Single chondrule K-Ar and Pb-Pb ages of Mexican ordinary chondrites as tracers of extended impact events

María del Sol Hernández-Bernal* and Jesús Solé

Instituto de Geología, Universidad Nacional Autónoma de México,
Circuito de la Investigación Científica s/n, Cd. Universitaria, Coyoacán, 04510 México D.F., Mexico.
** msol@geologia.unam.mx*

ABSTRACT

There is a good consensus about the age of the most primitive materials in the Solar System represented by carbonaceous chondrites. From these, a canonical age of the Solar System of 4567 Ma has been defined. Nevertheless, the age of the subsequent events that modified the accreted material that formed meteorites has been only partially constrained by geochronological methods. In this work, we report K-Ar and Pb-Pb ages for individual chondrules from eight Mexican chondrites: three H5 (Cosina, Nuevo Mercurio and Aldama), one LL5 (Tuxtuac), one L4 (Zapotitlán Salinas), one L5 (El Pozo), one L6 (Pácula), and one carbonaceous CV3 (Allende). Analysis were performed by using combined isotope dilution thermal ionization mass spectrometry and noble gas mass spectrometry. The purpose was to obtain some understanding of the thermal history of these meteorites and their parent bodies. The analyzed chondrules and matrix show a comprehensive K-Ar age range from the Solar System formation to 442 Ma, demonstrating that ordinary chondrites preserve an extensive record of disruption and accretion of their parent bodies.

The large time span recorded in the analyzed meteorites suggests that some chondrules were able to maintain a closed isotopic system, whereas the whole rock and other chondrules did not. To explain these ages, we suggest that partial heating from impact events, presumably from protracted bombardment of the parent body surface that also affected the surfaces of the Moon and Mars, is responsible for resetting the K-Ar chronometer.

It is remarkable that some of the studied chondrules show pre-solar ages similar to those reported for the Allende meteorite by the Ar-Ar method, implying that primordial bodies incorporated some kind of pre-solar materials, as suggested previously.

Key words: meteorites, impact processes, isotope dilution, K-Ar dating, Pb-Pb age, Mexico.

RESUMEN

La edad del Sistema Solar se ha establecido en 4567 Ma, tomando en cuenta la edad obtenida en condritas carbonáceas consideradas como el material más primitivo del Sistema Solar. Sin embargo, la edad de los eventos posteriores que modificaron los materiales primigenios ha sido definida sólo parcialmente a través del uso de diferentes métodos geocronológicos. Para establecer la historia térmica de ocho condritas mexicanas y sus cuerpos parentales, en este trabajo se ha utilizado una combinación de análisis isotópicos por espectrometría de masas con ionización térmica, dilución isotópica y espectrometría

Hernández-Bernal, M.S., Solé, J., 2010, Single chondrule K-Ar and Pb-Pb ages of Mexican Ordinary chondrites as tracers of extended impact events: Revista Mexicana de Ciencias Geológicas, v. 27, núm. 1, p. 123-133.

de masas de gases nobles aplicada a condros individuales a fin de obtener edades K-Ar y Pb-Pb. Las condritas analizadas son tres del tipo H5 (Cosina, Nuevo Marcurio y Aldama), una del tipo LL5 (Tuxtuac), una L4 (Zapotitlán Salinas), una L5 (El Pozo), una L6 (Pácula), todas ellas del tipo ordinario, además de una carbonácea CV3 (Allende). Los condros analizados y la matriz de algunos de ellos muestran un rango amplio de edades K-Ar que van desde 4581 hasta 442 Ma, señalando que las condritas preservan un registro extenso de perturbaciones en el proceso de acreción de sus cuerpos parentales.

Se sugiere que el calentamiento parcial de los cuerpos parentales es el responsable de la gran diversidad de edades registradas en los condros, roca total y matrices de los meteoritos analizados. Los eventos prolongados e intensos de impacto bien documentados en las superficies de Marte y la Luna pudieron generar calentamiento y reiniciar parcialmente el cronómetro K-Ar de los cuerpos parentales de estos meteoritos.

Algunos condros de este estudio muestran edades presolares, similares a aquéllas de Ar-Ar reportadas previamente en el meteorito de Allende, sugiriendo que los cuerpos primordiales incorporaron algún tipo de material presolar, como ya se ha propuesto anteriormente.

Palabras clave: meteoritas, procesos de impacto, dilución isotópica, fechamiento K-Ar, fechamiento Pb-Pb, México.

INTRODUCTION

Chondrules are spheres of silicates, which together with calcium-aluminum-rich inclusions (CAIs) are believed to be the oldest and earliest bodies solidified in the Solar System. The chronology of chondrules is of particular importance because they are the main components of chondrites and they are among the few materials we have to understand the origin and early evolution of our planet. There are unresolved questions about the thermal history of parent bodies of chondrites. The bulk of the meteorites (80%) among the observed falls are ordinary (H, L and LL) chondrites. For this reason, this group is receiving close attention in an attempt to establish their thermal history.

Chondrules ages can reflect the time of actual chondrule formation or a very early stage of thermal metamorphism, which is significant to our understanding of when and how the chondritic parent bodies formed, and of the heating-impact events they underwent. The content and distribution of the isotopes of noble gases in meteorites made it possible to suggest processes that took place at the early and middle stages of the evolution of the meteorite material, as well as the recent stages, after the segregation of the meteorites from the parent bodies as meter-sized and smaller objects.

Several isotopic methods have been used since decades to estimate the different ages preserved in meteorite components. In most cases those ages were obtained in whole-rock samples and mineral concentrates, and in some cases, in single CAIs and chondrules. The oldest reported ages, which vary in a narrow range from ~4570 to ~4550 Ma, have been obtained from Pb isotopic analysis and are thought to represent crystallization or accretion dates at early times. Isotopic systems like Rb-Sr or K-Ar seem to reflect thermal events at younger times.

Some authors have determined Ar-Ar ages in individual CAIs and chondrules of a carbonaceous chondrite (Jessberger *et al*., 1980) and K-Ar ages of ordinary chondrite whole-rock samples (*e.g.*, Alekseev, 1996; Mackiewicz and Halas, 2003 and references therein). In some studies of H and LL chondrites, histories for their parent bodies have been suggested on the basis of geochronological data (Bogard, 1995; Trieloff *et al*., 2003; Rubin, 2004). In this work we used the K-Ar and Pb-Pb geochronometers to obtain the crystallization ages and/or to recognize heating events in chondritic parent bodies. We report ages obtained in single chondrules, matrix, or whole rocks from eight Mexican chondrites.

SAMPLES

Eight chondrites were studied and reported here: Allende (CV3), Cosina, Nuevo Mercurio and Aldama (H5), Zapotitlán Salinas (L4), El Pozo (L5), Pácula (L6), and Tuxtuac (LL5). They all belong to the National Collection of Meteorites of the Instituto de Geología, UNAM, México. The samples were chosen on the basis of their availability in the collection and their description corresponds to that included in the Meteoritical Bulletin Database. Allende is the most studied meteorite in the world and for this reason it was chosen to compare with previous results and to test our methodology. Nuevo Mercurio is a H5 olivine-bronzite chondrite (olivine $Fa_{17.3}$) that fell about 10 km north of the Villa de Nuevo Mercurio, Zacatecas, on 15 December 1978. Cosina is an olivine-bronzite H5 fall (Cerro Cosina, Hgo., México, January 1844). Aldama (H5) was found in 1996, in Chihuahua; it is an olivine, $Fa_{18.7}$; pyroxene, $Fs_{16.5}$ $Wo_{1.6}$; plagioclase, $An_{12.4}$ $Or_{5.6}$; shock stage S2, weathering grade W3. Zapotitlán Salinas is an ordinary chondrite (L4) (olivine $Fa_{24.5}$, pyroxene $Fs_{20.3}$) found in 1984 near the town of Zapotitlán Salinas, Puebla, Mexico. El Pozo is an ordinary chondrite (L5) (olivine, $Fa_{23.6}$; pyroxene, $Fs_{22.2}$) found in summer 1998 in Chihuahua, Mexico. Pácula (L6) is an observed fall near the Pácula village, Hgo., Mexico in 1881. Tuxtuac is a LL5 olivine hypersthene fall in 16 October 1975 in Tuxtuac village, Zac., México.

ANALYTICAL TECHNIQUES

Potassium–Argon

The K-Ar method is a standard long-lived chronometer in which it is assumed that systems crystallized with negligible amounts of the daughter isotope, allowing ages to be calculated for each sample individually from the accumulation of the radiogenic isotope. One of the main problems in this kind of studies resides on the low weight of chondrule samples. For the K-Ar method, the K content is usually determined by X-ray Fluorescence or flame photometry, but these techniques require several hundreds of milligrams of material or, for Ar-Ar dating, the material has to be irradiated in a nuclear reactor. Since the mean K concentration in chondrules is about 800 μg/g, isotopic dilution (ID) is a suitable method for its determination.

Leaching, sample dissolution, K separation, and mass spectrometry measurements were carried out in the Laboratorio Universitario de Geoquímica Isotópica (LUGIS), at UNAM, México. Chondrules were separated from matrix using stainless steel tools, two new corundum mortars and a binocular microscope. Separated chondrules were rinsed several times in high purity ethanol with the aid of an ultrasonic bath in order to remove all matrix residues. All analyzed chondrules were spherical and clean, so it was not necessary to use magnetic or heavy liquids separation. The weight of each chondrule ranged from 7 to 40 milligram (Table 1). Each piece was further divided in several fragments; the mean-weight of the aliquots used for chemical separation in the K and Ar determinations was 3 mg.

Samples were dissolved by acid attack with concentrated and highly purified HF–HNO_3, followed by 6N HCl, in 10 mL PFA beakers. A ^{41}K enriched and calibrated spike was added to the samples before the dissolution and separation procedures. The chemical purification of K was carried out using an anion exchange quartz column with DOWEX 50WX12 (mesh 200-400). Potassium was recovered with 2N HCl before rubidium and strontium recovery. Concentration of K in analytical blanks was between 12 and 50 ηg/g, which means sample/blank ratios of 160 to 40 for the smaller chondrules.

For precise isotopic potassium determinations, a NIST-type thermal ionization mass spectrometer with 12” radius and a single Faraday collector was used; samples were loaded on Re outgassed filaments. Acquisition of isotopic ratios was done with a GPIB – Visual Basic protocol for drift correction. The isotopic relationships were corrected by a factor calculated with the accepted natural value of $^{39}K/^{41}K = 13.8567$ and an internal standard. External reproducibility lies within 2% (2σ).

Measurement of ^{40}Ar was accomplished by static vacuum noble gas mass spectrometry. Samples were fused with an infrared CO_2 laser. The constants for the calculations were taken from Steiger and Jäger (1977) and the equation used for age calculation is

$$t[\mathrm{Ma}] = 1804.1 \ln\left[1 + \frac{^{40}\mathrm{Ar}^{*} \times 3.1963 \times 10^{8}}{\%\mathrm{K}}\right] \quad (1)$$

where $^{40}Ar^*$ is the measured value in mol/g. A detailed description of the laser-based K-Ar technique used in this work can be found in Solé (2009).

Lead–Lead

Age determinations with the Pb-Pb method were carried out in samples of three chondrites: Cosina, Nuevo Mercurio and Allende. Procedures for chondrule separation and cleaning were similar to those described for potassium–argon analysis. Before sample dissolution, we applied a leaching procedure consisting in three 10 minutes cycles with 2N HCl in Savillex vials, and then a 30 minutes cycle with 6N HCl in an ultrasonic bath. For the digestion process we used highly purified HF plus HNO_3, followed by 3N HCl in PFA beakers. The chemical purification of Pb was carried out in columns filled with BioRad AG-1x8 (mesh 100-200). Lead was recovered with 6N HCl. Concentration in analytical blanks was between 40 and 65 ηg/g. The isotopic lead determinations were obtained with a secondary electron multiplier (SEM) using a Finnigan MAT262 Thermal Ionization Mass Spectrometer (TIMS) in dynamic mode; samples were loaded with H_3PO_4 and silica gel on Re outgassed filaments.

RESULTS

The reported K content in the chondrules of Richardton (H5; Evensen *et al*., 1979) ranges between 250 and 800 μg/g. The reported distribution of K contents in 114 falls is a Gaussian curve with a peak at a value of 782 ± 83 μg/g for H chondrites and 860 μg/g for L and LL type chondrites (Wasson and Kallemeyn, 1988; Kallemeyn *et al*., 1989). The concentration of K obtained in this study for Cosina chondrules ranges between 723 and 1489 μg/g and from 673 to 1135 μg/g in Nuevo Mercurio chondrules. We obtained a K concentration of 479 to 1208 μg/g for the chondrules of Tuxtuac (LL5), whereas the concentration reported for whole-rock samples of LL5 type chondrites ranges between 842 and 878 (Kallemeyn, *et al*., 1989). In this study, we obtained K concentrations in an interval between 310 and 1010 μg/g for Allende chondrules (CV3), in good agreement with previously reported contents of 250 to 1001 μg/g (Jessberger *et al*., 1980). The distribution of potassium content in all analyzed chondrules is described by a Gaussian behavior (Figure 1). A mean K concentration value of 946 μg/g was

Table 1. Summary of weight, diameter, and K-Ar ages obtained in this study for selected chondrules, whole-rock or matrix, from eight Mexican chondrites. Sufixes of sample numbers indicate sample type: WR: whole rock; Mx: matrix, C: chondrule.

Meteorite	Sample	Chondrule weight (g)	Diameter (mm)	K (µg/g)	$^{40}Ar^*$ (mol/g)	Age (Ma)	Error (Ma)
Allende [CV3] Fall	A-C13	0.00455	1.39	714	1.41E-09	3585	18
	A-C18	0.01128	1.88	624	1.83E-09	4219	19
	A-C19	0.00937	1.77	310	3.27E-10	2661	25
	A-C20	0.00199	1.05	1010	2.45E-09	3914	20
Cosina [H5] Fall	Cos-C1	0.00622	1.54	911	3.28E-09	4557	17
	Cos-C2	0.00093	0.60	1073	3.02E-09	4153	25
	Cos-C3	0.00086	0.64	854	2.36E-09	4122	46
	Cos-C4	0.00085	0.63	723	1.92E-09	4061	56
	Cos-C5	0.00110	0.71	1489	3.16E-09	3703	27
	Cos-C6	0.00108	0.72	918	3.35E-09	4581	28
	Cos-Mx	0.04692	–	656	1.27E-09	3565	17
Nuevo Mercurio [H5] Fall	NHg-C1	0.00277	1.18	926	3.35E-09	4565	18
	NHg-C2	0.00179	0.91	1076	4.52E-09	4816	26
	NHg-C3	0.00080	0.53	1135	3.45E-09	4278	65
	NHg-C4	0.00075	0.63	889	2.42E-09	4100	98
	NHg-C5	0.00069	0.68	672	2.49E-09	4604	100
	NHg-C6	0.00075	0.67	1017	3.53E-09	4496	72
	NHg-Mx	0.07519	–	849	2.74E-09	4376	18
Aldama [H5] Find	Aldama-WR	0.02020	–	937	8.13E-11	442	27
Tuxtuac [LL5] Fall	Txc-C1	0.00493	1.43	692	1.79E-09	4017	88
	Txc-C2	0.01361	2.00	865	2.92E-09	4452	17
	Txc-C3	0.00992	1.80	1208	4.28E-09	4532	17
	Txc-C4	0.01414	2.03	479	9.33E-10	3567	17
	Txc-C5	0.04008	2.87	737	1.71E-09	3847	17
	Txc-C6	0.00792	1.67	1004	3.23E-09	4370	17
	Txc-C7	0.01271	1.95	1208	2.68E-09	3770	19
	Txc-C8	0.00306	1.22	909	2.92E-09	4370	19
	Txc-Mx	0.01245	–	935	2.74E-09	4216	18
Zapotitlán Salinas [L4] Find	ZapSal-C1	0.00202	1.06	1253	3.06E-09	3923	18
	ZapSal-C2	0.00833	1.70	932	1.75E-09	3512	16
	ZapSal-C3	0.00220	1.09	1153	2.69E-09	3852	18
	ZapSal-C4	0.00196	1.05	1682	3.61E-09	3721	18
	ZapSal-C5	0.00177	1.01	1245	8.50E-10	2089	24
	ZapSal-Mx	0.01042	–	941	1.99E-09	3699	19
El Pozo [L5] Find	ElPozo-WR	0.08053	–	848	1.22E-09	3103	16
Pácula [L6] Fall	Pácula-WR	0.05053	–	870	2.50E-09	4188	17

found for chondrules of all studied chondrites, although a higher mean value was found for Zapotitlán Salinas (1253 µg/g), whereas CV3 Allende shows a lower mean value of 664 µg/g. The mean of all matrix and whole-rock (WR) samples of the studied chondrites is 862 µg/g, with a small difference between matrix and WR mean concentrations (845 and 885 µg/g, respectively).

The K-Ar ages obtained in this study for the several types of chondrites (including CV3, H5, LL5 and L4, L5 and L6 types) lie in a wide main range, from the canonical age of 4565 Ma to 3500 Ma, with only four lower ages of 36 measurements (Figure 2; Table 1).

The H5 chondrites show a broad time interval. The K-Ar ages calculated for Cosina chondrules range from 3703 to 4581 Ma, whereas the matrix has an age of 3565 Ma. Ages of Nuevo Mercurio chondrules are between a presolar age of 4816 and 4100 Ma, with an of 4376 Ma age obtained for the matrix. Aldama WR age is very young, with only 442 Ma. On the other hand, L chondrites show the following results: Zapotitlán Salinas (L4) chondrules are in the range from 3923 to 2089 Ma, and its matrix has an age of 3699 Ma; El Pozo (L5) WR age is 3103 Ma; Pácula (L6) WR age is 4188 Ma; and Tuxtuac (LL5) chondrules range from 4532 to 3567 Ma, with a matrix age of 4216 Ma. Finally, the ages of chondrules from Allende (CV3) lie in a time interval of 4219 to 2661 Ma.

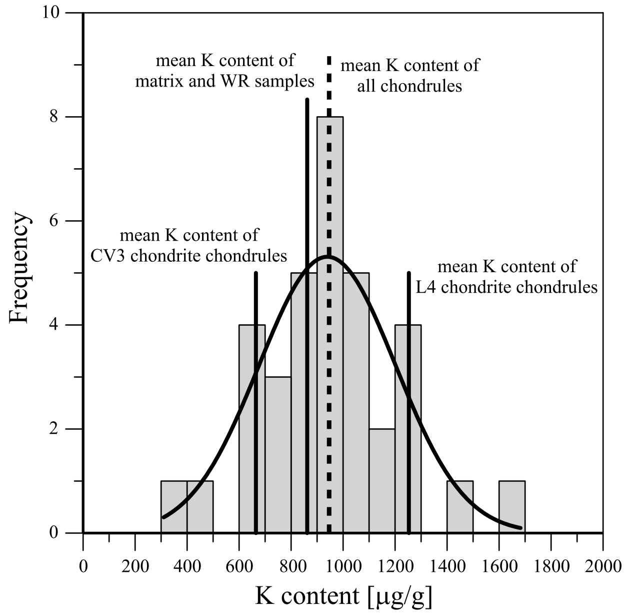

Figure 1. Frequency distribution of K concentration in chondrules from eight ordinary chondrites measured by ID-TIMS. Note that the mean K content in Allende (CV3) chondrules is lower while in Zapotitlán Salinas (L4) is higher than the mean K content for all samples.

Considering the K-Ar and Pb-Pb ages reported in this work (Tables 1 and 2), Cosina displays three age ranges (Figure 3a): a) the primordial Solar System age; b) a short hiatus interval between 4533 and 4425 (108 My); and c) a long and prolonged hiatus of 358 My, between 4061 and 3703 Ma. Taking account only post-solar ages, the total resetting interval registered in Cosina is at least 1000 My. For Nuevo Mercurio no ages were registered in two small periods between 4496 and 4380 Ma (116 My) and between 4202 and 4109 Ma (93 My) (Figure 3b). Sampling effects can not be excluded as cause of such hiatuses.

Tuxtuac was previously dated by the Pb-Pb method. Rotenberg and Amelin (2003) reported an age of 4493 ± 50 Ma for chondrules; Bouvier *et al*. (2007) a whole-rock age of 4547.4 ± 2.5 Ma and a chondrule age of 4555.3 ± 0.4 Ma; and Göpel *et al*. (1994) an age for phosphates of 4543.6 ± 2.1 Ma. Further, whole-rock K-Ar ages for this chondrite are 4391 and 4433 Ma (recalculated from Schultz and Kruse, 1989) and 4286 ± 4 Ma (Bernatowicz *et al*, 1988). Our K-Ar ages are lower than those previously obtained by the Pb-Pb method (Figure 3c); they range from 4532 to 3567 Ma, with a difference of 965 My between the minimum and maximum ages registered in the chondrules.

Zapotitlán Salinas show K-Ar ages from 3923 to 2089 Ma. Apparently, ages older than about 4 Ga have not been preserved in this meteorite (Figure 3d).

Allende displays a more complex behavior, with a main time span between ~4570 and 3585 Ma in both K-Ar and Pb-Pb ages of chondrules and CAIs (Figure 4), and two younger ages at 3223 and 2661 Ma are recorded. However, Allende also shows a wide pre-solar period, previously documented by Jessgberger *et al*. (1980), who reported ages as old as 5260 Ma.

The relationship between chondrite size, potassium concentration and K-Ar age is not so clear in our samples (Figure 5). Tuxtuac shows a positive correlation between potassium content and age, indicative of a mineralogical

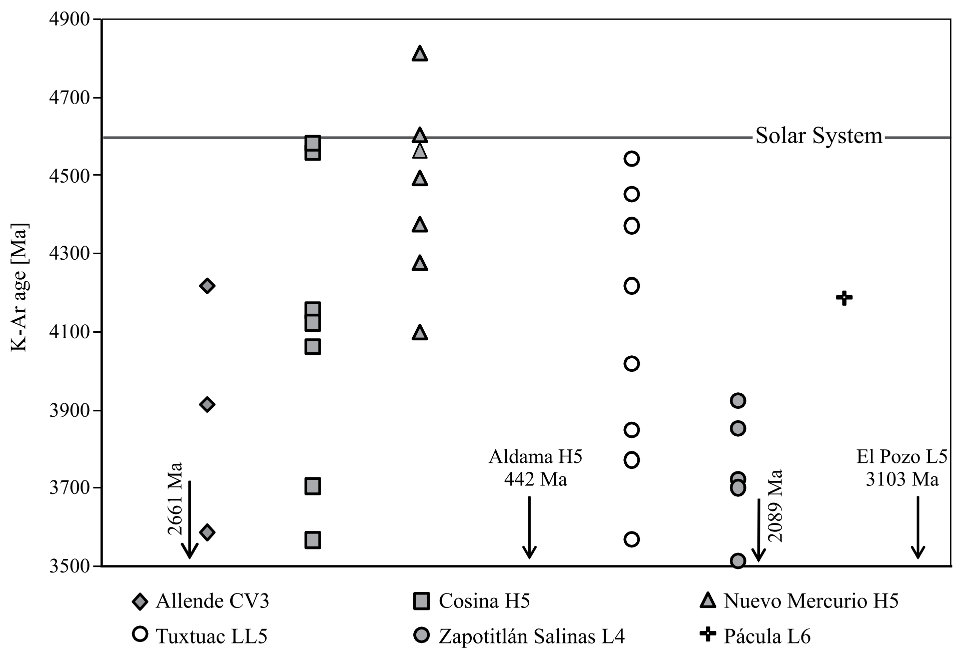

Figure 2. K-Ar ages from single chondrules obtained in seven ordinary and one carbonaceous chondrites. The time span covers about 1000 Ma, although some meteorites show narrow periods (Nuevo Mercurio and Zapotitlán Salinas). Ages of Aldama, El Pozo, one Zapotitlán Salinas and one Allende´s chondrule are not shown because they are out of scale (442, 3103, 2089 and 2661 Ma, respectively).

Table 2. Pb-Pb isotopic compositions and ages obtained in Cosina, Nuevo Mercurio and Allende chondrules. Samples types are: CAI: calcium-aluminum-rich inclusions; Mx: matrix; C: chondrule.

	Sample	**Weight (g)**	**$^{206}Pb/^{204}Pb$ (corr.)**	**$^{206}Pb/^{204}Pb$ error % 2σM**	**$^{207}Pb/^{204}Pb$ (corr.)**	**$^{207}Pb/^{204}Pb$ error % 2σM**	**$^{207*}Pb/^{206*}Pb$ (rad.)**	**% err $^{207*}Pb/^{206*}Pb$**	**$^{207*}Pb/^{206*}Pb$ edad (Ma)**	**Error [Ma]**
Cosina	C7	0.00639	21.21	0.5	18.78	0.6	0.713	0.90	4757	13
	C8	0.00240	46.16	5.0	35.29	4.8	0.678	1.27	4685	18
	C9	0.00059	22.62	1.2	18.71	1.2	0.632	1.04	4584	15
	C10	0.00159	45.21	0.5	33.45	0.4	0.658	2.29	4641	33
	C11	0.00211	21.98	0.6	18.91	1.0	0.680	1.63	4690	23
	C12	0.00112	19.98	0.5	16.26	0.3	0.559	12.58	4404	180
	C13	0.00118	23.76	0.8	18.41	0.5	0.562	13.38	4412	200
	C14	0.00142	33.88	0.4	24.22	0.2	0.567	4.08	4425	60
	C15	0.00175	28.66	0.5	21.10	0.4	0.556	7.64	4398	110
	C16	0.00223	31.28	0.6	21.96	0.6	0.531	9.10	4330	130
	C17	0.00296	43.10	1.0	30.92	1.0	0.610	8.49	4533	120
	C18	0.00153	22.36	0.5	16.86	0.3	0.503	10.80	4250	160
	C19	0.00147	23.72	1.4	17.48	0.9	0.499	24.35	4237	360
	C20	0.0013	19.30	0.4	15.45	0.3	0.516	12.02	4287	180
	Mx	0.11952	65.86	0.8	41.92	0.7	0.559	4.05	4404	59
Nuevo Mercurio	C7	0.00199	35.65	3.5	27.17	3.2	0.641	1.08	4603	16
	C8	0.00688	111.00	0.5	73.31	0.4	0.624	0.46	4566	7
	C9	0.00088	41.90	6.4	30.77	5.7	0.628	0.51	4575	7
	C10	0.00187	25.15	1.5	20.22	1.3	0.627	0.74	4572	11
	C11	0.0019	38.94	4.6	24.72	3.5	0.487	1.01	4202	15
	C12	0.00244	37.03	0.5	25.46	0.6	0.549	6.60	4373	96
	C13	0.00161	33.64	1.2	21.42	0.4	0.457	9.64	4109	143
	C14	0.00070	47.75	0.5	27.31	0.4	0.443	4.56	4060	68
	Mx	0.49110	55.27	0.5	34.91	0.3	0.536	3.02	4342	44
Allende	C1	0.00356	15.98	0.6	13.97	0.7	0.552	2.2	4385	33
	C2	0.00253	18.37	0.6	15.66	0.8	0.592	1.7	4488	24
	C3	0.00321	15.17	1.4	12.62	1.9	0.397	8.2	3897	120
	C4	0.00052	21.38	1.7	16.23	2.0	0.492	3.7	4216	55
	C5	0.00165	19.09	0.4	15.61	0.5	0.543	1.3	4363	18
	C6	0.0009	24.09	2.7	17.83	1.6	0.509	1.6	4269	23
	C9	0.0067	62.79	7.6	43.63	14.6	0.623	16.4	4563	240
	C15	0.01041	33.70	0.3	22.13	3.0	0.485	27.6	4197	410
	C12	0.00232	26.39	60.8	19.36	41.2	0.531	17.8	4329	260
	C16	0.01143	33.07	0.3	23.39	0.2	0.551	3.9	4385	57
	C17	0.00381	39.61	0.4	28.12	0.3	0.588	4.1	4480	60
	CAI-1	0.00036	31.19	4.4	15.90	4.0	0.256	7.4	3223	120
	CAI-2	0.00309	18.60	0.8	15.29	1.0	0.538	2.2	4349	33
	CAI-3	0.00195	23.17	1.4	18.72	1.6	0.608	2.1	4526	39
	CAI-4	0.00052	18.59	1.3	15.30	1.5	0.539	2.8	4352	42
	CAI-5	0.00188	26.64	2.5	16.26	2.4	0.344	5.5	3682	84
	CAI-6	0.00105	22.05	0.9	17.83	0.9	0.592	1.0	4488	15
	CAI-8	0.0146	13.48	4.1	13.08	5.0	0.669	15.1	4665	220
	CAI-10	0.03604	53.88	1.8	40.35	2.2	0.674	3.3	4677	48
	CAI-13	0.01608	25.44	5.9	21.31	6.1	0.683	3.5	4597	50

The average values and reproducibilities of NBS-981 at LUGIS are $^{206}Pb/^{204}Pb$ = 16.895, $^{207}Pb/^{204}Pb$ = 15.431, $^{208}Pb/^{204}Pb$ = 36.522 (2σ of 0.05%, 0.08 % and 0.10%, respectively, *n*=164). Error %$2\sigma_m$ is equal to $(2*\sigma\%/\sqrt{n})$, where *n* = number of measurements.

control of argon retention, but such correlation is not as evident in chondrules from other chondrites. Furthermore, Zapotitlán Salinas chondrules show a narrow age range, independently of the potassium content of the chondrule.

In the studied chondrules, both Pb-Pb and K-Ar ages of matrix and whole rocks samples fall in a major interval of almost 1000 My, if pre-solar Pb-Pb and K-Ar ages in CAIs and chondrules reported here and by Jessberger *et al*. (1980) are not taken into account. A comparison between our data and published whole-rock K-Ar ages of H and LL chondrites reveals that previously reported dates are younger or similar than the single chondrule dates obtained in this

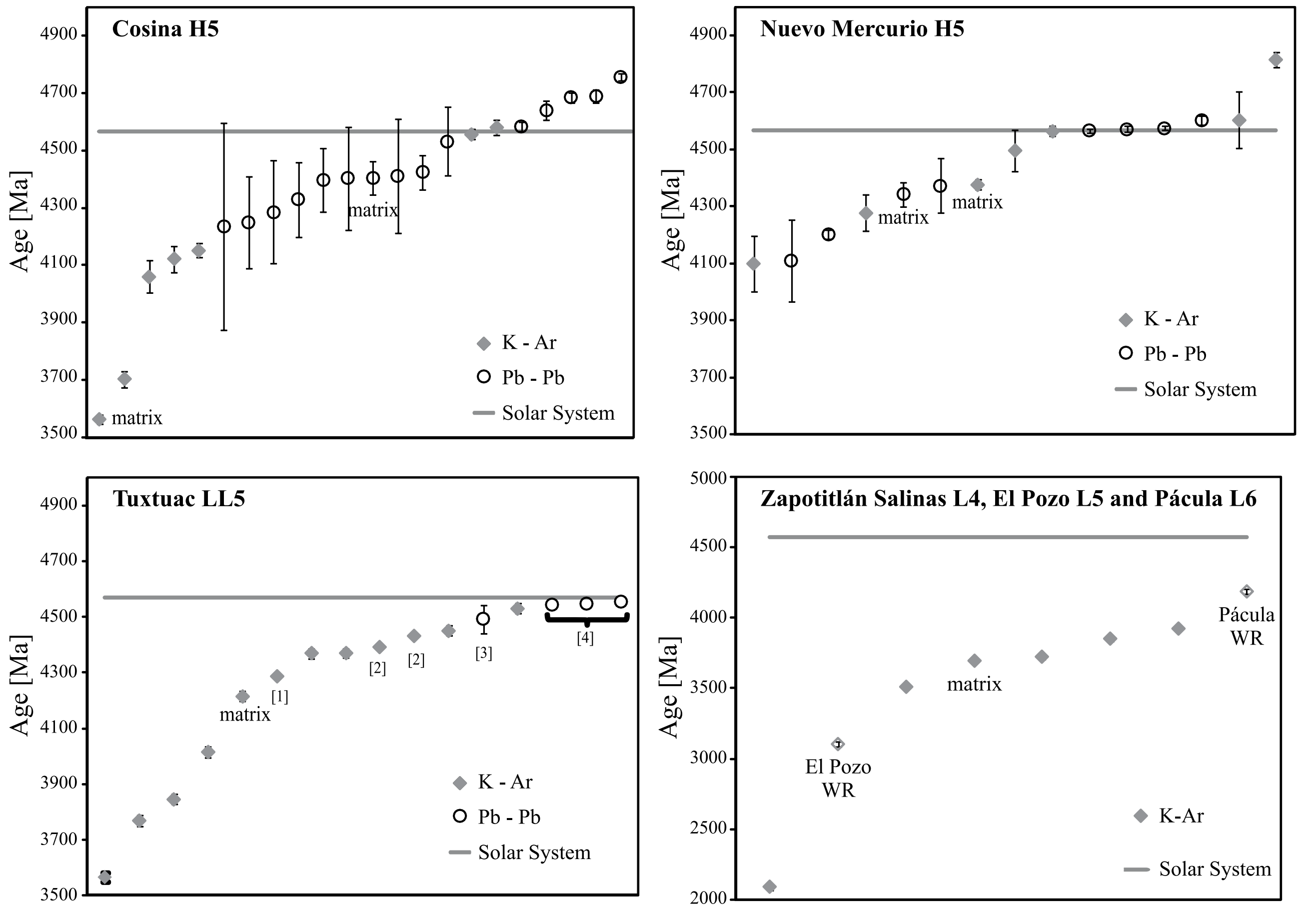

Figure 3. K-Ar and Pb-Pb ages of single chondrules from (a) Cosina, (b) Nuevo Mercurio, (c) Tuxtuac and (d) Zapotitlán Salinas, Pácula and El Pozo chondrites. We can observe that both geochronometers give similar ages, which suggests the existence of a disturbance period of at least 1 Ga duration, but not necessarily continuous. Pb-Pb and some K-Ar ages of Tuxtuac are from Bernatowicz *et al*. (1988) [1], calculated from Schultz and Kruse (1989) [2], Rotenberg and Amelin (2003) [3], and Bouvier *et al*. (2007) [4]. The rest of the ages are from this study. Presolar ages of Cosina and Nuevo Mercurio are worth mentioning.

study. Chondrules from every studied meteorite preserve a range of dates, whereas the whole-rock age is only a mean of chondrules and matrix ages.

For the previous discussion, it should be taken into account that some of the reported Pb ages have very large errors, although errors of pre-solar Pb ages for Cosina and Nuevo Mercurio are relatively small. We consider that the reasons for unsatisfactory precision of the Pb ages obtained in this study could be: disturbance of the U-Pb system during thermal processing on the parent bodies, redistribution of Pb during impact events, and terrestrial contamination. However, it must be observed that five of the eight studied chondrites are falls and should not have been exposed to heavy intense terrestrial contamination for long time.

DISCUSSION

A large amount of meteorites are marked with traces of thermal effects produced by metamorphism or melting and differentiation of the parent bodies at the early stages of evolution of the Solar System. To explain some of these traces there are a few models. Consistent with $^{26}Al/^{27}Al$ and Pb-Pb data, the entire period of chondrule formation took place over ~4–5 My after the time of CAIs formation, (Amelin and Krot, 2007). According to Huss *et al*. (2006), following metamorphism path can be traced in chondrites, relative to the time of CAIs formation: metamorphism of type 3.0–3.2 took place between 2 and 4 My later; in type 3.7–4 chondrite it lasted until 6 My later; and in type 6 chondrites it continued for >7 My after CAIs formed. The Pb-Pb ages, which reflect cooling below ~750 °K, indicate that metamorphism of H4 chondrites ended 4–6 My after the time of CAIs formation, consistent with estimates from ^{26}Al. This system also indicates that, for H5 and H6 chondrites, metamorphism ended 10–16 My and 45–63 My after CAIs formation, respectively. Fission tracks are retained at ~550 °K (pyroxene) or ~390 °K (merillite), so ^{244}Pu fission tracks reflect a later stage in the cooling history. These ages indicate that metamorphism ended ~10 My for H4, 50–65 My for H5, and 55–65 My for H6 after CAIs formed (Trieloff *et al*., 2003).

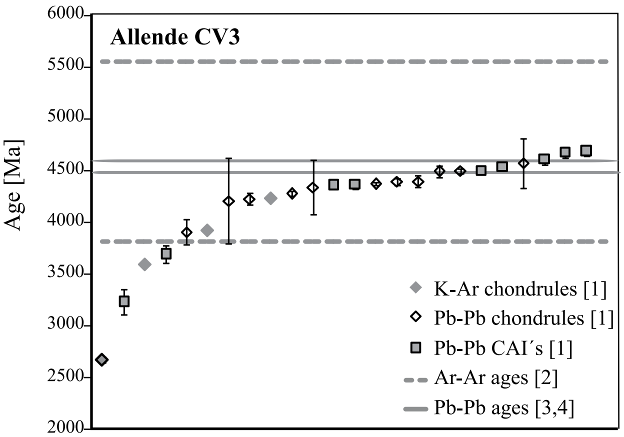

Figure 4. K-Ar and Pb-Pb ages of single chondrules and CAIs from the Allende meteorite. Pre-solar ages reported in this and in previous studies suggest the possibility that chondrules and CAIs have inherited components, anomalous isotopic composition or geologic alteration, although failures in analytical techniques cannot be completely excluded. [1] This study; [2] chondrules and CAIs (Jessberger *et al*., 1980); [3] and [4] chondrules, CAIs, whole rock and matrix (Chen and Tilton, 1976 and Tatsumoto *et al*, 1976, respectively).

This "onion shell" model predicts the structure of the parent bodies of ordinary chondrites with the most metamorphosed material (petrologic type 6) in the central part of the body and the degree of thermal metamorphism and petrologic type being reduced with the transition to the outer parts of the body (Trieloff *et al*., 2003). According with this model, the parent bodies of chondrites were formed during a short time interval [a few millions years (4.55–4.56 Ga)] and the thermal evolution of these bodies was fast and occurred within $10^7 – 10^8$ years after their accretion. At the same time, the age, characterizing the "freezing" time of the isotopic system invoked for dating, must be lower for the more metamorphosed material compared to that for the less metamorphosed material. Göpel *et al*. (1994) found a negative correlation between the Pb-Pb ages of phosphates isolated from H chondrites and the petrologic type of these chondrites, consistent with the "onion" structure of the H chondrites parent body and the *in situ* radioactive decay of short lived nuclei as internal thermal sources.

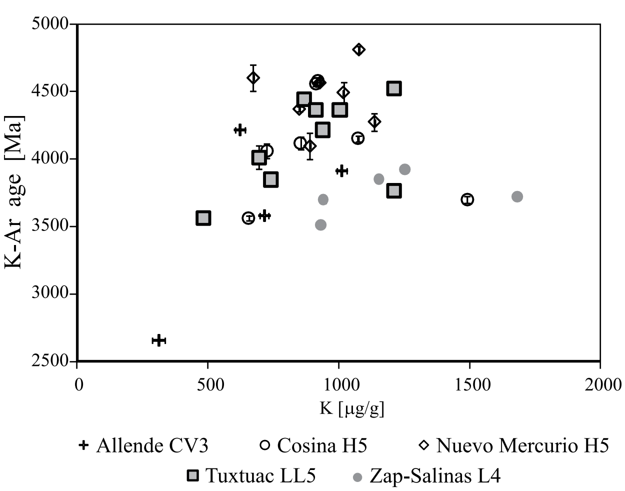

Figure 5. K-Ar ages versus potassium content. A direct relationship between these parameters is apparent only in Tuxtuac, whereas Zapotitlán Salinas shows a narrow time span, independently of K content.

On the other hand, theoretical research on the evolution of asteroids showed that collisions could lead to the disruption of asteroids to fragments. It seems that the parent bodies of H- and L-group ordinary chondrites broke up and reassembled after they experienced heating, metamorphism, and slow cooling. The lack of correlation between high metallographic cooling rates and petrographic type implies either that chondrite parent asteroids were not assembled originally with onion-shell structures or that, if they had been, they were broken due to self-gravitation; these fragments can integrate again, forming a "rubble pile", before they had cooled to below 500 °C. If the latter explanation is correct, these bodies apparently suffered at least two fragmentation and reassembly events since their formation (Taylor *et al*., 1987). Many facts, including the high cooling rates, the low density of asteroids, and their low rupture strength, suggest that the catastrophic fragmentation and reaccumulations of asteroids is the rule rather than the exception (Alexeev, 2005). Recent observation of asteroid Itokawa by a spatial probe (Fujiwara *et al*., 2006) show it as a rubble-pile with an L or LL composition.

Most impact ages of chondrites reflect partial rather than total loss of Ar. A reasonable, but not definitive, conclusion therefore is that Ar degassing was caused by large and extended impact events on the parent body, possibly one that caused its disruption. It is conceivable that Ar degassing from these meteorites was associated with events that initiated their cosmic-ray exposure (Bogard, 1995). Ar-Ar and some Rb-Sr ages of eucrites/howardites were partially to totally reset in a similar time period, as were ages for lunar highland rocks, with somewhat lower age distribution in howardite-eucrite-diogenite (HED) meteorites compared to lunar samples (Bogard, 1995 and Figure 6). For Bogard (1995), ordinary chondrites, however, suggest a different impact history from that of HED meteorites and the lunar highlands. Based on the old isotopic ages of most chondrites, he suggested that these early impacts did not produce widespread heating in cratering deposits for chondrites and would imply that the parent bodies of chondrites were even smaller than those of HED meteorites. However, in Figure 6 it can be see that K-Ar and Ar-Ar ages of chondrites reported in this study and by other authors cover at least the same period of time. The two types of ordinary chondrites, H and L, suggest impact heating more recently than 1.0 Ga ago and LL seems to have experienced episodic heating from 2 to 1 Ga. A sampling effect of the different groups cannot be excluded, because the LL group has been less sampled. In a chondrite study of Alekseev (1996), the LL group represents only the 5 % of 718 samples.

Alexeev (2005) made an analysis of U, Th-He and K-Ar age distribution in chondrites and found that the maximum K-Ar peak for the H, L and LL chondrites is at an age of 4.33 ± 0.02, 4.24 ± 0.03 Ga and 4.06 ± 0.06 Ga, respectively, although an important event in which heating ceased is recognized at 3.5 Ga for all groups. These peaks are close and, on average, about 200 My younger than currently assumed age of the Solar System, 4.56 Ga. The age values of 85 % of the H and LL chondrites and 50 % of the L chondrites are located around this peak. In Figure 7, it can be seen that the frequency distribution diagram for chondrules of this study show similar periods. Alekseev (1996) and Alexeev (2005) used about 700 noble gases isotopic signatures of Antarctic and non-Antarctic, H, L and LL chondrites for age calculation, and made use of mean whole rock concentrations for K, U, and Th. In this study, we used different chondrules of the same meteorite and the individual concentration of K determined for each one, and obtained the same age distribution as Alekseev (1996) and Alexeev (2005), but using only eight meteorites. The power of the single chondrule dating developed in this work is evidenced by these results.

A comparison between K-Ar chondrule dates (Table 1) and single chondrule ^{207}Pb-^{206}Pb ages (Table 2) of the same meteorites suggests that K-Ar ages very close to Pb ages are preserved in some chondrules. Another interesting point is that in the three chondrites dated by the Pb-Pb method, the K-Ar ages of individual chondrules are intercalated with Pb-Pb chondrule ages (Figures 3 and 4) and that the matrix K-Ar age is not always the youngest age, as it would be expected. It means that the diverse chondrules in the same meteorite kept different closure (or partial heating) events. We compared the results obtained using single chondrules K-Ar dating with those using Ar-Ar degassing steps in whole rock of a Tuxtuac sample (Bernatowicz *et al*., 1988) and it is clear that our ages are in agreement with several of the plateaus formed by degassing; the matrix age in this study is 4.21 Ga, whereas the Bernatowicz's age is 4.29 Ga for whole rock.

The intercalated K-Ar and Pb-Pb ages are difficult to explain because of the different closure temperatures of these systems. It is doubtful that two geochemically different isotopic clocks could be affected in a similar way in the same rock.One explanation could be that the chondrules come from different sources with a different thermal history. The fact that matrices of three of the specimens studied did not yield the youngest age, nor the oldest, and that only in one of the studied meteorites, Cosina, the matrix shows the youngest age, seems to point to the idea that the chondrules arrived from different environments, ages and alteration

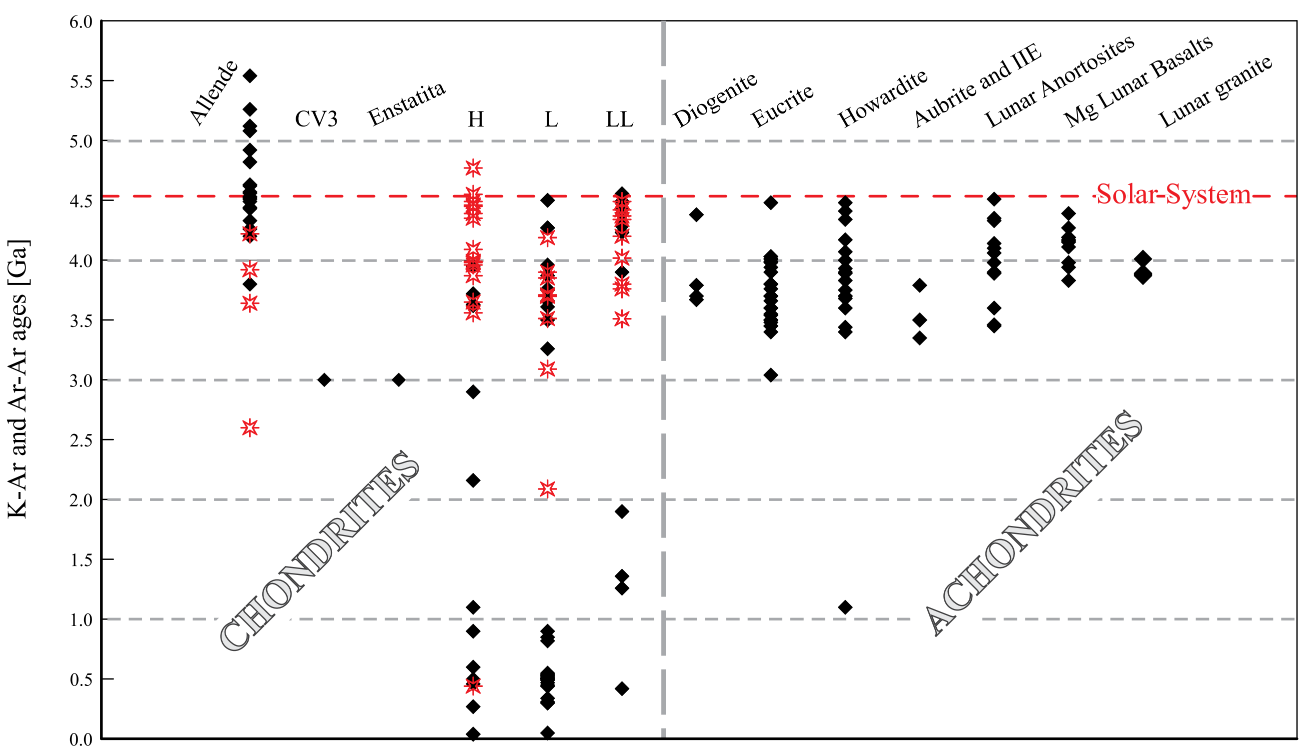

Figure 6. K-Ar and Ar-Ar ages of about 200 undifferentiated and differentiated meteorites and lunar rocks. Ages from this work (red stars) are also included. Most of the plotted points are WR ages and, in some few cases, they correspond to chondrule or matrix ages. Dates were compiled from Bernatowicz *et al*., (1988), Bogard (1995), Bouvier *et al*. (2007), Dixon *et al*. (2004), Mackiewicz and Halas (2003), Nyquist and Shih (1992), Rotenberg and Amelin (2003), and calculated from Schultz and Kruse (1989). The most significant feature is that achondrites and lunar rocks report ages between 4.0 and 3.0 Ga (with one exception), but not younger, whereas L, LL and H chondrites show a wider range.

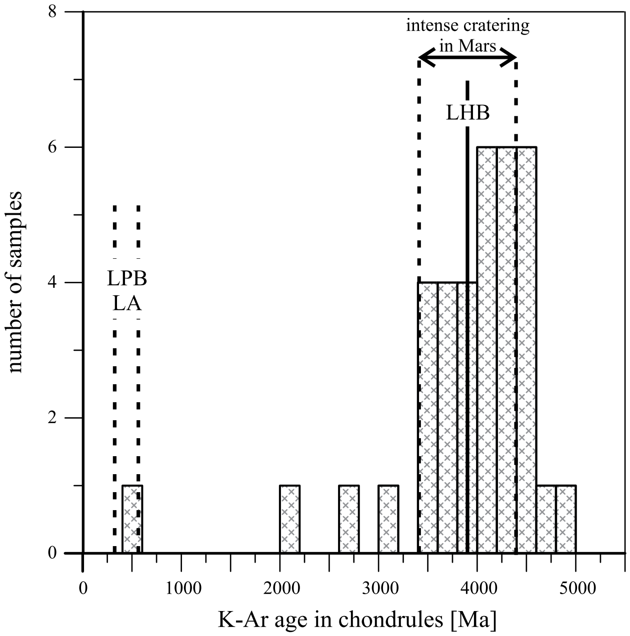

Figure 7. Frequency distribution diagram of ages obtained in single chondrules (this study). The age of the Late Heavy Bombardment (LHB) recorded in the Moon is shown, as well as the periods recorded in Mars (between 3.4 and 4.4 Ga, and Late Amazonian (LA, between 0.3 and 0.6 Ga) by impact crater density (dashed lines) (Chapman *et al*., 2007; Hartmann and Neukum, 2001). The L chondritic parent body fragmentation (LPB) event (0.46–0.48 Ga) is also shown (Korochantseva *et al*., 2006; Schmitz *et al*, 2001).

degree and that they were accreted into a body (rubble pile). The matrix is reflecting a mean value of the ages registered by chondrules.

Chondrules formed by several nebular processes (closed-system melting, condensation, and possibly evaporation) and at least one asteroidal process (impact in regoliths). Each chondrite component appears to have been built predominantly by brief high-temperature processes. Rapid cooling in the formation environment or removal to cooler localities ensured an extraordinary diversity of mineralogical and chemical compositions among chondritic components (Scott and Krot, 2005). The obtained ages in chondrules reflect a different original environment, possibly different mineralogy and thus different responses to impact events. Impact events are not single episodes; the wide spectrum of ages showed by chondrites and achondrites seems to be evidence that the impacts and thermal disruptions of meteorites parent bodies were protracted at least during the first 1000 My of the Solar System history, producing endogen metamorphism not so strong to melt the rocks. This is in agreement with Lunar and Martian cratering dating (Hartmann and Neukum, 2001).

Impact craters are one the most characteristic features of inner planetary bodies. The Late Heavy Bombardment (LHB) has played a significant role in the planetary science since it was proposed to have happened on the Moon. It has generally been presumed that all terrestrial planets – including the Earth– were heavily bombarded at the same time. At least for Mars, this assumption is the basis of their stratigraphic chronology (Chapman *et al*., 2007). The age of the LHB is constrained from 10–12 basin-forming impacts, which happened during the Nectarian from 3.90 – 3.85 Ga; thereafter, bombardment ended sharply, with only Orientale occurring a little bit later, ~3.82 Ga. Later cratering by smaller projectiles continued to decline by another order of magnitude until about 3.4 Ga, after which the cratering flux has been roughly constant to within a factor of two. The impact ages for the achondrites and the ordinary chondrites seem to provide evidence for a lunar-like LHB cataclysm affecting the meteorite parent bodies (Chapman *et al*., 2007 and Figure 7). These authors consider that lunar resetting ages span a period of 200 My, but when other reported lunar ages are used, the impact resetting in the Moon can be prolonged as far as 3.5 Ga in an anorthosite suite (Figure 6).

Finally, the pre-solar ages determined in this study and previously by other authors (Figure 4), suggest the possibility that chondrules have inherited components. Anomalous isotopic composition, geologic alteration or failures in analytical techniques can be also alternative explanations. With respect to the pre-solar Ar-Ar ages for Allende CAIs and chondrules reported by Jessberger *et al*. (1980), revisions of their analytical procedures and of the potassium isotopic signature concluded that this older ages should not be interpreted as evidence for the survival of pre-solar grains –although the ages are highly suggestive– until the carrier material of the extra ^{40}Ar is identified and further isotopic evidence is obtained (Jessberger and Dominik, 1979). At the same time, Stegmann and Begemann (1979) concluded that the isotopic composition of potassium in Allende inclusions is indistinguishable from that of normal terrestrial potassium (within ± 1 %). Potassium ratios in Allende show no evidence for an anomaly because this would imply an enrichment by about 35 % in ^{40}K. Besides, Yin *et al*. (2008) calculated pre-solar ages in Allende CAIs to be 10–14 Ga old, based on $^{232}Th/^{238}U$ ratios. It can be expected that some old pre-solar ages will be found in other chondritic materials.

CONCLUSIONS

Observing the dates from the eight different chondrites studied, we can suggest that their history was more complicated and less peacefully than some simple models predict. However, after the end of the major impacts documented in most of the bodies at about 3.5 Ga, it seems that only chondritic parent bodies and their typical structures (chondrules) were disturbed by multiple collisions throughout their history. It appears that achondritic bodies follow a distinct evolution path toward planetary environments. The ages obtained in matrix and chondrules of the same specimen support the rubble pile model, at least for a certain time span of meteorite's life. This model could apply for different petrologic types. The onion-like model can be possible for large meteorite bodies or during their first stages of evolution, *i.e.*, in the oldest age range (>4.4 Ga).

ACKNOWLEDGMENTS

We thank the National Collection of Meteorites of the Instituto de Geología (UNAM, México) for providing all the chondritic samples. We also thank Juan Morales, Gabriela Solís and Teodoro Hernández for analytical support at LUGIS. Two anonymous reviewers improved the paper. The work was supported by CONACyT Basic Research Program Project 43227 and 50619, a DGAPA-PASPA scholarship to M.S. Hernández, and PAPIIT grant IN112605-3 to J. Solé.

REFERENCES

Alekseev, V.A., 1996, Uranium-Thorium-Helium and Potassium-Argon ages of ordinary chondrites: Solar System Research, 3(3), 243-250.

Alexeev, V.A., 2005, The history of ordinary chondrites from the data on stable isotopes of noble gases (a review): Solar System Research, 39(2), 124-149.

Amelin, Y., Krot, A., 2007, Pb isotopic age of the Allende chondrules: Meteoritics and Planetary Science, 42(7-8), 1321-1335.

Bernatowicz, T.J., Podosek, F.A., Swindle, T.D., Honda, M., 1988, I-Xe systematics in LL chondrites: Geochimica et Cosmochimica Acta, 52, 1113-1121.

Bogard, D., 1995, Impact ages of meteorites: A synthesis: Meteoritics, 30, 244-268.

Bouvier, A., Blichert-Toft, J., Moynier, F., Vervoort, J., Albarède, F., 2007, Pb-Pb dating constraints on the accretion and cooling history of chondrites: Geochimica et Cosmochimica Acta, 71(6), 1583-1604.

Chapman, C.R., Cohen, B.A., Grinspoon, D.H., 2007, What are the real constraints on the existence and magnitude of the late heavy bombardment?: Icarus, 189(1), 233-245.

Chen, J.H., Tilton, G.R., 1976, Isotopic Lead investigations on the Allende carbonaceous chondrite: Geochimica et Cosmochimica Acta, 40, 635-643.

Dixon, E.T., Bogard, D.D., Garrison, D.H., Rubin, A.E., 2004, ^{39}Ar-^{40}Ar evidence for early impact events on the LL parent body: Geochimica et Cosmochimica Acta, 68(18), 3779-3790.

Evensen, N.M., Carter, S.R., Hamilton, P.J., O´Nions, R.K., Ridley, W.I., 1979, A combined chemical-petrological study of separated chondrules from the Richardton meteorite: Earth and Planetary Science Letters, 2(2), 223-236.

Fujiwara, A., Kawaguchi, J., Yeomans, D.K., Abe, M., Mukai, T., Okada, T., Saito, J., Yano, H., Yoshikawa, M., Scheeres, D.J., Barnouin-Jha, O., Cheng, A.F., Demura, H., Gaskell, R.W., Hirata, N., Ikeda, H., Kominato, T., Miyamoto, H., Nakamura, A.M., Nakamura, R., Sasaki, S., Uesugi, K., 2006, The rubble-pile asteroid Itokawa as observed by Hayabusa: Science, 312(5778), 1330-1334.

Göpel, C., Manhès, G., Allègre, C.J., 1994, U-Pb systematics of phosphates from equilibrated ordinary chondrites: Earth and Planetary Sciences Letters, 121(1-2), 153-171.

Hartmann, W.K., Neukum, G., 2001, Cratering chronology and the evolution Of Mars: Space Science Reviews, 96, 165-194.

Huss, G.R., Rubin, A.E., Grossman, J.N., 2006, Thermal metamorphism in chondrites, *in* Lauretta, D.S., McSween, H.Y. (eds.), Meteorites and the early solar system II: Tucson, The University of Arizona Press, 567-586

Jessberger, E.K., Dominik, B., 1979, Gerontology of the Allende meteorite: Nature, 277, 554-556.

Jessberger, E.K., Dominik, B., Staudacher, T., Herzog, G., 1980, ^{40}Ar-^{39}Ar ages of Allende: Icarus, 42(3), 380-405.

Kallemeyn, G.W., Rubin, A.E., Wang, D., Wasson, J.T., 1989, Ordinary chondrites: Bulk compositions, classification, lithofile-element fractionation, and composition-petrographic type relationships: Geochimica et Cosmochimica Acta, 53, 2747-2767.

Korochantseva, E.V., Trieloff, M., Buikin, A.I., Lorenz, C.A., Ivanova, M.A.,Schwarz, W.H., Hopp, J., Jessberger, E.K., 2006, L-chondrite asteroid breakup tied to Ordovician meteorite shower by multiple isochron ^{40}Ar–^{39}Ar dating, *in* Proceedings of 69th Annual Meeting of the Meteoritical Society: Zurich, Switzerland, Meteorite Planetary Science, 41, p. 5087.

Mackiewicz, P., Halas, S., 2003, Datowanie meteorytów kamiennych metodą potasowo-argonową (Potassium-Argon dating of stone meteorites): Przegląd Geologiczny, 51(7), 594-596.

Nyquist, L.E., Shih, C.Y., 1992, The isotopic record of lunar volcanism: Geochimica et Cosmochimica Acta, 56(6), 2213-2234.

Rotenberg, E., Amelin, Y., 2003, Age variations among ordinary chondrites: U-Pb chronology of chondrules, *in* 34th Lunar and Planetary Science Conference, abstract 1902, 2 p.

Rubin, A.E., 2004, Postshock annealing and postannealing shock in equilibrated ordinary chondrites: Implications for the thermal and shock histories of chondritic asteroids: Geochimica et Cosmochimica Acta, 68(3), 673-689.

Schmitz, B., Tassinari, M., Peucker-Ehrenbrink, B., 2001, A rain of ordinary chondritic meteorites in the Early Ordovician: Earth and Planetary Science Letters, 194(1-2), 1-15.

Schultz, L., Kruse H., 1989, Helium, neon and argon in meteorites –A data compilation: Meteoritics, 24, 155-172.

Scott, E.R.D., Krot, A.N., 2005, Chondrites and their component, *in* Davis, A.M. (ed.), Meteorites, Comets and Planets: Oxford, Elsevier-Pergamon, Treatise on Geochemistry (Holland, H.D., Turekian, K.K., eds.), v. 1, pp. 143-200.

Solé, J., 2009, Determination of K-Ar ages in milligram samples using an infrared laser for argon extraction: Rapid Communications in Mass Spectrometry, 23, 3579-3590.

Stegmann, W., Begemann, F., 1979, Allende meteorite-old age but normal isotopic composition of potassium: Nature, 282, 290-291.

Steiger, R.H., Jäger, E., 1977, Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronolgy: Earth and Planetary Science Letters, 36(3), 35-362.

Tatsumoto, M., Unruh, D.M., Desborough, G.A., 1976, U-Th-Pb and Rb-Sr systematics of Allende and U-Th-Pb systematics of Orgueil: Geochimica et Cosmochimica Acta, 40, 617-634.

Taylor, G.J., Maggiore, P., Scott, E.R.D., Rubin, A.E., Keil, K., 1987, Original structures, and fragmentation and reassembly histories of asteroids: Evidence from Meteorites: Icarus, 69(1), 1-13.

Trieloff, M., Jessberger, E.K., Herrwerth, I., Hopp, J., Fiéni, C., Ghelis, M., Bourot-Denise, M., Pellas P., 2003, Structure and thermal history of the H-chondrite parent asteroid revealed by thermochronometry: Nature, 422, 502-503.

Wasson, J.T., Kallemeyn, G.W., 1988, Compositions of chondrites: Philosophical Transactions of the Royal Society of London. Series A325, 535-544.

Yin, Q., Jacobsen, B., Moynier, F., Amelin, Y., Krot, A.N., Nagashima, K., Hutcheon, I., Palme, H., 2008, ^{26}Al-^{26}Mg and ^{207}Pb-^{206}Pb systematic of Allende CAIs: Reinstated canonical solar initial ^{26}Al/ ^{27}Al ratio, variable κ-values (^{232}Th/ ^{238}U) and the age of the galaxy, *in* 39th Lunar and Planetary Science Conference, LPI Contribution 1391, p.1525.

Manuscript received: July 7, 2008
Corrected manuscript received: April 22, 2009
Manuscript accepted: November 23, 2009