U-PB AGE OF REFRACTORY INCLUSIONS FROM THE CV CARBONACEOUS CHONDRITES ALLENDE AND EFREMOVKA. Y. Amelin[1], L. Grossman[2], A. N. Krot[3], T. Pestaj[1], S. B. Simon[2], and A. A. Ulyanov[4], [1]Department of Earth Sciences, Royal Ontario Museum, Toronto, ON M5S 2C6, Canada, yuria@rom.on.ca, [2]Department of the Geophysical Sciences, University of Chicago, Chicago, IL 60637, USA, [3]Hawaii Institute of Geophysics and Planetology, SOEST, University of Hawaii, Honolulu, HI 96822, USA, [4]Moscow State University, Moscow 117999, Russia.

CAI age controversy: Ca-Al-rich inclusions (CAIs) found in carbonaceous chondrites are thought to represent the earliest solids formed in the solar system. Their age is a fundamental reference point for cosmochronology. However, the debate about the timing of the CAI formation started with the first U-Pb age determinations published in 1975 [1, 2] and is still not settled. Subsequent studies [3-5] achieved more radiogenic Pb isotope composition and better precision, however age estimates obtained in these studies and in data re-evaluations using compilations and alternative data treatment [6, 7] vary between 4559-4566 Ma. Moreover, a recent estimate [8] based on ^{53}Mn-^{53}Cr isotopic systematics and the precise Pb-Pb age of angrites [9] as a link to the absolute time scale gives the CAI age as old as 4571 Ma.

This variation in the age estimates is unacceptably large for modern chronology of the solar system formation, which is mainly concerned with the first 10 Ma following the beginning of accretion. On the other hand, the refinement of U-Pb analytical and data treatment techniques since the previous studies of CAIs suggests that obtaining more precise and accurate data than before is feasible.

Choice of materials: We have dated CAIs from two CV3 chondrites: Allende and Efremovka. All previous U-Pb chronological studies of CAIs were performed only on the Allende inclusions. Both meteorites are reasonably well preserved, however neither is perfect: Allende is an oxidized CV chondrite and experienced more extensive late-stage, Fe-alkali-metasomatic alteration than the reduced CV chondrite Efremovka [10]; the latter, however, experienced relatively strong shock metamorphism [11]. This gives an opportunity to evaluate the effects of these disturbing processes on U-Pb systems of CAIs.

The mineralogy, chemical and isotopic compositions of these inclusions have been reported previously [12-17]. These inclusions represent various types of CAIs in the currently accepted classification [18]. The analyzed splits from Allende CAIs F-2 (Type B2), TS-32 (Compact Type A, or CTA) and TS-33 (B1) are aliquots of powders prepared for representative chemical analyses of bulk CAIs. The Efremovka CAI E-60 is a forsterite-bearing Type B (Fo-B) inclusion composed of Al-diopside, melilite ($Åk_{22-86}$), anorthite, spinel, and forsterite; anorthite is a secondary mineral replacing melilite [16]. E-60 has a canonical $(^{26}Al/^{27}Al)_I$ ratio of $(4.63±0.44)×10^{-5}$ (Hutcheon, unpubl.) The Efremovka CAI E-49a (CTA) inclusion is composed largely of melilite and spinel; Al-diopside, perovskite, and anorthite are accessory. Melilite is corroded by Al-diopside and anorthite. Secondary nepheline is a minor phase in both E-49a and E-60. Fragments of these CAIs were crushed to 50-100 micron pieces at the ROM.

Procedures and results: Pulverized samples of the Allende CAIs were separated using bromoform and methylene iodide into fractions with density of <2.85g/cm^3, 2.85-3.15 g/cm^3 and >3.15 g/cm^3, enriched in plagioclase, melilite and pyroxene, respectively. The fragments of the Efremovka CAIs were hand-picked to avoid weathered domains (e.g. marked with rusty staining) and analyzed without mineral separation.

The selected fractions were washed in 0.5N – 2.0N HCl with ultrasonic agitation to minimize contamination related to weathering and handling. Both acid washes and residues were analyzed using standard U-Th-Pb procedures adopted at the ROM Geochronology Lab. Acid washes contain common Pb with $^{206}Pb/^{204}Pb$ between 15.7-18.3 and low U/Pb ratios. In contrast, washed CAI minerals and bulk fractions contain much more radiogenic Pb. Three very small (0.07-0.35 mg) plagioclase-rich fractions of Allende CAIs yielded Pb with relatively low $^{206}Pb/^{204}Pb$ of 39-120 and imprecise U-Pb data and are not considered here. Six other Allende separates (melilite- and pyroxene-rich) and all five analyzed Efremovka fractions yielded highly radiogenic Pb isotopic compositions with $^{206}Pb/^{204}Pb$ between 270-1010, suitable for precise U-Pb and Pb-Pb age calculations (Table 1).

Various methods have been applied to the treatment of U-Pb data. Single-stage $^{207}Pb/^{206}Pb$ model ages calculated assuming primordial Pb isotopic composition from [19] are 4566.3-4568.9 Ma (Table 1, col. 9). The 3D linear isochron regression of all highly radiogenic analyses presented in Table 1 yields an age estimate of 4567±6 Ma, independent of assumption of a certain initial Pb isotopic composition. The initial Pb isotopic compositions $^{206}Pb/^{204}Pb=19.0±3.3$ and $^{207}Pb/^{204}Pb=16.5±2.6$ are obtained from the same 3D isochron. This method of age calculation assumes, however, that the analyses are concordant and the initial Pb is isotopically homogeneous. High MSWD=66 indicates that at least one of these assumptions is incorrect. Including analyses of acid washes to the 3D linear isochron regression greatly increases the spread of U/Pb ratios. The isochron yields an age of 4568±9 Ma (MSWD=1326), and more precise $^{206}Pb/^{204}Pb$ = 16.32±0.45 and $^{207}Pb/^{204}Pb$ = 14.50±0.49. These Pb isotopic ratios are intermediate between modern terrestrial common Pb, on one hand, and primordial Pb [19] and Allende matrix Pb [1,2,4], on the other. The common Pb present in the CAIs is therefore likely to be a mixture of two or three components: initial, redistributed from or contaminated by the matrix, and terrestrial contamination. The average common Pb isotopic composition in CAIs obtained from the 3D isochron regression can be used as an alternative common Pb value for the $^{207}Pb/^{206}Pb$ model ages calculations. The model ages vary from 4567.1 - 4570.2 Ma (Table 1, col. 10), and are 0.4-1.5 Ma older than the model ages obtained with the primordial Pb (the difference decreases with increasing $^{206}Pb/^{204}Pb$ in the fraction).

None of the methods used in U-Pb and Pb-Pb data treatment: model ages, 2D or 3D U-Pb concordia diagrams, or Pb-Pb isochrons, can account for both U-Pb isotopic disturbance and heterogeneity of the common Pb. Only one of these methods: the 3D planar regression, is designed to analyze the systems with variable common Pb composition. The 3D planar regression through all Efremovka and Allende CAI analyses (residues) yielded an age of 4568±15 Ma, MSWD=3.9.

Precise and accurate ages from imperfect U-Pb systems: The data presented above suggest that U-Pb isotopic systems in Allende and Efremovka CAIs are complicated by heterogeneity of common Pb, and by recent U and/or Pb migration. We therefore apply common Pb isotopic composition determined from 3D linear U-Pb regression to calculation of radiogenic Pb isotopic ratios. If the measured $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ are sufficiently high, and realistic errors are assigned to the common Pb values, the $^{207}Pb/^{206}Pb$ model ages or concordia intercept ages are accurate within error limits. This approach yields the concordia intercept ages of 4568.71±0.77 Ma, MSWD=1.3, for the Efremovka CAIs, 4568.05±0.65 Ma, MSWD=0.33 for the Allende CAIs, and 4568.04±0.43 Ma, MSWD=1.3 for the combined data set. Zero (within error) lower intercepts and the absence of excess scatter argue against ancient U-Pb disturbance. The latter age value is our preferred estimate for the age of the CAIs. This value is consistent with the Pb-Pb isochron age of 4566.6±1.7 Ma based on the same data. No age heterogeneity is detected between the two meteorites or between individual CAIs.

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Table 1. U-Pb data for refractory inclusions from carbonaceous chondrites Efremovka and Allende.

Meteorite, CAI	Type	Fraction (density)	Weight mg	U ppb	$^{206}Pb/^{204}Pb$ measured (1)	$^{238}U/^{204}Pb$ (2)	$^{206}Pb^*/^{238}U$ Age, Ma(2,3)	$^{207}Pb^*/^{206}Pb^*$ Age, Ma(2,3)	$^{207}Pb^*/^{206}Pb^*$ Age, Ma(2,4)
Efremovka									
E49	CTA	Bulk	3.66	19	448.8	592.4	4382±23	4566.6±0.8	4567.3±1.3
E60	Fo-B	Bulk	4.88	33	334.1	328.7	4665±12	4568.9±0.9	4570.2±2.0
E60	Fo-B	Bulk	4.14	33	270.9	265.4	4646±18	4568.1±0.9	4569.6±2.4
E60	Fo-B	Bulk	2.92	29	524.8	531.3	4695±19	4567.9±0.8	4568.6±1.3
E60	Fo-B	Bulk	7.17	36	349.0	325.9	4675±10	4567.4±0.8	4568.6±2.0
Allende									
F2	B2	(>3.15)	0.52	99	686.8	807.0	4654±29	4567.0±0.7	4567.5±1.0
TS32	CTA	(>3.15)	2.18	78	406.3	395.6	4604±10	4566.9±0.8	4567.9±1.7
TS33	B1	(>3.15)	2.37	89	402.6	381.1	4670±16	4567.6±0.9	4568.6±1.8
F2	B2	(2.85-3.15)	0.86	45	425.5	454.0	4762±38	4566.3±0.8	4567.1±1.5
TS32	CTA	(2.85-3.15)	3.75	58	1010.5	1049.0	4573 ± 9	4567.8±0.8	4568.2±1.0
TS33	B1	(2.85-3.15)	1.38	56	353.7	341.9	4716±20	4566.7±0.7	4567.8±1.9

(1) Measured isotopic ratios, no corrections applied. (2) Corrected for fractionation, spike and blank. (3) Radiogenic Pb isotopic ratios and ages are calculated using the primordial Pb isotopic composition from Tatsumoto et al. (1973) assuming zero errors. (4) Ages are calculated using the common Pb isotopic composition ($^{206}Pb/^{204}Pb$=16.32±0.45, $^{207}Pb/^{204}Pb$=14.50±0.49, Rho=0.9) determined from 3D linear regression of the complete data set of Allende and Efremovka CAI U-Pb analyses, including both washes and residues. Errors are 2 σ.