

Investigating the effects of acid leaching on the U-Th-Pb system in CAIs from the CV chondrite NWA 4502.
M. S. Sapah, Y. Amelin and T.R. Ireland, Research School of Earth Sciences, Building 142 Mills Road, The Australian National University, Canberra ACT 0200, Australia (marian.sapah@anu.edu.au)

Introduction: Inconsistencies in the ages of CV CAIs have been observed in U-Pb dating studies over the last decade [e.g.1-4]. These inconsistencies can have multiple causes, which should all be considered. Along with variability of $^{238}\text{U}/^{235}\text{U}$ ratio [5], the apparent ages can be influenced by secondary processing of the host meteorites, which may affect the U-Pb isotope systematics of CAIs. Acid leaching applied to remove contamination, weathering products and non-radiogenic Pb [3,6], can also induce fractionation of radiogenic $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ [7].

The importance of complete removal of non-radiogenic Pb for precise and accurate Pb isotopic dating of meteorites and their components is now well established [8-10]. Phases rich in non-radiogenic Pb can be removed by a combination of ultrasonic agitation and acid leaching. However, intensive acid leaching for meteorite components such as CAIs and chondrules may disturb the U-Pb, making accurate determination of $^{207}\text{Pb}/^{206}\text{Pb}$ age dates difficult [2-4, 11]. Acid leaching also reduces the total amount of radiogenic Pb available for analysis, and this affects precision. It is important to develop more selective leaching procedures, which would preferentially extract common Pb but preserve radiogenic Pb.

In this study, we investigate the effect of acid leaching and the use of citrate-bicarbonate-dithionite (CBD) which was developed for removal of weathering products such as Fe hydroxide in soil studies [12] on CAIs from the CV chondrite NWA 4502.

Samples and Methods: The CAIs used in this study are type A CAIs 6 and 7, type B CAI 1 and FoB CAI 5 [13]. All sample preparations were carried out under clean lab conditions. The analysed samples consist of mineral fractions obtained after disaggregation, cleaning and coarse crushing of CAI fragments. All fractions were pre-cleaned repeatedly with agitation in distilled acetone, ethanol and water before acid leaching.

Procedure 1: Mild acid leaching following [6] was applied to 3-9 mg melilite and pyroxene concentrates (100-275 μm) from CAIs 1, 5, 6 and 7. The first acid leaching step (W1) is an ultrasonic wash with 1ml of 0.5 M HNO_3 with 10 min ultrasonic agitation, repeated 5 times. This was followed by a 1 hour hot (110 $^\circ\text{C}$) acid washing with 7 M HNO_3 and 6 M HCl two times each, combined as W2.

Procedure 2: A slightly more intensive procedure was applied to two aliquots (~ 20 mg) each of cleaned bulk/mix fractions (<100 μm) of CAIs 1 and 6. One portion of each CAI was treated with CBD, the other

was acid leached without CBD treatment. The CBD protocol used in this study was modified after [12]. A solution of 40 ml sodium citrate and 5 ml sodium bicarbonate was added to samples and heated to 80 $^\circ\text{C}$. At this temperature, 0.5 g of sodium dithionite was added and stirred thoroughly. The samples were kept at a constant temperature (110 $^\circ\text{C}$) for an hour with stirring every 15 min. The liquid was separated after cooling and the residue was thoroughly rinsed with ethanol and deionised water. Acid leaching included W1 and W2 as in procedure 1, followed by additional 10 min ultrasonic wash in 0.2 M HF collected as W3, and a 1 hour (110 $^\circ\text{C}$) hot wash in 1 M HF collected as W4.

Procedure 3: This procedure usually referred to as progressive dissolution is modified after [3,4] and is the most intensive in this study. It was applied to 20-30 mg bulk (<100 μm), fine (<100 μm) and coarse (>275 μm) melilite-rich fractions of CAI 1. This acid leaching procedure consists of 7 steps of a combination of hot and ultrasonic washing in the following order: 1 ml 0.3 M HBr, 1 ml 0.5 M HNO_3 , 1 ml 2 M HCl, 1 ml 6 M HCl, 1 ml 6 M HCl (110 $^\circ\text{C}$, 6 hr, and 15 min ultrasonication), 1 ml 1 M HF (15 min), and 1 M HF (110 $^\circ\text{C}$, 6 hr, and 15 min ultrasonication). Washes are denoted as L1, L2...L7.

Residues from all procedures were decomposed with concentrated HF + HNO_3 . All washes and residues were spiked with ^{202}Pb - ^{205}Pb - ^{233}U - ^{235}U isotope tracer, and analysed using procedures of [7].

Results: Uranium and Pb are preferentially extracted during the early stages of acid leaching. The total amounts of U and Pb in acid leached mineral fractions calculated using sample weights before leaching vary from ~0.01-2 ng and ~0.01-18 ng respectively. Total procedural blanks are <1 pg for Pb and <0.1 pg for U in all three procedures.

The Pb isotopic ratios in mineral fractions from CAI 1, 5, 6 and 7 in procedure 1 are variably radiogenic. In general, the isotopic composition of the Pb extracted in progressively stronger HNO_3 becomes more radiogenic. The most radiogenic signatures occur in some second leachates (W2) of melilite-rich fractions and all final residues. The measured $^{206}\text{Pb}/^{204}\text{Pb}$ after correction for fractionation, spike, and analytical blank are between 17-32 (W1), 38-334 (W2) and 98-5884 (Residues). Mineral fractions from the FoB CAI 5 contain the most radiogenic Pb. All other CAIs have similar amounts of radiogenic Pb in both their pyroxene-rich and melilite-rich fractions.

In procedure 2, the Pb isotopic ratios in both CBD-treated and untreated mineral fractions from CAI 1 and 6 are progressively radiogenic, CBD-treated samples are consistently more radiogenic than untreated samples. The first application of HF yielded Pb slightly more radiogenic than previous HNO₃ and HCl steps. A second application of HF liberates Pb that is still more radiogenic. The ²⁰⁶Pb/²⁰⁴Pb ratios are between 24-464 (W1-R) for CBD-treated samples and 20-250 (W1-R) for untreated samples.

The progressive acid leaching procedure 3, yielded Pb isotopic ratios in leachates becoming progressively more radiogenic from L1-R especially for coarse (>275 μm) grained fractions. The first leaching steps with weak HBr and HNO₃ (L1-L2) removes non-radiogenic Pb but did not extract significant quantities radiogenic Pb. Subsequent steps (L3-L5) of progressively stronger HCl extracted progressively more radiogenic Pb. Application of HF liberates Pb more radiogenic than previous steps, and final residues contain the most radiogenic Pb. Fractions <100 μm depart from this pattern where pre-HF steps have more radiogenic signatures. The HNO₃ and HCl steps (L2-L4) contain a more radiogenic signature than the subsequent HF step (L6) but are less radiogenic than the second HF step (L7) and residue. The most radiogenic signature occurs in the second concentrated HCl step (L5). The ²⁰⁶Pb/²⁰⁴Pb ratios are between 21-83 (<100 μm mixed fraction), 24-464 (<100 μm melilite-rich fraction) and 32- 895 (>275 μm melilite-rich fraction).

Comparing the degree to which the final residues of mineral fractions from CAI 1 are radiogenic in all three procedures; melilite and pyroxene rich fractions (100-275 μm) in procedure 1 yielded ²⁰⁶Pb/²⁰⁴Pb of ~98 and 450 respectively. Mix fraction residues in procedure 2 not treated with CBD have a ²⁰⁶Pb/²⁰⁴Pb value of 245 while CBD treated samples have a ²⁰⁶Pb/²⁰⁴Pb value of 405. Mix fraction residues in procedure 3 produced a ²⁰⁶Pb/²⁰⁴Pb of 52 about 5 times lower compared to those in procedure 1. Melilite-rich fractions (<100 - >275 μm) yielded the most radiogenic CAI 1 residues with values from 463-895.

Applying the ²³⁸U/²³⁵U of 137.808 for NWA 4502 CAIs [14] to ²⁰⁷Pb/²⁰⁶Pb-²⁰⁶Pb/²⁰⁴Pb isochron ages of the most radiogenic fractions in all procedures, residue analyses in procedure 1 yielded an age of 4567.40±0.27 Ma (MSWD =2.0) [14]. Leachate 7 and residues of coarse melilite-rich fractions in procedure 3 give an age of 4567.2 ± 1.3 Ma (MSWD =1.4), while W4 and residues in procedure 2 CBD-treated and untreated samples give less precise ages of 4574 ± 25 Ma (MSWD=161) and 4561.0± 8.6 (MSWD =52) respectively.

Discussion: Repeated pre-cleaning by ultrasonication in distilled ethanol, acetone and water effectively

removes terrestrial contamination in samples analysed as reported in other studies [3,6]. Non-radiogenic Pb was preferentially removed during acid leaching processes. Procedure 2 shows that additional cleaning with CBD is effective in further removing non-radiogenic Pb and terrestrial contamination. Procedure 1 produces variably radiogenic leaching steps compared to procedure 2 and 3 which gave progressively radiogenic leaching steps.

Leaching with HNO₃ usually separates the least radiogenic component of the dissolution series. However, increasing concentrations of HNO₃ and HCl with longer and higher temperature yields more radiogenic Pb fractions. HF is most effective in liberating radiogenic signatures. This has also been observed for CV chondrite chondrules [3].

It is not clear which mineral phase is the dominant Pb carrier in these CAIs. Both melilite and pyroxene contain comparable amounts of radiogenic Pb and are suitable for U-Pb dating. A more aggressive procedure 3 significantly reduces the total amount of radiogenic Pb analysed compared to the other procedures. Also, variable radiogenic Pb signatures obtained for fine fractions compared to coarse fractions in procedure 3 may indicate that the mineral that hosts non-radiogenic Pb is more readily removed from coarse grained fractions.

While U and Pb were highly and variably fractionated during procedures 2 and 3, the residues of CAIs obtained with procedure 1 gave the most accurate and precise Pb-Pb age for NWA 4502 CAIs so far. Even though this study has provided some insights into the effects of acid leaching on U-Pb isotope systems of NWA 4502 CAIs, further studies are required because there is still much to be understood.

References: [1] Amelin, Y. et al. (2002) *Science*, 297, 1678. [2] Amelin, Y. et al. (2009) *GCA*, 73, 5212-5223. [3] Connelly, J. N. and Bizzarro, M. (2009) *Chemical Geology*, 259, 143-151. [4] Bouvier, A and Wadhwa, M. (2010) *Nature geoscience*, 3, 637-641. [5] Brennecka, G. A. et al. (2010) *Science*, 327, 449-451. [6] Amelin, Y. (2008) *GCA* 72, 221-232 [7] Amelin, Y. et al. (2010) *EPSL* 300, 343-350. [8] Lugmair, G. W and Galer, S. J. G. (1992) *GCA* 56, 1673-1694. [9] Göpel, C. et al. (1994) *Earth and Planet. Sci.* 121,153-171. [10] Amelin, Y. (2006) *Meteorit & Planet. Sci.* 41, 7-17. [11] Tera, F. et al., (1997) *GCA* 61, 1713-1731. [12] Van Oorschot, I. H. M. and Dekkers, M. J. (1999) *Earth and Planet. Sci.* 167, 283-295. [13] Sapah, M. S. et al. (2013) *LPSC abstract* [14] Amelin, Y. et al. (2013) *LPSC abstract*. [15] Bouvier, A. et al. (2011) *Workshop on Formation of the First Solids in the Solar System*, 9054. [16] Connelly J. N. et al. (2012) *Science*, 338, 651-655.