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Pb isotopic age of the Allende chondrules

Yuri AMELIN[1†*] and Alexander KROT[2]

[1]Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada, K1A 0E8
[2]Hawai'i Institute of Geophysics and Planetology, School of Ocean, Earth Science and Technology,
University of Hawai'i at Manoa, Honolulu, Hawai'i 96822, USA
[†]Present address: Research School of Earth Sciences, The Australian National University, 61 Mills Road, Canberra, ACT 0200, Australia
[*]Corresponding author. E-mail: yuri.amelin@anu.edu.au

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Abstract–We have studied Pb-isotope systematics of chondrules from the oxidized CV3 carbonaceous chondrite Allende. The chondrules contain variably radiogenic Pb with a $^{206}Pb/^{204}Pb$ ratio between 19.5–268. Pb-Pb isochron regression for eight most radiogenic analyses yielded the date of 4566.2 ± 2.5 Ma. Internal residue-leachate isochrons for eight chondrule fractions yielded consistent dates with a weighted average of 4566.6 ± 1.0 Ma, our best estimate for an average age of Allende chondrule formation. This Pb-Pb age is consistent with the range of model ^{26}Al-^{26}Mg ages of bulk Allende chondrules reported by Bizzarro et al. (2004) and is indistinguishable from Pb-Pb ages of Ca-Al-rich inclusions (CAIs) from CV chondrites (4567.2 ± 0.6 Ma) (Amelin et al. 2002) and the oldest basaltic meteorites. We infer that chondrule formation started contemporaneously with or shortly after formation of CV CAIs and overlapped in time with formation of the basaltic crust and iron cores of differentiated asteroids. The entire period of chondrule formation lasted from 4566.6 ± 1.0 Ma (Allende) to 4564.7 ± 0.6 Ma (CR chondrite Acfer 059) to 4562.7 ± 0.5 Ma (CB chondrite Gujba) and was either continuous or consisted of at least three discrete episodes. Since chondrules in CB chondrites appear to have formed from a vapor-melt plume produced by a giant impact between planetary embryos after dust in the protoplanetary disk had largely dissipated (Krot et al. 2005), there were possibly a variety of processes in the early solar system occurring over at least 4–5 Myr that we now combine under the umbrella name of "chondrule formation."

INTRODUCTION

Chondrules (millimeter- to submillimeter-sized spherules composed mostly of mafic silicates) are the most abundant component in most chondrites (Zanda 2004). Chondrules in most meteorites are believed to have formed by melting of solid precursors, including fine-grained dust, chondrules of earlier generations and refractory inclusions, in the protoplanetary disk (e.g., Jones et al. 2005 and references therein; Russell et al. 2005). Age relationships between chondrules and their more refractory counterparts, Ca-Al-rich inclusions (CAIs), which are considered the earliest solids formed in the solar system (Amelin et al. 2002), would therefore provide an estimate for the lifespan of the protoplanetary disk (Russell et al. 2006 and references therein). Although petrographic, mineralogical, chemical, and isotopic observations suggest that CAIs predate chondrule formation (Russell et al. 2005 and references therein), the absolute age difference between these components remains poorly constrained.

The relative ages of chondrules and CAIs have been determined in many studies, using mostly isotopic effects produced by decay of short-lived, now extinct radionuclides, including ^{26}Al ($t_{1/2}$ ~ 0.73 Myr), ^{53}Mn ($t_{1/2}$ ~ 3.7 Myr), and ^{129}I ($t_{1/2}$ ~ 16 Myr) (Kita et al. 2005 and references therein). Using extinct-nuclide chronometers to measure the time difference between CAI and chondrule formation requires assumptions of homogeneous initial distribution of the parent nuclides in the CAI- and chondrule-forming regions, and both extinct- and extant-nuclide chronometers require the lack of subsequent disturbance of these isotope systematics during parent body processing, such as metamorphism and aqueous alteration. Although the parent body effects on isotopic systematics of chondrules and CAIs can be minimized by studying mineralogically primitive chondrites, the assumption of homogeneous distribution of short-lived radionuclides in the CAI- and chondrule-forming regions may not be necessarily true, considering (i) variable and in some cases, large isotopic anomalies of many elements in CAIs (e.g., Ireland 1990), (ii) the possible irradiation origin of ^{10}Be (McKeegan et al. 2000) and ^{7}Be (Chaussidon et al. 2006) in CAIs, and (iii) the proposed irradiation origin, sole or partial, of other short-lived radionuclides (^{26}Al, ^{41}Ca, ^{53}Mn) commonly used for relative chronology (Goswami et al. 2005 and references therein). We note that, from bulk Mg isotope measurements of chondrites, Martian meteorites, and terrestrial samples, Thrane et al. (2006) inferred uniform distribution of ^{26}Al in the inner protoplanetary disk, where CAIs and chondrules probably formed, but the matter needs further investigation.

Chronometers based on long-lived (extant) nuclides do not require the assumption of initial homogeneous distribution of the parent nuclide. Instead, the distribution can be verified by measuring the present-day abundance of the nuclide (high-precision U isotope data for Allende have been reported by Stirling et al. 2006). Recent improvements in the precision of Pb isotopic dating allow us to tackle the question of the CAI-chondrule formation interval. Using modern Pb-isotope dating techniques, we resolved the difference in the time of formation between CAIs from the reduced CV3 chondrite Efremovka (4567.2 ± 0.6 Ma) and chondrules from the CR2 carbonaceous chondrite Acfer 059 (4564.7 ± 0.6 Ma) (Amelin et al. 2002). However, application of this result to the estimation of the time difference between CAI and chondrule formation involves general uncertainty related to the origin of chondrules and CAIs in different chondrite groups (e.g., Shu et al. 2001; Russell et al. 2005; Scott and Krot 2005) and the lack of Pb-isotopic dating of CAIs from CR chondrites or chondrules from CV chondrites. For example, according to the X-wind model, CAIs and chondrules in a chondrite group formed contemporaneously near the X-point and were subsequently transported to their accretion region(s) by X-wind (Shu et al. 2001). These uncertainties can be eliminated if Pb-isotopic dates are determined from chondrules and CAIs extracted from the same meteorite, or at least from meteorites of the same group, probably originating from the same parent body.

Here we present the results of Pb isotopic dating of chondrules from the oxidized CV chondrite Allende. During this study, we have found that complete removal of common Pb, a condition for precise and accurate Pb-isotopic dating, from Allende chondrules is hard to achieve (here all Pb other than in situ accumulated radiogenic Pb is referred to as common Pb). To circumvent this problem, we have developed an alternative approach to chondrule age determination based on the use of combined acid leachate and leaching residue Pb isotopic compositions. We also discuss the consequences of possible age heterogeneity in the Allende chondrule population, suggested by a recent ^{26}Al-^{26}Mg study of bulk Allende chondrules (Bizzarro et al. 2004), for Pb isotopic dating.

ALTERATION OF CHONDRULES FROM CV CHONDRITES

CV chondrites are currently subdivided into the reduced (CV_{red}) and two oxidized subgroups, Allende-like (CV_{oxA}) and Bali-like (CV_{oxB}) (McSween 1977; Weisberg and Prinz 1998), which largely reflect their complex alteration history (Krot et al. 1995, 1998a, 1998b, 2004). Chondrules in the CV_{oxB} chondrites (e.g., Kaba, Bali) experienced aqueous alteration resulting in the replacement of primary mineral phases (mostly mesostasis and Fe,Ni metal; low-Ca pyroxene is only slightly altered; olivine is almost unaltered) by secondary phyllosilicates, magnetite, Fe,Ni sulfides, Fe,Ni carbides, fayalite ($Fa_{>90}$), salite-hedenbergite pyroxenes ($Fs_{10-50}Wo_{45-50}$), and andradite. Chondrules in the CV_{oxA} chondrites, including Allende, experienced iron-alkali metasomatic alteration resulting in replacement of their primary minerals by nepheline, sodalite, salite-hedenbergite pyroxenes, andradite, Fe,Ni sulfides, magnetite, Ni-rich metal, and ferrous olivine ($Fa_{\sim 40-50}$). Most of the opaque nodules and mesostasis of the Allende chondrules are replaced by secondary minerals; replacement of low-Ca pyroxene by ferrous olivine and enrichment of olivine in FeO decrease toward chondrule cores. The CV_{red} chondrites Efremovka and Leoville experienced alteration similar to that of CV_{oxA}, but to a smaller degree (see Krot et al. 1998a, 1998b, 2004 for details).

From the petrographic and mineralogical observations and isotopic data, including ^{26}Al-^{26}Mg, ^{53}Mn-^{53}Cr, and ^{129}I-^{129}Xe chronology of secondary phases and their oxygen isotopic compositions, it is inferred that secondary mineralization in CV chondrites resulted from prolonged (>10 Myr) fluid-assisted thermal metamorphism postdating accretion of the CV parent asteroid, and the CV subgroups represent its different lithologies (Krot et al. 2006 and references therein).

Physico-chemical conditions (pressure, temperature, pH, fO_2, water/rock ratio) of the CV alteration remain poorly constrained, which partly reflects its complex, multistage nature (aqueous alteration followed by thermal metamorphism) (e.g., Krot et al. 1998a, 1998b; Bonal et al. 2006 and references therein). For example, the petrographic type assigned to Allende varies from 3.2 based on the thermoluminescence studies of CV chondrites (Guimon et al. 1995), to 3.6, suggested by Bonal et al. (2006) on the basis of a Raman spectroscopy study of structural order of organic matter in CV chondrites. From thermodynamic analysis of secondary mineralization in CV chondrites, Krot et al. (1998a) and Zolotov et al. (2006) inferred that aqueous alteration of CV chondrites occurred below ~350 °C, at a total pressure below 100 bars and with a relatively low water/rock ratio (<0.2). Allende may have then experienced thermal metamorphism with peak metamorphic temperatures of ~400–550 °C (McSween 1977; Blum et al. 1989; Weinbruch et al. 1994).

PREVIOUS ISOTOPIC STUDIES

Allende is arguably the most extensively studied meteorite. CV chondrites contain larger and more abundant CAIs than other chondrites, and Allende is by far the most plentiful CV chondrite, therefore Allende CAIs in particular have received a lot of attention from cosmochemists. The number of radiogenic isotope studies of Allende chondrules is much smaller. Early U-Th-Pb studies by Chen and Tilton (1976) and Tatsumoto et al. (1976), in which all components of the Allende meteorite (CAIs, chondrules, and matrix) were analyzed, yielded Pb isotopic dates of 4565 ± 4 Ma, and 4553 ± 4 Ma, respectively, from combined isochron regressions including chondrules, CAIs and matrix. Chondrules, CAIs and other components from Allende were also analyzed for U-Pb by Arden and Cressey (1984), but these authors did not report any age calculations. Rubidium-Sr data for Allende chondrules, reported by Gray et al. (1973) and Tatsumoto et al. (1976), form scattered arrays suggesting late re-distribution of Rb and/or Sr. A more recent Rb-Sr study by Shimoda et al. (2005) indicates two stages of disturbance, the first episode at 4.41 ± 0.12 Ga (the authors use a ^{87}Rb decay constant of 1.402×10^{-11} yr^{-1} following Begemann et al. 2001), followed by later continuous or episodic processes. A recent high-precision MC-ICP-MS (multicollector inductively coupled plasma mass spectrometry) study of ^{26}Al-^{26}Mg systematics of bulk Allende chondrules (Bizzarro et al. 2004) suggests that formation of Allende chondrules continued for at least 1.2 Myr and the oldest chondrules may have formed contemporaneously with CAIs. We note that model ages of the Allende chondrules based on bulk Mg isotope measurements may represent ages of chondrule precursors rather than crystallization ages of chondrules; the latter requires knowledge of internal Al-Mg systematics of chondrules, which are typically measured with less precision in situ by secondary ion mass spectrometry (SIMS). Preliminary SIMS data on Mg isotopic compositions of mineral phases in chondrules from primitive chondrites suggest initial ^{26}Al/^{27}Al ratios in chondrules less than 1.5×10^{-5} so far (Kita et al. 2005 and references therein). An independent evidence for the minimum age interval of Allende chondrule formation of 1 Myr is determined obtained from an ^{26}Al-^{26}Mg SIMS study of a compound chondrule, made of two chondrules of different ages (Akaki et al. 2007).

ANALYTICAL PROCEDURES

We analyzed chondrules from two specimens of the Allende meteorite. For this study, we processed an ~30 g specimen, completely covered with fusion crust, from the meteorite collection of the Royal Ontario Museum. The sample was crushed and chondrules were separated as described previously for the Richardton chondrite (Amelin et al. 2005). Additional chondrules were picked from the sample earlier processed at the Washington University.

Data reported here have been acquired in four analytical sessions between March 2002 and May 2004. Sample washing, chemistry and mass spectrometry varied between the sessions. Detailed descriptions of analytical procedures used in each session are summarized in the Electronic Annex EA-1. All chondrules were washed in acids to remove loosely bound common Pb. Throughout the text, acid-washed materials are referred to as "residues" or simply "chondrules," whereas the material extracted to acidic solutions during washing is referred to as "leachate."

Isochrons, weighted means and medians and their uncertainties were calculated using Isoplot/Ex version 3.00 (Ludwig 2003). All isochrons, weighted mean and median errors have 95% confidence intervals, unless indicated otherwise.

RESULTS

U-Th-Pb Systematics

Pb isotopic data, Pb, U and Th concentrations, and ^{238}U/^{206}Pb* and ^{207}Pb*/^{206}Pb* model dates are presented in Table 1. A complete form of this table, which contains all isotopic ratios with errors and error correlations necessary for isochron calculations, is available online at http://meteoritics.org. Uranium and Pb concentrations in acid-washed chondrules are lower and more variable than the concentrations reported for Allende chondrules analyzed without acid leaching by Chen and Tilton (1976) and Tatsumoto et al. (1976). For set 4, where acid washes were analyzed along with residues, U and Pb concentrations before washing have been calculated as the sums of concentrations in both washes and the residue. Uranium concentrations between 14–22 ppb and total Pb concentrations between 69–150 ppb are more consistent than the concentrations in acid-washed chondrules, indicating evidence for substantial and variable Pb and U loss during acid washing of chondrules.

Lead isotopic ratios in chondrules are variably radiogenic, with measured ^{206}Pb/^{204}Pb between 19.5–268 (or 19.3–658 after correction for fractionation, spike, and analytical blank). These ratios are less radiogenic than the values obtained from chondrules in CR chondrite Acfer 059 and H5 chondrite Richardton (Amelin et al. 2002, 2005) using similar techniques. Elevated content of common Pb in Allende chondrules, even after acid leaching, is a concern in isochron dating (Amelin 2006).

A complete set of leachate and residue analyses obtained for eight groups of chondrules during analytical session 4 allows comparison of Pb isotopic compositions on acid-soluble and insoluble portions of chondrules. Acid leachates contain less radiogenic Pb than residues of the same fractions:

Table 1. U-Th-Pb data.

Fraction	Set	Number of chondrules	Weight (g)	U (ppm)	Th (ppm)	Pb (ppm)	Pb (pg)	$^{206}Pb/^{204}Pb$ (raw)	$^{206}Pb/^{204}Pb$ (total)	$^{204}Pb/^{206}Pb$ (total)	$^{204}Pb/^{206}Pb$ % error	$^{207}Pb/^{206}Pb$ (total)	$^{207}Pb/^{206}Pb$ % error	$^{238}U/^{206}Pb^*$ date (Ma)	$^{207}Pb^*/^{206}Pb^*$ date (Ma)	$^{207}Pb^*/^{206}Pb^*$ date error
Residues																
1	1	1	0.00208	0.0097	nm	0.0418	87	47.36	47.70	0.02096	0.79	0.72000	0.15	4536	4570.5	3.2
2	1	1	0.00257	0.0071	nm	0.0283	73	42.15	42.27	0.02366	0.68	0.73185	0.17	4423	4570.0	3.6
3	1	1	0.00417	0.0137	nm	0.0485	202	43.42	43.54	0.02297	0.46	0.72885	0.18	4536	4570.2	4.0
4	1	1	0.00550	0.0158	nm	0.0477	263	64.95	65.43	0.01528	0.67	0.69205	0.19	4483	4563.5	3.7
5	1	1	0.00319	0.0120	nm	0.0346	110	89.80	92.21	0.01085	0.84	0.67385	0.11	4614	4568.0	1.9
6	2	1	0.00154	0.0058	nm	0.0200	31	50.85	51.88	0.01927	1.5	0.70711	0.22	4659	4555.4	3.7
7	2	1	0.00657	0.0033	nm	0.0146	96	30.37	30.66	0.03261	0.50	0.76892	0.11	4569	4560.2	2.1
8	2	1	0.00464	0.0007	nm	0.0065	30	19.47	19.34	0.05171	0.49	0.85276	0.23	5526	4550.3	9.5
9	2	1	0.00655	0.0028	nm	0.0151	99	29.68	29.94	0.03340	0.80	0.76978	0.25	5147	4551.2	7.1
10	2	1	0.00339	0.0071	nm	0.0211	72	87.42	93.66	0.01068	3.3	0.67062	0.23	4791	4561.6	1.8
11	2	2	0.00596	0.0047	nm	0.0170	101	64.12	66.30	0.01508	1.9	0.69172	0.35	5180	4565.0	6.5
12	2	1	0.00509	0.0130	nm	0.0714	363	171.4	182.2	0.00549	2.8	0.64879	0.11	4733	4565.3	1.1
13	2	2	0.00586	0.0056	nm	0.0190	111	79.56	83.04	0.01204	2.0	0.67785	0.16	4875	4564.5	1.6
14	2	2	0.00696	0.0054	nm	0.0172	120	60.11	61.72	0.01620	1.2	0.69749	0.14	4590	4567.1	1.7
15	2	6	0.00483	0.0072	nm	0.0285	138	80.66	84.11	0.01189	1.9	0.67651	0.20	4824	4562.7	2.6
16	2	4	0.00598	0.0056	nm	0.0178	106	71.73	74.43	0.01344	1.7	0.68339	0.16	4798	4562.5	1.8
17	2	4	0.01007	0.0060	nm	0.0224	225	57.85	58.73	0.01703	0.83	0.69896	0.13	4850	4561.0	2.4
18	3	Multiple 1)	0.00600	nm	nm	0.0077	46	45.96	48.04	0.02082	3.6	0.71782	0.38		4566.2	3.6
19	3	Multiple 2)	0.00900	nm	nm	0.0088	79	33.89	34.40	0.02907	1.23	0.75717	0.17		4573.6	3.1
20a	3	Multiple 3)	0.01500	nm	nm	0.0126	189	27.98	28.12	0.03557	0.44	0.78448	0.10		4568.1	3.1
20c	3	Multiple 3)	0.01500	nm	nm	0.0058	86	132.7	146.5	0.00683	9.1	0.65646	0.48		4569.4	7.6
21	4	12	0.01441	0.0051	0.0205	0.0171	247	163.5	180.7	0.00553	7.7	0.64910	0.31	5396	4565.6	3.3
22	4	8	0.00335	0.0047	0.0140	0.0115	39	207.9	661.5	0.00151	165	0.63127	1.52	4879	4566.1	4.5
23	4	19	0.00733	0.0061	0.0226	0.0201	147	174.5	208.6	0.00479	14.1	0.64680	0.44	5462	4568.1	3.4
24	4	21	0.00893	0.0053	0.0210	0.0177	158	112.0	123.4	0.00811	7.4	0.66004	0.35	5345	4564.1	2.3
25	4	16	0.00680	0.0051	0.0206	0.0165	112	137.4	164.2	0.00609	14.2	0.65227	0.51	5336	4567.3	2.4
26	4	9	0.00758	0.0068	0.0300	0.0291	221	268.5	319.9	0.00313	13.5	0.63862	0.27	6945	4566.3	1.8
27	4	14	0.00664	0.0073	0.0311	0.0252	168	177.6	208.8	0.00479	12.6	0.64588	0.37	5604	4565.9	2.0
28	4	20	0.02271	0.0056	0.0249	0.0219	498	154.6	161.8	0.00618	3.4	0.65199	0.15	5956	4565.6	1.7
29	5	Multiple	0.01353	nm	nm	0.0125	168	122.4	131.2	0.00762	4.5	0.65748	0.22		4563.1	1.7
30	5	Multiple	0.01143	nm	nm	0.0192	219	71.7	73.7	0.01357	1.8	0.68349	0.16		4561.3	2.0
31	5	Multiple	0.00605	nm	nm	0.0088	53	104.3	124.7	0.00802	12.9	0.65999	0.59		4565.0	2.8
32	6	Multiple	0.00684	nm	nm	0.0132	90	159.6	215.6	0.00464	26.2	0.64468	0.73		4564.6	3.0
33	6	Multiple	0.01015	nm	nm	0.0303	308	105.3	111.1	0.00900	4.1	0.66386	0.22		4563.5	2.2
35	6	Multiple	0.00840	nm	nm	0.0322	271	248.0	292.0	0.00342	12.8	0.63979	0.28		4565.9	1.7
Acid leachates																
21 HNO_3	4	12	0.01441	0.0087	nm	0.0878	1265	14.94	14.93	0.06696	0.29	0.92077	0.22	4525	4542.3	13.0
21 HCl	4	12	0.01441	0.0024	nm	0.0068	98	69.45	94.19	0.01062	31	0.67271	1.78	4281	4567.7	7.3
22 HNO_3	4	8	0.00335	0.0126	nm	0.0782	262	22.21	22.39	0.04466	0.94	0.81614	0.13	4950	4531.8	7.3
22 HCl	4	8	0.00335	0.0033	nm	0.0607	203	24.83	25.25	0.03960	1.74	0.75014	0.48	10,066	4360.9	9.8
23 HNO_3	4	19	0.00733	0.0132	nm	0.0618	453	23.65	23.83	0.04197	0.71	0.81038	0.103	4151	4557.7	4.9
23 HCl	4	19	0.00733	0.0030	nm	0.0091	66	74.29	122.82	0.00814	58	0.66164	2.68	4842	4567.7	11.0
24 HNO_3	4	21	0.00893	0.0072	nm	0.0488	436	18.34	18.34	0.05453	0.60	0.86740	0.15	4399	4559.0	9.0
24 HCl	4	21	0.00893	0.0010	nm	0.0025	23	39.99	72.17	0.01386	96	0.69455	6.61	3926	4587.1	35.6

Table 1. *Continued.* U-Th-Pb data.

Fraction	Set	Number of chondrules	Weight (g)	U (ppm)	Th (ppm)	Pb (ppm)	Pb (pg)	$^{206}Pb/^{204}Pb$ (raw)	$^{206}Pb/^{204}Pb$ (total)	$^{204}Pb/^{206}Pb$ (total)	$^{204}Pb/^{206}Pb$ % error	$^{207}Pb/^{206}Pb$ (total)	$^{207}Pb/^{206}Pb$ % error	$^{238}U/^{206}Pb^*$ date (Ma)	$^{207}Pb^*/^{206}Pb^*$ date (Ma)	$^{207}Pb^*/^{206}Pb^*$ date error
25 HNO_3	4	16	0.00680	0.0089	nm	0.0640	435	16.56	16.52	0.06054	0.48	0.89524	0.18	4092	4562.9	8.2
25 HCl	4	16	0.00680	0.0017	nm	0.0051	35	52.27	95.93	0.01042	85	0.67537	4.73	4756	4576.7	20.1
26 HNO_3	4	9	0.00758	0.0100	nm	0.0432	327	22.48	22.64	0.04417	0.80	0.81912	0.12	3855	4552.9	6.5
26 HCl	4	9	0.00758	0.0054	nm	0.0124	94	84.95	123.54	0.00809	38	0.66120	1.76	4175	4567.1	6.5
27 HNO_3	4	14	0.00664	0.0113	nm	0.0581	386	21.49	21.60	0.04630	0.52	0.83179	0.10	4125	4565.3	5.4
27 HCl	4	14	0.00664	0.0031	nm	0.0082	55	54.71	80.62	0.01240	44	0.68341	2.86	4208	4574.8	13.2
28 HNO_3	4	20	0.02271	nm	nm	0.0600	1363	17.38	17.40	0.05748	6.2	0.87135	3.97	1799	4511.2	200.5
28 HCl	4	20	0.02271	0.0017	nm	0.0043	99	59.16	74.23	0.01347	22	0.68574	1.56	3986	4568.4	7.4

nm = not measured.
Numbers of chondrules-multiple chondrule fractions: 1 = olivine-rich light-colored; 2 = darker, mostly pyroxene-rich; 3 = dark with sulfides and matrix overgrowths.
Weights before leaching. U, Th, and Pb concentrations are calculated using these weights.
Isotopic ratios denoted "raw" are measured ratios without any corrections.
Isotopic ratios denoted "total" are corrected for fractionation, blank, and spike.
Errors are 2 sigma of the mean.
Isotopes marked with asterisk are "radiogenic": corrected for fractionation, spike, blank, and primordial Pb isotopic composition from Tatsumoto et al. (1973) as initial Pb.
Ages calculated using the primordial Pb isotopic composition from Tatsumoto et al. (1973).
"Rho" is error correlation.

nitric acid leachates (first washing cycle) have measured $^{206}Pb/^{204}Pb$ between 14.9–23.7, hydrochloric leachates (second cycle) have measured $^{206}Pb/^{204}Pb$ between 24.8–84.9, whereas the residues contain Pb with $^{206}Pb/^{204}Pb$ between 112–268.

Residue U-Pb and Pb-Pb Isochrons

The results of the U-Pb and Pb-Pb isochron calculations are shown in Table 2. We have calculated conventional Pb-Pb and U-Pb isochrons and three-dimensional linear regressions (Ludwig 1998). U-Pb isochrons, both conventional and three-dimensional, show large scattering of points (MSWD between 31–571), suggesting that U-Pb systems were disturbed by incoherent migration of U and Th in natural environments and/or during laboratory treatment, and cannot be used for age determination.

Pb-Pb isochrons show more coherent behavior. We use "inverse" isochrons, which provide direct reading of the date from the y-axis intercept, and have much smaller error correlations than "normal" isochrons. Isochron dates for individual analytical sessions are between 4563 ± 13 Ma and 4568 ± 27 Ma, and agree with each other within error. Isochron regression of all residue analyses yields 4565.3 ± 1.5 Ma (MSWD = 6.0). If analyses with low $^{206}Pb/^{204}Pb$, potentially more affected by variations in common Pb composition, are excluded, then the data scattering decreases. The MSWD value decreases from 6.0 for the isochron including all analyses, to 0.60 (no scattering outside of analytical errors) for the isochron including only data points with $^{206}Pb/^{204}Pb > 200$ (two of the isochrons are shown, as examples, in Fig. 1).

This pattern is consistent with the presence of more than one component in common Pb. The decrease in the data dispersion, however, is not matched by the decrease in the error of the date, which remains, almost unchanged, between ±1.5–2.5 Ma, and even increases for the regression based on the most radiogenic data only ($^{206}Pb/^{204}Pb > 200$). The relatively large errors of ±2.5 to ±4.2 Ma for the isochron with no excess scattering is produced by expansion of the isochron error envelope when extrapolated to the y-axis. A more "precise" isochron date with the error of less than ±1 Ma can be obtained by excluding the most deviant points, irrespective to their $^{206}Pb/^{204}Pb$ ratio, from the data set. However, we have no a priori reasons for excluding these data points from regression, and would consider such an exercise invalid, and "high precision" obtained this way unfounded. Therefore we need to look for alternative ways of data treatment that might help us to improve the precision of the dates.

Pb-Pb Model Dates

We have calculated weighted averages of single-stage model dates, based on primordial Pb of Tatsumoto et al. (1973), for the same data sets as the Pb-Pb isochron regressions. The data are presented in Table 2. The average of model dates for each data set agrees within error with the isochron date for the same set, and the averages of model dates are more precise than the isochron dates. Agreement between model dates and isochron dates suggests that the isotopic composition of prevailing common Pb components in Allende chondrules is not very different from the primordial Pb. For example, common Pb in the chondrules can be dominated by Pb redistributed from the Allende matrix ($^{206}Pb/^{204}Pb$ between 9.7–10.1) (Chen and Tilton 1976; Tatsumoto et al. 1976), which is only slightly more radiogenic than the primordial Pb. However, there is no guarantee that the common Pb in chondrules is identical to the primordial Pb or to the matrix Pb, and that the isotopic composition of the chondrule common Pb is homogeneous. Therefore, there is no reason to assume that the model dates are necessarily accurate within their random errors. On the contrary, the lack of reproducibility between the average model dates measured in different analytical sessions (using different leaching procedures) suggests that at least two common Pb components are present, and one is more easily removed by acid leaching than the other. Despite the agreement between isochron dates and model dates and apparently high precision of the latter, model dates may be biased to an uncertain degree. For the highest measured $^{206}Pb/^{204}Pb$ ratios, about 200–300, the potential bias in model dates due to inaccurate common Pb assumption can be as large as 4–6 Ma, and as large as 15 Ma for a sample with $^{206}Pb/^{204}Pb = 100$ if the common Pb varies between primordial and average modern terrestrial isotopic compositions (Amelin 2006). Even the difference between matrix Pb and primordial Pb can cause a significant bias for less radiogenic samples. Model dates are therefore suitable only for reconnaissance age determination.

Residue—Leachate Isochrons

The precision of Pb-isotopic dating can be potentially improved by including Pb isotopic composition of acid leachates in age calculations, using an approach similar to the single mineral Pb-Pb dating of Frei and Kamber (1995). If a chondrule contains two or more common Pb components, then it can be expected that some of these components, for example those associated with surface contamination or with more soluble minerals, are more easily leached by acids than the others. Sequential acid leaching of such a chondrule would produce a series of fractions with variable common Pb content and isotopic composition. The common Pb composition in any of these fractions can also differ from common Pb in the residue: therefore, two-point internal residue-leachate isochrons including any leaching fraction or combined leachates might yield inaccurate dates. Data for multiple acid leachates from the same chondrule would produce a scattered or curved array in the isochron diagram if

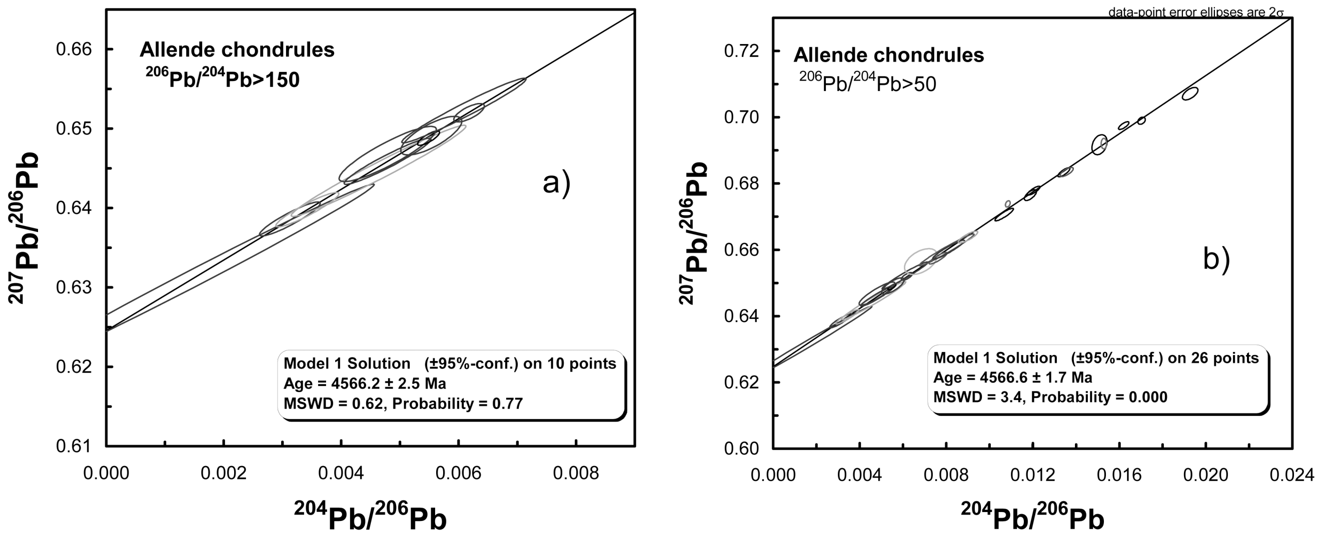

Fig. 1. Pb-Pb isochrons for acid-washed individual chondrules and chondrule fractions from Allende. a) Ten fractions containing most radiogenic Pb with measured $^{206}Pb/^{204}Pb > 150$. b) 27 fractions with measured $^{206}Pb/^{204}Pb > 50$.

the common Pb-isotopic composition varies between the leaching steps. Co-linearity of the points, on the other hand, would be proof of the uniform common Pb composition and would suggest that the date is accurate. If multiple leachates are analyzed from several chondrules or chondrule groups from the same meteorite, then internal residue-leachate isochrons without excess scattering would yield precise (and presumably accurate) dates, whereas the dates from scattered isochrons would be less precise. Calculation of the age of chondrules as a weighted average of internal residue-leachate isochrons thus favors more accurate internal isochron dates.

Another method of age determination from residue-leachate isochrons is based on the assumption that the more soluble common Pb component is removed by the first leaching step, whereas the second leachate and the residue contain only the second, relatively insoluble component. Two-point isochrons for "residue-second wash" pairs for individual fractions would then give accurate and consistent dates. If this assumption is wrong, then the residue-second wash isochron dates would be irreproducible.

The validity of both approaches will be confirmed if internal residue-leachate isochrons for several chondrules give consistent dates. The first method is more stringent because it has two tests for consistency: between leaching steps and between chondrules. In contrast to isochron dating using multiple chondrule residues combined in one isochron, internal residue-leachate isochrons do not require uniform common Pb composition among chondrules. This is an important advantage if we study a chondrule population with variable mineralogy and/or degree of alteration (which may be the case for the Allende chondrules).

Two-point and three-point isochron dates for Allende chondrules analyzed during analytical session 4 are presented in Table 3. Five out of eight three-point isochrons have no dispersion outside of analytical errors (MSWD range between 0.0024 and 0.85), whereas three other isochrons show substantial excess scattering. All eight three-point isochrons yield consistent dates (Fig. 2), with the weighted average of 4566.6 ± 1.0 Ma.

Two-point isochron residue-first wash and residue-second isochron dates have more uniform precision, but their weighted average of 4566.6 ± 1.0 Ma and 4566.8 ± 2.8 Ma, respectively, are identical to the average of three-point isochron dates. The residue-second isochron dates are less precise, because most second leachates contained very little Pb and their analyses are relatively imprecise. All residue-leachate isochron dates and their averages agree with the isochron dates for residues only (Table 2). Agreement between the dates calculated using various methods residue-only isochrons, model dates, and leachate-residue isochrons supports the above suggestion that variation in common Pb composition between Allende chondrules is relatively small.

DISCUSSION

Advantages and Drawbacks of Acid Leaching in Pb Isotopic Analysis of Chondrules

Analyzing acid-leached chondrules has two advantages compared to analysis of untreated chondrules. Removal of common Pb is the main virtue of acid leaching. There are two reasons why reducing common Pb content to a negligible level is important. First, it eliminates the major, nonanalytical uncertainty in $^{207}Pb/^{206}Pb$ age calculations. The possible inaccuracy of model dates and isochron dates (and the isochron date uncertainty due to excess scatter) decreases as the ratio of radiogenic Pb to common Pb increases (Allègre et al. 1995; Amelin et al. 2005; Amelin 2006). The second

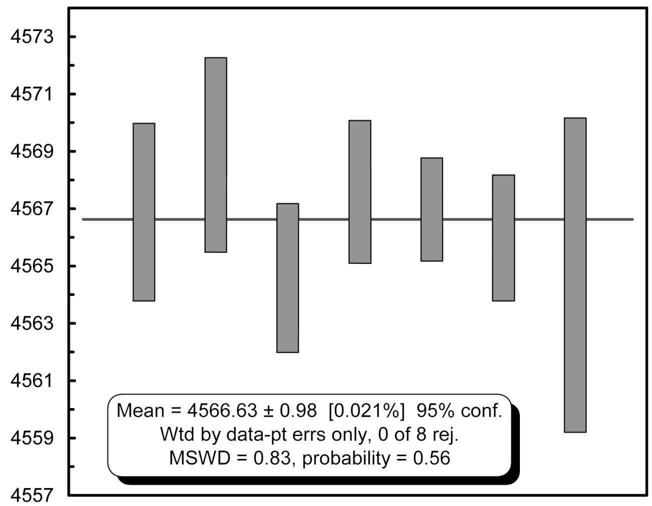

Fig. 2. Weighted average of three-point internal Pb-Pb isochrons (HNO_3 wash, HCl wash, residue) for each of eight fractions of Allende chondrules (fractions 21–28 in Table 1). The data point for the fraction 22, with large error bar, is omitted from the figure for clarity, but is included in the weighted average calculation. Omission of this point from calculation has trivial effect on the weighted average value.

reason is that it is easier to recognize the patterns of multi-stage evolution in the systems containing radiogenic Pb but no common Pb. The importance of complete removal of common Pb for precise and accurate Pb-isotopic dating can hardly be overestimated. Reduction of common Pb content is the main reason of improved precision of meteorite ages in recent Pb isotopic studies.

The second advantage of leaching is the possibility of Pb isotopic dating using internal residue-leachate isochrons. These isochrons can yield accurate dates for individual chondrules and are indispensable for studying chondrule populations with heterogeneous age and/or common Pb isotopic composition. For chondrule populations with uniform age but variable common Pb, precision of the age determination can be increased by averaging internal isochron dates for individual chondrules. In addition, residue-leachate isochrons can help, if remaining common Pb in the residues compromises the precision of dating with a conventional "residue-only" isochron—a case described in this paper.

The drawbacks of acid leaching are related to the loss of uranium and radiogenic Pb. Incongruent extraction of U and radiogenic Pb during leaching steps (Fig. 3) makes it impossible to study natural discordance in the U-Pb system and to determine the timing of secondary processes using concordia diagram.

It is interesting that acid leaching caused disturbance of the U-Pb system in chondrules from CV3 chondrite Allende (this study), but chondrules from H5 chondrite Richardton, leached using a similar procedure, have concordant U-Pb systems (Amelin et al. 2005). This difference in chondrule

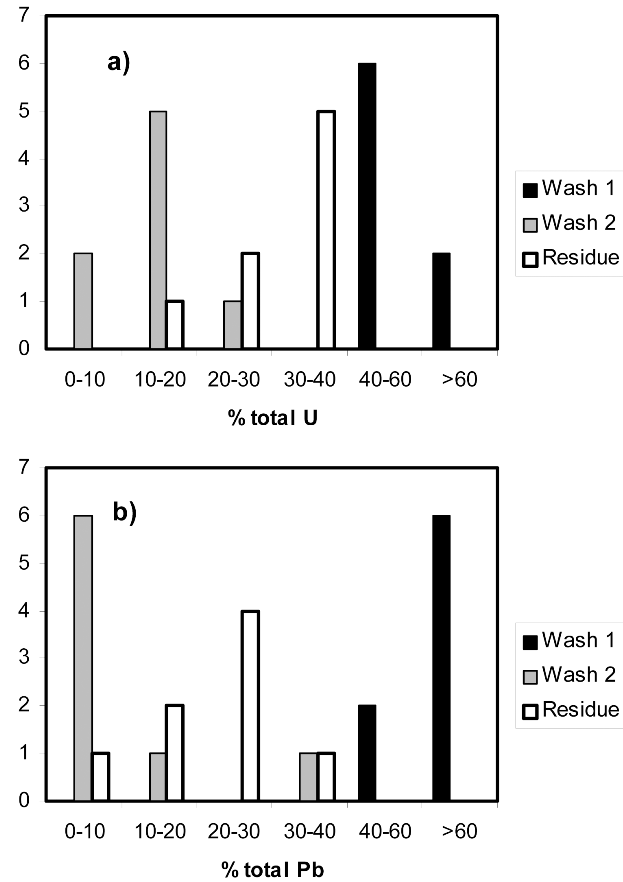

Fig. 3. Distribution of U (a) and total Pb (b) between HNO_3 leachates (Wash 1), HCl leachates (Wash 2), and residues of eight chondrule fractions analyzed during analytical session 4. The distributions for U and Pb are not identical, suggesting decoupled extraction of U and Pb. These results show that over 50% of U and Pb in chondrules are relatively poorly bound and are extracted during the first leaching step.

behavior may be a result of more intensive recrystallization of Richardton chondrules during high-temperature metamorphism.

Another downside of leaching is the reduction of the total amount of radiogenic Pb available for analysis, with resulting deterioration of precision. The distribution of Pb between two washes and the residue, illustrated by Fig. 3b, shows that the residues contain between 8–34% of the total Pb content, and 66–92% of Pb is in the leachates. Of course, a large part of Pb extracted during acid leaching is common Pb, but the loss of radiogenic Pb also occurs, as indicated by relatively radiogenic Pb isotopic compositions in the second leachates. In order to compensate for the loss of radiogenic Pb and to achieve reasonable precision of analyses, we have to analyze fractions of several chondrules together rather than individual chondrules, thus losing the ability to detect potential age differences between the chondrules.

Although the drawbacks of leaching are important, the advantages clearly exceed them. The drawbacks of leaching

Table 2. Summary of Pb-Pb isochron and model date calculations (residues only).

Fractions	Number of fractions Pb-Pb	$^{204}Pb/^{206}Pb$-$^{207}Pb/^{206}Pb$ isochron date (Ma)	MSWD	Weighted average of model dates calculated using primordial Pb	MSWD	Number of fractions U-Pb	3-dimensional total Pb/U isochron date (Ma)	Initial $^{206}Pb/^{204}Pb$	Initial $^{207}Pb/^{204}Pb$	MSWD
Set 1 (fractions 1–5)	5	4563 ± 13	2.5	4568.3 ± 2.9	2.7	5	4567 ± 23	8.68 ± 0.73	9.95 ± 0.80	31
Set 2 (fractions 6–17)	12	4565.6 ± 3.3	5.4	4563.5 ± 1.8	8.2	12	4565.6 ± 8.6	12.3 ± 1.2	12.11 ± 0.82	67
Set 3 (fractions 18a–20c)	4	4568 ± 27	4.4	4569.6 ± 5.6	3.8	nd	nd	nd	nd	nd
Set 4 (fractions 21–28)	8	4567.3 ± 2.4	0.74	4565.94 ± 0.79	0.85	8	4574 ± 18	65 ± 16	44 ± 10	57
Sets 5+6 (fractions)	6	4566.9 ± 1.9	0.49	4563.8 ± 1.8	2.8	nd	nd	nd	nd	nd
All	35	4565.3 ± 1.5	6.0	4564.8 ± 1.0	6.5	25	4564 ± 19	11.0 ± 1.9	11.3 ± 1.3	503
$^{206}Pb/^{204}Pb$_total>40	30	4565.2 ± 1.8	4.8	4564.87 ± 0.90	4.9	22	4563 ± 29	11.1 ± 2.2	11.4 ± 1.8	571
$^{206}Pb/^{204}Pb$_total>50	26	4566.6 ± 1.7	3.4	4564.65 ± 0.89	4.5	19	4565 ± 30	16.1 ± 3.8	14.4 ± 2.7	485
$^{206}Pb/^{204}Pb$_total>70	21	4567.1 ± 1.6	2.2	4564.75 ± 0.85	3.5	14	4570 ± 35	20.6 ± 6.2	17.1 ± 4.3	519
$^{206}Pb/^{204}Pb$_total>100	15	4566.8 ± 1.6	0.86	4565.32 ± 0.67	1.4	9	4573 ± 21	51 ± 18	36 ± 11	172
$^{206}Pb/^{204}Pb$_total>150	10	4566.2 ± 2.5	0.62	4565.81 ± 0.60	0.58	8	4573 ± 22	52 ± 20	37 ± 13	191
$^{206}Pb/^{204}Pb$_total>200	6	4565.8 ± 4.2	0.60	4566.07 ± 0.91	0.50	4	4571 ± 18	111 ± 69	74 ± 43	31

MSWD = mean square of weighted deviates.

Table 3. Summary of residue-wash Pb-Pb isochron calculations for individual fractions.

				Three-point isochron			Residue + HNO_3 wash		Residue + HCl wash	
Fraction	206/204 residue	207*/206* model date (Ma)	207*/206* model date error	Date	2σ error (Ma)	MSWD	Date	2σ error (Ma)	Date	2σ error (Ma)
21	181	4565.6	3.3	4566.9	3.1	0.58	4566.4	3.4	4563.0	11
22	662	4566.1	4.5	3348.0	66,000	1045	4566.7	3.5	4570.8	4.7
23	209	4568.1	3.4	4568.9	3.4	0.0024	4568.9	3.6	4569.0	16
24	123	4564.1	2.3	4564.6	2.6	1.50	4564.5	2.6	4535.0	110
25	164	4567.3	2.4	4567.6	2.5	0.85	4567.5	2.5	4555.0	51
26	320	4566.3	1.8	4567.0	1.8	0.35	4566.9	1.8	4565.8	4.9
27	209	4565.9	2.0	4566.0	2.2	1.7	4565.9	2.2	4561.0	12
28	162	4565.6	1.7	4564.7	5.5	0.68	4569.0	10	4563.5	6.9
Weighted mean		4565.94	4566.63				4566.58		4566.80	
2-sigma% err. of mean		0.80	0.98				0.96		2.80	
MSWD		0.85	0.83				0.79		0.86	
Probability of fit		0.55	0.56				0.60		0.54	

$^{207}Pb^{*}/^{206}Pb^{*}$ model dates are calculated using the primordial Pb isotopic composition from Tatsumoto et al. (1973).

MSWD = mean square of weighted deviates.

Probability of fit is the probability that, if the only reason for scatter is the analytical errors assigned to the data points, the scatter of the data points will exceed the amount observed for the data (Ludwig 2003).

can be minimized by developing more selective leaching procedures, which would extract common Pb without moving radiogenic Pb and U. This can be achieved by a systematic study of the effects of acid leaching on chondrule mineralogy and chemical composition, currently underway.

Residue-Leachate Isochrons—One Possible Solution for the Deficiency of Conventional Isochron Model

The "conventional" Pb-Pb isochron approach (for example, linear fitting using the algorithm of York [1969], with error propagation using the maximum-likelihood estimation algorithm of Titterington and Halliday [1979]), such as used in Isoplot) has a fundamental flaw: an unfavorable shape of the isochron error envelope, produced by currently available isochron regression models, results in many cases in very inefficient use of analytical data, and in unreasonably large isochron date errors. An isochron based on data points with low but almost invariable $^{204}Pb/^{206}Pb$ can give a very imprecise y-axis intercept (i.e., $^{207}Pb/^{206}Pb$ date), whereas an addition of one or more much less radiogenic point radically changes the shape of the error envelope and increases precision of the isochron date. With the current isochron regression models, it often appears advantageous to include unradiogenic data points into regressions. This conclusion may be counterintuitive, but it is confirmed by many regressions of both simulated and observational data sets, and by considerations of isochron formalism. In the case of a small spread of the $^{204}Pb/^{206}Pb$ ratios, the isochron date can be many times less precise than the model date for any of the points, even for a true isochron with no excess scatter. The cause of this problem is that the assumptions of the isochron models do not reflect the geochemical reality of the U-Pb isotopic systems in meteorites.

There are three possible solutions to this problem. The first is separating and analyzing fractions that contain no common Pb other than analytical blank. Such data do not require isochron regression—the age is calculated as a weighted average of $^{207}Pb/^{206}Pb$ dates of individual fractions. The validity of the age is further verified by checking concordance of the U-Pb isotopic systems. This is the best approach, both straightforward and model-independent, identical to the approach used in terrestrial U-Pb (e.g., zircon) geochronology in the cases where high precision and accuracy are required, for example, in time scale studies. Complete removal of common Pb can be achieved for some materials, for example, CAIs and angritic pyroxenes (Amelin 2007), but unfortunately this is not possible for chondrules with currently available techniques.

If fractions free from common Pb cannot be obtained, then the other two approaches can be used to optimize the shape of the isochron error envelope and to use the precision of analyses more efficiently. One approach is developing a geochemically realistic isochron regression model, which would account for the possible presence of two or more common Pb components in meteoritic materials. In such a model, the weight of analysis in isochron regression would depend on the ratio of radiogenic Pb to common Pb, as well as on the analytical error. One of the authors (Y. A.) has recently initiated a project aimed at development of such a model.

The final approach is using leachate analyses to constrain the common Pb isotopic composition in the studied materials. The rationale of using three-point internal isochrons consisting of a residue analysis and two step leachate analyses was discussed by Krot et al. (2005), and in the Residue-Leachate Isochrons section. Co-linear position of residue and two (or more) leachate data points in the isochron diagram indicates that the isotopic composition of common Pb in all three fractions is identical within error, i.e., that the three-point residue-leachate isochron is a true isochron. If the assumption of the uniform isotopic composition of common Pb, released during leaching, is not satisfied, then we can expect scattering both among the data points in the internal isochron, and among internal isochron dates for various fractions. These scattered data receive low weights in the calculations of weighted averages of the dates, and are discriminated against unscattered, and therefore more precise, internal isochron dates.

Pb-Pb Isochrons for a Chondrule Population with Heterogeneous Age

An assumption that the samples combined in an isochron regression formed simultaneously is a basic condition of constructing an isochron. ^{26}Al-^{26}Mg dating of bulk Allende chondrules (Bizzarro et al. 2004) has revealed variations in the initial $^{26}Al/^{27}Al$ ratio, which correspond to the range of ages of 1.2 Ma. A possible bias of Pb-Pb isochron dates for the Allende chondrules due to age heterogeneity has been explored by applying a distribution of ^{26}Al-^{26}Mg ages reported by Bizzarro et al. (2004) to a simulated Pb-Pb isochron data set (adapted from Amelin et al. 2005) with or without random scatter caused by analytical uncertainties. For consistency with real chondrule analyses, we used model Pb-Pb isochrons in $^{207}Pb/^{206}Pb$ versus $^{204}Pb/^{206}Pb$ coordinates. Each model isochron consists of 11 data points with each point being a mixture between primordial Pb and radiogenic Pb, with the fraction of primordial Pb between 0.5% and 10%. Errors assigned to each point are similar to the typical errors in thermal ionization mass spectrometry (TIMS) analysis of small fractions of Pb with external normalization: a fixed error of 0.08% is assigned to $^{207}Pb/^{206}Pb$, whereas the error of $^{204}Pb/^{206}Pb$ varies between 4.3% for the most radiogenic point with $^{206}Pb/^{204}Pb$ = 1861 and 1.2% for the least radiogenic point with $^{206}Pb/^{204}Pb$ = 143, due to changing counting statistics on ^{204}Pb (the error is inversely proportional to the square root of ^{204}Pb abundance). Error correlation between $^{204}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ is 0.9.

Table 4. Model Pb-Pb isochron calculations for Allende chondrules.

		Model description					
Model	Run	Mass bias variations	Age variations	Isochron age (Ma)	Error (Ma)	MSWD	Probability of fit
1	1	No	No	4567.20	0.47	0.00	1.000
2	1	No	Random	4566.23	0.47	1.16	0.310
2	2	No	Ordered up	4567.43	0.48	0.10	1.000
2	3	No	Ordered down	4566.00	0.47	0.19	0.995
3	1	Yes	No	4567.07	0.47	1.16	0.320
3	2	Yes	No	4567.26	0.47	0.60	0.790
3	3	Yes	No	4566.77	0.47	0.53	0.860
3	4	Yes	No	4567.16	0.47	0.60	0.800
3	5	Yes	No	4567.31	0.47	1.06	0.390
4_1	1_1	Yes	Random	4566.03	0.81	2.60	0.006
4_1	2_1	Yes	Random	4566.27	0.68	1.70	0.092
4_1	3_1	Yes	Random	4565.87	0.74	2.20	0.022
4_1	4_1	Yes	Random	4566.20	0.63	1.50	0.130
4_1	5_1	Yes	Random	4566.25	0.75	2.40	0.010
4_2	1_2	Yes	Ordered up	4567.31	0.48	0.84	0.580
4_2	2_2	Yes	Ordered up	4567.49	0.48	0.59	0.800
4_2	3_2	Yes	Ordered up	4567.00	0.47	0.44	0.910
4_2	4_2	Yes	Ordered up	4567.39	0.48	0.80	0.620
4_2	5_2	Yes	Ordered up	4567.55	0.48	1.02	0.420
4_3	1_3	Yes	Ordered down	4565.70	0.60	1.80	0.069
4_3	2_3	Yes	Ordered down	4566.06	0.47	0.97	0.460
4_3	3_3	Yes	Ordered down	4565.57	0.47	0.64	0.770
4_3	4_3	Yes	Ordered down	4565.96	0.47	0.93	0.500
4_3	5_3	Yes	Ordered down	4565.92	0.60	1.60	0.110

MSWD = mean square of weighted deviates.

Probability of fit is the probability that, if the only reason for scatter is the analytical errors assigned to the data points, the scatter of the data points will exceed the amount observed for the data.

Model isochron calculations are shown in Table 4. Model 1 represents an "ideal" isochron calculated with fixed radiogenic Pb isotopic composition corresponding to 4567.2 Ma (the age of the CV CAIs) (Amelin et al. 2002). The error of the isochron date of 0.47 Ma is propagated from the assigned errors.

In model 2, radiogenic Pb isotopic compositions are modified to match the age differences between the CV CAIs and Allende chondrules found by Bizzarro et al. (2004). The average of ^{26}Al-^{26}Mg chondrule ages, 0.52 Ma after CAIs, is considered the true average chondrule age. The results of Pb isochron regressions in this model depend on whether the ages of chondrules are correlated with the ^{206}Pb/^{204}Pb ratio. If we apply the ^{26}Al-^{26}Mg chondrule ages in the same sequence as they are presented in the Bizzarro et al. (2004) paper (presumably random sequence, run 1), then the isochron date agrees, within error, with the true average chondrule age. If the ^{26}Al-^{26}Mg chondrule ages positively correlate with the ^{206}Pb/^{204}Pb ratio, then the isochron date is too old, and vice-versa (runs 2 and 3, denoted "ordered up" and "ordered down," respectively). Model isochrons for "ordered" chondrule ages (runs 2 and 3) have smaller excess scattering than the "random sequence" isochron.

In model 3, random scattering, simulating mass bias variations in Pb isotopic analysis, is applied to ^{207}Pb/^{206}Pb ratios (the effect on ^{204}Pb/^{206}Pb is negligible). Five runs with different sets of random numbers produced isochrons with the ages within error of 4567.2 Ma, and probabilities of fit between 0.32–0.86.

In model 4, mass bias variations (with the same sets of random numbers as in model 3) and age variations (as in model 2) are applied together. This superposition of age variations and mass bias variations produces isochrons with increased scattering compared to the isochrons with only one source of variations. Combined random age variations and mass bias variations (runs 1_1 to 5_1) yield isochrons with the largest scattering and low probability of fit between 0.006–0.13 and thus lower precision. Combined ordered age variations and mass bias variations (runs 1_2 to 5_3) produce less scattered (and thus more precise) isochrons with biased dates.

The models described above show that the effect of age variations in a chondrule population on Pb-Pb dating depends on the range of age variations and precision of Pb-isotopic analysis, and, more importantly, on possible correlation between chondrule chemistry and age. If ^{206}Pb/^{204}Pb ratios and chondrule ages are not correlated, then age variations, combined with analytical dispersion, can produce a scattered and less precise isochron. If, however, chondrule ages and chondrule chemistry (and thus $^{206}Pb/^{204}Pb$) are correlated or anti-correlated, then the isochron date can be biased. This problem can be solved in several ways. Getting highly radiogenic Pb (ideally, pure radiogenic Pb) and ^{26}Al-^{26}Mg and/or ^{53}Mn-^{53}Cr ages for the same chondrules would help to distinguish variations in chondrule formation ages from possible multi-stage evolution. Another possibility is to date each chondrule using an internal residue-leachate isochron. The ^{26}Al-^{26}Mg and ^{53}Mn-^{53}Cr dating can be used in this case as well, either by analysis of separate unleached fragments of chondrules, or by re-combining column washes from Pb-isotopic separations of residues and leachates.

The Age of Allende Chondrules

Ages of eight individual groups of Allende chondrules (fractions 21–28), determined with leachate-residue isochrons, agree within error. We can therefore regard our set of dates as homogeneous, and average individual dates. We consider the weighted average of three-point residue-leachate isochrons of 4566.6 ± 1.0 Ma as the best estimate for the average age of Allende chondrules. All other estimates, from two-point internal isochrons and from combined residue-only isochrons, agree with this number.

The agreement between Pb-isotopic ages of individual groups of chondrules may seem to contradict the age variability among Allende chondrules demonstrated by the bulk ^{26}Al-^{26}Mg data (Bizzarro et al. 2004). In fact there is no disagreement between these data sets. Each of our fractions analyzed with step leaching was composed of multiple chondrules (between 8 and 21), and thus the age variations are averaged. In addition, the entire range of age variations resolved with the ^{26}Al-^{26}Mg method is 1.2 Ma, smaller than the confidence interval of the most precise internal Pb-Pb isochron. The relative ages after CAI formation, measured with ^{26}Al-^{26}Mg and Pb-Pb, agree very well: the average of eleven ^{26}Al-^{26}Mg chondrule ages is 0.52 Ma after CAIs, whereas the average of eight Pb-isotopic ages of 4566.6 Ma post-dates CAIs by 0.6 Ma. This agreement confirms earlier suggestions that ^{26}Al-^{26}Mg and Pb-Pb chronometers give consistent readings of time in the early solar system (Zinner and Göpel 2002; Amelin et al. 2002).

The Time Span of Chondrule Formation

According to Pb-Pb and ^{26}Al-^{26}Mg systematics, Allende chondrules are the oldest currently known chondrules. Their formation might have started contemporaneously with the CV CAI formation or shortly after, and lasted for 1–2 million years. Chondrules in Allende are distinctly older than those in CR (4564.7 ± 0.6 Ma) and CB chondrites (4562.7 ± 0.5 Ma), which were dated by Pb-Pb systematics as well (Amelin et al. 2002; Krot et al. 2005). These observations indicate that chondrules formed during several episodes (minimum two episodes, if we exclude CB meteorites, or minimum three episodes if we consider them), or possibly continuously between ~4567–4562 Ma. We note, however, that chondrules in CB chondrites may have formed from a vapor-melt plume produced by a giant impact between planetary embryos after dust in the protoplanetary disk had largely dissipated (Krot et al. 2005), and hence may not be considered as typical products of the protoplanetary disk.

The timing of formation of Allende chondrules overlaps with the timing of formation of the oldest basaltic crust and metal-silicate segregation on differentiated asteroids—the sources of eucrites and angrites, as indicated by Pb-Pb ages of the angrites Sahara 99555 (between 4566.18 ± 0.14 Ma [Baker et al. 2005] and 4564.41 ± 0.65 Ma [Amelin 2007]; the age needs to be verified) and D'Orbigny of 4564.48 ± 0.24 Ma (Amelin 2007), and eucrite Asuka-881394 of 4566.52 ± 0.33 Ma (Wadhwa et al. 2005; Amelin et al. 2006), as well as ^{182}Hf-^{182}W ages of magmatic irons relative to the Allende CAIs (Kleine et al. 2005; Markowski et al. 2006). Assuming that ^{26}Al was the major heating source of differentiated asteroids (consistent with the lack of evidence for presence of ^{60}Fe in these asteroids) (Bizzarro et al. 2007), theoretical modeling suggests that these asteroids must have accreted within 0.7 Myr after formation of the CV CAIs (Bizzarro et al. 2005). Since chondrule formation lasted over a period of at least 4–5 Myr, the latest generations of chondrules postdate accretion and early differentiation of some asteroids. However, the old Al-Mg and Pb-Pb ages of the Allende chondrules and CAIs may provide an indirect evidence that the early differentiated asteroids could have consisted of typical chondritic components as well.

It has been recently concluded that desegregation of early differentiated asteroids was a common phenomena in the protoplanetary disk (e.g., Asphaug et al. 2006; Yang et al. 2006). As a result, one may expect that fragments of differentiated or extensively thermally metamorphosed asteroids could have been present among chondrule precursors. Reported discoveries of annealed differentiated clasts inside chondrules (Libourel et al. 2006; Sokol and Bischoff 2006) may support this hypothesis.

Based on the emerging picture of early accretion (i.e., within ~1 Myr of CAI formation) of differentiated planetesimals and the existence of undifferentiated chondrite parent asteroids, it seems inevitable that the latter accreted late (Kleine et al. 2005; Bizzarro et al. 2005; Baker et al. 2005). This is consistent with the presence of relatively young chondrules in primitive chondrites (e.g., Kunihiro et al. 2004). How primitive materials such as presolar grains, CAIs, chondrules, and low-temperature minerals found in chondrite matrices could survive a few million years in the protoplanetary disk (i.e., until they were accreted into chondrite parent bodies) alongside the accreting and differentiating asteroids is still unclear. A better understanding of the dynamics within a protoplanetary disk would help to clarify this.

CONCLUSIONS

1. Allende chondrules leached in acids contain variably radiogenic Pb with measured $^{206}Pb/^{204}Pb$ ratios between 19.5–268 (or 19.3–658 after correction for fractionation, spike, and blank). These ratios are less radiogenic than in some previously studied chondrules in other meteorites. Pb-Pb isochron regression for ten most radiogenic analyses with $^{206}Pb/^{204}Pb > 150$ yielded the date of 4566.2 ± 2.5 Ma.
2. Acid leaching is a crucial step in Pb-isotopic dating of chondrules.
3. Acid leachates have been analyzed, along with residues after leaching, from eight chondrule fractions. Internal residue-leachate isochrons yielded consistent dates with a weighted average of 4566.6 ± 1.0 Ma, our best estimate for the age of Allende chondrules. These are the oldest chondrules studied so far.
4. Measurements of the time interval between formation of CAIs and Allende chondrules using Pb isotopes (this study) and ^{26}Al-^{26}Mg (Bizzarro et al. 2004) agree very well.
5. Modeling Pb isochron for a set of chondrules with variable ages, as suggested for Allende chondrules by ^{26}Al-^{26}Mg data, shows that the Pb-Pb isochron date is accurate, even if less precise, if there is no correlation between $^{206}Pb/^{204}Pb$ and the age for individual chondrules. The isochron date may be biased if $^{206}Pb/^{204}Pb$ and the age are correlated. This problem does not exist if the age is determined from internal residue-leachate isochrons.
6. Formation of Allende chondrules may have started simultaneously with, or shortly after formation of the CV CAIs, and possibly overlapped in time with formation of the oldest basaltic crust and iron cores of differentiated asteroids.
7. The entire period of chondrule formation continued for about 4–5 Myr, and included at least three discrete episodes, or possibly was continuous. There were probably a variety of processes in the early solar system that we now call "chondrule formation."

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