the previous steps including those involving HF as already observed by [5].

Due to the limited range of $^{206}Pb/^{204}Pb$ ratios and their unradiogenic values, extracting a precise isochron date was challing. Only the data from the HF steps and residues yield a mixing line between a radiogenic component and initial Pb. A regression line of these data passes through the values of primordial Pb, but the data display some scatter that limits precision of the isochron date. By removing data points that have large uncertanties or show Pb isotopic ratios close to terrestrial contamination Pb, the remaining data fail to yield a reliable date even when the regression is anchored to the primordial Pb. The mathematical recombinasion of several successive steps was attempted but is did not considerably improve the date. Following the procedure used by [3], removing the few data points that plot marginally below the line between the most radiogenic Pb data and primordial Pb yields a regression that allow the calculation of an isochron date of 4569.1 ± 2.2 Ma. A date of 4566.9 ± 1.4 Ma is obtained when the regression is constrained to the value of primordial Pb. Despite being less precise, is in the range of both multi-chondrule fractions by [1-4] and single chondrules determined by [3].

References: [1] Amelin Y. and Krot A. N. 2007. *Meteoritics and Planetary Sciences* 42:1321–1335. [2] Amelin Y. et al. 2009. *Geochimia Cosmochimica Acta* 73:5212–5223. [3] Connelly J. et al. 2012. *Science* 338:651–655. [4] Connelly J. et al. 2008. *The Astrophysical Journal* 675:121–124. [5] Connelly J. and Bizzarro M. 2009. *Chemical Geology* 259:143–151. [6] Amelin Y. et al. 2014. Abstract # 2646. 45th Lunar & Planetary Science Conference. [7] Huyskens et al. 2016. Abstract # 2727. 47th Lunar & Planetary Science Conference.