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Chondrites and the Protoplanetary Disk

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Constraints on the Origin of Chondrules and CAIs from Short-Lived and Long-Lived Radionuclides

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Abstract. The high time resolution Pb-Pb ages and short-lived nuclide based relative ages for CAIs and chondrules are reviewed. The solar system started at 4567.2±0.6Ma inferred from the high precision Pb-Pb ages of CAIs. Time scales of CAIs (≤0.1Myr), chondrules (1-3Myr), and early asteroidal differentiation (≥3Myr) inferred from ^{26}Al relative ages are comparable to the time scale estimated from astronomical observations of young star; proto star, classical T Tauri star and week-lined T Tauri star, respectively. Pb-Pb ages of chondrules also indicate chondrule formation occur within 1-3 Myr after CAIs. Mn-Cr isochron ages of chondrules are similar to or within 2 Myr after CAI formation. Chondrules from different classes of chondrites show the same range of ^{26}Al ages in spite of their different oxygen isotopes, indicating that chondrule formed in the localized environment. The ^{26}Al ages of chondrules in each chondrite class show a hint of correlation with their chemical compositions, which implies the process of elemental fractionation during chondrule formation events.

1. Introduction

1.1. Principle of Radionuclide Chronometers

One of the challenges of cosmochemistry is to understand the timing of events in the early solar system through the examination of tiny materials preserved in primitive meteorites from a variety of origins. Geological inferences from detailed microscopic mineralogical observations provide important basic information that nevertheless is only qualitative. For example, the occurrence of relict Calcium-Aluminum Inclusions (CAIs) inside Al-rich chondrules implies that CAI formation predated chondrule formation, though the time difference is difficult to evaluate. In order to discuss the time scale of events in the proto-planetary disk more quantitatively, we focus on the results of so-called "short-lived" chronometers available in the early solar system, as applied to CAIs and chondrules.

Many radionuclides have been used for dating meteorites in order to understand origin of solar system and the timing of planetary evolution. "Long-lived" nuclides are those with half-lives ($t_{1/2}$) longer than 300 million years (Myr) and some portion of their initial solar system inventory still exists today. They have been used to establish absolute ages of meteorites and give the ages of 4.5-4.6 billion years, commonly referred as the age of the solar system (e.g., Patterson 1955; Tastumoto, Knight, & Allègre 1973; Chen & Tilton 1976; Minster, Birck, & Allègre 1982). However, because of the slow decay rates, these chronometers have relatively low time resolution (≥20Myr) limited by small changes in isotopic abundances over the history of the solar system. This limitation makes it very difficult to measure the small (≤1Myr) differences in time for events occurring 4.5 billion years ago, required to compare meteoritic evidence with the time scale inferred from astronomical observations of young stars as well as from theoretical studies of planetary evolution (~10Myr). Since the first observation of excess ^{129}Xe from the decay of ^{129}I (Jeffery and Reynolds 1961), the former existence of short-lived nuclides has been confirmed from the excesses of their daughter nuclide in meteorites. These nuclides are now extinct because of their short half-lives (≤100 Myr). The short-lived nuclides potentially provide much more precise chronometers than most of the long-lived nuclides and can be used to establish small time differences between events in the earliest solar system.

Table 1.Radionuclide used for meteorite chronology

Short-lived Nuclide	$\tau_{1/2}$ (Myr)	Initial Solar Abundance		Long-lived Nuclide	$\tau_{1/2}$ (Gyr)†
^{41}Ca-^{41}K	0.1	^{41}Ca/^{40}Ca	1.4E-8 [1]	^{40}K-^{40}Ar	1.25
^{36}Cl-^{36}S	0.3	^{36}Cl/^{35}Cl	≥5.0E-6 [2]	^{87}Rb-^{87}Sr	48.8
^{26}Al-^{26}Mg	0.73	^{26}Al/^{27}Al	5.0E-5 [1]	^{147}Sm-^{143}Nd	106
^{10}Be-^{10}B	1.5	^{10}Be/^{9}Be	~7E-4 [3]	^{187}Re-^{187}Os	41.6
^{60}Fe-^{60}Ni	1.5	^{60}Fe/^{56}Fe	(3-16)E-7 [4,5]	^{232}Th-^{208}Pb	13.9
^{53}Mn-^{53}Cr	3.7	^{53}Mn/^{55}Mn	~9E-6 [1]	^{235}U-^{207}Pb	0.704
^{107}Pd-^{107}Ag	6.5	^{107}Pd/^{108}Pd	2E-5 [1]	^{238}U-^{206}Pb	4.468
^{182}Hf-^{182}W	9	^{182}Hf/^{180}Hf	1.0E-4 [1]		
^{129}I-^{129}Xe	16	^{129}I/^{127}I	1.0E-4 [1]		
^{244}Pu (SF)	80	^{244}Pu/^{238}U	7.0E-3 [1]		
^{146}Sm-^{142}Nd	103	^{146}Sm/^{144}Sm	8E-3 [6]		

[1] McKeegan & Davis (2003), [2] Lin et al. (2004), [3] MacPherson et al. (2003), [4] Huss & Tachibana (2004), [5] Mostefaoui et al. (2004), and [6] Nyquist et al. (1994).
†Data sources: Steiger & Jäger (1977) and Begemann et al. (2001).

In principle, the age of an object, *t,* can be determined from the abundance of the radioactive parent nuclide (P_t) at the time of the formation and the abundance of the radiogenic daughter nuclide (D^*) produced by decay since its formation. The relationship between parent and daughter nuclides is expressed as a simple radionuclide decay equation as follows;

$$P = P_t \exp(-\lambda t) = (P + D^*)\exp(-\lambda t)$$
$$\frac{D^*}{P} = \exp(\lambda t) - 1 \qquad (1)$$
$$\lambda = \tau^{-1} = \ln(2)/\tau$$

where λ and τ are the decay constant and mean life of the nuclide, and P is the measured abundance of parent nuclide.

In the case of short-lived nuclide, we can no longer detect the parent nuclide P, but can estimate amount of P_t from its decay product, D^*. Instead of obtaining the age t, we obtain the isotopic ratio of the short-lived nuclide to its stable isotope, (P_t/P_S). Under the assumption the solar system was initially homogeneous in isotopic abundance, the change in the isotopic ratio with time and can be expressed by the initial isotopic ratio (P_0/P_S) at time t_0 and the relative age $\Delta t = t - t_0$ as follows;

$$\frac{P_t}{P_S} = \frac{D^*}{P_S} = \frac{P_0}{P_S}\exp(-\lambda \Delta t) \qquad (2)$$

Note that definition of age t for long-lived chronometer is to count the age backwards from the present to the past and is called as "absolute age". However, the relative age Δt is defined as time after reference age t_0, where the age is count forward from past to the present, because age t_0 corresponds to the beginning of the solar system if the (P_t/P_S) is equal to the initial isotopic ratios of the solar system. Unit of age used for the absolute age is "Ma (Mega Annum=10^6 yeas ago)" and that for the relative age is "Myr (Mega years=10^6 yeas)" throughout the chapter.

This simple application of the radioactive decay equation usually is not available in practice. In many cases, the measured amount of the daughter nuclide (D) consists of both radiogenic (D^*) and non-radiogenic (D_0) components, which were initially contained in the samples at the time of crystallization. Therefore, Eq. (1) and (2) are usually replaced with a formula consisting of measurable properties,

$$\frac{D}{D_S} = \frac{D_0 + D^*}{D_S} = \frac{D_0}{D_S} + \frac{P}{D_S}\left[\exp(\lambda t) + 1\right] \qquad \text{for long-lived nuclide (1')},$$

$$\frac{D}{D_S} = \frac{D_0 + D^*}{D_S} = \frac{D_0}{D_S} + \frac{P_S}{D_S}\left(\frac{P_0}{P_S}\right)\exp(-\lambda \Delta t) \qquad \text{for short-lived nuclide (2')},$$

where D_S is a stable isotope of the daughter nuclide. The introduction of D_S makes it easier to estimate the amount of radiogenic daughter that is detected as an elevation of the isotopic ratio of D/D_S. By obtaining multiple measurement sets of D/D_S and P/D_S or P_S/D_S for phases in a single sample that differ in $(P \text{ or } P)/D_S$, t (or Δt) and D_0/D_S are determined by the linear regression of these data, where the best-fit line is called an "isochron".

In order to obtain accurate age information from the isochron diagrams, three criteria must be met. First, the object to be dated must have been initially isotopically homogeneous, *i.e.,* constant D_0/D_S and P_t/P_S, at the time it formed. Second, chemical fractionation must have taken place during the event, producing phases with different parent-to-daughter elemental ratios P/D_S. The event being dated should produce both the isotopic homogenization and chemical fractionation in the object. This event can be a melting and subsequent crystallization event, during which atoms move freely to homogenize a system isotopically, and then crystallization of minerals from the melt produces chemical fractionation among the

mineral phases. Alternatively, evaporation of bulk solar-system material can produce isotopic homogeneity in the resultant gas phase, and condensation of minerals from the gas can produce the chemical fractionation necessary for isotopic dating. A third requirement is that the "system" (the entire object being dated) must have remained isotopically closed since the event that is being dated.

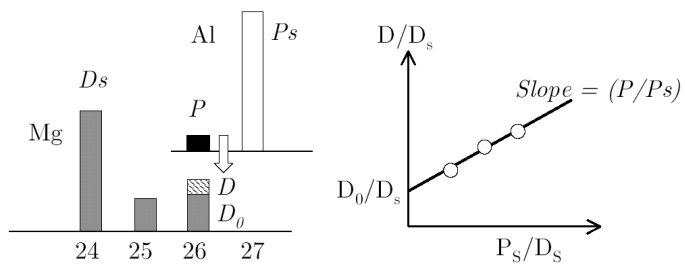

Fig. 1. Example of an isochron diagram for ^{26}Al decay to ^{26}Mg.

There are numerous other ways to start, or restart, isotopic clocks. For example, diffusion of isotopes and chemical reactions among the phases can disturb or even destroy the correlations in an isochron diagram. Therefore, we must be careful in choosing the right meteorite samples for which parent body events or terrestrial weathering have not affected the isotopic systematics, as we are interested in processes in the proto-planetary disk that occurred before the parent body formed.

Even when these criteria are met for individual samples and the initial abundance of the parent nuclide is correctly deduced, the relative time obtained from Eq. (2') by using short-lived nuclide is still based on the assumption that the solar nebula (the bulk reservoir from which the objects formed) was isotopically homogeneous. However, there are no means to directly prove this assumption. If the inferred differences in initial isotopic abundances between objects instead reflect a heterogeneous nebula, then the data have no chronological significance. One way to evaluate the assumption of isotopic homogeneity is to compare the ages obtained by multiple chronometers. If the relative ages are consistent, then the assumption of isotopic homogeneity probably holds for all the chronometers. As will be apparent in succeeding sections, searching for evidence of synchronicity in the ages obtained from short-lived chronometers is a main theme in age-determination studies.

In this Chapter, we discuss evidence for differences in the formation times of calcium-aluminum-rich inclusions (CAIs), chondrules, and other constituents in chondrites that formed in the proto-planetary disk. The primary evidence comes from short-lived nuclides with half-lives less than 5 Myr (^{10}Be, ^{26}Al, ^{41}Ca, ^{53}Mn, and ^{60}Fe) and also from the long-lived U-Pb system where high precision ^{207}Pb-^{206}Pb ages are applied. All these systems allow us to determine time differences of less than 1 Myr, short enough to elucidate the history of the proto-planetary disk. Among these chronometers, we focus on the results from Pb-Pb, ^{26}Al-^{26}Mg and ^{53}Mn-^{53}Cr dating, systems which have been applied to various meteorites groups with consistent relative ages. In addition, recent progress in ^{60}Fe-^{60}Ni system is also discussed.

In order to obtain accurate isotopic ratios of the daughter nuclide, three types of mass spectrometers, which are specialized for high precision isotopic ratio analyses, are often used; Thermal Ionziation Mass Spectrometer (TIMS), Secondary Ion Mass Spectrometer (SIMS) and Induced Coupled Plasma Mass Spectrometer (ICP-MS). TIMS and ICP-MS yield high ionization efficiency and suitable for high precision isotopic analyses (0.01-0.1%). Analyzed

elements in the sample should be chemically separated from acid dissolved sample solutions, and these instruments are used for U-Pb and ^{53}Mn-^{53}Cr dating of bulk CAIs and chondrules. SIMS is often called as ion microprobe, because micro-beam of primary ion (≤10 μm) is focused on the sample surface to produce secondary ions by sputtering. SIMS is suitable for studying small grains in meteorites, which are difficult to separate mechanically. Although the precisions of isotopic ratio analyses are not as high as TIMS and ICP-MS, SIMS is useful in detecting a large isotopic excess of daughter nuclide in the specific phases with high P/D ratios. SIMS is widely used for short-lived chronology in meteorite, such as ^{26}Al-^{26}Mg, ^{60}Fe-^{60}Ni, ^{53}Mn-^{53}Cr, ^{10}Be-^{10}B, and ^{41}Ca-^{41}K. Micro-analytical technique has also been applied to ICP-MS by ablating the sample using a focused laser beam (≤100 μm), called as laser ablation (LA) ICP-MS. Currently, LA-ICP-MS is used only for detecting a small ^{26}Mg excess (≤0.1%) in some minerals in CAIs with low Al/Mg ratios.

1.2. Fractionation between parent-daughter nuclide

In the proto-planetary disk, major chemical fractionation occurred by evaporation and condensation of solids at high temperature, which effectively homogenized isotopes through the gas phase. Relevant processes could have been the condensation of solids from hot nebula gas, as well as evaporation and re-condensation of solids during heating events to produce chondrules. The concept of "50% condensation temperatures" (T_C) in the solar nebula is the temperature at which a half of the abundance of a given element is present in solid condensates from the gas of the bulk solar composition (e.g., Lodders 2003), shown in Fig.2a, and useful for comparing the volatility of various elements. This concept has been applied successfully in describing the chemical fractionation trend among chondrites and their components (e.g., Grossman & Larimer, 1974). Another major elemental fractionation occurred by melting and crystallization to form chondrules and CAIs. The experimentally determined mineral/melt partition coefficients (Fig.2b) are useful in describing differences in element partitioning into certain minerals within chondrules and igneous CAIs. Thus, the distribution of elements within chondrules and CAIs results from a superposition of volatility-related and igneous fractionation.

Al and U, both are the parent nuclides, are *ultra-refractory* elements (T_C>1650K) that are initially condensed into hibonites and grossite, and then into other refractory minerals present in CAIs. Their daughters, Mg (a *common* element enriched in Mg silicates, T_C~1300K) and Pb (a *moderately volatile* element, T_C=727K), have much lower condensation temperatures. Thus, CAIs, made of refractory condensates, have highly radiogenic Pb isotopic compositions and large ^{26}Mg excesses. The bulk CAI ^{26}Al-^{26}Mg and ^{206}Pb/^{207}Pb dates may therefore reflect the timing of condensation of the precursor material. U-Pb dating, especially ^{206}Pb/^{207}Pb dating because of its high precision, is well suited to dating formation of CAIs. Thus, ^{26}Al-^{26}Mg and ^{206}Pb/^{207}Pb ages of CAIs can be considered as starting from the same time and when combined provide the most widely accepted reference point (t_0) for early solar system chronology. Crystallization of a CAI melt produced anorthite (Ca-plagioclase) – an Al-rich mineral that effectively excludes Mg during crystallization. Most ^{26}Al-^{26}Mg age determinations of CAIs are based on large ^{26}Al excesses in anorthite and therefore reflect the time of the melt crystallization. The melting of chondrules causes homogenization of Mg isotopic compositions and enrichment of Al/Mg in glass (or plagioclase), to which SIMS Al-Mg dating is applied. Therefore, SIMS Al-Mg dating of chondrules determines the time of the melting.

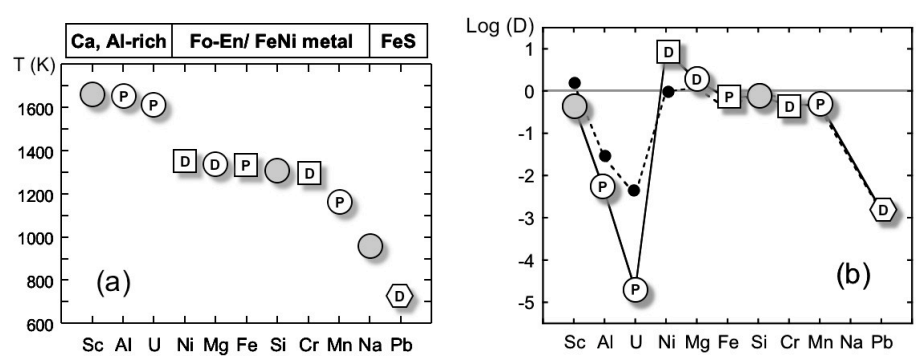

Fig. 2. Chemical fractionation among parent/daughter nuclide pairs. "P" indicates parents, "D" daughter nuclide, and others reference elements. (a) The 50% condensation temperatures in the solar nebular ($P=10^{-4}$ atm, after Lodders, 2003). Circles, squares and hexagons indicate lithophile (condensed as oxide and silicates), siderophile (metals), and chalcophile (sulfide) elements. (b) Experimental mineral/ melt distribution coefficients (Kennedy et al. 1993). Solid line; olivine (T=1525˚C), dashed line; orthopyroxene (T=1440˚C). Values for Sr are used as an approximation for Pb. The same symbols are used as in (a) though metal and sulfides phases are absent in the system.

Nebular volatility plays a lesser role in causing a large degree of fractionation of other parent-daughter pairs, for example, Fe-Ni and Mn-Cr. These elements do not form high temperature refractory condensates and are less suitable for dating CAIs. Both Fe and Ni initially condense into metallic iron alloy with nearly identical condensation temperatures (T_C=1334 K and 1353 K, respectively) and limited fractionation between them is expected during initial condensation (Fe/Ni ratios between 3-30) within a small temperature range. Enhancements of ^{60}Ni in chondritic materials have been observed from troilite (FeS) and FeO-rich chondrules in unequilibrated ordinary chondrites (UOCs), showing extremely high Fe/Ni ratios (>10,000). In troilite, the large Fe/Ni fractionation is caused by more *chalcophile* (sulfur-loving) tendency of Fe than Ni. In FeO-rich chondrules, Fe/Ni fractionation may reflect a precursor formed under more oxidizing conditions (in which Fe becomes lithophile and has much higher volatility as FeO) than in the typical solar nebula. Because these materials may not be condensates from the nebula, it is difficult to estimate the initial ^{60}Fe abundance of the solar system from these data; this issue is currently under debate, as discussed in Section 2.4.

There is a modest difference in the condensation temperatures of Mn and Cr; T_C=1296 K for Cr and 1158 K for Mn. These two elements begin condensing into different initial phases: Cr into Fe alloy and Mn into Mg silicates (forsterite and enstatite). However, a trace amount of Cr condenses into forsterite at a temperature higher than or similar to the condensation temperature of Mg. Thus, one might expect some enrichment of Cr in the highest temperature forsterites and of Mn in lower temperature condensates. This expectation has led to the application of the ^{53}Mn-^{53}Cr chronometer to chondrules, which are mainly composed of Mg-rich silicate minerals and show significant variation in their bulk Mn/Cr ratios. If the Mn/Cr fractionation in early condensates was incorporated into chondrule precursors and preserved during chondrule-forming events (closed system formation), the ^{53}Mn-^{53}Cr systematics of bulk chondrules would provide the time of nebular Mn/Cr fractionation. However, because Mn and Cr are both more volatile than Mg, the Mn-Cr system may well not have remained closed during chondrule formatoion. The extent to which chronological information has been retained in the ^{53}Mn-^{53}Cr systematics of bulk chondrules is a question open to examination. Attempts to apply internal isochron methods based on partitioning of Mn and Cr during crystallization have led to puzzling results for the ^{53}Mn-^{53}Cr system. These issues are discussed in more detail in Sections 2.3 and 3.2.

2. Age determinations of CAIs and chondrules

2.1. ^{207}Pb-^{206}Pb system

The Pb-Pb method was the first isotope chronometer used to date meteorites (Patterson 1955; 1956), and remained widely used until the early 1980's (see reviews by Tilton 1988a; 1988b). In these early days of Pb-isotope cosmochronology, it was rarely possible to obtain ages with a precision of better than 5 to 10 Myr, and the accuracy of the ages was usually uncertain, due to ubiquitous U and Pb mobility, extensive contamination with terrestrial Pb, and the presence of excess radiogenic Pb of unknown origin. Short-lived chronometers became the main tools for studying the chronology of early solar system processes, despite the fact they can only measure time intervals. In order to link relative ages based on short-lived chronometers to the absolute time scale, we have to use high precision Pb isotopic dates from the same meteorite components. High precision and accuracy of Pb isotopic dates for chondrules and CAIs are, therefore, crucial for building a comprehensive isotopic timescale of the early solar system.

The U-Pb dating method (Faure 1986; Dickin 1995) includes two isotopes of uranium that decay into two different isotopes of lead at different rates (Table 1). This dual decay scheme allows an age to be calculated from the ratio of the radiogenic isotopes ^{207}Pb* and ^{206}Pb* alone, without using U/Pb ratios. Combining Eq. (1') for two U-Pb decay systems gives Pb-Pb isochron equation as follows;

$$\left(\frac{^{206}Pb}{^{204}Pb}\right) = \left(\frac{^{206}Pb}{^{204}Pb}\right)_t + \left(\frac{^{238}U}{^{204}Pb}\right)\left(\exp(\lambda_{238}t) - 1\right)$$

$$\left(\frac{^{207}Pb}{^{204}Pb}\right) = \left(\frac{^{207}Pb}{^{204}Pb}\right)_t + \left(\frac{^{235}U}{^{204}Pb}\right)\left(\exp(\lambda_{235}t) - 1\right)$$

$$\frac{\left(\frac{^{207}Pb}{^{204}Pb}\right) - \left(\frac{^{207}Pb}{^{204}Pb}\right)_t}{\left(\frac{^{206}Pb}{^{204}Pb}\right) - \left(\frac{^{206}Pb}{^{204}Pb}\right)_t} = \left(\frac{^{235}U}{^{238}U}\right)\frac{\exp(\lambda_{235}t) - 1}{\exp(\lambda_{238}t) - 1} \qquad (3)$$

The left side of the above formula is equal to the radiogenic Pb isotopic ratio (^{207}Pb*/^{206}Pb*), so that the age t is obtained without the knowledge of parent/daughter ratios:

$$\frac{^{207}Pb^*}{^{206}Pb^*} = \frac{^{235}U}{^{238}U}\frac{\exp(\lambda_{235}t) - 1}{\exp(\lambda_{238}t) - 1} = \frac{1}{137.88}\frac{\exp(\lambda_{235}t) - 1}{\exp(\lambda_{238}t) - 1} \qquad (4)$$

The ^{207}Pb*/^{206}Pb* method is unique among isotopic chronometers in two ways. First, since the date is determined from the ratio of isotopes of one element, it is insensitive to recent fractionation between parent and daughter elements, caused either by natural processes, e.g. recent impact or terrestrial weathering, or induced by laboratory treatment, e.g. partial dissolution. Second, high ^{235}U/^{238}U ratio in the early solar system (about 90 times higher than the present value) coupled with the half-life of ^{235}U, shortest among long-lived nuclides, results in rapid growth of radiogenic ^{207}Pb*/^{206}Pb*, allowing quite small age differences to be resolved. For example, the ^{207}Pb*/^{206}Pb* ratio for a 4560 Ma material, measured with a relative error of 0.05% (a typical 2σ uncertainty of a TIMS analysis with external correction for instrumental mass bias) yields a ^{207}Pb*/^{206}Pb* age with an uncertainty of 0.72 Myr. This precision rivals the precision of state-of-the-art short-lived nuclide dating techniques. Because of its high time resolution, the ^{207}Pb*/^{206}Pb* method is the only way to obtain "absolute" ages

suitable for studies of solar nebula evolution. Thus, this is also the only method used for linking extinct nuclide chronometers to the absolute time scale.

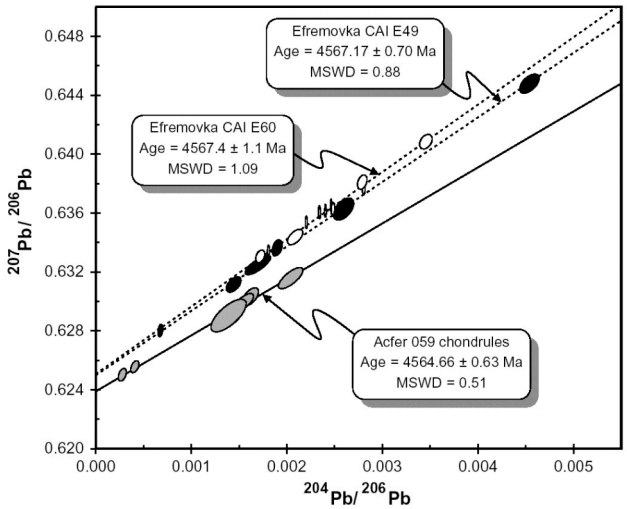

Fig.3. Pb-Pb isochrons for chondrules and CAIs (Amelin et al., 2002).

The $^{207}Pb^*/^{206}Pb^*$ ratio and, hence, age, is determined from a Pb-Pb isochron, a plot of measured $^{207}Pb/^{206}Pb$ ratios versus $^{204}Pb/^{206}Pb$ for a set of samples (as in Fig. 3). As shown in Eq. (3) ^{204}Pb is the non-radiogenic stable isotope and is, therefore, used as a gauge of the amount of non-radiogenic Pb. The intercept of the isochron with the Y-axis gives the $^{207}Pb^*/^{206}Pb^*$ ratio of Eq. (4), which corresponds to the time of the event that caused parent-daughter elemental fractionation.

Amelin et al. (2002) demonstrated high precision Pb-Pb age determination for two CAIs from Efremovka (CV3) and a group of chondrules from Acfer 059 (CR), as shown in Fig. 3. The result indicated the time difference between CAIs and chondrules was 2.5±1.2 Myr, consistent with the ~2Myr difference inferred from the Al-Mg systems (Russell et al. 1996; Kita et al. 2000). Thus, the absolute Pb-Pb chronometer has proved that the chondrule formation (for CR chondrites) post-dated CAIs formation (for CV chondrites). Pb-Pb age of 4566.7 ±1.0 Ma for chondrules from CV chondrite Allende (Amelin et al., 2004) indicate that chondrule formation in the nebular settings have started simultaneously or shortly after CAI formation, and continued for at least 2 Myr.

There are three major sources of possible systematic errors in Pb-Pb isochron dates: (1) The presence of multiple non-radiogenic Pb components (called "common Pb") including initial Pb in the samples and contaminated Pb from both parent body and terrestrial environments; (2) The possible open system behaviour of U and Pb; and (3) Variations in formation ages within a population of chondrules. These errors may introduce scatter or curvature into the array of data points. Our ability to recognize a true isochron (within error) from an errorchron (an isochron with a dispersion of data points in excess of analytical errors) depends on the precision of analyses. This is why high precision is important for checking the accuracy of isochron dates.

Complete removal of common Pb from chondrules and CAIs prior to the Pb-isotopic analyses is the only efficient solution for problems caused by the presence of multiple common Pb components (Amelin 2004; Amelin et al. 2002; 2005). It is also possible to reliably recognize open system behaviour of radiogenic Pb, and multi-stage evolution of the U-Pb

system (for example, incorporation of radiogenic Pb that was accumulated in a chondrule or CAI precursor) only if common Pb is absent (Amelin 2004). Elimination of common Pb is, therefore, the most important condition for precise and accurate Pb-isotopic dating. Low levels of common Pb in analyses of chondrules and CAIs are achieved by choosing minerals that do not incorporate Pb due to their structural properties (such as pyroxene) and conditions of formation (such as CAIs), and removal of adhering phases rich in common Pb (e.g. chondrite matrix) by a combination of air abrasion, ultrasonic agitation and acid leaching. However, the same procedures that effectively remove common Pb from chondrules in some chondrites work poorly for other chondrites, currently hampering precise Pb-isotopic dating of chondrules from many chondrites (Amelin 2004).

The best solution for resolving small differences in age within a single population of CAIs or chondrules would be to construct internal isochrons by analysis of multiple fragments from the same chondrule or CAI. However, the usefulness of this approach is restricted by the small sizes of most chondrules and CAIs and the low abundance of U and radiogenic Pb in their constituent phases. A typical 1mm chondrule (ca. 1.5mg in weight) may contain only 15pg and 9pg of radiogenic ^{206}Pb and ^{207}Pb, respectively. Extensive acid washing, necessary for removal of common Pb, further reduces the content of radiogenic Pb to 20-30% of the original amount. These amounts are at the limit of modern techniques for precise Pb isotopic analysis. Sub-milligram fragments of from chondrules contain an insufficient amount of radiogenic Pb to yield useful precision. Internal isochron Pb-Pb dating is therefore problematical for typical chondrules, but may be possible for exceptionally large chondrules with diameters of 3 mm or larger, and for large CAIs from CV chondrites.

Pb-isotopic ages of chondrules and CAIs can be affected by aqueous alteration and shock metamorphism on U-Pb and other isotopic chronometers. For example, the chondrule ages of 4562.7±0.5 Ma in Gujba and 4562.8 ±0.9 Ma in CB chondrite Hammadah al Hamra 237 (Amelin & Krot, 2005) are the youngest precise absolute ages of chondrules determined from unequilibrated chondrites, and are distinctly younger than the ages of chondrules in CR and CV chondrites (Amelin et al. 2002; 2004). Very metal-rich CB chondrites are thought to have formed from metal and silicate droplets by evaporation and/or condensation in an impact-generated vapor plume (Rubin et al. 2003). If this model is correct and formation of CB chondrites was not a nebular process, then the age of chondrules in CB chondrites does not constrain the lifespan of the nebula. It is possible that the lifetime of the nebula was shorter, about 2-3 Myr, as determined from the ages of CR-chondrite chondrules, and CV-chondrite CAIs and chondrules discussed above.

2.2 ^{26}Al-^{26}Mg system

The ^{26}Al has a half-life of 0.73 Myr, making it suitable to investigate the earliest several million years of solar system history. Since the earliest observations of excess, radiogenic ^{26}Mg in CAIs from the Allende meteorite (Gray & Compston 1974; Lee & Papanastassiou 1974), large numbers of CAIs have been studied, yielding unambiguous evidence for the former existence of live-^{26}Al in the solar system with an initial ^{26}Al/^{27}Al ratio of ~5×10^{-5}. MacPherson, Davis, & Zinner (1995) summarized the available data collected prior to 1995 and reached three important conclusions: (1) the distribution of inferred initial ^{26}Al/^{27}Al ratios is bimodal with most CAIs showing an initial ^{26}Al/^{27}Al ratio of ~5×10^{-5}, often referred as the "canonical value" for the solar system; (2) no CAIs formed with ^{26}Al/^{27}Al ratios significantly greater than 5×10^{-5}; and (3) many CAIs experienced secondary metamorphism leading to Mg isotope re-equilibration and lower inferred initial ^{26}Al/^{27}Al ratios. Additional studies over the past 10 years have added many new CAIs, including inclusions from ordinary and enstatite chondrites, but have not significantly changed the picture that most CAIs formed over a short time interval characterized by an ^{26}Al/^{27}Al of ~5 x 10^{-5}. An important advances was the addition of new data for chondrules from a diverse suite of unequilibrated carbonaceous and ordinary chondrites and for some achondritic plagioclase (see, e.g. McKeegan & Davis 2003). The great majority of

the data discussed here are recent data for CAIs and chondrules collected using SIMS, which offers permil level precision and accuracy coupled to *in situ* analysis with micrometer spatial resolution. The past several years also have seen increasing application of ICP-MS, which provides much higher precision (better than 50 ppm) in Mg isotope ratio measurements. These new data, which are under the on-going debates (see also in Davis et al. 2005), will be also described.

The use of the ^{26}Al- ^{26}Mg system as a chronometer is predicated on the assumption that the initial ^{26}Al/^{27}Al ratio of the solar system was homogeneous. With this assumption, ^{26}Al-^{26}Mg ages can be calculated relative to the time the ^{26}Al/^{27}Al ratio of the solar system was equal to the canonical value:

$$\Delta t_{CAI} = -\ln\left\{(^{26}\mathrm{Al}/^{27}\mathrm{Al})_{sample}/(^{26}\mathrm{Al}/^{27}\mathrm{Al})_{CAI}\right\} \times \tau_{26} \qquad (5)$$

where τ_{26} is the mean life of ^{26}Al (1.02 Myr). In the following discussion we assume a homogeneous distribution of ^{26}Al and express differences in inferred initial ^{26}Al/^{27}Al in terms of age relative to CAI formation.

Range of initial ^{26}Al/^{27}Al ratios in CAIs:

Large numbers of CAIs from C chondrites (CV, CO, CM, and CR) have been measured for the ^{26}Al-^{26}Mg system, and the initial ^{26}Al/^{27}Al of most CAIs falls between 4×10^{-5} and 5×10^{-5}, corresponding to time differences of less than 0.3 Myr (data summarized by Wadhwa & Russell 2000; McKeegan & Davis 2003). Although other groups of chondrites (O and E) contain few CAIs (<0.1%), CAIs in LL3 and EH3 chondrites showed initial ^{26}Al/^{27}Al ratios consistent with the canonical value of 5×10^{-5} within analytical uncertainties (Russell et al. 1996; Guan et al. 2000; Huss et al. 2001). No SIMS data show well-defined isochrons with initial ^{26}Al/^{27}Al ratios significantly higher than the canonical value. All of the data plotting to the left side of the reference isochron come from low Al/Mg phases, possibly as the result of a disturbed system (Podosck et al. 1991). However, some recent ICP-MS bulk CAI data indicate significantly higher initial ^{26}Al/^{27}Al ratios. Galy et al (2000) reported a model isochron for one Allende CAI with slope corresponding to (^{26}Al/^{27}Al) = $(6.24 \pm 0.23)\times10^{-5}$ and, in a more extensive study, Galy, Hutcheon, & Grossman (2004) used "whole rock" analyses of 11 CAIs from Allende, Leoville and Efremovka to construct an isochron with slope corresponding to (^{26}Al/^{27}Al) = $(6.78 \pm 0.85)\times10^{-5}$. Although these data are fairly scattered from the regression line, most data lie significantly above the canonical isochron with initial (^{26}Al/^{27}Al)= 5×10^{-5}. Bizzarro et al. (2004) also reported high precision ICP-MS ^{26}Al-^{26}Mg analyses of micro-drilled Allende CAIs. In contrast to the results of Galy et al. (2000; 2004), the 6 CAIs well define an isochron with slope corresponding to (^{26}Al/^{27}Al) = $(5.25 \pm 0.10)\times10^{-5}$; none lie significantly above the canonical 5 x 10^{-5} isochron. More investigations are clearly required to solve this inconsistency.

MacPherson et al. (1995) pointed out that significant numbers of CAIs have ^{26}Al-^{26}Mg isotope compositions lying off the reference isochron, implying that the ^{26}Al-^{26}Mg isotopic systems were locally disturbed by secondary events, occurring over several Myr. Many CAIs have experienced complex thermal histories, either by reprocessing in the nebula or by being metamorphism in parent bodies. Hsu, Wasserberg, & Huss (2000) have demonstrated that petrologically distinct zones of Allende CAI 5241 have distinct initial ^{26}Al/^{27}Al ratios corresponding to relative age differences of 0.1 Myr and 0.4 Myr. This result strongly suggests that there were sequential nebular heating events affecting some CAIs extending over a time scale of a few times 10^5 years.

There are also a number of CAIs exhibiting local heterogeneity in ^{26}Al-^{26}Mg in which some part of the inclusion contains the canonical ^{26}Al/^{27}Al ratios while other parts display much

lower initial $^{26}Al/^{27}Al$ ratios (Hutcheon 1982a; Podosek et al 1991; MaPherson & Davis 1993; Caillet, MacPherson, & Zinner 1993; Imai & Yurimoto 2000; Kita et al. 2004). Anorthite, the pahse with highest Al/Mg ratio in most CAIs, is a particularly bad actor with data often show very little or no resolvable excess radiogenic $^{26}Mg^*$ in spite of very high $^{27}Al/^{24}Mg$ ratios (>100). These disturbed isotope systematics are generally interpreted in terms of secondary, metamorphic events, taking place after ^{26}Al had decayed, several Myr following CAI crystallization. Whether these secondary events represent nebular processes or parent body processes remains controversial and the topic of on-going research.

Insofar as the isotopic disturbance of the ^{26}Al-^{26}Mg system is controlled by Mg diffusion within and among coexisting CAI minerals, the different diffusivities for Mg can be used to place limits on the temperature and time of metamorphism. LaTourrette & Wasserburg (1998) measured Mg self-diffusion in anorthite and concluded temperatures extant during parent body metamorphism were too low for Mg diffusion to play a dominant role for Allende and other C chondrites. However, both LaTourrette & Hutcheon (2000) and Yurimoto et al. (2001) demonstrated that coupled Mg diffusion between melilite and anorthite could explain the disturbed Mg isotope systematics in many type B CAIs. Processes other than solid-state diffusion may also play a role. There is ample evidence of the parent body metamorphism and fluid transport in many C-chondrites. Reactions such as the replacement of anorthite by nepheline require open system behavior and suggest the Mg isotope record of CAIs reflects the influence of a variety of metamorphic processes.

There are minor groups of CAIs, particularly many of the hibonite- and grossite-bearing CAIs in CM and CH chondrites, which show only very small or unresolved ^{26}Mg excesses, but systematically contain significant isotopic anomalies in other elements, Ca and Ti, especially. Included in this group are inclusions exhibiting large mass-dependent isotopic fractionation of oxygen, Mg and Si, the so-called FUN (Fractionation and Unknown Nuclear) inclusions. Because of the large nuclear isotope anomalies and highly refractory chemical compositions, these CAIs are most plausibly considered to be derived from an isotopically heterogeneous region of the nebula, which was missing the ^{26}Al characteristic of "normal" solar system material. Whether this lack of ^{26}Al is due to very early formation, before the "late" ^{26}Al addition from a stellar source or to a more pervasive ^{26}Al heterogeneity in the nebula is a key issue for the utility of the ^{26}Al-^{26}Mg chronometer for deciphering early solar system history.

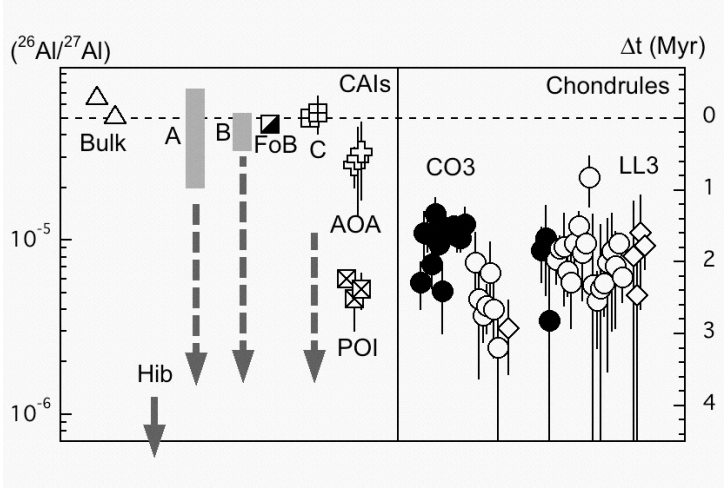

Fig. 4. Initial $^{26}Al/^{27}Al$ ratios of CAIs and chondrules. Bulk CAIs: Galy et al (2000), Bizzarro et al. (2004), CAIs: MacPherson et al. (1995), Imai & Yurimoto (2000), Itoh et al. (2002), Amelin et al. (2002), Hsu et al. (2003), Kita et al. (2004), Chondrules; Hutcheon & Hutchison (1989), Russell et al. (1996); Kita et al. (2000); McKeegan et

al. (2000); Huss et al. (2001); Yurimoto & Wasson (2003); Kunihiro et al. (2004); Kurahashi et al. (2004).

Variation of initial $^{26}Al/^{27}Al$ ratios among CAI types

Major element compositions and mineral compositions of CAIs indicate that the varieties of CAIs might be related to condensation sequences, starting from ultra-refractory hibonite- and grossite-bearing inclusions, type A, to type B, and then to less refractory type C and FoB (forsterite bearing type B) CAIs. There are no significant differences between the highest $^{26}Al/^{27}Al$ ratios among different CAI types, indicating that all of these CAIs formed within the time resolution of ^{26}Al-^{26}Mg dating (<0.5Myr). Earlier data on type C and FoB CAIs show much lower initial $^{26}Al/^{27}Al$ than the canonical value ($<6\times10^{-6}$; Hutcheon, 1982b), indicating that these less refractory inclusions formed at least 2 Myr after type A and B CAIs. However, Amelin et al. (2002) showed a well-correlated isochron with initial $^{26}Al/^{27}Al= 4.5\times10^{-5}$ from FoB CAI, E60 in Efremovka. Recent data on type C CAIs (Imai & Yurimoto 2000; Kita et al. 2004) also showed that pyroxene and melilite data plot along the canonical isochron, while anorthite data show little or no ^{26}Mg excess. Although the reasons for younger ages or later disturbance of type C and FoB CAIs are not well understood, recent results indicate that at least some of them formed at the same time as type A and B CAIs.

Amoeboid olivine inclusions (AOA) are much less refractory showing intermediate compositions between CAIs and chondrules. Itoh et al. (2002) reported initial $^{26}Al/^{27}Al$ ratios $\sim3\times10^{-5}$, corresponding to ages 0.5 Myr younger than CAIs. Plagioclase-olivine inclusions (POI) span a wide range in chemical composition, falling between ferromagnesian chondrules and fine-grained CAIs (Sheng, 1992; Sheng, Hutcheon, & Wasserberg 1991; 1992). POIs define isochrons with initial $^{26}Al/^{27}Al$ ratios less than 10^{-5} (Sheng et al., 1991; Hsu, Wasserberg, & Huss 2003; Kita et al. 2004), a behavior similar to chondrules. Together with increasing numbers of chondrule data described below, these results from the ^{26}Al-^{26}Mg chronometer give us some hints of the overall sequence of material forming in the solar system starting from refractory inclusions, AOA, POIs and to varieties of chondrules.

Chondrules

Chondrules usually do not contain Al-rich minerals with high Al/Mg ratios, making it difficult to investigate their initial $^{26}Al/^{27}Al$ ratios. However, UOC and CC contain small numbers of Al-rich chondrules spanning a wide variety of texture and compositions (Bischoff & Keil, 1984; Krot & Keil, 2002). These chondrules contain plagioclase and/or glass with high Al/Mg, and are potential targets for ^{26}Al chronology. The first detection of radiogenic ^{26}Mg was not from an Al-rich chondrule, but from the "clast chondrule" CC1 in Semarkona (LL3.0), a non-porphyritic, plagioclase bearing chondrule, showing an initial $^{26}Al/^{27}Al$ ratio of $(7.7\pm2.1)\times10^{-6}$ (Hutcheon & Hutchison 1989). Based on the high and strongly fractionated REE contents in plagioclase and pyroxene, CC1 was considered to be a fragment of an igneous rock set into the chondritic host. In this model the ^{26}Al-^{26}Mg age dates the time of igneous activity on the asteroidal body as early as 2 Myr after CAI formation. Later studies on similar objects (Kita et al., 2000; Mostefaoui, 2002; Tachibana et al. 2003) indicated that these chondrules are a minor type of FeO-rich and alkali-poor chondrules without igneous fractionation in their major element chemistry. In this scenario, CC1 has a nebular rather than planetary origin and provides the first evidence of live ^{26}Al at the time of chondrule formation.

Extensive studies on chondrule ^{26}Al chronology were led by the pioneering work of Hutcheon, Huss, & Wasserberg (1994) and Russell et al. (1996), who observed resolvable ^{26}Mg excesses in two Al-rich chondrules from UOCs, with relative ages of ~2 Myr after CAIs. These authors also reported the lack of excess ^{26}Mg from many other Al-rich chondrules, and inferred an extended period of chondrule formation between 2 to more than 6 Myr after CAIs. In a subsequent study, Huss et al. (2001) suggested that apparently younger ages of some

chondrules could be the result of parent body metamorphism, rather than representing primary formation ages. Al-rich chondrules and POIs in C chondrites showed similar results with relative ages of 2-3 Myr or longer relative to CAIs (Shen et al. 1991; Hutcheon, Krot, & Ulyanov 2000; Srinivasan, Huss, & Wasserberg 2000; Hsu et al. 2003; Kita et al. 2004). Hutcheon et al. (2000) also suggested that the fraction of Al-rich chondrules without detectable ^{26}Mg excesses increases with increasing degree of metamorphism of the host meteorite. Therefore, it is very important to work on the least metamorphosed chondrites (types 3.0-3.1) to obtain primary crystallization ages of chondrules.

The first evidence of live ^{26}Al in more common ferromagnesian chondrules was provided by Kita et al. (2000), who measured glassy mesostasis among Ca-pyroxene microcrystalites in type II chondrules from Semarkona. Data from total of more than 40 ferromagnesian chondrules from Semarkona, Bishunpur and Krymka (LL3.0-3.1; Hutcheon and Hutchison 1989; Kita et al. 2000; McKeegan et al. 2000, Mostefaoui et al. 2002; Kita et al. 2005) and also from Y81020 (CO3.0; Yurimoto and Wasson, 2003; Kunihiro et al., 2004; Kurahashi et al., 2004) now indicate the formation of chondrules took place between ~1 and ~3 Myr after CAIs. Chondrules from carbonaceous chondrites and ordinary chondrites show significant differences in their oxygen isotopic compositions and their bulk chemical compositions. However, the total range of chondrule formation times (1-3Myr) are the same for both chondrite class. These results strongly indicate LL and carbonaceous chondrules formed in two regions of the proto-planetary disk that were isolated from each other, but which underwent chondrule formation events at the same time. Mostefaoui et al. (2002) reported that there is a hint of olivine-rich chondrules being systematically older than pyroxene-rich ones. This is the first indication of a correlation between ages and properties of chondrules. Tachibana et al. (2003) further reported that chondrule ages correlate with bulk Mg/Si ratios, implying chemical fractionation of chondrule precursors with time in the proto-planetary disk. A limited number of data imply that type II chondrules are systematically younger than type I in the same meteorite (Yurimoto and Wasson, 2003; Kunihiro et al., 2004; Kurahashi et al., 2004).

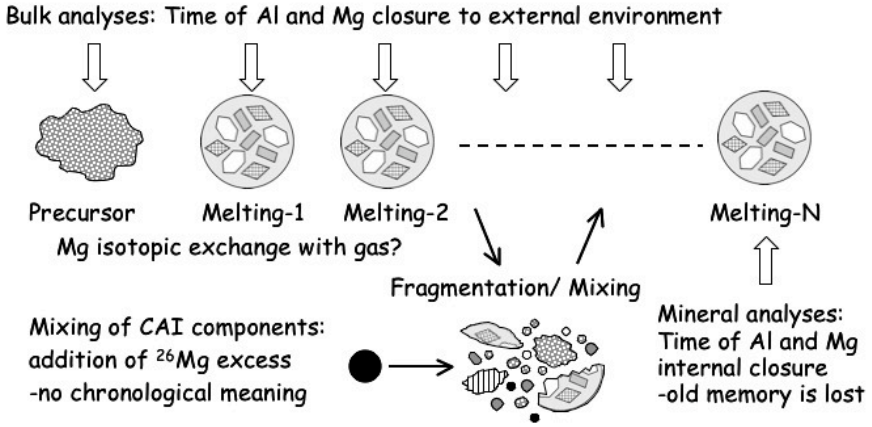

Fig. 5. Events dated by different analytical method.

The Al-Mg ages discussed above were obtained by ion microprobes and the analyses are made of glass and plagioclase, which are first phases to melt in chondrules. Many chondrules are considered to be recycled (or remelted) from previous generations (Nagahara 1981; Jones 1996) and any ^{26}Mg excess accumulated in small Al-rich areas could be easily erased. Therefore, these ^{26}Al ages should be considered to date the last melting events and may not be identical to the time distribution of chondrule forming events. Bizzarro et al. (2004) recently

reported high precision ICP-MS ^{26}Al-^{26}Mg analyses of micro-drilled Allende chondrules. Data for 15 chondrules show model isochrons with initial $^{26}Al/^{27}Al$ ratios ranging from $(1.4 \pm 0.5) \times 10^{-5}$ to values as high as $(5.7 \pm 0.8) \times 10^{-5}$, systematically higher than ion microprobe data for chondrules in the same meteorite. At value, the Bizzarro et al. (2004) results suggest chondrule formation began contemporaneously with CAI formation and continued for at least 1.5 Ma. High initial ratios may not directly indicate old formation ages of chondrules if they are produced by simple mixing of old CAI components to chondrule precursors (Galy et al., 2000). However, the fact that many data plot along the canonical CAI isochron strongly suggests formation of (at least a part of) some chondrule precursors contemporaneously with CAIs (Fig. 6). If chondrule formation actually started as early as that of CAIs, many older chondrules formed within the first million years must have been lost or recycled because SIMS ^{26}Al ages, corresponding to the last chondrule melting events, are at least 1 Myr younger than CAIs.

2.3 ^{53}Mn-^{53}Cr system

The first suggestion of the former presence of ^{53}Mn was derived from ^{53}Cr deficits in lower Mn/Cr fractions of CAIs, implying an initial $^{53}Mn/^{55}Mn$ ratio of 4.4×10^{-5} (Birck & Allègre 1985). However, the $^{53}Mn/^{55}Mn$ initial ratio estimated from CAIs is not considered to represent the initial solar system value for two reasons. First, the 53Cr deficit is associated with a ^{54}Cr anomaly of nucleosynthetic origin, making it difficult to distinguish between radiogenic and nucleogenetic sources. Nyquist et al. (2003), e.g., argued that the source of the ^{53}Cr deficit in CAIs could be very refractory spinels which preserved the early Cr isotopic heterogeneity of the solar system. Second, the inconsistency between the initial $^{53}Mn/^{55}Mn$ ratio and high precision Pb-Pb ages of CAIs (~4567Ma) relative to the LEW86010 angrites (Pb-Pb age of 4557.8±0.5Ma; Lugmair and Galer, 1992 a Second, a Mn-Cr chronology based on the CAI value is inconsistent with high precision Pb-Pb ages for differentiated meteorites (Lugmair and Galer, 1992; Nyquist et al., 1994) as well as with the recent Al-Mg ages for chondrules discussed above. Because the initial ^{53}Mn abundance in CAIs is not well understood, ^{53}Mn-^{53}Cr time scale is now commonly expressed relative to the age of the LEW86010 angrite as follows;

$$\Delta t = -\tau_{53} \ln\left\{\left(^{53}Mn/^{55}Mn\right)/\left(^{53}Mn/^{55}Mn\right)_{LEW}\right\} \quad (6)$$

where τ_{53} is mean life of ^{53}Mn (5.3 Myr).

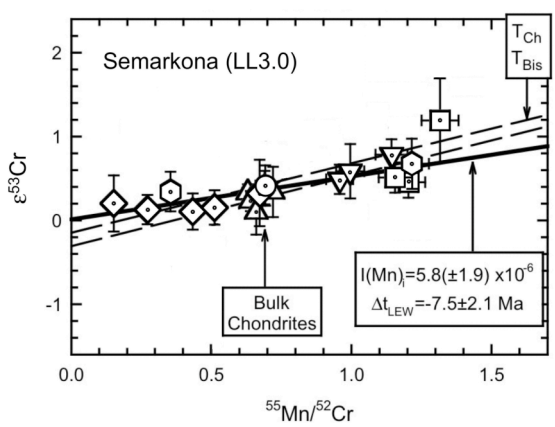

Fig. 6. Mn-Cr isochron diagram for Semarkona chondrules (Nyquist et al., unpublished). Y axis: ε^{53}Cr is excess ^{53}Cr in parts in 10^4 compared to the terrestrial value. Triangles: bulk chondrites (Nyquist et al., 2001); diamonds: PO, hexagonals: BO, circles: POP, inverted triangles: PP, and squres; RP. T_{CH} and T_{BIS} are isochrones for Chainpur and Bishunpur (Nyquist et al., 2001).

Nyquist et al. (2001) obtained whole chondrule ^{53}Mn-^{53}Cr isochrons from Bishunpur and Chainpur UOCs giving initial ^{53}Mn/^{55}Cr ratios of $(9.4\pm3.1)\times10^{-6}$ and $(9.5\pm1.7)\times10^{-6}$, respectively (Fig. 6). By applying Eq. (6), these initial ratios correspond to the ages 10 Myr older than LEW86010 with errors of 1-2 Myr, which is very similar to the time of CAI formation. From to the major and trace element concentrations in these chondrules, as measured by Instrumental Neutron Activation Analysis (INAA), Nyquist et al. (2001) also argued that the Na, Fe, and Sc abundances were consistent with chondrule formation from precursors, without significant elemental fractionation. However, because variations in the relative abundances of Sc, Mn, and Cr form a pronounced and well-defined trend (Fig. 7), they argued that the elemental abundances in the precursors were volatility-controlled. As seen from Fig. 2(a), these elements differ substantially in their condensation temperatures. Sc is an ultrarefractory element whereas Cr is a "common" element condensing initially into iron-alloy and then forsterite, whereas Mn is a relatively mo has a somewhat lower 50% condensation temperature, and condenses later into forsterite plus enstatite. Because the trend of Mn/Sc is volatility-controlled, there is a strong inference that the Mn/Cr trend in Fig. 7 is volatility controlled as well.

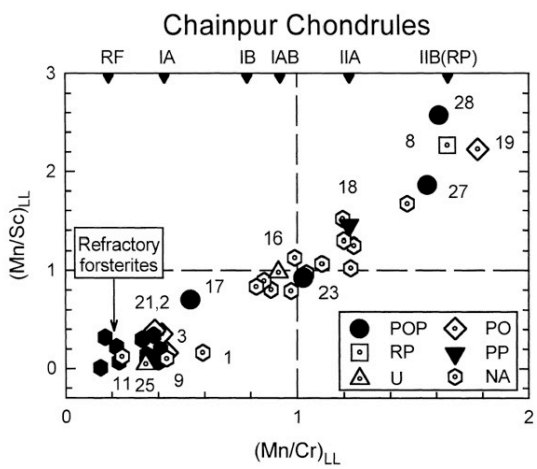

Fig. 7. LL-chondrite-normalized Mn/Cr and Mn/Sc ratios for Chainpur chondrules studied by Nyquist et al. (2001). Data for refractory forsterites (RF) are from Weinbruch et al. (2000). More refractory compositions are at the lower left in the figure, less refractory compositions are at the upper right.

The most volatile element, Mn, is depleted in Type IA porphyritic olivine (PO) chondrules, but is preferentially enriched in radial pyroxene (RP) chondrules. Data for refractory forsterites from Allende (Weinbruch, Palme, & Spettel 2000) have even lower chondrite-normalized Mn/Sc and Mn/Cr ratios than the most refractory Type IA chondrules, as shown in Fig. 7. Weinbruch et al. (2000), as well as earlier authors, argued that these refractory forsterites (RF) acquired their compositional characteristics by condensation from the solar

nebula. Thus, Nyquist et al. (2001) suggested that they represent a starting composition as well as an end-member composition for chondrule precursors. Palme et al. (2004) concluded that RFs formed in a well defined, very reducing high temperature environment, provided either by direct condensation from the solar nebula, or by crystallization from very refractory melts, only slightly less refractory than the parental melts of CAIs. In either case, RFs are the most refractory, earliest-formed olivines, and thus the oldest Mg-silicates in chondritic meteorites. Nyquist et al. (2001) argued that the Mn-Cr isotopic parameters provided by the isochrons characterize a portion of the solar nebula at the time when chondrule precursors were forming. The nearly equivalent value of $(^{53}Mn/^{55}Mn)_{I,CC} = (8.5\pm1.5)\times10^{-6}$ obtained for bulk carbonaceous chondrites (Shukolyukov, Lugmair, & Bogdanovski 2003) is consistent with the very plausible assumption that carbonaceous chondrites are derived from primitive materials in the solar nebula accreted on undifferentiated asteroids. In this connection, it is noteworthy that RFs occur as isolated grains within the matrices of carbonaceous chondrites, and also as relict grains in chondrules (Palme et al., 2004).

In addition to the results for Bishunpur and Chainpur chondrules published by Nyquist et al. (2001), a Mn-Cr isochron also has been determined for Semarkona chondrules (Fig. 6, JSC unpublished data). The slope of the isochron for these Semarkona data shown in Fig. 6 determines an initial $(^{53}Mn/^{55}Mn)$ ratio of $(5.8\pm1.9)\times10^{-6}$, corresponding to an age 7.5±2.1 Myr older than LEW86010. Although this value is somewhat less than the values found for the Chainpur and Bishunpur chondrules in the earlier study, it nevertheless is in adequate agreement with the earlier work considering both analytical uncertainties.

2.4. ^{60}Fe-^{60}Ni system

Iron-60 decays to ^{60}Ni with a half life of ~1.5 Myr. It is the only one of the short-lived nuclides known to have been present in the early solar system that is produced only in stars. Thus, ^{60}Fe is a key to understanding the origin of the short-lived nuclides in the solar system (see Chapter xx by Goswami et al. 2005). Detecting evidence for ^{60}Fe in solar system materials is quite challenging. The daughter isotope, ^{60}Ni, is the second most abundant nickel isotope at 26.22%, so the isotopic effects of ^{60}Fe decay must be identified as small additions to a large isotopic bucket. This requires either very-high-precision data or very favorable Fe/Ni ratios.

The first hint for ^{60}Fe in solar system materials was found in Allende CAIs (Birck & Lugmair 1988). Small excesses of ^{60}Ni found in several inclusions were tentatively attributed to the decay of ^{60}Fe, corresponding to an initial $(^{60}Fe/^{56}Fe)$ ratio of 1.6×10^{-6} for the time that CAIs crystallized can be calculated (Birck & Lugmair 1988). However, these excesses were sometimes accompanied by excesses in ^{64}Ni and ^{62}Ni, which are best explained as residual nucleosynthetic anomalies from a stellar source, as in the case of the ^{53}Cr anomaly in CAIs. The first evidence that ^{60}Fe was alive in the early solar system was found in the Chervony Kut and Juvinus eucrites, basaltic meteorites consisting of minerals with very high Fe/Ni ratios (up to $\sim3\times10^{5}$) due to preferential partitioning of Ni into the parent asteroid's metallic core (Shukolyukov & Lugmair 1993a; 1993b; 1996). The $(^{60}Fe/^{56}Fe)$ ratios inferred for the eucrites are significantly lower than that inferred for Allende CAIs and also differ significantly from one another (Chervony Kut = $(3.9\pm0.6)\times10^{-9}$; Juvinas = $(4.3\pm1.5)\times10^{-10}$). The large difference in $(^{60}Fe/^{56}Fe)$ for the eucrites contrasts with their similar initial $(^{53}Mn/^{55}Mn)$ ratios (Lugmair & Shukolyukov 1998), implying that the ^{60}Fe-^{60}Ni system is more susceptible to secondary disturbance than is the ^{53}Mn-^{53}Cr system (Lugmair & Shukolyukov 1998).

More recent attempts to find evidence of ^{60}Fe in CAIs and chondrules by the ion microprobe technique were not successful in detecting resolvable ^{60}Ni excess (Choi et al., 1999; Kita et al., 2000). The first clear evidence for ^{60}Fe in chondrites came from SIMS measurements on troilite (FeS) in Bishunpur, Krymka (LL3.1), and Semarkona (Tachibana & Huss 2003a; 2003b; Mostefaoui et al. 2003). Their high Fe/Ni ratios (up to 2×10^{5} for Bishunpur and Krymka troilites and up to 5×10^{4} for Semarkona troilites) made it possible to

detect ^{60}Ni excesses. The inferred (^{60}Fe/^{56}Fe) ratios for Bishunpur and Krymka troilites were in the range of 1-2×10^{-7}, from which Tachibana and Huss (2003a, 2003b) inferred a (^{60}Fe/^{56}Fe) ratio for the early solar system of 2.8x10^{-7} to 4 x 10^{-7}. Semarkona troilites gave a higher (^{60}Fe/^{56}Fe) ratio of ~7×10^{-7}, which implies an initial ratio for the early solar system of >1×10^{-6} (Mostefaoui et al., 2003). Later measurements give (^{60}Fe/^{56}Fe)$_0$ = (1.24±0.18)×10^{-6} for the combined data from several Semarkona troilites (Mostefaoui, Lugmair, & Hoppe 2004). Once it was clear that ^{60}Fe had been present in chondrites and could be detected in sulfides, Guan et al. (2003a) and Guan, Huss, & Leshin (2003b) measured sulfides in type 3 enstatite chondrites for both ^{60}Fe-^{60}Ni and ^{53}Mn-^{53}Cr systematics. They found clear evidence of ^{60}Fe and of ^{53}Mn in many of the sulfides. However, the initial (^{60}Fe/^{56}Fe)$_0$ ratios ranged from ~1×10^{-7} to ~1×10^{-5}, even among sulfides from the same meteorite! Mn-Cr "isochrons" were also quite variable from grain to grain and did not closely correlate with the (^{60}Fe/^{56}Fe) ratios. It seems clear that many, if not all, of the sulfides in enstatite chondrites experienced temperature of ~500°C on its parent body (similar to temperature experienced by Qingzhen; Huss & Lewis 1994) and did not record the (^{60}Fe/^{56}Fe) ratio in the nebula when the sulfides originally formed (Guan et al. 2003a; 2003b; Guan, Huss, & Leshin 2004).

Faced with unreliable sulfide data from enstatite chondrites, one must consider the possibility that the ^{60}Fe-^{60}Ni system of sulfides in other meteorites may have also been reset or disturbed, even those from the least metamorphosed ordinary chondrites. It is therefore important to find evidence for ^{60}Fe in minerals which are less susceptible to thermal resetting. Two non-sulfide minerals in chondrites have now shown evidence for ^{60}Fe. Magnetite from Semarkona, a secondary mineral most likely produced by aqueous alteration on the meteorite parent body with Fe/Ni of up to 6×10^{5}, gives (^{60}Fe/^{56}Fe) ≈ 1.4×10^{-7} (Mostefaoui et al. 2004). FeO-rich pyroxene chondrules from Semarkona and Bishunpur with Fe/Ni ratios up to ~3×10^{4} gave (^{60}Fe/^{56}Fe) ≈ (2-5) x10^{-7} (Huss & Tachibana 2004; Tachibana et al. 2005). Although there has been no data on Fe-Ni diffusion in orthopyroxene, if we assume that the Fe-Ni diffusion rate in orthopyroxene is similar to that for Fe-Mg (Ganguly & Tazzoli 1994), the closure temperature for several micron-sized pyroxene would be higher than 1000°C when the chondrule melt was cooled at the rate of 100 K/hr. Semarkona and Bishunpur has experienced metamorphic temperatures no higher than ~260 ºC and ~300˚C, respectively (e.g., Rambaldi & Wasson 1981; Alexander, Barber, & Hutchison 1989; Huss & Lewis 1994), most likely much too low for diffusion of Fe and Ni. The metamorphic temperatures experienced by Semarkona do not seem to have affected the chondrule silicates (e.g., Grossman, 2004). Thus, in Semarkona and Bishunpur, silicates are likely to preserve evidence of the original (^{60}Fe/^{56}Fe) ratios acquired during chondrule formation, while magnetite in Semarkona may record the timing of parent body aqueous alteration. So far, non-sulfides have not given the high (^{60}Fe/^{56}Fe) ratios observed in Semarkona troilites.

Although the current data are very limited, some first order chronological interpretations are possible. Two different interpretations can be constructed for Semarkona depending on which data one thinks is most reliable. One starting point is to assume that the highest (^{60}Fe/^{56}Fe) ratio measured in Semarkona troilites, (1.24±0.18)×10^{-6} by Mostefaoui et al. (2004), is the best value for formation of the main constituents of chondrites. An (^{60}Fe/^{56}Fe) ratio for the solar system can be inferred by assuming that the toilites are contemporaneous with the chondrules in Semarkona and formed ~1 Myr after CAIs (e.g., Kita et al., 2000). The calculated (^{60}Fe/^{56}Fe) ratio for the solar system is then very similar to the (^{60}Fe/^{56}Fe) ratio inferred for CAIs (1.6x10^{-6}; Birck & Lugmair 1988). The Semarkona chondrule with evidence of ^{60}Fe is then constrained to have formed, or to have been last altered ~4 Ma after the Semarkona troilite. In this interpretation, the Semarkona chondrule cannot be recording the formation of the majority of chondrules in the meteorite. The Semarkona magnetite is constrained to have formed ~0.75 Ma after the Semarkona chondrule, or ~4.75 Ma after CAIs.

This time line implies that an extended period of accretion and parent-body alteration is recorded in Semarkona.

An alternative timeline assumes that FeO-rich pyroxene chondrules contain the most reliable record of the ($^{60}Fe/^{56}Fe$) ratio at the time chondrules formed. If so, then the inferred $(^{60}Fe/^{56}Fe)_i$ ratio for the earliest epoch of the solar system, when CAIs formed, is 5×10^{-7} -1×10^{-6} (Huss & Tachibana 2004; Tachibana et al. 2005). Many sulfides and most magnetites in Semarkona are secondary, having formed during parent-body aqueous alteration (e.g., Krot et al., 1997). The secondary sulfides are typically Ni-rich (i.e., Fe-poor). In this interpretation, the ($^{60}Fe/^{56}Fe$) ratio inferred for the pyroxene-rich chondrules record the time of chondrule formation and the Fe-Ni data for Semarkona magnetite reflects the time of parent-body aqueous alteration. The time interval between these two events, during which accretion of the parent body would have taken place, was 0.5-2 Ma. The Semarkona sulfides have lost iron and do not give a reliable record of $^{60}Fe/^{56}Fe$ at the time when the major constituents of Semarkona formed, and the ($^{60}Fe/^{56}Fe$) ratio inferred from uncorrelated ^{60}Ni excesses in CAIs are not due to *in situ* decay of ^{60}Fe. The sulfides in Bishunpur and Krymka may not have experienced sufficient aqueous alteration to cause iron loss, but instead may have recorded gentle thermal metamorphism in the host meteorites that reset their isotopic clocks 0.5-1 Ma after chondrules formed.

The data base for ^{60}Fe is likely to grow rapidly over the next few years. Target minerals have been identified, and the new generation of high-transmission ion microprobes make measurements of the small excesses of ^{60}Ni in phases with relatively low Fe/Ni ratios (e.g., chondrule olivines) possible. The ^{60}Fe-^{60}Ni system could well provide the bridge that permits cross correlation of the ^{26}Al-^{26}Mg and ^{53}Mn-^{53}Cr systems to give a coherent chronological picture of the early solar system, and may also provide some insights into the stellar contribution to the short-lived nuclides in the early solar system.

3. Implications for the history of the proto-planetary disk

3.1. Comparison of multiple chronometers and an overview of meteorite ages

Initial homogeneity in the abundances of short-lived nuclides throughout the early solar nebula was assumed in order to apply the short-lived chronometers. One way to test the validity of this assumption is to compare the ages of individual meteorites as dated by various short-lived chronometers and the Pb-Pb method. Fig. 8 compares three chronometers, Pb-Pb, Al-Mg, and Mn-Cr, for various types of meteorite samples. Generally, these chronometers agree well within analytical uncertainties, indicating that at least ^{26}Al and ^{53}Mn were reasonably homogeneous in the early solar nebula. There are some minor inconsistencies, which could be interpreted as initial isotopic heterogeneity of these nuclides (e.g., Gounelle & Russell, 2005). However, these could be due to differences in closure temperatures for different chronometers especially if the parent bodies were slowly cooled and/or experienced some form of thermal processing (due to meteorite impacts, etc.) at lower temperature. It should be worth mentioned that polymict ureilite clasts showing well-preserved primary igneous texture have consistent ^{26}Al and ^{53}Mg ages within analytical errors of 0.4 Myr (Goodrich et al., 2002; Kita et al., 2003). This example rather supports the homogeneous distribution of these nuclides in the early solar system.

The summarized data for the meteorites show that there is a preferred order of ages, from CAIs, to chondrules, and then to planetary-differentiated meteorites and thermally equilibrated chondrites. The time period of this evolution is comparable to the time period of proto-star, classical T-Tauri, and week-lined T-Tauri stages of low mass stars (Calvet, Hartmann & Strom 2000). A short time scale of no more than 0.1 Myr is inferred for the formation of a variety of CAIs with similar initial $^{26}Al/^{27}Al$ ratios near the canonical value of 5×10^{-5}, implying that they formed during the proto-star stage when the proto-planetary disk was very active due to high

accretion rates. Chondrules formed ages within a few Myr of CAIs. This time period is similar to the average lifetime of the classical T-Tauri stage for low mass stars and may represent the lifetime of the proto-planetary disk. The earliest differentiated meteorites postdated the youngest chondrule ages by only ~1 Myr. Therefore, it is very likely that planetary formation started (at least in the asteroidal belt) a few Myr after most CAIs were formed. Melting and differentiation in early formed asteroidal bodies started quickly due to heat generated by the decay of ^{26}Al and ^{60}Fe. These results indicate that chondrule formation probably occurred in the proto-planetary disk, rather than on a parent body (Hutchison et al., 2001) or other processes require existing large planetesimals (Weidenschilling, Marzari, & Hood 1998). Furthermore, ^{26}Al ages among chondrules in the same chondrites vary by least 1 Myr (see Fig. 4), indicating chondrule-forming events must have been repeated many times over an interval of about a million years.

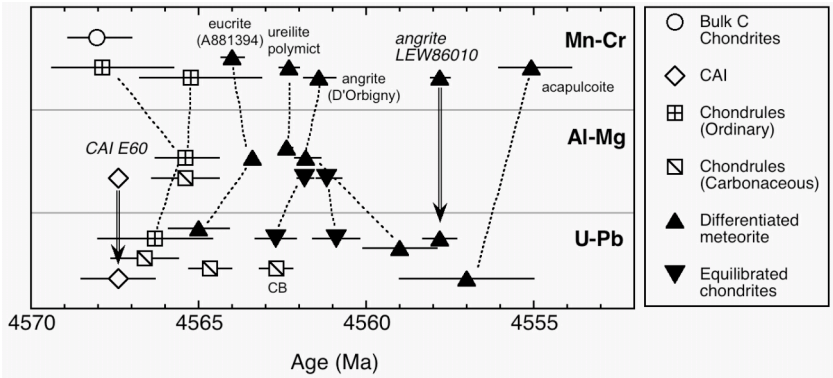

Fig. 8. Comparison of three chronometers. The relative Al-Mg and Mn-Cr ages are converted to an absolute ages using Pb-Pb ages obtained for CAI E60 (4567.2±0.6Ma; Amelin et al. 2002) and LEW86010 angrite (4557.8±0.5Ma; Lugmair & Galer 1989), respectively. Dashed lines indicate the data obtained from the same meteorites. Chondrule Al-Mg data represent the range shown in Fig. 4. Other data are from Shukolyukov et al. (2003), Nyquist et al. (2001; 2003; unpublished), Jagoutz et al. (2002), Wadwha et al. (2005?), Goodrich et al. (2002), Kita et al. (2003), another angrites, Göpel et al. (1992), Lugmair & Shukolyukov (1998), Göpel et al. (1994), Zinner & Göpel (2002), Amelin et al. (2004; unpublished), Amelin & Krot (2005).

3.2. Chondrules from ordinary chondrites; Did volatile element abundance increase with nebular residence time?

As described earlier, the initial ^{26}Al/^{27}Al ratios of chondrules from LL3.0-3.1 chondrites (the least equilibrated ordinary chondrites) show a hint of decreasing with increasing bulk Si/Mg ratios (Fig. 9). Tachibana et al. (2003) and Tomomura et al. (2004) showed that bulk Si/Mg ratios correlate with the abundance of moderately volatile elements, such as Mn and Na. Tachibana et al. (2003) suggested a mechanism for enhancing the volatile content of later formed chondrules by repeated chondrule formation accompanying gas/solid fractionation for Mg, Si, and other volatile elements (Fig. 10). They suggested that Si was selectively lost from earlier generations of chondrules because Si is more volatile than Mg and evaporates more rapidly from a chondrule melt. If these early-formed Mg-rich chondrules were separated from the chondrule-forming region and the evaporated Si-rich materials added to the next generation of chondrule precursors as fine grained re-condensed dusts, the chondrule precursors would become more Si rich than earlier precursors. If this process was repeated many times, the

later-formed chondrules would become progressively more Si- and volatile-rich than early formed ones.

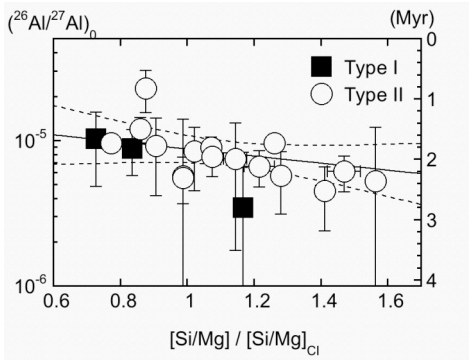

Fig. 9. Correlation of ^{26}Al ages with bulk Si/Mg ratios for chondrules from LL3.0-3.1 chondrites (After Tachibana et al. 2003 and Kita et al. 2005).

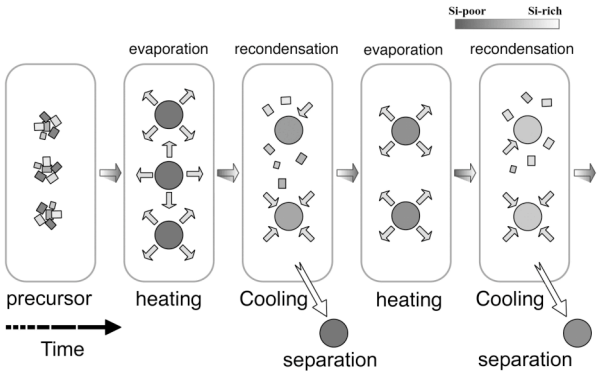

Fig. 10. Volatile enrichment in later formed chondrules (Tachibana et al. 2003).

This open system chondrule formation scenario predicts that the bulk Mn and Cr contents of chondrules should change with time, because Mn and Cr are more volatile than Si (Fig. 2). Indeed, Nyquist et al. (2001) observed Mn/Cr enrichments in pyroxene rich chondrules from LL3 chondrites. Considering that the age difference between the youngest and oldest ^{26}Al ages (~1Myr; between 1.5-2.5Myr after CAIs) is significantly shorter than the half life of ^{53}Mn (3.7 Myr), Mn-Cr isochron for chondrules would be expected to give an average age ~2 Myr younger than CAIs. As discussed in detail earlier, the published data of Nyquist et al. (2001) indicated Mn-Cr isochron ages older than the ^{26}Al ages of chondrules and closer to the formation ages of CAIs. However, more recent unpublished data for Semarkona chondrules (Fig. 6) are consistent with the range of ^{26}Al chondrule ages. The uncertainties of the Mn-Cr isochron ages are 1-2 Myr, so we obviously need more data to solidify this conclusion. If the Mn-Cr chondrule age really is as old as CAIs, then the volatile element abundances were likely fixed in the precursors before the chondrule forming period (closed system). If the Mn-Cr age is shown to be consistent with the ^{26}Al chondrule ages, and ~2 Myr after CAIs, then moderately volatile elements might be redistributed among chondrule precursors by evaporation and re-condensation as illustrated in Fig. 10 (open system).

4. Concluding Remarks

In the last 5-10 years, increasing numbers of new data have been obtained with high precision chronometers and give a general overview of early solar system chronology are generally given from analyses of meteoritic materials. The starting time (t=0) for the solar system 4567.2±0.6 Ma ago can be inferred from the high precision Pb-Pb ages of CAIs. The real time "t_0" may not be exactly the same as the CAI formation time (if CAI formed within the proto-planetary disk, then the disk was already there), this age may well represent the beginning of the solar system within analytical uncertainty. The time scales of CAIs (≤0.1Myr), chondrules (2-3Myr), and early asteroidal differentiation (≥3Myr) inferred from ^{26}Al relative ages are consistent with the time scale estimated from astronomical observations of young stars; that is, the protostar stage with an active disk (~0.1 Myr), the classical T-Tauri stage with a dusty proto-planetary disk (2-3 Myr) and a weak-lined T-Tauri star without a dusty disk (~10 Myr). However, we still need more data with higher precision, in order for the meteorite chronology to be used as strong constraints for theoretical models of solar system evolution. For example, the mechanisms of CAI and chondrule formation are still in full of debate and there is a lack of consensus as to whether CAI and chondrule formation periods overlapped. If they did overlap, CAI and chondrule formation could, but need not, be caused by the same mechanism. If the age data clearly demonstrate separate formation periods, such as CAI formation within a few times 10^5 yr of "t_0", while chondrules began forming ~1 Myr later, either the formation mechanisms were different, or there were large differences in the environments of the two events.

A better understanding of the exact meaning of the various ages may be necessary to better constrain the time scale of early nebular evolution. More experimental data may be needed to help in understanding the chemical behavior of parent-daughter nuclides during the various processes that occurred in the early solar system, such as evaporation, condensation and element-partitioning into minerals. Furthermore, the effects of diffusion and alteration during parent body processes may lead us to misinterpret some of the data. Chronologists try to avoid these secondary effects by using the least metamorphosed chondrites (such as types 3.0-3.1), although in actual fact, no meteorites completely avoided any secondary processing.

The instrumentation needed for analyzing small quantities of materials (such as large-radius ion microprobes and LA-ICP-MS) is still improving, so that higher precision data can be expected within the next decade. The potential for applying other chronometers, such ^{60}Fe and ^{36}Cl (Tachibana & Huss 2003; Lin et al. 2004), is especially important to answer many specific unsolved questions about the evolution of solid matter in the proto-planetary disk. Like ^{53}Mn, these parent nuclides are more volatile than U and ^{26}Al. Once they are established as useful relative chronometers, they can be applied to volatile element fractionation processes in the proto-planetary disk. Such processes include lower temperature gas-solid reactions (or nebular alterations) for CAIs and refractory components as well as evaporation and re-condensation of volatiles during chondrules formation. The results from such studies may have further implications to the compositions of larger planetary bodies, such as the Earth, the Moon, and Mars, all of which show significant depletions and fractionation in these moderately volatile elements compared to chondritic abundances.

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