The Chronology of Asteroid Accretion, Differentiation, and Secondary Mineralization

L. E. Nyquist[a], T. Kleine[b], C.-Y. Shih[c], Y. D. Reese[d]

[a]Mail Code KR, NASA Johnson Space Center, Houston, TX 77058-3696, USA,

[b]Inst. Isotope Geochemistry and Mineral Resources, ETH Zurich, Switzerland,

[c]Mail Code JE-23, ESCG/Jacobs Sverdrup, P.O. Box 58477, Houston, TX 77258-8477, USA,

[d]Mail Code JE-23, ESCG/Muniz Engineering, Houston, TX 77058, USA.

Corresponding author. Fax: +1 281 483 1573
E-mail address: laurence.e.nyquist@nasa. gov (L. Nyquist)

ABSTRACT

We evaluate initial $(^{26}Al/^{27}Al)_I$, $(^{53}Mn/^{55}Mn)_I$, $(^{182}Hf/^{180}Hf)_I$, and $^{207}Pb/^{206}Pb$ ages for igneous differentiated meteorites and chondrules from ordinary chondrites for consistency with radioactive decay of the parent nuclides within a common, closed isotopic system, i.e., the early solar nebula. We find that the relative abundances of ^{26}Al, ^{53}Mn, and ^{182}Hf, here denoted by $I(Al)_{CAI}$, $I(Mn)_{CAI}$, and $I(Hf)_{CAI}$, are consistent with decay from common initial values for the bulk solar system. $I(Mn)_{CAI}$ and $I(Hf)_{CAI} = 9.1\pm1.7 \times 10^{-6}$ and $1.06\pm0.09 \times 10^{-6}$, respectively, correspond to the canonical value of $I(Al)_{CAI} = 5.1 \times 10^{-5}$. $I(Hf)_{CAI}$ thus determined is consistent with $I(Hf)_{CAI} = 1.003\pm0.045 \times 10^{-6}$ directly determined in separate work. $I(Mn)_{CAI}$ is within error of the lowest value directly determined for CAI. We suggest that erratically higher values directly determined for CAI in carbonaceous chondrites reflect proton irradiation of unaccreted CAIs by the early Sun after other asteroids destined for melting by ^{26}Al decay had already accreted. The ^{53}Mn incorporated within such asteroids would have been shielded from further "local" spallogenic contributions. The relative abundances of the short-lived nuclides are less consistent with the $^{207}Pb/^{206}Pb$ ages of the corresponding materials with the best consistency being obtained between $(^{182}Hf/^{180}Hf)_I$ and $^{207}Pb/^{206}Pb$ ages of angrites. $(^{182}Hf/^{180}Hf)_I$ decreases with decreasing $^{207}Pb/^{206}Pb$ ages at the rate expected from the 8.90 ± 0.09 Ma halflife of ^{182}Hf. However, the model "CAI age" thus determined, $T_{CAI,\,Hf\text{-}W} = 4568.6\pm0.7$ Ma, is older than the commonly accepted directly measured value $T_{CAI} = 4567.1\pm0.2$ Ma. $I(Al)_I$ and $(^{53}Mn/^{55}Mn)_I$ are less consistent with $^{207}Pb/^{206}Pb$ ages, but determine $T_{CAI,\,Mn\text{-}Cr} = 4568.3\pm0.5$ Ma relative to $I(Al)_{CAI} = 5.1 \times 10^{-5}$ and a $^{207}Pb/^{206}Pb$ age of 4558.6 Ma for the LEW86010 angrite. However, the $(^{53}Mn/^{55}Mn)_I$ and $^{207}Pb/^{206}Pb$ ages of "intermediate" age D'Orbigny-clan angrites and Asuka 881394 are inconsistent with radioactive decay from CAI values with a ^{53}Mn halflife of 3.7 ± 0.4 Ma, in spite of consistency between $(^{53}Mn/^{55}Mn)_I$ and $(^{26}Al/^{27}Al)_I$. Nevertheless, it appears that the Mn-Cr method with $I(Mn)_{CAI} = 9.1\pm1.7 \times 10^{-6}$ can be used to date primary igneous events and also secondary mineralization on asteroid parent bodies. We summarize ages thus determined for igneous events on differentiated asteroids and for carbonate and fayalite formation on carbonaceous asteroids.

1. INTRODUCTION

We examine the chronology of differentiated asteroids as obtained by applying the ^{26}Al-^{26}Mg ($t_{1/2}$ = 0.73±0.03 Ma; 1 Ma = 10^6 years), ^{53}Mn-^{53}Cr ($t_{1/2}$ = 3.7±0.4 Ma), ^{182}Hf-^{182}W ($t_{1/2}$ = 8.90±0.09 Ma), and ^{146}Sm-^{142}Nd ($t_{1/2}$ = 103 Ma) chronometers in combination with ^{207}Pb-^{206}Pb ages. To consider the chronology of asteroid processes, it is necessary to know which processes can be dated. It is also necessary to have a reference point in time. As is customary in discussing earliest solar system history, we take the zero of time ("t = 0") to be that time when dust in the nebula solidified to form CAIs and chondrules. We assume these mm-sized solids accreted into asteroidal-sized bodies on a time scale that was rapid in comparison to the half-lives of the nuclides used as radiometric chronometers. Geochemical studies tell us that after accretion many asteroids underwent global chemical differentiation accompanied by fractionation of radioactive parent nuclides from stable daughter nuclides, allowing asteroid chemical differentiation to be dated. That some asteroids underwent chemical differentiation implies that they contained heat sources adequate to melt their interiors, causing basaltic magmatism. Asteroid 4 Vesta, believed to be the parent body of the HED (Howardite-Eucrite-Diogenite) meteorites is one example. The angrite parent body (APB) is another. Most basaltic eucrites on the HED parent body (HEDPB) were thermally metamorphosed by a mechanism that remains unclear. Dating the time of metamorphism provides clues to its cause, but is not a topic of this paper. Some asteroids apparently did not contain heat sources adequate to melt rock, but ice on or within them was melted, leading to secondary alteration of some of their mineral constituents. The processes and timescales of secondary alteration on parent asteroids of chondritic meteorites were recently reviewed by Krot et al. (2006), and also will be omitted from the present discussion.

Collisions among asteroids have played a role throughout asteroid history. Recent numercial simulations suggest that early "hit-and-run" collisions may have stripped the iron cores of the parent bodies of iron meteorites of overlying mantle and crust (Asphaug et al., 2006). Such collisions may well have been of fundamental importance in determining the subsequent geochemical evolution of some asteroids. Chemical differentiation appears to been driven by the decay of ^{26}Al, and thus is constrained to have followed rapidly on the heels of parent body accretion. "Hit-and-run" collisions may have been contemporaneous with accretion and differentiation, but considering their effects is beyond the scope of this paper. This paper emphasizes those non-random processes that are expected to have followed directly as a consequence of parent body accretion, melting, and chemcial differentiation.

2. APPROACH: RADIOACTIVE DECAY IN A CLOSED ISOTOPIC SYSTEM

Prerequisites for determining the earliest asteroid chronology are that the chronometers are reliable and have sufficiently fine time resolution so that differences in the times of occurrence of important events are resolved. Earlier work has shown that among the traditional methods of geochronology, only the ^{207}Pb-^{206}Pb method has sufficient time resolution to distinguish events occurring within the first 10 Ma of solar system history. Methods based on decay of the short-lived (for geochronlogy) nuclides ^{26}Al, ^{53}Mn, and ^{182}Hf with half-lives of 0.73±0.03 Ma, 3.7±0.4 Ma and 8.90±0.09 Ma, respectively, have sufficient time resolution by virtue of having halflives that are $\leq$ 10 Ma , but rely on the assumptions that their isotopic abundances relative to a stable isotope of the same element were initially the same everywhere in the solar system. That is, after being synthesized in different nucleosynthetic processes, these short-lived nuclides were homogeneously mixed throughout the solid matter condensing and accreting to become asteroid parent bodies. This cannot be assumed to be true *a priori*, and determining whether the short-lived nuclides were homogeneously or heterogeneously distributed throughout the solar nebula at "t = 0" is an active area of research addressed in this paper.

A criterion that must be satisfied for each short-lived chronometer is that the relative ages it gives for different early solar system materials are consistent with the differences in their absolute ages. In practice, this requirement becomes equivalent to requiring that time differences as measured by a short-lived chronometer should be the same as time differences as measured by the ^{207}Pb/^{206}Pb chronometer. This topic has received considerable recent attention, particularly with respect to the difference in formation times of CAIs and chondrules. (See Kita et al., 2005, for a review). Most recently, attention has focused on applying the same criterion to differentiated meteorites, which by virtue of having crystallized from molten material can be assumed to have most reliably recorded parent-daughter partitioning (e.g., Amelin, 2008). However, determining ^{207}Pb/^{206}Pb ages at the required level of precision is difficult, suggesting that the alternate approach of comparing relative formation intervals as determined by different short-lived chronometers is useful also. We consider both approaches here.

The decay equation governing the relative abundances of a radioactive parent isotope, P_R, and a stable reference isotope, P_S, at time, t, is simply

$$(P_R/P_S)_t = (P_R/P_S)_0 \exp[-\lambda(t_0-t)] \qquad \text{Eq. 1}$$

where subscript "0" refers to the zero of time, and λ is the decay constant for the radionuclide in question. Values of t_0 and $(P_R/P_S)_0$ can be chosen to correspond to a particular reference sample. The equation then is conveniently written in logarithmic form:

$$\ln (P_R/P_S)_t = \ln (P_R/P_S)_{REF} - \lambda(t_{REF}-t) \qquad \text{Eq. 2}$$

The decay interval of interest here is the ~10 Ma interval between formation of CAI and solidification of the LEW86010 angrite. Angrites Sahara 99555 and D'Orbigny formed in the middle of this interval. The formation times of both CAIs and angrites have been used as absolute age "anchors" by which formation intervals determined by short-lived nuclides can be converted to absolute ages. Fig. 1 shows the predicted decay of $^{26}Al/^{27}Al$, $^{53}Mn/^{55}Mn$, and $^{182}Hf/^{180}Hf$ with increasing time (decreasing absolute age) since formation of CAI at 4567.11±0.16 Ma ago (Amelin et al., 2006, Table 1).

Because ^{26}Al decay is very rapid on a geologic timescale, ^{26}Al had nearly vanished before the angrite LEW86010 solidified, so the "LEW" anchor is inappropriate for Al-Mg ages. Conversely, $^{53}Mn/^{55}Mn$ in LEW86010 is well determined, but $^{53}Mn/^{55}Mn$ is difficult to determine for CAI, which has made the CAI anchor inappropriate for Mn-Cr ages. However, both initial $^{53}Mn/^{55}Mn$ and initial $^{26}Al/^{27}Al$ have been determined for several samples with ages intermediate to those of CAIs and LEW86010, respectively. In such cases, plotting the initial $^{26}Al/^{27}Al$ versus initial $^{53}Mn/^{55}Mn$ ratios present in the samples when they formed shows whether or not the ^{26}Al and ^{53}Mn abundances were controlled by simple radioactive decay from defined starting conditions as determined from analyses of the reference sample. This approach requires that both the Al-Mg and Mn-Cr systems closed at the same time. Given that these two systems have different closure temperatures in most cases, the most suitable samples for such an intercomparison are rapidly cooled samples such as CAIs, chondrules and igneous-textured angrites.

Applying Eq. 2 to two different parent radionuclides, P_{R1} and P_{R2}, isotopes of elements "1" and "2", respectively, decaying over the same time interval Δt, allows Δt to be eliminated to obtain a linear relationship between $\ln(P_{R1}/P_{S1})_t$ and $\ln(P_{R2}/P_{S2})_t$, i.e.,

$$\ln(P_{R1}/P_{S1})_t = (\lambda_1/\lambda_2)\ \ln(P_{R2}/P_{S2})_t + K \qquad \text{Eq. 3}$$

where K is a constant of the decay determined from the "t = 0" CAI values. That is

$$K = \ln(P_{R1}/P_{S1})_{REF} - (\lambda_1/\lambda_2)\ \ln(P_{R2}/P_{S2})_{REF} \qquad \text{Eq. 4}$$

where REF denotes a reference sample for which the parameters have been determined. For example, radioactive decay within a single, closed reservoir with determined values of $(^{26}Al/^{27}Al)_{REF}$ and $(^{53}Mn/^{55}Mn)_{REF}$ will lead to later, correlated abundances of $(^{26}Al/^{27}Al)_I$ and $(^{53}Mn/^{55}Mn)_I$. Here, subscript "I" replaces "t" to denote the isotopic ratios initially present in the rock when it crystallized from a melt. Several samples from the same reservoir should lie on a single straight line of slope, "*m*" where

$$m = [t_{1/2}\ (^{26}Al)/t_{1/2}\ (^{53}Mn)] \qquad \text{Eq. 5}$$

and is determined by the ratio of the decay constants for ^{26}Al and ^{53}Mn, respectively, or, equivalently, their half-lives (Fig. 2). For ^{53}Mn and ^{26}Al, the ratio of halflives is ~ 0.2, with some uncertainty arising from the uncertainty in the half-lives. The ribbon-like field shown in Figs. 2 and 6 allows for the halflife uncertainties. The reference values for these figures are taken from analyses of the angrites D'Orbigny and Sahara 99555 (Amelin, 2008, Table 1). Allowed values of $^{26}Al/^{27}Al$ and $^{53}Mn/^{55}Mn$ for samples formed from the same initial isotopic reservoir as these angrites lie within the ribbon-like field shown in the figures. Provided that initial isotopic heterogeneity can be excluded, samples could only plot outside this field if the Al-Mg and Mn-Cr systems closed at different times due to differing closure temperatures. This could be the case for slowly cooled metamorphic samples, for example.

The linear relationships defined by Eqs. 2 and 3 allow sample data for short-lived radionuclides to be tested for decay within the same isotopic reservoir. To apply Eq. 2, we use the $^{207}Pb/^{206}Pb$ ages obtained via decay of long-lived ^{238}U and ^{235}U to ^{206}Pb and ^{207}Pb, respectively, as approximations of absolute time. The analytically determined values of ln $(P_R/P_S)_t$ are plotted versus $^{207}Pb/^{206}Pb$ age and fit by linear regression to determine if all data in the set correspond to simple radioactive decay within in the same isotopic reservoir. To test whether two short-lived nuclides both indicate simple decay within a common isotopic reservoir we plot $\ln(P_{R1}/P_{S1})_t$ versus $\ln(P_{R2}/P_{S2})_t$ and test for a linear relationship within the data set with a slope given by the ratio of the decay constants of the two radionuclides.

2.1 Comparison of Al-Mg and $^{207}Pb/^{206}Pb$ ages for angrites, HEDs, and CAI

Several studies have shown generally good agreement between the Al-Mg formation intervals for chondrules relative to CAI and differences in $^{207}Pb/^{206}Pb$ absolute ages, as summarized, for example, by Kita et al. (2005). However, the time intervals for formation of most chondrules are short, only ~1-2 Ma, and the uncertainties in the ages are significant in comparison. Comparing the $^{207}Pb/^{206}Pb$ and Al-Mg ages of CAI to those of differentiated meteorites is a more sensitive test of the assumption of initial isotopic homogeneity in the solar system because (a) the time interval of comparison is longer, and (b) although the parent asteroids are not known with certainty, asteroid 4 Vesta is the probable parent of the HED meteorites, and can serve as a place of reference. Spectroscopic studies can identify possible candidate parent bodies for some of the other differentiated meteorites as well.

Fig. 3 shows $^{26}Al/^{27}Al$ ratios (Log_{10}) vs $^{207}Pb/^{206}Pb$ (Pb-Pb) ages. Pb-Pb ages are from Amelin (2008) and mineral separate isochron values of $^{26}Al/^{27}Al$ for angrites and the oldest eucrite, Asuka 881394 (red squares and blue hexagons, resp.) are from Nyquist et al. (2003), Wadhwa et al. (2005), and Spivak-Birndorf et al. (2005). A decay-equiline slope corresponding to the 0.73 Ma halflife of ^{26}Al and anchored to the D'Orbigny and Sahara (Sah) 99555 angrites does not include data for rocks from the HED parent body, or widely accepted values for CAI. Because the equiline represents radioactive decay in the same or equivalent isotopic reservoirs, this failure implies some heterogeneity in $^{26}Al/^{27}Al$ between the formation locations of the Angrite Parent Body (APB), the HED Parent Body, i.e., asteroid 4 Vesta, and Efremovka CAI E60. The latter has been dated at ~4567.11 Ma (Amelin, et al., 2006). The problem is relieved if the

SIMS $^{26}Al/^{27}Al$ data are taken for A881394 (Srinivasan, 2002, yellow hexagon), and is further relieved for the highest "model $^{26}Al/^{27}Al$" calculated for eucrites by Bizzarro et al. (2005) (HEDPB, half-filled hexagon). These latter data appear to imply an age of ~4569.5 Ma for the solar system as suggested originally by Baker et al. (2005). However, the $^{207}Pb/^{206}Pb$ age for Sah 99555 upon which the latter suggestion was based has been revised (Connelly et al., 2008). Those authors caution that the Pb isotopic data of the angrites, at least of Sah 99555, have complexities requiring further investigation before Sah 99555, and presumably angrites of the same clan, can serve as robust anchors for the timescale of the early solar system. The data for these angrites are clearly inconsistent with an age of 4567.11 Ma for CAI at the "canonical" value of $^{26}Al/^{27}Al = 5 \times 10^{-5}$. For CAI and D'Orbigny-clan angrites to represent decay in the same isotopic reservoir, either the $^{207}Pb/^{206}Pb$ age of the angrites must be lower, or the CAI age should be higher. The former option would increase the difference between the angrite and HED ages. Thus, angrite and HED meteorites could no longer be considered as lying on the same equiline. Moreover, a higher $^{207}Pb/^{206}Pb$ age of 4568.5±0.5 Ma has been proposed for CAI (Bouvier et al., 2007). Thus, these data imply an older age for the solar system than ~4567 Ma, although the latter has obtained wide acceptance as the "best" age for the solar system.

It must also be noted that identification of Asuka 881394 as an HED meteorite has been challenged on the basis of its non-HED O-isotopic composition (Scott et al., 2008). Removal of A881394 from the HED clan affects only the datum labelled "HEDPB" in Fig. 1 because the other data shown in the Fig. 1 are for direct measurements on a single rock, whatever its origin. Considering only the remaining data strengthens somewhat the implication that the absolute CAI age must be older than ~4567 Ma in order for it to be consistent with the angrite and A881394 $^{207}Pb/^{206}Pb$ ages. An alternative implication is that ^{26}Al was heterogeneously distributed in the early solar system. In fact, this conclusion is weakly supported by the data for the angrites and A881394 alone, if (a) the $^{207}Pb/^{206}Pb$ ages are accurate within the stated error limits, and if (b) the initial $(^{26}Al/^{27}Al)_I$ values from the TIMS mineral separate data (Nyquist et al., 2003; Spivak-Birndorf et al., 2005) are preferred to the SIMS data. The discrepancy between the TIMS and SIMS data (Srinivasan et al., 2002) might be explained by partial re-equilibration of the Mg-isotopic composition in this rock, which has a granulitic texture (Nyquist et al., 2003). Alternatively, the Al-Mg system in A881394 might have closed later than the U-Pb system. This is conceivable given that the Al-Mg closure temperature for feldspar, the major host of radiogenic Mg in A881394, is ~450 °C (LaTourette and Wasserburg 1998), whereas Pb diffusion in pyroxenes, the major host of radiogenic Pb in A881394, ceased before cooling below ~700 °C (Cherniak 1998). The D'Orbigny-clan have sub-ophitic textures, and it is unlikely that their Mg isotopic compositons were re-equilibrated subsequently to initial crystallization. Also, the D'Orbigny-clan angrites cooled so rapidly that the aforementioned differences in closure temperatures could not result in resolvable age differences. Because both the initial $(^{26}Al/^{27}Al)_I$ and the $^{207}Pb/^{206}Pb$ ages of the D'Orbigny clan meteorites have been very well determined, it is difficult to avoid the conclusion that either (a) CAI have older absolute ages than the widely accepted ~4567 Ma value, or (b) ^{26}Al was initially heterogeneously distributed in the nebula.

2.2 Comparison of $^{207}Pb/^{206}Pb$ and Mn-Cr ages for angrites, HEDs, and CAI

Because of the longer halflife of ^{53}Mn, the relatively "young" LEW86010 angrite can be included in the comparison of $^{207}Pb/^{206}Pb$ and Mn-Cr ages (Fig. 4). A curious feature of Fig. 4 is that the mineral isochron data for the LEW86010 and D'Orbigny-clan angrite groups and A881394 are collinear along a line corresponding to an apparent ^{53}Mn decay halflife of ~4.7 Ma rather than to the accepted value of ~3.7 Ma. This observation is especially troubling since both angrite groups have been used as anchors for the early solar system timescale. According that role to LEW86010 allows "absolute" ages to be inferred for the angrite parent body (APB) and the HED parent body (HEDPB) from determined values of $(^{53}Mn/^{55}Mn)_I$. The isotopic data for the Ste. Marguerite H-chondrite is consistent within uncertainites with the LEW86010 data, but inconsistent with the data of the D'Orbigny-clan and A881394. Initial $(^{53}Mn/^{55}Mn)_I$ data determined for whole chondrule isochrons for Semarkona chondrules (Kita et al., 2005) and Chainpur chondrules (Yin et al., 2007) are only slightly greater than the values found for chemical differentiation of the HED and A881394 parent bodies, This observation is interesting because in the commonly accepted view of the normal sequence of events at a single radial location in the solar system, accretion proceeds to solids of ever-increasing size, with chemical differentiation of a large body further delayed relative to chondrule formation both by an additional accretion time, and by the thermal inertia of heating a large asteroid several hundred km in diameter. The delay between the time of chondrule formation and differentiation of these parent bodies is <~1-2 Ma.

The meaning of whole chondrule isochrons is imprecise. The primary event dated is apt to be elemental fractionation of Mn from Cr in chondrule precursors rather than in the chondrules themselves. (See Nyquist et al. (2001) for a discussion.) Whole chondrule isochrons also were determined for Chainpur and Bishunpur by Nyquist et al. (2001) and suggest earlier formation of some chondrules. Chondrule formation is likely to have been an ongoing process. Moreover, the whole-chondrule approach is subject to intrinsic uncertainties, so variations in results from that approach are not unlikely. Even those isochrons giving the youngest apparent ages, i.e., the Semarkona data of Kita et al. (2005), and the Chainpur data of Yin et al. (2007) imply chondrule formation could have been as early as ~4568 Ma ago for a D'Orbigny-clan anchor. $^{207}Pb/^{206}Pb$ ages of chondrules are younger, more consistent with a LEW86010 anchor, but also probably are affected by parent body processes. For example, the Pb-Pb isochron date for Richardton (H5) chondrules is 4562.7±1.7 Ma, compared to 4550.7±2.6 Ma for phosphate fractions from the same meteorite (Amelin et al., 2005). The difference is interpreted by the authors to be due to different isotopic closure temperatures for pyroxenes and phosphates on the H-chondrite parent body. That the ~4563 Ma age of the Richardton chondrules is ~2 Ma younger than the Mn-Cr age of the Semarkona (LL3.0) and Chainpur LL (3.3) chondrules is plausibly attributed to thermal metamorphism on the H-chondrite parent body. The Chainpur chondrules, at least, also are subject to some degree of Cr-isotopic equilibration on their parent body since Cr is to a large extent exsolved ferroan olivines (Grossman and Brearley, 2005). Whole chondrule isochrons for all but the least metamorphosed chondrites (e.g., Semarkona) are thus likely to give lower limits to the time of primary Mn/Cr fractionation in chondrule precursors, itself an upper limit on the time of chondrule formation. Subsequent to formation, many chondrules likely partook in secondary processes of partial melting following chondrule-chondrule collisions in the nebula (Tachibana et al., 2003; Kita et al., 2005). Finally there is likely to have been some degree of Cr isotopic re-equilibration on the parent body, which could vary according to chondrule size or type. Thus, variations in Mn-Cr whole-chondrule isochron ages are to be expected, and should be interpreted with the above caveats in mind. Initial $(^{53}Mn/^{55}Mn)_I$ for the carbonaceous chondrite whole rock isochron (Shukolyukov and Lugmair, 2006) and CAI "Big Al" (Bognanovski et al., 2002; Papanastassiou et al., 2002, 2005) imply a solar system age near ~4568-4569 Ma even for the LEW86010 anchor.

Discounting the possibility that the accepted halflife of ^{53}Mn is in error by ~20-25%, the data most strongly suggest some unresolved analytical issues. The alternative, heterogeneity in initial ^{53}Mn is excluded if LEW86010 and the D'Orbigny-clan are from the same parent asteroid. This possibility could be invoked for the A881394 data, if it is indeed from a parent body distinct from the HEDPB (Scott et al., 2008). However, it can be argued on textural grounds that the D'Orbigny clan meteorites are igneous rocks, which are very unlikely to have undergone post-crystallization isotopic disturbance. Thus, their data are likely to be the most reliable and the A881394 data are in agreement with them. Thus, we do not favor an interpretation of the data in Fig. 4 as suggestive of ^{53}Mn heterogeneity in the early solar system.

2.3 Comparison of $^{207}Pb/^{206}Pb$ and Hf-W ages for angrites and CAI

The comparison of $^{207}Pb/^{206}Pb$ and Hf-W ages can be made for several angrites including D'Orbigny, Sahara 99555 and Northwest Africa 2999, 4590, and 4801. In Fig. 5, the initial $^{182}Hf/^{180}Hf$ ratios of these angrites are plotted against their Pb-Pb ages. The angrites D'Orbigny and Sahara 99555 as well as Northwest Africa 4590 and 4801 plot on a straight line, whose slope is identical to the one predicted from the ^{182}Hf half-life. Northwest Africa 2999 plots slightly below but within uncertainty of this line. This might reflect a slight disturbance of the Hf-W system in this sample, consistent with the observation that some fractions of this meteorite plot off the isochron. An important feature of Fig. 5 is that, unlike for the ^{53}Mn-^{53}Cr system, the calibration of the Hf-W system onto an absolute timescale yields consistent results regardless of which of the four angrites, D'Orbigny, Sahara 99555, Northwest Africa 4590 or 4801 is used. This provides evidence that the absolute Hf-W ages calculated relative to these angrites are robust and accurate. This approach yields an absolute Hf-W age of 4568.6±0.7 Ma for CAIs and provides further evidence that the formation of CAIs occurred later than indicated by the Pb-Pb age of 4567.11±0.16 Ma (Amelin et al., 2006).

The H chondrites Ste. Marguerite (H4) and Richardton (H5) could in principle be included in the comparison of ^{207}Pb-^{206}Pb and Hf-W ages but in these slowly cooled metamorphic rocks - in contrast to the rapidly cooled angrites and CAIs - differences in the Hf-W and Pb-Pb closure temperatures (T_c) could have resulted in age differences. For Richardton the Hf-W age of 4562.9±0.9 Ma (relative to the D'Orbigny/Sahara 99555 age anchor) is indistinguishable from a ^{207}Pb-^{206}Pb age of Richardton pyroxenes of 4562.7±1.7 Ma (Amelin et al., 2005). The Hf-W age for Ste. Marguerite (H4) of 4566.9±0.5 Ma is slightly older than, but overlaps the ^{207}Pb-^{206}Pb model age of 4565.5±1.2 Ma for chondrule residues measured by Bouvier et al. (2007). Kleine et al. (2008) showed that T_c for the Hf-W system in H chondrites is similar to, but slightly above T_c for the U-Pb system. This is consistent with the generally good agreement between Hf-W and ^{207}Pb-^{206}Pb ages for Ste. Marguerite and Richardton. It is important to note that, if the Hf-W ages were calculated using the ^{207}Pb-^{206}Pb CAI age of 4567.11±0.16 Ma as an anchor, the Hf-W age for Richardton would be younger than its ^{207}Pb-^{206}Pb pyroxene age. This would be inconsistent with the relative diffusivities of W and Pb and provides further evidence that CAIs formed earlier than ~4567 Ma.

2.4 (^{26}Al/^{27}Al)$_I$ and (^{53}Mn/^{55}Mn)$_I$ and (^{182}Hf/^{180}Hf)$_I$ for angrites, A881394, HEDPB, and CAI

Suggestions of isotopic heterogeneity vanish when the ^{207}Pb/^{206}Pb ages are omitted from the comparisons. Fig. 6 shows the data set for ureilites (Goodrich et al., 2002; Kita et al., 2003), the two D'Orbigny-clan angrites, A881394, the HEDPB at the time of its differentiation, and Semarkona chondrules. These data are collinear along a line of slope m = 0.23±0.04, within error of the expected value, 0.20±0.02, given by the ratio of the ^{26}Al and ^{53}Mn half-lives. The best-fit line can be extended in either direction to a value of ^{53}Mn/^{55}Mn as low as measured for

LEW86010, and to a value of $^{26}Al/^{27}Al$ as high as measured for CAI. With the assumption that the CAI and LEW86010 would lie on the line if we could measure the missing parameter in each case, and assuming a 4558.62 Ma age for LEW from Amelin et al. (2008), gives 4568.3 Ma as the corresponding age for CAI at the canonical value of $^{26}Al/^{27}Al = 5.1 \times 10^{-5}$ (Lee et al., 1977). We suggest that these two values for the absolute ages of LEW86010 and CAI are most consistent with the short-lived nuclide data for the D'Orbigny-clan angrites, i.e., the angrite parent body, A881394, the HEDPB, and Semarkona chondrules. We note also that this age is in agreement with 4568.6±0.7 Ma derived by Kleine et al. (2008) from Hf-W data anchored to the D'Orbigny clan angrites. These observations suggest homogeneous distribution of ^{26}Al, ^{53}Mn, and ^{182}Hf at least throughout the asteroid belt.

In view of Fig. 4, a curious feature of Fig. 6 is that the relative ^{26}Al and ^{53}Mn half-lives using currently accepted values seem to be consistent with the meteorite data. Although this seems encouraging, it is nevertheless surprising given the discrepancy between the ^{207}Pb-^{206}Pb and ^{53}Mn-^{53}Cr ages for angrites and A881394 described above. These appear to be more consistent with a ~4.7 Ma half-live for ^{53}Mn instead of the accepted value of ~3.7 Ma. However, a ~4.7 Ma half-life does not seem to be consistent with the ^{26}Al-^{26}Mg and ^{53}Mn-^{53}Cr ages shown in Fig. 6. There are several possible interpretations of these observations. First, the ^{207}Pb-^{206}Pb ages for some of the angrites may not accurately date the crystallization of these rocks. This interpretation seems plausible, given that different high-precision ^{207}Pb-^{206}Pb ages have been reported for SAH 99555 by Baker et al. (2005) and Connelly et al. (2008), and the ^{207}Pb-^{206}Pb age of D'Orbigny has undergone substantial revision since the initial report of an age of 4559±1 Ma, within ~1 Ma of the LEW 86010 age (Jagoutz et al., 2002). Various analytical groups have now reached convergence on the ^{207}Pb-^{206}Pb ages of most angrites, and the resultant ^{207}Pb-^{206}Pb ages appear robust. However, Connelly et al. (2008) report the presence of an "anomalous Pb component" in at least SAH99555 due either to very radiogenic initial Pb, or to post-crystallization redistribution of Pb. This result may explain some of the earlier divergent ^{207}Pb-^{206}Pb ages that have been reported for D'Orbigny-clan meteorites, and causes Connelly et al. (2008) to urge caution in using the ages of the D'Orbigny-clan as an anchor for early solar system chronology. Nevertheless, because the age of the D'Orbigny-clan is favorable for comparing the results from short-lived nuclides of varying halflives, we rely heavily on them in this paper, but are open to the possibility that they could undergo further revision as the relevant analytical approaches are further investigated and refined. As outlined above and illustrated in Fig. 5, the Hf-W and ^{207}Pb-^{206}Pb for a suite of angrites provides consistent results, providing strong evidence that the ^{207}Pb-^{206}Pb angrite ages are indeed robust.

A second possibility is that the good correlation between $^{26}Al/^{27}Al$ and $^{53}Mn/^{55}Mn$ may be less significant than it appears. For example, it could be argued on textural grounds that A881394 cooled slowly enough that differences in closure temperatures, T_c, between the Al-Mg and Mn-Cr systems resulted in different ages. The closure temperature for Mn-Cr is probably >800 °C. Ganguly et al. (2007) estimated a closure temperature of 830-980 °C for the cumulate eucrite Serra de Magé), whereas T_c for the Al-Mg system is ~500 °C (LaTourrette and Wasserburg 1998). The granulitic texture of A881394 is unique among eucrites (Nyquist et al., 2003), and differs from that of cumulate eucrites, but is nevertheless indicative of relatively slow cooling. It therefore seems possible that the Al-Mg age for A881394 could be younger than its Mn-Cr age, steepening somewhat the slope of a regression line including the D'Orbigny-clan meteorites. The initial $^{53}Mn/^{55}Mn$ for Semarkona chondrules plotted in Fig. 6 is obtained from a whole-chondrule isochron, whereas the initial $^{26}Al/^{27}Al$ is based on internal isochrons for several chondrules. The latter clearly date chondrule crystallization and, hence, formation, but whether the Mn-Cr fractionation among bulk chondrules is related to the same event is less clear. It could also reflect volatile loss of chondrule precursors (Nyquist et al. 2001), which could well predate chondrule formation. Lastly, initial $^{53}Mn/^{55}Mn$ of the HEDPB is obtained from a whole-rock isochron for several eucrites, whereas the initial $^{26}Al/^{27}Al$ is obtained from a model isochron defined by eucrites (with identical $^{26}Mg/^{24}Mg$) and chondrites (Bizzarro et al. 2005). Therefore, in spite of the good correlation between $^{53}Mn/^{55}Mn$ and $^{26}Al/^{27}Al$, these data do not completely rule out the possibility of a ^{53}Mn half-life of ~4.7 Ma. This value is ~27% higher than the currently accepted value, and would cause a regression line of corresponding slope through the D'Orbigny-clan meteorite data to pass somewhat below the lower edge of the ±20% error envelope shown in Fig. 5. As a consequence, the estimated value of $(^{53}Mn/^{55}Mn)_I$ for CAI would be lowered. However, in view of self-consistent results for the absolute ages of LEW86010, D'Orbigny-clan angrites, and CAIs which the correlation shown in Fig. 5 provides, we consider that the probability that the currently accepted halflife of ^{53}Mn could be in error by the requisite ~27% is relatively low.

2.5 Best estimate $^{207}Pb/^{206}Pb$ age for CAI

Fig. 7 graphically compares the above-estimated $^{207}Pb/^{206}Pb$ age (CAI Best Estimate), to direct measurements of the Pb-Pb age of CAIs. This "best" estimate is obtained by averaging the results from "calculated" and "measured" values of $(^{53}Mn/^{55}Mn)_0$ at the canonical value $(^{26}Al/^{27}Al)_0 = 5.1 \times 10^{-5}$ (Lee et al., 1977) obtained from alternate linear regressions to the data shown in Fig. 6. These alternate values of $(^{53}Mn/^{55}Mn)_0$ (hereafter $I(Mn)_{CAI}$) were then used to calculate the time interval between CAI formation and crystallization of LEW86010, and the results were added to the 4558.62 Ma age of LEW86010 to obtain estimates of the CAI age. The "measured" values for this process were obtained from the best fit linear regression which has a slope $m = 0.23\pm0.04$, i.e., the blue line in Fig. 6. Because the slope of this line differs slightly, but within error limits, from the slope $m = 0.20 \pm 0.02$ calculated from the ratio of the ^{26}Al and ^{53}Mn halflives, a second line through the center of gravity of the data set, but with the $m = 0.2$ slope, was also fit to the data to yield the "calculated" value of $(^{53}Mn/^{55}Mn)_0$ The "Best Estimate" was then taken to be the average result of these two approaches. The best agreement of this estimated value, which is normalized to an age of 4558.62±0.18 Ma for LEW86010 Amelin (2008), to a directly measured CAI age is with the age 4568.5±0.5 Ma reported by Bouvier et al. (2007). Our estimated value is also consistent with the Hf-W age for CAIs of 4568.6±0.7 Ma using the D'Orbigny/Sahara 99555 anchor (Fig. 5). We also note that if only the Al-Mg data for angrites and CAIs as well as the ^{207}Pb-^{206}Pb age for D'Orbigny are used, the "absolute" Al-Mg of CAIs is 4569.1±0.2 Ma. So, there is considerable support for an age of CAI which is slightly older than the age of 4567.11±0.16 Ma reported by Amelin et al. (2006), although the latter has gained wide acceptance as "the" CAI age. The age of 4569.5±0.2 Ma suggested as the solar system age by Baker et al. (2005) is higher than any of the above estimates as well as the directly measured ages of CAI. The ~4569.5 Ma age was suggested by Baker et al. (2005) based on their analysis of Sah 99555. That it is very likely too high is consistent with the recently suggested revision of the $^{207}Pb/^{206}Pb$ age of Sah 99555 (Connelly et al., 2008).

2.6 Best estimate $I(Mn)_{CAI}$ compared to directly measured values

Fig. 8 illustrates the $^{53}Mn/^{55}Mn$ vs. $^{26}Al/^{27}Al$ correlation for the same data set fit with the "best estimate" slope yielding the "best estimate" $I(Mn)_{CAI} = (9.1 \pm 1.7) \times 10^{-6}$. A slightly lower value of $I(Mn)_{CAI} = \sim 6.9 \times 10^{-6}$ is obtained from a similar approach using initial $^{53}Mn/^{53}Mn$ and $^{182}Hf/^{180}Hf$. In this case, however, the estimated value for $I(Mn)_{CAI}$ is largely based on the data for D'Orbigny and Sahara 99555 because Mn-Cr and Hf-W data are not available for other suitable samples. The initial $(^{182}Hf/^{180}Hf)$ of CAIs is $(1.003 \pm 0.045) \times 10^{-4}$, for D'Orbigny/Sahara 99555 it is $(7.31 \pm 0.16) \times 10^{-5}$. The estimates for $I(Mn)_{CAI}$ will be lower if a ^{53}Mn half-life of ~4.7 Ma instead of ~3.7 Ma is used. Therefore, our estimates may be upper limits. The value derived here compares favorably with some of the directly measured initial $(^{53}Mn/^{55}Mn)_I$ values (Papanastassiou et al. 2002, 2005), but all the measured values show slight to considerable excesses. It is tempting to speculate that the excesses are due to variable amounts of ^{53}Mn produced by "local" particle irradiation of "residual" CAI after accretion of differentiated asteroid parent bodies. Because the Cr isotopic compositions of CAI are anomalous compared to terrestrial and chondritic compositions (*cf.*, for example, Nyquist et al., 2001), such an explanation also requires an anomalous starting Cr isotopic composition for CAI, but this does not seem to be a serious objection. The likely circumstances of the hypothetical particle irradiation would be during an early active phase of the Sun. This hypothesis also requires that (a) accretion of differentiated asteroids occurred early during the irradiation, and (b) unaccreted CAI were shielded to varying degrees during the irradiation. The criteria suggest that accretion of the undifferentiated carbonaceous asteroids in which CAI are found occurred relatively slowly. But, slow accretion is consistent with lack of sufficient ^{26}Al to cause melting and differentiation, and rapid accretion of differentiated asteroids ((a), above) is consistent with their inclusion of enough ^{26}Al to cause melting. Thus, this hypothesis appears to warrant further evaluation.

Another intriguing observation that is similar is that the Al-Mg and Hf-W formation intervals between D'Orbigny/Sahara 99555 and CAIs do not match exactly (Burkhardt et al. 2008). From this comparison, ^{26}Al in CAIs appears to be slightly overabundant relative to the predicted value, which possibly could reflect some ^{26}Al production by particle irradiation also, as proposed above for ^{53}Mn. These intriguing possibilities call for more quantitative evaluations that are, however, beyond the scope of the present paper.

2.7 I(Hf)$_{CAI}$

Fig. 9 applies an analogous approach to that illustrated in Fig. 8 to estimate the value of initial ^{182}Hf/^{180}Hf corresponding to I(Mn)$_{CAI}$ = 8.9×10^{-6}. That is, a line of slope 2.41±0.26, corresponding to the ratio of the ^{182}Hf and ^{53}Mn half lives, is drawn through the initial (^{53}Mn/^{55}Mn)$_I$ and (^{182}Hf/^{180}Hf)$_I$ values determined for the D'Orbigny angrite, the HEDPB, and the Ste. Marguerite H-chondrite. The value found in this manner is $(1.06\pm0.09) \times 10^{-4}$, agrees within error limits with the directly determined value of $(1.003\pm0.045)\times10^{-4}$ (Burkhardt et al. 2008). As discussed more fully elsewhere (Kleine et al., this volume), some earlier estimates of this parameter were too high. The good agreement between the estimated and directly determined values is strong verification of the approach used here to estimate $I(Mn)_{CAI}$ and $I(Hf)_{CAI}$..

3. DISCUSSION

3.1 Rapid differentiation of asteroids

With the foregoing validation of the short-lived chronometers and determination of a Best Estimate Solar System age, we can compare the times of early events on a variety of asteroids parental to the meteorites, relying mostly on the Mn-Cr chronometer (Fig. 10). As shown in the figure $(^{53}Mn/^{55}Mn)_I$ for carbonaceous chondrites (Shukolyukov and Lugmair, 2006) yields an age indistinguishable from the age for CAIs. Moynier et al. (2007) interpreted this to reflect the timing of parent body accretion, implying that the parent asteroids of carbonaceous chondrites formed nearly contemporaneously with CAIs. However, there are several problems with this interpretation. First, the Mn-Cr fractionation among the different carbonaceous chondrites may reflect volatile element depletion in the solar nebula and as such could well be unrelated to parent body accretion. Second, and most importantly, Al-Mg and Pb-Pb ages indicate that chondrules from the CO and CR chondrites formed more than ~2 Ma after CAIs (Kunihiro et al., 2004; Amelin et al., 2002). Since chondrule formation must predate chondrite accretion, these chondrule ages provide strong evidence that accretion of the parent bodies of at least some carbonaceous chondrites occurred more than ~2 Ma after formation of CAIs.

Initial $(^{53}Mn/^{55}Mn)_I$ data for whole chondrule isochrons for Bishunpur and Chainpur chondrules (Nyquist et al., 2000) also indicate ages as old as CAIs, but recently reported data for Chainpur chondrules (Yin et al., 2007) indicate a younger age. The JSC value of $(^{53}Mn/^{55}Mn)_I$ for Semarkona chondrules (Kita et al., 2005) also is somewhat lower than the earlier data for Chainpur and Bishunpur. The cause for variations in $(^{53}Mn/^{55}Mn)_I$ as obtained from whole chondrule isochrons is in our opinion unexplained. As discussed earlier in the paper, the whole-chondrule Mn-Cr ages could in principle date chondrule formation - and the younger Chainpur and Semarkona chondrule ages seem to support this view - but this interpretation requires that the Mn-Cr fractionation among the bulk chondrules occurred at the time of chondrule formation. However, the Mn-Cr fractionation also could have occurred in the chondrule precursors, in which case ages between ~0 and 2 Ma after formation of CAIs would be expected. It is interesting to note that all the Mn-Cr chondrule ages taken together appear to fall into this time period, which suggests that a signature of earlier Mn-Cr fractionation events has been preserved in some chondrules.

A note of caution related to the presence of nucleosynthetic Cr isotope anomalies in many early solar system materials seems to be in place here. The chronological interpretation outlined above relies on the assumption that is $I(Mn)_{CAI}$ ~$8.9x10^{-6}$. However, as mentioned above, other observations suggest $I(Mn)_{CAI}$ could be as low as ~$6.9x10^{-6}$, in which case the $(^{53}Mn/^{53}Mn)_I$ of the chondrite whole-rock isochron and whole-chondrule isochrons for some data sets give $I(Mn)_{CAI}$ that are too high. Chondrules may be subject to ongoing processes of formation and destruction in the nebula (Tachibana et al., 2003; Kita et al., 2005), which could disturb their isotopic systematics. Mechanisms affecting the Mn-Cr systematics of bulk chondrites are more difficult to envision, but could include secondary alteration on the surface of the parent body and/or nucleosynthetic Cr isotope anomalies present to varying extents in bulk chondrites. These possibilities complicate interpretation of chondrule and chondrite Mn-Cr data, and require continual evaluation for consistency with other chronological approaches. However, most chronological methods also require careful evaluation. Often "anomalous" results provide hints of important processes that may have affected the systems under consideration.

It is interesting to note that the Chainpur LL3.4-chondrite chondrule isochron age of Yin et al. (2007) overlaps the Mn-Cr age of the Ste. Marguerite H4-chondrite (Polnau and Lugmair, 2001). Chondrule formation should, of course, predate thermal metamorphism on chondrite parent bodies. The Mn-Cr isochron for Ste. Marguerite was obtained by chemical leaching of more soluble silicates from residual chromites, and could in priniciple have been affected by thermal metamorphism of the parent body. However, the ^{207}Pb-^{206}Pb age of Ste. Marguerite phosphates of 4562.7±0.6 Ma is close to the whole rock ^{207}Pb-^{206}Pb age 4566.7±1.6 Ma, and is the oldest age obtained for phosphates from ordinary chondrites (Göpel et al., 1994). Moreover, Type 4 chondrites were only heated to temperatures of ~675-750°C (Kessel et al., 2007), and at least for the Hf-W system this seems not to have been sufficient to reset the age (Kleine et al., 2008b). If the Mn-Cr closure temperature (T_c) is similar to that of Hf-W, then the Mn-Cr age may not have been significantly reset. Ganguly et al. (2007) found that T_c for Mn-Cr was relatively high (>800°C). These observations suggest that the Mn-Cr age of the Ste. Marguerite silicates may not differ significantly from the chondrule age.

The HEDPB, i.e., 4 Vesta, underwent global differentiation at a time contemporaneous with the Ste. Marguerite "silicate" age, and shortly thereafter eucrite A881394 crystallized as a magma on or near the surface of its parent body. Although earlier O-isotope data suggested that A881394 also came from the HEDPB, very recent data reported by Scott et al. (2008) suggests that was not the case. Global differentiation of the angrite parent body (APB) occurred slightly later than that of the HEDPB and the parent body of A881394. High-Mn/Cr phases in the core of the IIIAB iron meteorite parent body formed, or at least closed to Cr isotopic equilibration, contemporaneously with formation of APB. Among the differentiated meteorites, ureilites appear to have been last on the scene. It is interesting to speculate that the ureilite parent body was slow to accrete, thereby delaying its differentiation.

In comparison to the above period of ~5-6 Ma for some asteroid parent bodies to differentiate, the unradiogenic $^{182}W/^{184}W$ ratios for magmatic iron meteorites indicate that their parent bodies accreted and differentiated within less than ~1 Ma after formation of CAIs (Kleine et al., 2005; Burkhardt et al., 2008). A Hf-W age for the H4 chondrite Ste. Marguerite reflects chondrule formation at 1.7±0.7 Ma after CAI formation, consistent with Al-Mg ages of ~2 Ma for L and LL chondrules (cf., Kita et al., 2005). The Hf-W age for global differentiation of the HED parent body is currently uncertain (Kleine et al., this volume; Touboul et al. 2008) but the Hf-W data are not inconsistent with the Mn-Cr age obtained from the eucrite whole-rock isochron. Hafnium-tungsten ages for zircons from eucrites A881388 and A881467 (Srinivasan et al., 2007) provide evidence for magmatic activity on the surface of Vesta between ~4 and 10 Ma after CAI formation. Basalt extrusion on the angrite parent body, as determined by Hf-W ages for D'Orbigny and Sahara 99555, appears to have occurred somewhat earlier, at ~4 Ma after CAI formation and may have extended until ~10 Ma, as given by the Hf-W age of angrite Northwest Africa 4590. Hf-W ages when they exist are generally in good agreement with the Mn-Cr ages summarized in Fig. 10. Detailed comparison of the two data sets would require consideration of isotopic closure temperatures in the context of models for the thermal evolution of the parent bodies, and is beyond the scope of the present paper. Such an attempt ought also to include a larger set of isotopic chronometers, with both relatively high and relatively low closure temperatures. Considering that the Cr isotopic systems may have remained open until a closure temperature of ~800-900°C was reached (Ito and Ganguly 2006 , Ganguly et al. 2007), the ages shown in Fig. 10 should be considered lower bounds to the ages of the corresponding igneous events on the asteroid parent bodies.

3.2 ^{207}Pb/^{206}Pb ages and short- lived chronometer formation intervals

We have attempted to present a relatively complete and unbiased presentation of literature data pertaining to the time-resolution of events during the first ~10 Ma of solar system history as they pertain to the accretion and geochemical differentiation of rocky asteroids. We believe the values of $I(Al)_I$, $I(Mn)_I$, and $I(Hf)_I$ derived here constitute a self-consistent set for calculating formation intervals using the Al-Mg, Mn-Cr, and Hf-W chronometers. These values are nearly, but not completely, consistent with "absolute" ^{207}Pb-^{206}Pb ages of ancient igneous rocks from asteroid parent bodies. A comparison especially of Mn-Cr formation intervals and ^{207}Pb-^{206}Pb ages shows that some issues remain. Hf-W formation intervals appear to be in relatively good agreement with the relative ^{207}Pb-^{206}Pb ages for angrites (Fig. 5), but for the angrite anchor require an apparent CAI age of 4568.6±0.7 Ma, older than the widely accepted age of 4567.11 Ma for CAI (Amelin, 2006). Thus, some issues remain for the Hf-W chronometer as well. Al-Mg ages extend only over a portion of the time interval in question and provide a less complete comparison, but also reveal some unresolved issues. Note that all the short-lived chronometers considered here seem to require a CAI age that is older than ~4568 Ma when anchored to the D'Orbigny-clan angrites.

Fig. 11 shows Al-Mg and Mn-Cr "absolute ages" calculated relative to (a) $I(Mn)_{CAI} = (9.1\pm1.7)\times10^{-6}$ as derived for CAI in this paper anchored to the "Best Estimate" CAI age of 4568.3 Ma (CAI anchor) and (b) $I(Mn)_{LEW} = (1.35\pm0.05) \times 10^{-6}$ as the weighted average of JSC and UCSD data for LEW86010 (Lugmair and Galer 1992, Nyquist et al., 1994), anchored to the ^{207}Pb-^{206}Pb age of 4558.62 Ma (LEW anchor) respectively, versus measured ^{207}Pb-^{206}Pb ages of the D'Orbigny-clan angrite and A881394. The figure shows that there is good agreement between the Mn-Cr formation interval for

LEW86010 as calculated relative to $I(Mn)_{CAI}$ ~9.1 x 10^{-6} and the ~10 Ma difference between the LEW86010 ^{207}Pb-^{206}Pb age of 4558.62 Ma and our "Best Estimate" CAI age of 4568.3 Ma. However, both the Al-Mg and the Mn-Cr formation intervals for A881394 and the D'Orbigny-clan meteorites are significantly longer than the difference between their ^{207}Pb-^{206}Pb ages and the CAI age. The discrepancies are, of course, greater for a CAI age of 4567.1 Ma (Amelin, 2006).

Yin et al. (2007) have reported that their revision of I(Mn) = (5.1±1.6) x 10^{-6} for Chainpur chondrules results in a consistent chronology for the early solar system based on ^{207}Pb-^{206}Pb ages and the short-lived chronometers. We disagree with the significance of the revision, and are unable to reproduce their Fig. 3 purporting to show the concordance of all chronometers for CAI and LEW anchors at I(Mn) = (8.5±1.5) x 10^{-6} at 4567.2 Ma ago and I(Mn) = (1.25±0.07) x 10^{-6} at 4558.2 Ma ago, respectively. For the Chainpur chondrules, their figure plots a derived age of ~(4567.2-2.5) = ~4564.7 Ma as the "absolute" age based on an average $^{26}Al/^{27}Al$ formation age of (2.5±1.0) for chondrules attributed to Kita et al. (2005). From Fig. 10 of Kita et al. (2005) we take instead an average chondrule formation age of (2.0±1.0) Ma, which yields a calculated $I(Mn)_{CAI}$ = (7.4±1.6) x 10^{-6}. Fig. 12 shows Al-Mg and Mn-Cr "absolute ages" calculated relative to this CAI anchor. The LEW anchor and other features of the figure are unchanged relative to Fig. 11. This choice of $I(Mn)_{CAI}$ shortens all the calculated Mn-Cr formation intervals, bringing the CAI-anchored ages of A881394 and the D'Orbigny clan meteorites closer to the 1:1 line, but causing the CAI-anchored ages of LEW86010 and ADOR to move from the 1:1 line. It is apparent that shifting the absolute value of the age anchor from 4568.3 Ma as used here to 4567.2 Ma as used by Yin et al. (2007) has the effect of increasing the "kink" between A881394 and CAI in the data trend from ADOR and LEW through the D'Orbigny-clan and A881394 to CAI, but does not change the apparent linear trend of the angrites and A881394, which does *not* parallel the 1:1 line. Thus, we do not concur with Yin et al. (2007) that revising I(Mn) for Chainpur chondrules has significantly improved the mutual consistency of the ^{207}Pb-^{206}Pb and short-lived chronometers.

Determining an appropriate value of $I(Mn)_{CAI}$ has been a considerable problem in early solar system chronology. In their pioneering study of CAI, Birck and Allègre (1985) a proposed value much higher than any discussed here, i.e., $(4.4\pm1.1) \times 10^{-5}$, as an average for CAI. In the first report on Chainpur chondrules, Swindle et al. (1996) favored an alternate value of 3.7×10^{-5} obtained from an internal Mn-Cr mineral isochron for Allende inclusion BR1. Continuing the chondrule study, Nyquist et al. (2001) proposed $I(Mn)_{CAI} = 2.8 \times 10^{-5}$ from the average Mn-Cr systematics or chondrules and bulk chondrites and initial $^{53}Cr/^{52}Cr$ = -1.3 ε-units for CAI spinels. Papanastassiou et al. (2002, 2005) found I(Mn) to be variable among CAI, as illustrated in Fig. 8, with the lowest value $(^{53}Mn/^{55}Mn)_I \sim 1.04 \times 10^{-5}$. The basis for assigning $I(Mn)_{CAI} = (8.5\pm1.5) \times 10^{-6}$ from the whole chondrite isochron for carbonaceous chondrites is somewhat unclear, but the result is in agreement with the value deduced here from Al-Mg and Mn-Cr parameters for chondrules and *differentiated* meteorites (Fig. 6). An independent approach is to combine the chondrule-determined I(Mn) with the Al-Mg formation ages of chondrules as above. The strongest justification can be made for using $I(Mn) = (5.8\pm1.9) \times 10^{-6}$ for Type 3.0 Semarkona as reference because the Cr distribution in Semarkona should be undisturbed. Correction for 2.0 Ma of ^{53}Mn decay yields $I(Mn)_{CAI} = (8.4\pm1.9) \times 10^{-6}$, in agreement with the bulk carbonaceous chondrite value. Thus, a value near 8.5×10^{-6} can be justified by three independent ways: (a) from the bulk carbonaceous chrondrite isochron, (b) from differentiated igneous meteorites and the HEDPB differentiation (Fig. 6), (c) from chondrules from the Semarkona unequilibrated ordinary chondrite, corrected for 2.0 Ma of ^{53}Mn decay as inferred from the average Al-Mg ages of chondrules. These results are summarized in Table 2.

Although the above considerations seem to provide a self-consistent estimate for $I(Mn)_{CAI}$, a slight inconsistency appears when Hf-W data are included in these estimates. Combining the $I(Hf)_I$ for CAIs and the angrite D'Orbigny with $I(Mn)_I$ for this angrite results in a calculated $I(Mn)_{CAI}$ of $\sim 6.9\times10^{-6}$. This value is difficult to reconcile within error limits with the value of $\sim 8.5 \times 10^{-6}$ deduced above. The reason for this inconsistency is currently unclear. However, this ~23% uncertainty in the deduced $I(Mn)_{CAI}$ is minor compared to the range of directly measured $I(Mn)_{CAI}$. A combined Mn-Cr and Hf-W investigation of a range of samples is needed to clarify this remaining issue.

3.3 ^{53}Mn-^{53}Cr timescale for secondary mineralization on carbonaceous asteroids

The ^{53}Mn-^{53}Cr chronometer is useful for dating secondary mineralization on planetary surfaces as well as primary igneous events. Both carbonates and fayalites are well suited to Mn-Cr dating by SIMS techniques because they can have extremely high Mn/Cr ratios. It is not unusual for enrichments in radiogenic ^{53}Cr* to exceed 1000 ‰ in both minerals. This topic has been reviewed recently by Krot et al. (2006). Here we note only a few results because of their relevance to the question of initial ^{53}Mn/^{55}Mn for the solar system. The Kaidun polymict chondrite breccia is of particular relevance in this regard. The Cr-isotopic composition of calcite and dolomite grains from three different lithologies within Kaidun give a well-defined isochron corresponding to $(^{53}Mn/^{55}Mn)_I = (9.4 \pm 1.6) \times 10^{-6}$ (Hutcheon et al., 1999). This result is coincident within error limits with the higher values for $I(Mn)_I$ summarized in Table 2 and is inconsistent with a value of $I(Mn)_I$ as low as 7.4×10^{-5}, for example. Fig. 13 shows additional Mn-Cr data for carbonates and fayalites as summarized in the review by Krot et al. (2006). It shows that secondary mineralization began early and appears to have lasted only about 10 Ma post-CAI on the CV, CI, and CM parent bodies. Interestingly, but perhaps not unexpectedly, it appears to have begun essentially simultaneously with planetesimal formation. Note that there are two other cases in which secondary mineralization on the CM parent body appears to have preceded formation of LL chondrules if only the revised data for Chainpur chondrules are accepted. In that case one would have to say that CM chondrites formed before LL-chondrules, which seems counter-intuitive. Clearly, further investigations of the Mn-Cr systematics of chondrules are justified.

4. CONCLUSIONS:

Short-lived chronometers define a mostly-consistent chronology for events in the early solar system. Values of $I(Mn)_{CAI} \sim 9.1 \times 10^{-6}$ and $I(Hf)_{CAI} \sim 1 \times 10^{-5}$ corresponding to canonical $I(Al)_{CAI} \sim 5.1 \times 10^{-5}$ have been derived from data for differentiated meteorites from asteroids which accreted early enough for decay of ^{26}Al to provide the heat source for melting. We believe this to be a significant observation consistent with early isolation of the ^{53}Mn they contained from additional contributions from the nebula. We suggest that the difference between $I(Mn)_{CAI}$ derived here and the directly measured values in CAI can be plausibly attributed to proton irradiation of unaccreted CAI by an early active sun. ^{56}Fe is a most abundant target nuclide for spallation production of excess ^{53}Mn by irradiation processes, and would be enriched in the mafic mineral phases which determine isochron slopes in Mn-Cr isochron plots. Although Fe is in overall low abunance in CAI, phases having high Mn/Cr ratios would be enriched in olivines and pyroxenes containing more abundant Fe then low Mn/Cr phases such as hibonites. Because spallogenic ^{53}Mn would be produced more abundantly in phases having high Mn/Cr ratios the slope of Mn-Cr isochrons would in general be rotated to higher-than-normal values resulting in higher calculated $(^{53}Mn/^{55}Mn)_I$ ratios. Individual CAI could have been exposed to the irradiation under highly variable conditions, thereby accounting for apparent initial $(^{53}Mn/^{55}Mn)_I$ values that are erratically higher than the solar system baseline value.

The Best Estimate Solar System Age of 4568.3±0.5 Ma relative to 4558.62 Ma for LEW86010 that is derived from the Al-Mg and Mn-Cr data is consistent with the independently derived age of 4568.6±0.7 Ma form Hf-W data. The $^{207}Pb/^{206}Pb$ ages of the D'Orbigny-clan angrites strongly influence these age estimates, which are older than the widely-accepted directly measured $^{207}Pb/^{206}Pb$ ages of 4567.1±0.2 Ma for CAI.

We believe the present work has clarified some issues related to using the so-called "short-lived" chronometers to determine early solar system chronolgy. Nevertheless, much remains to be done. The new generation of instruments and techniques will allow isotopic data to be determined with greater precision. Collaborative studies using different techniques and multiple isotopic systems are clearly critical to verify basic assumptions. Many different events appear to have occurred within a limited amount of time in the early nebula, so rather broad consistency criteria can be developed. Thus, for example, it appears that secondary mineralization occurred on undifferentiated asteroids rapidly enough that SIMS study of these secondary minerals, which have more extreme parent/daughter nuclide ratios than most igneous materials, can form a useful check on studies of the chronology of igeneous differentiation and magmatism on differentiated asteroids.

Acknowledgments: L. N. acknowledges the generosity of the organizing committee of the *Workshop on the Chronology of Meteorites and the Early Solar System* for inviting his participation in the workshop. Thanks are due especially to Sasha Krot for suggesting a topic to be reviewed, and to Ed Scott for hosting a delightful post-conference field trip to the Kilauea volcano. Noriko Kita provided ureilite data for the conference abstract and also for this paper and encouragement in the writing both. Financial support was provided by NASA RTOP 344-31 and the Swiss National Science foundation.

REFERENCES

Amelin Y., Krot A. N., Hutcheon I. D., Ulyanov A. A. (2002) Lead Isotopic Ages of Chondrules and Calcium-Aluminum–Rich Inclusions. *Science* **297,** 1678-1683.

Amelin Y., Ghosh A., and Rotenberg E. (2005) Unraveling evolution of chondrite parent asteroids by precise U-Pb dating and thermal modeling. *Geochim. Cosmochim. Acta* **69,** 505-518.

Amelin, Y., Wadhwa, M., and Lugmair, G. W., 2006. Pb-isotopic dating of meteorites using ^{202}Pb-^{205}Pb double spike: comparison with other high-resolution chronometers. In *37th Lunar and Planetary Science Conference*, abstract #1970 (CD-ROM).

Amelin Y. (2007). The ages of angrites. *Lunar and Planetary Science XXXVIII*, Lunar Planet. Inst., Houston. #1669 (abstr).

Amelin Y. and Irving, A. J. (2007). Seven million years of evolution on the angrite parent body from Pb-isotopic data. *Workshop on the chronology of meteorites and the early solar system,* LPI Contribution No. 1374, p.20-21.

Amelin Y. (2008). U-Pb ages of angrites. *Geochim. Cosmochim. Acta* **72,** 221-232.

Asphaug, E., Agnor, C. B., and Williams, Q., 2006. Hit-and-run planetary collisions. Nature 439, 155-160.

Baker J. Bizarro M. Wittig N., Connelly J., and Haack H. (2005) Early planetesimal melting from an age of 4.5662 Gyr for differentiated meteorites. *Nature* **436,** 1127-1131.

Birck J.-L. and Allègre C. J. (1985) Evidence for the presence of ^{53}Mn in the early solar system. *Geophys. Res. Lett.* **12,** 745-748.

Bizzarro M, Baker J. A., Haack H., and Lundgaard K. L. (2005) Rapid timescales for accretion and melting of differentiated planetesimals inferred from ^{26}Al-^{26}Mg chronometry *Ap. J.* **632,** L41-L44.

Bouvier A., Blichert-Toft J., Moynier F., Vervoort J. D., Albarede F. (2007) Pb-Pb dating constraints on the accretion and cooling history of chondrites. *Geochim. Cosmochim. Acta* **71,** 1583-1604.

Bogdanovski O., Papanastassiou D. A., and Wasserburg G. J. (2002) Cr isotopes in Allende Ca-Al-rich inclusions. *Lunar and Planetary Science XXXIII,* Abstract #1802.

Burkhardt, C., Kleine, T., Palme, H., Bourdon, B., Zipfel, J., Friedrich, J., and Ebel, D. (2008) Hf-W isochrons for CAIs and timescales for planetesimal accretion, *Geochim. Cosmochim. Acta,* submitted.

Cherniak (1998) Pb diffusion in clinopyroxene. *Chemical Geology* **150,** 105–117

Connelly J. N., Amelin Y., Bizarro M., Thrane K., and Baker J. A. (2008) The Pb-Pb age of angrite SAH 99555 revisited. *Lunar and Planetary Science XXXIX,* Abstract #2386.

Ganguly, J., Ito, M., and Zhang, X. (2007) Cr diffusion in orthopyroxene: Experimental determination, ^{53}Mn-^{53}Cr thermochronology, and planetary applications. *Geochim. Cosmochim. Acta* **71,** 3915-3925.

Goodrich C.A., Hutcheon I.D. and Keil K. (2002) ^{53}Mn-^{53}Cr age of a highly-evolved, igneous lithology in polymict ureilite DaG 165. *Meteorit. Planet. Sci.* **37,** A54 (abstract).

Glavin D., Kubny P. A., Jagoutz E. and Lugmair G. W. (2004) Mn-Cr isotope systematics of the D'Orbigny angrite. *Meteorit. Planet. Sci.* **39,** 693-700.

Göpel C., Manhès G., and Allegrè C.-J. (1994) U-Pb sytematics of phosphates from equilibrated ordinary chondrites. *Earth and Planet. Sci. Lett.* **121,** 153-171.

Grossman J. N. and Brearley A. J. (2005) The onset of metamorphism in ordinary and carbonaceous chondrites. *Meteoritics and Planet. Sci.,* **40,** 87-122.

Ito, M. and Ganguly, J. (2006) Diffusion kinetics of Cr in olivine and 53Mn-53Cr thermochronology of early solar system objects. *Geochim. Cosmochim. Acta* **70,** 799-809.

Jagoutz E., Jotter R., Varela M. E., Zartman R., Kurat G., and Lugmair G. W. (2002) Pb-U-Th isotopic evolution of the D'Orbigny angrite. *Lunar and Planetary Science XXXIII,* Abstract #1043.

Jogo K., Nakamura T. and Noguchi T. (2006) Secondary fayalite in the Vigarano CV3 carbonaceous chondrite: Occurrence and formation age. *Meteoritics and Planet. Sci.,* **41,** abstract #5242.

Kessel R., Becckett J. R., and Stolper E. M. (2007) The thermal history of equilibrated ordinary chondrites and the relationship between textural maturity and temperature. *Geochim. Cosmochim. Acta* **71,** 1855-1881.

Kita N.T., Ikeda Y., Shimoda Y., Morishita and Y. Togashi S. (2003) Timing of basaltic volcanism in ureilite parent body inferred from the ^{26}Al ages of plagioclase-bearing clasts in DaG-319 polymict ureilite. In *34th Lunar and Planetary Science Conference*, abstract #1557(CD-ROM).

Kita N. T., Huss G. R., Tachibana S., Amelin Y., Nyquist L.E., and Hutcheon I. D. (2005) Constraints on the origin of chondrules and CAIs from short-lived and long-lived radionuclides. In Chondrules and the Protoplanetary Disk, ASP Conference Series, Vol 341, pp. 558-587.

Kleine, T., Mezger, K., Palme, H., Scherer, E., and Münker, C., 2005. Early core formation in asteroids and late accretion of chondrite parent bodies: Evidence from 182Hf-182W in CAIs, metal-rich chondrites and iron meteorites. *Geochim. Cosmochim. Acta* **69,** 5805-5818.

Kleine, T., Touboul, M., Van Orman, J. A., Bourdon, B., Maden, C., Mezger, K., and Halliday, A., 2008b. Hf-W thermochronometry: closure temperature and constraints on the accretion and cooling history of the H chondrite parent body. *Earth Planet. Sci. Lett.* subm.

Kleine T., Bourdon B., Burkhardt C., and Irving A. J. (2008) Hf-W chronometry of angrites: Constraints on the absolute age of CAIs and planetesimal accretion timescales. *Lunar and Planetary Science XXXIX,* Abstract #2367.

Krot A. N., Hutcheon I. D., Brearley A. J., Pradivtseva O. V., Petaev M. I., and Hohenberg C. M. (2006) Timescales and settings for alteration of chondritic meteorites. *Meteorites and the Early Solar System II.* Univ. of Arizona Press. pp. 525-553.

Kunihiro T., Rubin A. E., McKeegan K. D., Wasson J. T. (2004) Initial ^{26}Al/^{27}Al in carbonaceous chondrite chondrules: Too little ^{26}Al to melt asteroids. *Geochim. Cosmochim. Acta* **68,** 2947-2957.

LaTourrette T. and Wasserburg G. J. (1998) Mg diffusion in anorthite: implications for the formation of early solar system planetesimals. *Earth Planet Sci. Lett.,* **158,** 91-108.

Lee T., Papanastassiou D. A., and Wasserburg G. J. (1977) Aluminum-26 in the early solar system: Fossil or fuel? Ap. J. **211,** L107-110.

Lugmair G. W. and Shukolyukov A. (1998) Early solar system timescales according to ^{53}Mn-^{53}Cr systematics. *Geochim. Cosmochim. Acta* **62,** 2863-2886.

Lugmair G.W. and Galer S. J. G. (1992) Age and isotopic relationships among the angrites Lewis Cliff 86010 and Angra dos Reis. *Geochim. Cosmochim. Acta,* **56,** 1673-1694.

Moynier F., Yin Q.-Z., and Jacobsen B. (2007) Dating the first stage of planet formation Ap. J. **671,** L181-183.

Nyquist L., Bansal b., Wiesmann H., and Shih C.-Y. (1994) Neodymium, strontium and chromium isotopic studies of the LEW86010 and Angra dos Reis meteorites and the chronology of the angrite parent body. *Meteoritics* **29,** 872-885.

Nyquist L., Lindstrom D., Shih C.-Y., Wiesmann H., Mittlefehldt D., Wentworth S., and Martinez R. (2001) Mn-Cr formation intervals for chondrules from the Bishunpur and Chainpur meteorites. *Meteoritics and Planetary Sciences* **36,** 911-938.

Nyquist L. E., Reese Y., Wiesmann H., Shih C.-Y., and Takeda, H. (2003a) Fossil ^{26}Al and ^{53}Mn in the Asuka 881394 eucrite: evidence of the earliest crust on asteroid 4 Vesta. *Earth Planet. Sci. Lett.* 214, 11-25.

Nyquist L. E., Shih C.-Y., Wiesmann H., and Mikouchi, T. (2003b) Fossil ^{26}Al and ^{53}Mn in D'Orbigny and Sahara 99555 and the timescale for angrite magmatism. In *Lunar and Planet. Sci. XXXIV,* Abstract #2003, Lunar and Planetary Institute, Houston (CD-ROM).

Papanastassiou D.A., Bognanovski O., and Wasserburg G.J. (2002) ^{53}Mn-^{53}Cr systematics in Allende refractory inclusions. *Meteoritics & Planetary Science,* **37,** suppl., A114 (abstract).

Papanastassiou D. A., Wasserburg G. J., and Bogdanovski O. (2005) The ^{53}Mn-^{53}Cr system in CAIs: an update. *Lunar and Planetary Science,* Abstract #2198.

Polnau E. and Lugmair G. W. (2001) Mn-Cr isotope systematics in the two ordinary chondrites Richardton (H5) and Ste. Marguerite (H4). *Lunar and Planetary Science XXXII,* abstract #1527 (CD-ROM).

Scott E. R. D., Greenwood R. C., Franchi I. A., Barrat J.-A., and Sanders I. S. (2008) Oxygen isotopic constraints on the number and origin of basaltic achondrite parent bodies. *Lunar and Planetary Science XXXIX,* Abstract #2344.

Shukolyukov A. and Lugmair G. W. (2006) Manganese-chromium isotope systematics of carbonaceous chondrites. *Earth Planet. Sci. Lett.* **250,** 200-213.

Spivak-Birndorf L., Wadhwa M., and Janney P. E. (2005) ^{26}Al-^{26}Mg chronology of the D'Orbigny and Sahara 99555 angrites. *Meteoritics and Planetary Sciences* **40,** A145 (abstract).

Srinivasan G. (2002) ^{26}Al-^{26}Mg systematics of A881394 eucrite (abstract). In *33rd Lunar and Planetary Science Conference*, abstract #1489 (CD-ROM).

Srinivasan G., Whitehouse M. J., Weber I., and Yamaguchi A. (2007) The crystallization age of eucrite zircon. *Science* **317,** 345-347.

Sugiura N., Miyazaki A., and Yanai K. (2005) Widespread magmatic activities on the angrite parent body at 4562 Ma ago. *Earth Planets Space* **57,** e13-e16.

Tachibana S., Nagahara H., Mostefaoui S., and Kita N. T. (2003)Correlation between relative ages inferred from ^{26}Al and bulk compositions of ferromagnesian chondrules in least equilibrated ordinary chondrites. *Meteoritics and Planetary Sciences* **38,** 939-962.

Wadhwa, M., Shukolyukov, A., Davis, A. M., Lugmair, G. W., and Mittlefehldt, D. W., 2003. Differentiation history of the mesosiderite parent body: Constraints from trace elements and manganese-chromium isotope systematics in Vaca Muerta silicate clasts. Geochim. Cosmochim. Acta 67, 5047-5069.

Wadhwa M., Amelin Y., Bogdanovski O., Shukolyukov A., Lugmair G. W., and Janney P., (2005) High precision relative and absolute ages for Asuka 881394, a unique and ancient basalt. In *36th Lunar and Planetary Science Conference*, abstract #2126(CD-ROM).

Yin Q.-Z., Jacobsen B., Moynier F., and Hutcheon I. D. (2007) Toward consistent chronology in the early solar system: High-resolution ^{53}Mn-^{53}Cr chronometry for chondrules. *Ap. J.* **662,** L43-L46.

FIGURE CAPTIONS

Fig. 1 . Illustrating Eq. 2 for the relationship between Al-Mg, Mn-Cr, and Hf-W ages and absolute age for the first ~10 Ma of solar system history. The absolute ages for CAI, LEW, and D'Orbigny/Sahara 99555 are approximated by their $^{207}Pb/^{206}Pb$ ages (Table1). "Anchors for each system are shown by solid symbols.

Fig. 2. Illustrating Eq. 3 for the relationship between the Al-Mg and Mn-Cr formation intervals for the currently accepted halflives $t_{1/2}$ = 0.73±0.03 Ma and 3.7±0.4 Ma , for ^{26}Al and ^{53}Mn, respectively.

Fig. 3. Measured $^{26}Al/^{27}Al$ ratios and ^{207}Pb-^{206}Pb ages in D'Orbigny, Sah99555, A881394, and CAI. $^{26}Al/^{27}Al$ for the HEDPB (Bizzarro et al., 2005) is shown as a half-filled symbol plotted on the ^{27}Al decay line passing through the D'Orbigny-clan meteorites. The corresponding value on the x-axis is thus the "absolute" Al-Mg age of the HEDPB relative to the ^{207}Pb-^{206}Pb ages of the D'Orbigny-clan meteorites. Data references and numerical values are given in Table 1.

Fig. 4. Measured $^{53}Mn/^{55}Mn$ ratios and $^{207}Pb/^{206}Pb$ ages in some early solar system materials. Data references and numerical values are given in Table 1. Alternate choices of the $^{207}Pb/^{206}Pb$ age of Ste. Marguerite correspond to different mineral phases, the central datum is for ol and px residues (Bouvier et al., 2007).

Fig. 5. Measured $^{182}Hf/^{180}Hf$ ratios and $^{207}Pb/^{206}Pb$ ages in angrites and CAI. Figure after Kleine et al. (2008). Hf-W data are from Burkhardt et al (2008), and $^{207}Pb/^{206}Pb$ ages are from Amelin et al. (2008).

Fig. 6. Initial $(^{53}Mn/^{55}Mn)_I$ for ureilites, two D'Orbigny-clan angrites, the HEDPB, and Semarkkona chondrules plotted against initial $(^{26}Al/^{27}Al)_I$ for the same or similar samples. The best fit regression line has a slope m = 0.23±0.04, within uncertainty of m = 0.20±0.02 expected from the ratio of the halflife of ^{26}Al to that of ^{53}Mn. The short-lived nuclide data imply an absolute age of CAI of 4568.3±0.5 Ma when anchored to an age of 4558.62 Ma for LEW 86010 (Amelin et al., 2008). Data references and numerical values are given in Table 1.

Fig. 7. Absolute ages estimated for CAI from the Al-Mg and Mn-Cr data, normalized to an age of 4568.3 Ma for the LEW 86010 angrite and to $^{26}Al/^{27}Al = 5.1 \times 10^{-5}$ for CAI compared to reported values of directly measured $^{207}Pb/^{206}Pb$ ages for CAI. "Measured" means the age was calculated using the slope m

~0.23 of the best fit line in Fig. 6, "calculated" means the age was calculated using m ~0.20 as obtained from the ratio of halflives.

Fig. 8. Using the correlation between initial $(^{53}Mn/^{55}Mn)_I$ and initial $(^{26}Al/^{27}Al)_I$ to determine the value of initial $(^{53}Mn/^{55}Mn)_I$ that corresponds to $(^{26}Al/^{27}Al)_I = 5.1 \times 10^{-5}$. These values are here called $I(Al)_{CAI}$ and $I(Mn)_{CAI}$, respectively. $I(Mn)_{CAI}$ thus defined has the value $(9.1\pm1.7) \times 10^{-6}$.

Fig. 9. Using the correlation between initial $(^{53}Mn/^{55}Mn)_I$ and initial $(^{182}Hf/^{180}Hf)_I$ to determine the value of initial $(^{182}Hf/^{180}Hf)_I$ corresponding to initial $(^{53}Mn/^{55}Mn)_I = (9.1\pm1.7) \times 10^{-6}$. $I(Hf)_{CAI}$ thus derived is $(1.06\pm0.09) \times 10^{-4}$ in good agreement with the directly determined value of 1.003±0.045 (Burckhardt et al., 2008).

Fig. 10. T_{LEW} $^{53}Mn/^{55}Mn$ ages and measured $^{207}Pb/^{206}Pb$ ages (filled red circles and stars) in early solar system objects and materials. Arranged in order of increasing age from top to bottom. Data references and numerical values are given in Table 1.

Fig. 11. Al-Mg and Mn-Cr "absolute ages" calculated relative to (a) $I(Mn)_{CAI} = (9.1\pm1.7)\times10^{-6}$ as derived for CAI in this paper anchored to the "Best Estimate" CAI age of 4568.3 Ma (CAI anchor) and (b) $I(Mn)_{LEW} = (1.35\pm0.05) \times 10^{-6}$ as the weighted average of JSC and UCSD data for LEW86010 (Lugmair and Galer (1992, Nyquist et al., 1994), anchored to the ^{207}Pb-^{206}Pb age of 4558.62 Ma (LEW anchor) respectively, versus measured ^{207}Pb-^{206}Pb ages of the D'Orbigny clan angrite and A881394 (Amelin et al., 2006). Mn-Cr ages relative to the LEW anchor are shown as blue hexagons, those relative to the CAI anchor are shown as red triangles. Al-Mg ages relative to CAI for $I(Al)_{CAI} = 5.1 \times 10^{-5}$ are shown as green diamonds.

Fig. 12. Al-Mg and Mn-Cr "absolute ages" calculated relative to (a) $I(Mn)_{CAI} = (7.4\pm1.6) \times 10^{-6}$ as derived from the $I(Mn) = (5.1\pm1.6)\times10^{-6}$ for Chainpur chondrules (Yin et al., 2007) corrected for 2.0 Ma of decay (Kita et al., 2005) anchored to the "Best Estimate" CAI age of 4568.3 Ma (CAI anchor). The LEW anchor and other features of the figure are unchanged from Fig. 11.

Fig. 13. Comparison of initial $(^{53}Mn/^{55}Mn)_I$ for chondrules, carbonates. and secondary fayalites in carbonaceous chondrites. Data for secondary minerals are from the summary by Krot et al. (2006) and as reported by Jogo et al. (2006) for Vigarano fayalite. Time post-CAI is shown calculated relative to

$I(Mn)_{CAI} = 9.1 \times 10^{-6}$ and can be normalized to a CAI age $T_{CAI, Mn\text{-}Cr} = 4568.3$ Ma as determined by this study. Chondrule data are from Nyquist et al. (2001, Bishunpur (Bi) and Chainpur (Ch)), Kita et al., (2005, Semarkona (Smk), and Yin et al. (2007, Ch(Y)).

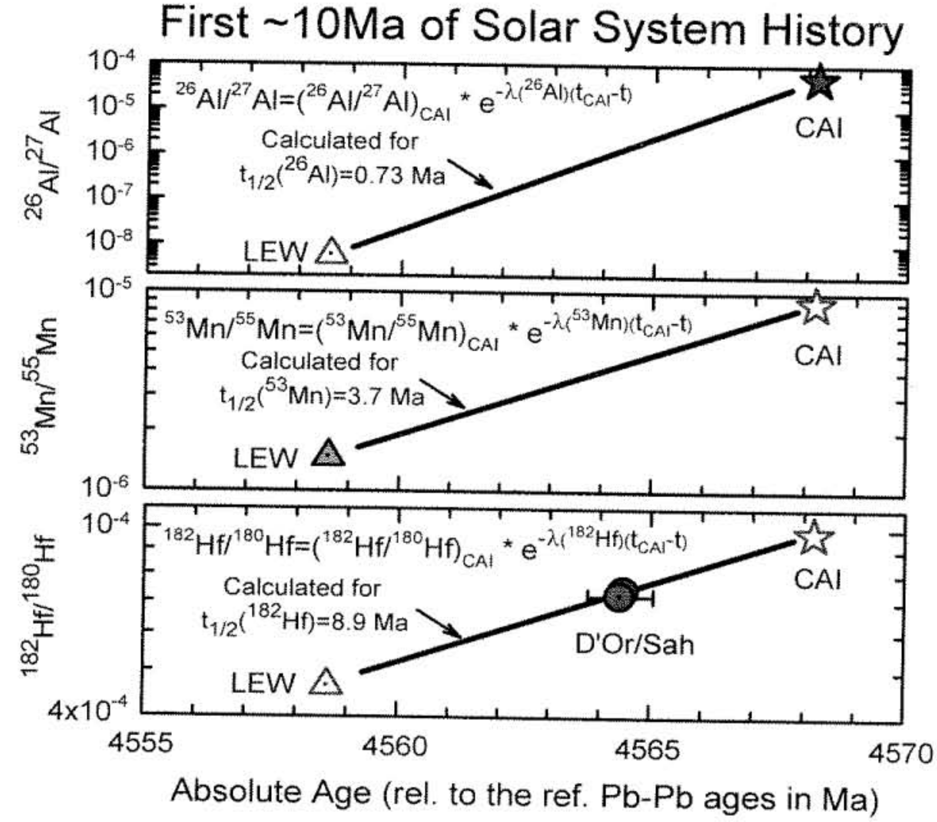

First ~10Ma of Solar System History
26Al/27Al=(26Al/27Al)CAI * e-λ(26Al)(tCAI-t)
Calculated for
t1/2(26Al)=0.73 Ma
LEW
CAI
53Mn/55Mn=(53Mn/55Mn)CAI * e-λ(53Mn)(tCAI-t)
Calculated for
t1/2(53Mn)=3.7 Ma
LEW
CAI
182Hf/180Hf=(182Hf/180Hf)CAI * e-λ(182Hf)(tCAI-t)
Calculated for
t1/2(182Hf)=8.9 Ma
D'Or/Sah
LEW
CAI
26Al/27Al
53Mn/55Mn
182Hf/180Hf
Absolute Age (rel. to the ref. Pb-Pb ages in Ma)

Fig. 1

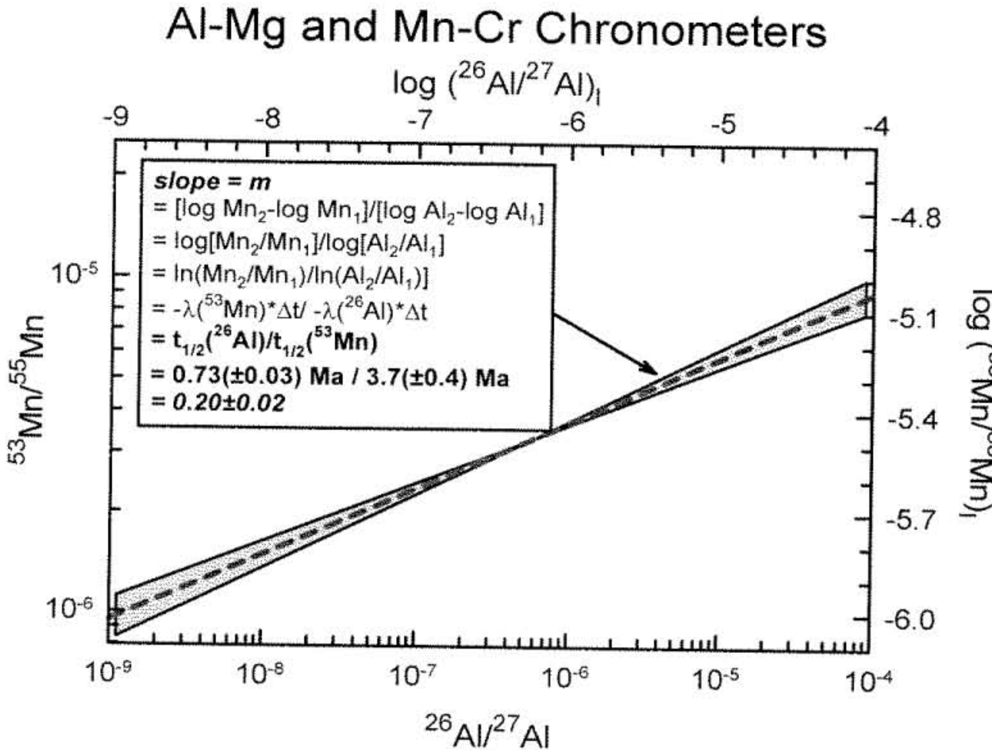

Al-Mg and Mn-Cr Chronometers
log (26Al/27Al)I
-9
-8
-7
-6
-5
-4
slope = m
= [log Mn2-log Mn1]/[log Al2-log Al1]
= log[Mn2/Mn1]/log[Al2/Al1]
= ln(Mn2/Mn1)/ln(Al2/Al1)]
= -λ(53Mn)*Δt/ -λ(26Al)*Δt
= t1/2(26Al)/t1/2(53Mn)
= 0.73(±0.03) Ma / 3.7(±0.4) Ma
= 0.20±0.02
53Mn/55Mn
10-5
10-6
-4.8
-5.1
-5.4
-5.7
-6.0
log (53Mn/55Mn)I
10-9
10-8
10-7
10-6
10-5
10-4
26Al/27Al

Fig. 2

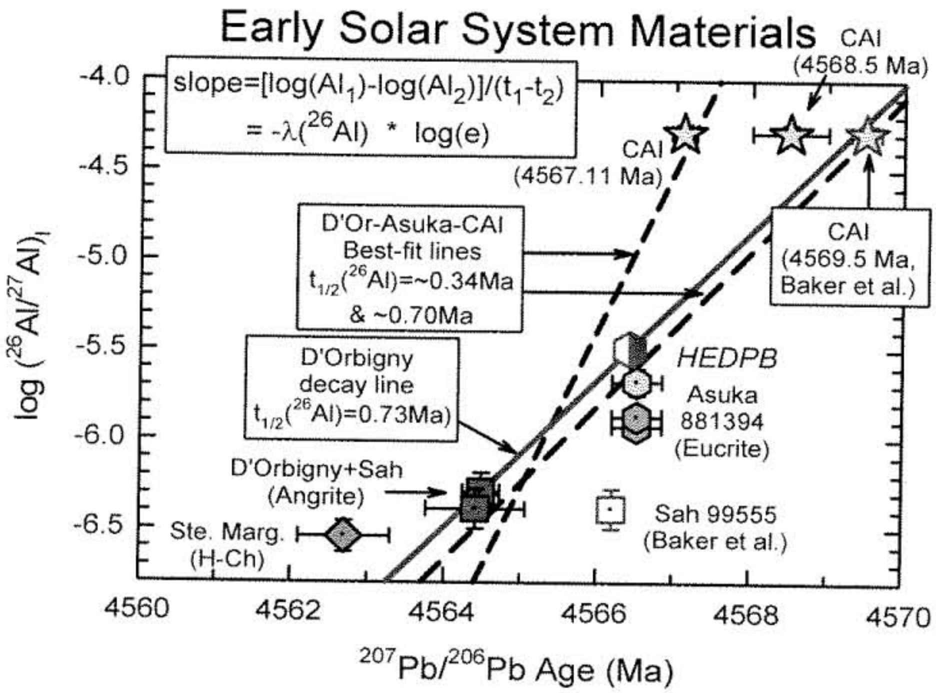

Early Solar System Materials
slope=[log(Al1)-log(Al2)]/(t1-t2)
= -λ(26Al) * log(e)
CAI
(4568.5 Ma)
CAI
(4567.11 Ma)
D'Or-Asuka-CAI
Best-fit lines
t1/2(26Al)=~0.34Ma
& ~0.70Ma
CAI
(4569.5 Ma,
Baker et al.)
D'Orbigny
decay line
t1/2(26Al)=0.73Ma)
HEDPB
Asuka
881394
(Eucrite)
D'Orbigny+Sah
(Angrite)
Ste. Marg.
(H-Ch)
Sah 99555
(Baker et al.)
log (26Al/27Al)I
207Pb/206Pb Age (Ma)
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
4560
4562
4564
4566
4568
4570

Fig. 3

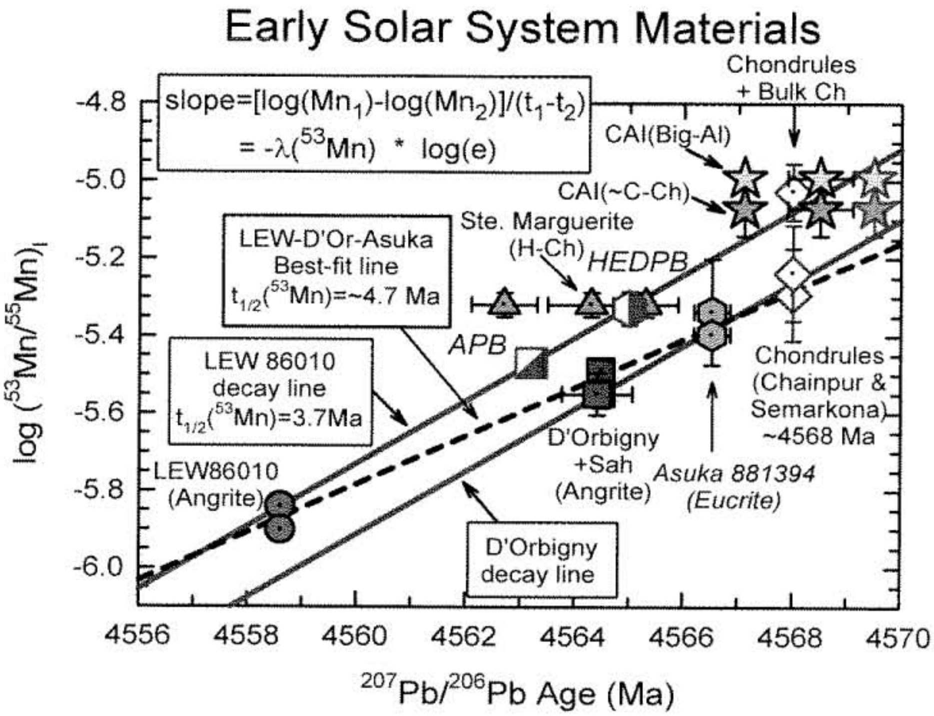

Early Solar System Materials
slope=[log(Mn1)-log(Mn2)]/(t1-t2)
= -λ(53Mn) * log(e)
Chondrules
+ Bulk Ch
CAI(Big-Al)
CAI(~C-Ch)
Ste. Marguerite
(H-Ch)
HEDPB
LEW-D'Or-Asuka
Best-fit line
t1/2(53Mn)=~4.7 Ma
APB
LEW 86010
decay line
t1/2(53Mn)=3.7Ma
Chondrules
(Chainpur &
Semarkona)
~4568 Ma
D'Orbigny
+Sah
(Angrite)
Asuka 881394
(Eucrite)
LEW86010
(Angrite)
D'Orbigny
decay line
log (53Mn/55Mn)I
207Pb/206Pb Age (Ma)

Fig. 4

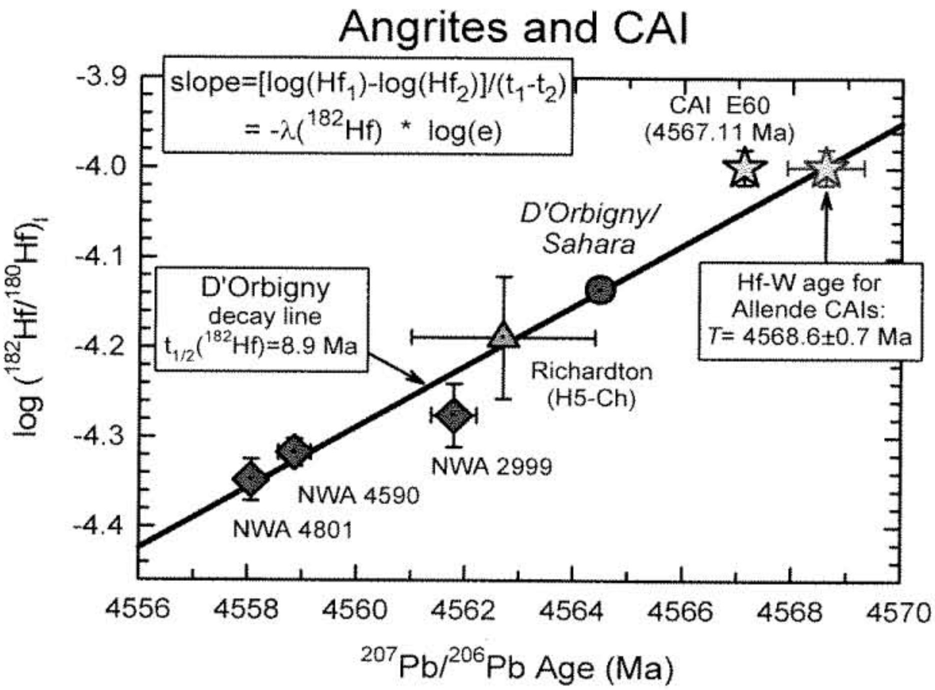

Angrites and CAI
slope=[log(Hf1)-log(Hf2)]/(t1-t2)
= -λ(182Hf) * log(e)
CAI E60
(4567.11 Ma)
D'Orbigny/
Sahara
D'Orbigny
decay line
t1/2(182Hf)=8.9 Ma
Hf-W age for
Allende CAIs:
T= 4568.6±0.7 Ma
Richardton
(H5-Ch)
NWA 2999
NWA 4590
NWA 4801
log (182Hf/180Hf)I
207Pb/206Pb Age (Ma)
-3.9
-4.0
-4.1
-4.2
-4.3
-4.4
4556
4558
4560
4562
4564
4566
4568
4570

Fig. 5

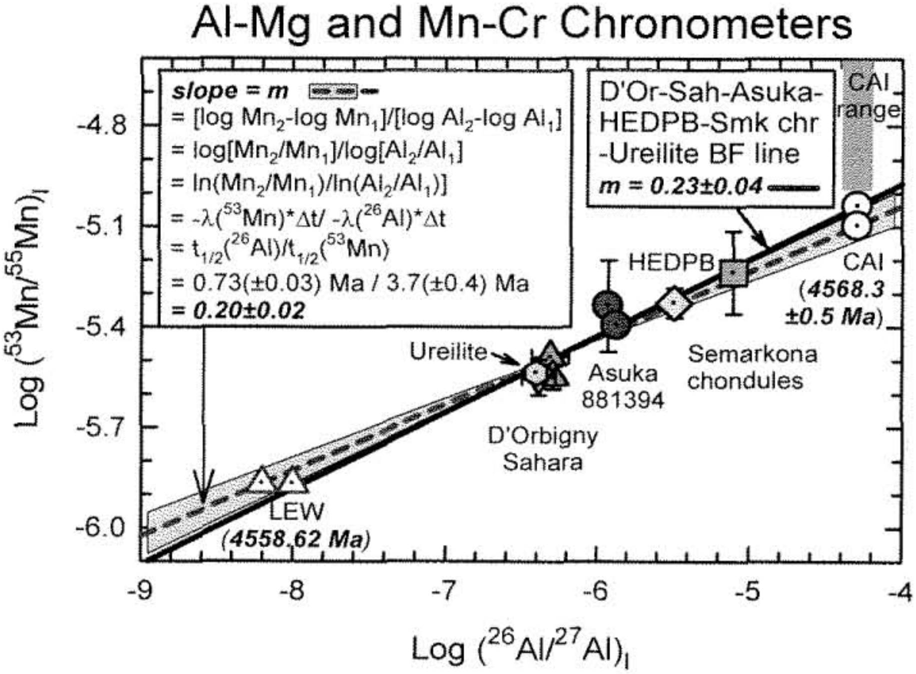

Al-Mg and Mn-Cr Chronometers
slope = m
= [log Mn2-log Mn1]/[log Al2-log Al1]
= log[Mn2/Mn1]/log[Al2/Al1]
= ln(Mn2/Mn1)/ln(Al2/Al1)]
= -λ(53Mn)*Δt/ -λ(26Al)*Δt
= t1/2(26Al)/t1/2(53Mn)
= 0.73(±0.03) Ma / 3.7(±0.4) Ma
= 0.20±0.02
D'Or-Sah-Asuka-
HEDPB-Smk chr
-Ureilite BF line
m = 0.23±0.04
CAI range
HEDPB
CAI
(4568.3
±0.5 Ma)
Ureilite
Asuka
881394
Semarkona
chondules
D'Orbigny
Sahara
LEW
(4558.62 Ma)
Log (53Mn/55Mn)I
Log (26Al/27Al)I
-4.8
-5.1
-5.4
-5.7
-6.0
-9
-8
-7
-6
-5
-4

Fig. 6

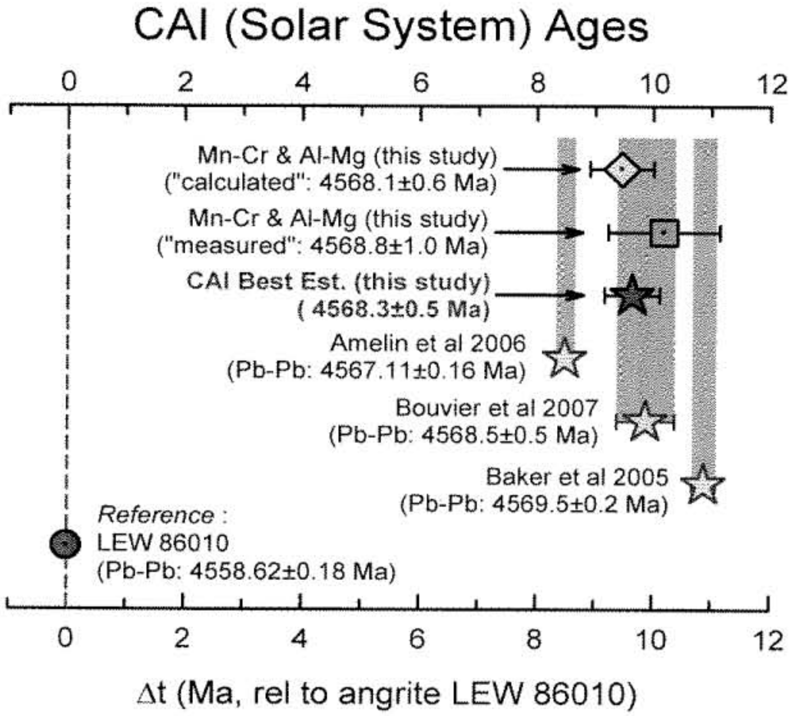

CAI (Solar System) Ages
0
2
4
6
8
10
12
Mn-Cr & Al-Mg (this study)
("calculated": 4568.1±0.6 Ma)
Mn-Cr & Al-Mg (this study)
("measured": 4568.8±1.0 Ma)
CAI Best Est. (this study)
(4568.3±0.5 Ma)
Amelin et al 2006
(Pb-Pb: 4567.11±0.16 Ma)
Bouvier et al 2007
(Pb-Pb: 4568.5±0.5 Ma)
Baker et al 2005
(Pb-Pb: 4569.5±0.2 Ma)
Reference :
LEW 86010
(Pb-Pb: 4558.62±0.18 Ma)
Δt (Ma, rel to angrite LEW 86010)

Fig. 7

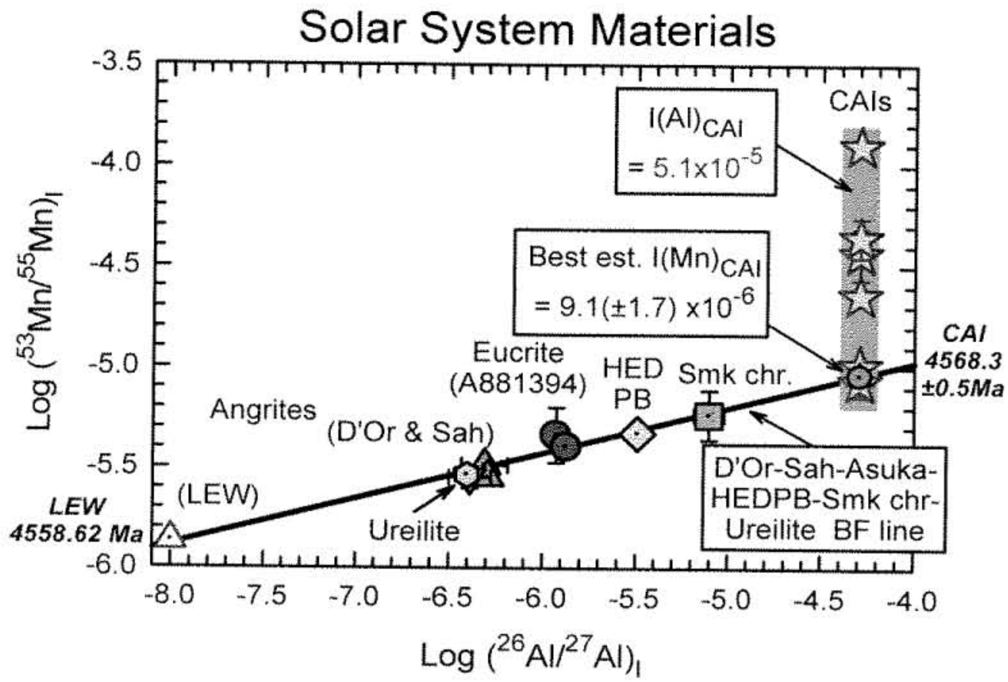

Solar System Materials
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
Log (^{53}Mn/^{55}Mn)$_I$
CAIs
I(Al)$_{CAI}$
= 5.1x10^{-5}
Best est. I(Mn)$_{CAI}$
= 9.1(±1.7) x10^{-6}
CAI
4568.3
±0.5Ma
Eucrite
(A881394)
HED
PB
Smk chr.
Angrites
(D'Or & Sah)
D'Or-Sah-Asuka-
HEDPB-Smk chr-
Ureilite BF line
LEW
4558.62 Ma
(LEW)
Ureilite
-8.0
-7.5
-7.0
-6.5
-6.0
-5.5
-5.0
-4.5
-4.0
Log (^{26}Al/^{27}Al)$_I$

Fig. 8

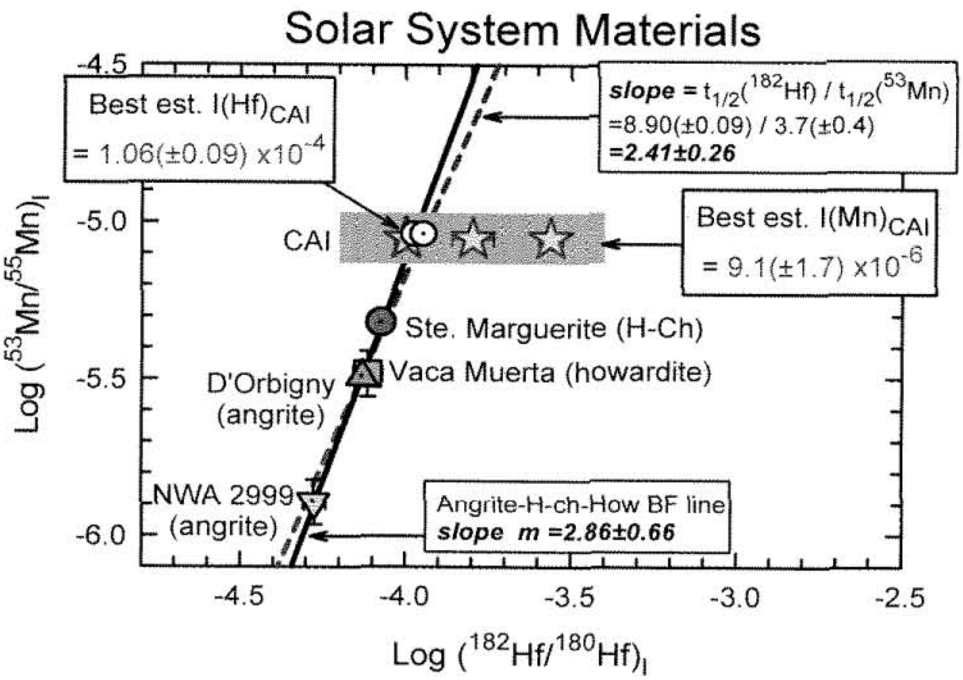
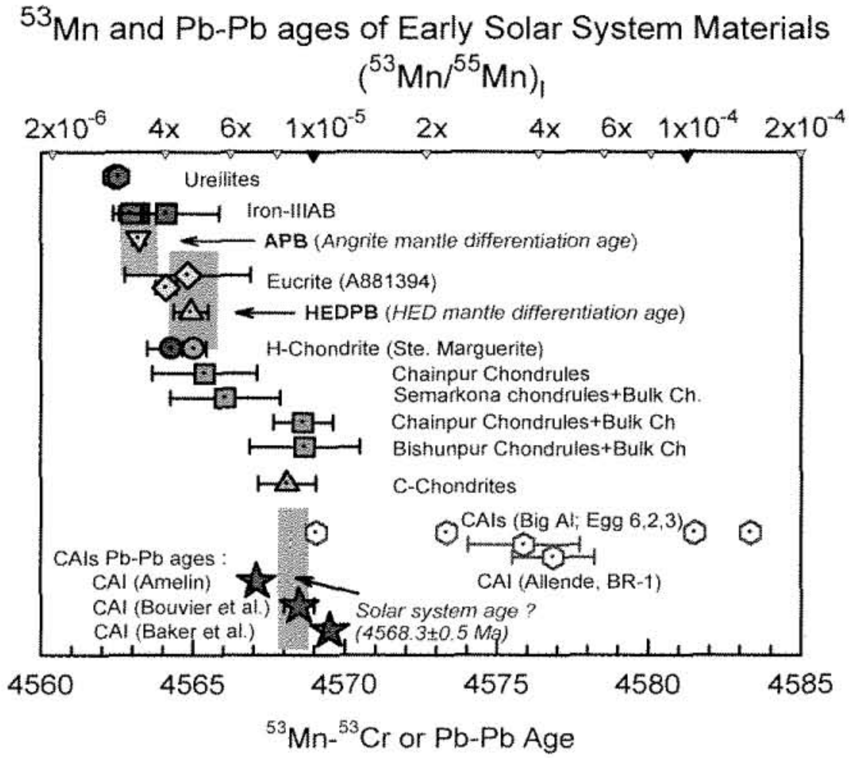

Solar System Materials
Best est. I(Hf)CAI
= 1.06(±0.09) x10-4
slope = t1/2(182Hf) / t1/2(53Mn)
=8.90(±0.09) / 3.7(±0.4)
=2.41±0.26
CAI
Best est. I(Mn)CAI
= 9.1(±1.7) x10-6
Ste. Marguerite (H-Ch)
D'Orbigny
(angrite)
Vaca Muerta (howardite)
NWA 2999
(angrite)
Angrite-H-ch-How BF line
slope m =2.86±0.66
-4.5
-5.0
-5.5
-6.0
-4.5
-4.0
-3.5
-3.0
-2.5
Log (53Mn/55Mn)I
Log (182Hf/180Hf)I

Fig. 9



^{53}Mn and Pb-Pb ages of Early Solar System Materials
(^{53}Mn/^{55}Mn)$_I$
2x10^{-6} 4x 6x 1x10^{-5} 2x 4x 6x 1x10^{-4} 2x10^{-4}
Ureilites
Iron-IIIAB
APB (Angrite mantle differentiation age)
Eucrite (A881394)
HEDPB (HED mantle differentiation age)
H-Chondrite (Ste. Marguerite)
Chainpur Chondrules
Semarkona chondrules+Bulk Ch.
Chainpur Chondrules+Bulk Ch
Bishunpur Chondrules+Bulk Ch
C-Chondrites
CAIs (Big Al; Egg 6,2,3)
CAI (Allende, BR-1)
CAIs Pb-Pb ages :
CAI (Amelin)
CAI (Bouvier et al.)
CAI (Baker et al.)
Solar system age ?
(4568.3±0.5 Ma)
4560 4565 4570 4575 4580 4585
^{53}Mn-^{53}Cr or Pb-Pb Age

Fig. 10

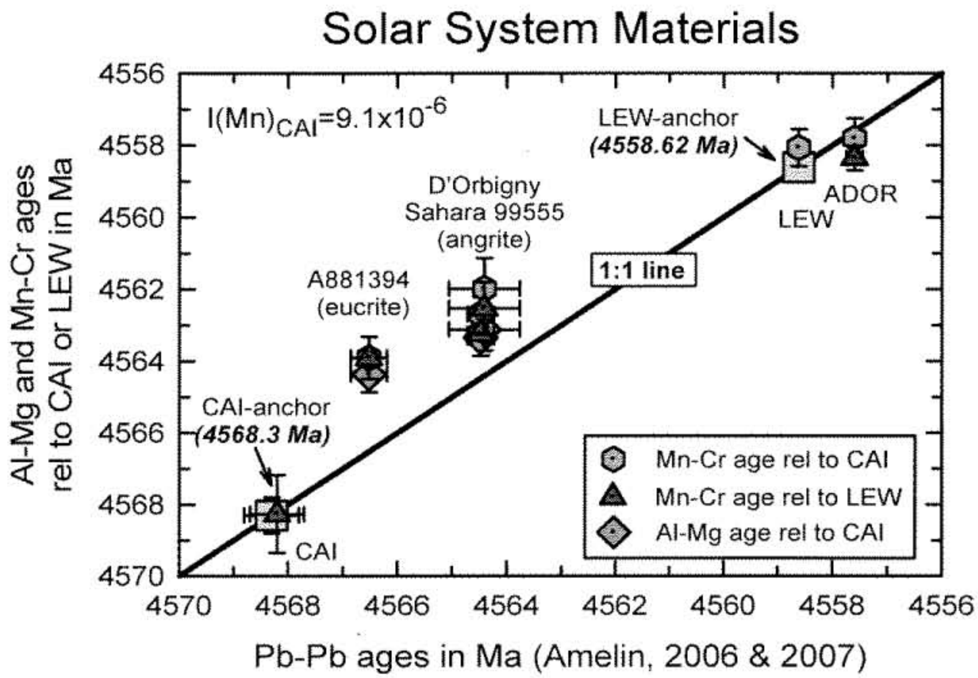
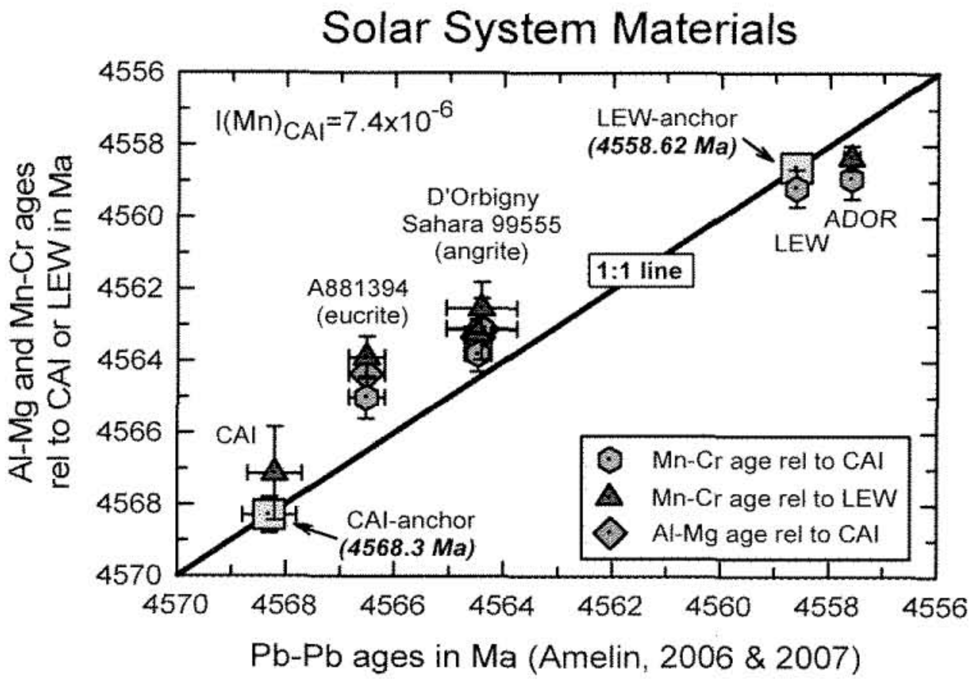
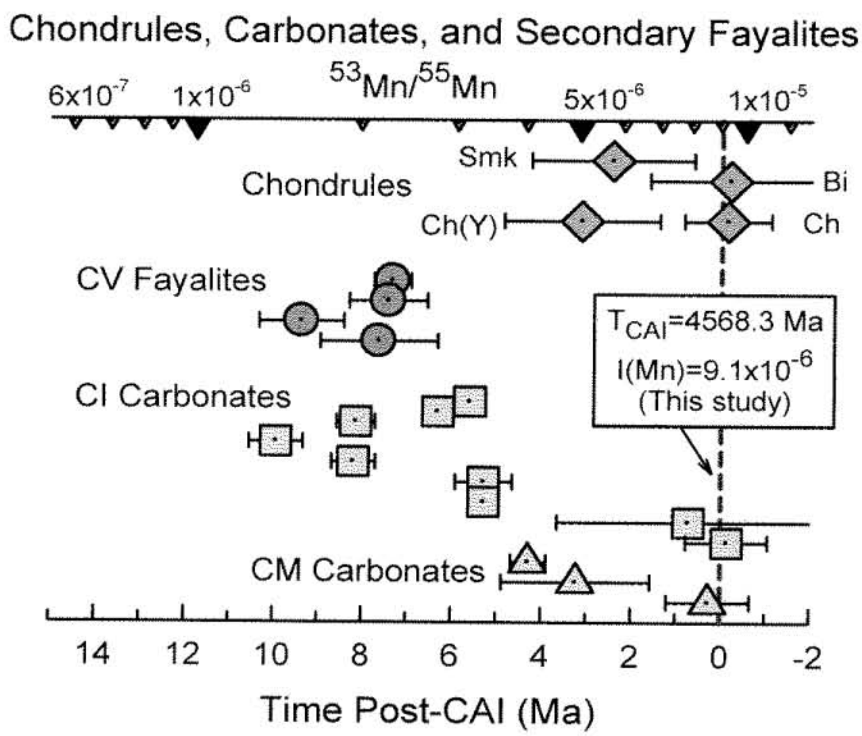

Solar System Materials
I(Mn)CAI=9.1x10-6
LEW-anchor
(4558.62 Ma)
ADOR
LEW
D'Orbigny
Sahara 99555
(angrite)
1:1 line
A881394
(eucrite)
CAI-anchor
(4568.3 Ma)
CAI
Mn-Cr age rel to CAI
Mn-Cr age rel to LEW
Al-Mg age rel to CAI
Al-Mg and Mn-Cr ages
rel to CAI or LEW in Ma
Pb-Pb ages in Ma (Amelin, 2006 & 2007)
4556
4558
4560
4562
4564
4566
4568
4570

Fig. 11



Solar System Materials
I(Mn)CAI=7.4x10-6
LEW-anchor
(4558.62 Ma)
D'Orbigny
Sahara 99555
(angrite)
A881394
(eucrite)
1:1 line
ADOR
LEW
CAI
CAI-anchor
(4568.3 Ma)
Mn-Cr age rel to CAI
Mn-Cr age rel to LEW
Al-Mg age rel to CAI
Al-Mg and Mn-Cr ages rel to CAI or LEW in Ma
Pb-Pb ages in Ma (Amelin, 2006 & 2007)
4556
4558
4560
4562
4564
4566
4568
4570

Fig. 12



Chondrules, Carbonates, and Secondary Fayalites
53Mn/55Mn
6x10-7
1x10-6
5x10-6
1x10-5
Smk
Chondrules
Bi
Ch(Y)
Ch
CV Fayalites
TCAI=4568.3 Ma
I(Mn)=9.1x10-6
(This study)
CI Carbonates
CM Carbonates
14
12
10
8
6
4
2
0
-2
Time Post-CAI (Ma)

Fig. 13

Table 1. Values and references for data used in this paper.			
Sample	$^{26}Al/^{27}Al$	±	Ref.
Asuka 881394	1.18E-06	1.40E-07	Nyquist et al. (2003)
	1.34E-06	5.00E-09	Wadhwa et al. (2005)
	2.10E-06	4.00E-07	Srinivasan 2002
D'Orbigny	4.90E-07	1.60E-07	Nyquist et al (2003) to be re-vised
	5.10E-07	3.00E-08	Spivak-Birndorf (2005)
Sahara 99555	4.10E-07	1.20E-07	Spivak-Birndorf (2005)
HED PB	3.22E-06	4.20E-07	Bizzarro et al. (2005)
CAI	5.10E-05	6.00E-06	Lee et al. (1977)

Sample	$^{53}Mn/^{55}Mn$	±	Ref.
Asuka 881394	4.60E-06	1.70E-06	Nyquist et al. (2003)
	4.02E-06	2.60E-07	Wadhwa et al. (2005)
D'Orbigny	3.24E-06	4.00E-08	Glavin et al. (2004)
	2.83E-06	2.50E-07	Nyquist et al (2003)
	2.83E-06	2.40E-07	Sugiura et al. (2005)
Sahara 99555	2.82E-06	3.70E-07	Sugiura et al. (2005)
LEW 86010	1.44E-06	7.00E-08	Nyquist et al (1994)
	1.25E-06	7.00E-08	Lugmair & Shukulyukov (1998)
APB	3.40E-06	1.40E-07	
HED PB	4.70E-06	5.00E-07	Lugmair & Shukulyukov (1998)
Ste. Marguerite	4.80E-06	3.60E-07	Polnau and Lugmair (2001)
Chondrule +Bulk Ch	9.40E-06	1.70E-06	Nyquist et al (2001)
Chainpur ch.	5.10E-06	1.60E-06	Yin et al (2007)
Semarkona + Bulk Ch	5.80E-06	1.90E-06	Kita et al. (2005)
Bishunpur + Bulk Ch	9.50E-06	3.10E-06	Nyquist et al (2001)
CAI (C-Ch)	8.50E-06	1.50E-06	Yin et al (2007)
CAI (Big Al)	1.04E-05	1.68E-05	Papanastassiou et al. (2005)
CAI (Egg 3)	1.48E-04		Papanastassiou et al. (2005)

	$^{207}Pb/^{206}Pb$	±	
CAI	4568.50	0.50	Bouvier et al., 2007
	4567.11	0.16	Amelin et al., 2006
	4569.50	0.20	Baker et al., 2005
Asuka 881394	4566.52	0.33	Amelin et al. (2006)
D'Orbigny	4564.42	0.12	Amelin (2008)
Sahara 99555	4564.64	0.54	Amelin (2007)
			Amelin (2007)
LEW 86010	4558.55	0.15	Amelin (2008)
APB			
HED PB			
Ste. Marguerite	4564.3	0.8	Bouvier et al., 2007

Table 2. Summary of $I(Al)_{CAI}$, $I(Mn)_{CAI}$, and $I(Hf)_{CAI}$.

Parameter	SSI	Comment/reference
$I(Al)_{CAI}$	5.1×10^{-5}	Normalization: (Lee et al., 1977)
$I(Mn)_{CAI}$	$(9.1 \pm 1.7) \times 10^{-5}$	I(Mn) vs. I(Al): Diff. Met. & Smk Chondrules (Fig. 8)
	$(8.4 \pm 1.9) \times 10^{-5}$	I(Mn) for Smk + 2.0 Ma of ^{53}Mn decay (Kita et al., 2005)
	$(7.4 \pm 1.6) \times 10^{-5}$	I(Mn) for Chnp + 2.0 Ma of ^{53}Mn decay (Kita et al., 2005)
	$(8.5 \pm 1.5) \times 10^{-5}$	Bulk CC isochron (Shukolyukov and Lugmair (2006).
$I(Hf)_{CAI}$	$(1.06 \pm 0.09) \times 10^{-4}$	I(Mn) vs. I(Hf): Diff. Met. & Ste. M. Chondrules (Fig. 8)
	$(1.003 \pm 0.045) \times 10^{-4}$	Direct measurement of CAI (Burkhardt et al. (2008)

SSI = Best estimate solar system initial value.
Smk = Semarkona LL3.0 chondrite.
Ste. M = Ste. Marguerite H chondrite.
Chnp = Chainpur