

# **Time Scales of Planetesimal Differentiation in the Early Solar System**

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Chronological constraints on the formation times of a variety of meteoritic materials indicate that planetesimal differentiation occurred rapidly in the early solar system. Some planetesimals only experienced the earliest stage of the onset of melting and were subsequently arrested in that state. On some of these bodies, such incipient melting began within  $\sim 2$  to 5 Myr of the formation of calcium-aluminum-rich inclusions (CAI), but possibly extended to  $\geq 10$  Myr on others. Extensive differentiation took place on yet other planetesimals to form silicate crust-mantle reservoirs and metallic cores. Crust formation began within  $\sim 4$  Myr of CAI formation, and likely extended to at least  $\sim 10$  Myr. Global mantle differentiation, which established the source reservoirs of the crustal materials, occurred contemporaneously for the angrites and eucrites, within  $\sim 3$  to 4 Myr of CAI formation. Metal segregation on different planetesimals occurred within a narrow time interval of  $\leq 5$  Myr; in the specific case of the Howardite-Eucrite-Diogenite (HED) parent body, the process of core formation is estimated to have occurred  $\sim 0.6$  Myr before global mantle differentiation. Following metal segregation, core crystallization is likely to have occurred over a time interval of 10 Myr or more.

## **1. INTRODUCTION**

Within the last decade, significant advances have been made in our understanding of the time scales involved in the differentiation history of planetesimals in the early solar system. In

particular, the application of several chronometers based on short-lived radionuclides (i.e., with half-lives less than  $\sim 100$  Myr) has allowed unprecedented time resolution (often  $\leq 1$  Myr for events that occurred close to  $\sim 4.6$  Ga ago).

The earliest differentiation events in solar system history were those that occurred between nebular gas and the earliest condensates that are represented by components within chondritic meteorites. Time scales involved in such events, which likely occurred during the accretion disk phase of the nebula, are discussed elsewhere in this book (McKeegan, 2004; Russell et al., 2004). In this chapter, we will focus on the *time scales* involved in the differentiation events that occurred on *planetesimals*, defined here as small asteroidal-sized bodies (up to hundreds of kilometers in diameter) that accreted from nebular dust and the earliest condensates and, in the process, resulted in the clearing of the nebular accretion disk. The *processes* likely to be involved in planetesimal differentiation are discussed in more detail in the chapter by McCoy et al. (2004).

The meteoritic record includes a variety of materials resulting from planetesimal differentiation. These materials are primarily composed of two types, (1) primitive achondrites that have near-chondritic bulk compositions (e.g., brachinites, acapulcoites, lodranites, and winonaites) and formed during the earliest stages of melting on planetesimals (which were subsequently arrested at this stage and did not differentiate further), and (2) meteorites that resulted from more extensive differentiation such that their bulk compositions are significantly different from those of chondrites. The latter are in turn comprised of three classes of materials, (1) achondrites that formed within the silicate crust of differentiated planetesimals, such as, eucrites, diogenites and howardites (or HED meteorites), angrites, and HED-like silicate clasts in mesosiderites, (2) metal-silicate meteorites (pallasites) that may have been formed near the core-mantle boundary, and (3) metal-rich meteorites that are the products of metal segregation from essentially chondritic precursors and some of which may represent the cores of extensively differentiated planetesimals.

Age determinations on these meteoritic materials with the appropriate chronometers then make it possible to constrain the timing of planetesimal differentiation events ranging from incipient melting to more extensive processing involving silicate differentiation (including crust formation and fractionation within the mantle), metal segregation and core crystallization. Thus far, chronometers based on both long- and short-lived radionuclides have been applied

extensively for age-dating such events. Long-lived chronometers, however, typically do not have the time resolution required to resolve events occurring within the first tens of millions of years of solar system history. In contrast, short-lived chronometers can have high time resolution (i.e., a million years or less) and are thus capable of precisely age dating the earliest solar system events. Nevertheless, the application of chronometers based on short-lived radionuclides is not without its challenges. In particular (and provided there are no other complications such as heterogeneity in the initial distribution of the parent radionuclide and/or disturbance of the isotope systematics subsequent to initial closure), isochrons based on a short-lived radionuclides can provide only relative ages since the slope of such an isochron reflects the abundance of the now extinct radionuclide at the time of last chemical equilibration. Therefore, since the high resolution chronometers based on short-lived radionuclides can provide only relative time differences between early solar system events, it is essential to have a “time anchor” (i.e., a sample that allows one to determine the value of the parameter  $(R^*/R)_T$  at a precisely defined absolute time  $T$ , where  $R^*$  is the abundance of the radioisotope and  $R$  is that of a stable isotope of the same element) so as to map the relative ages derived from such a chronometer on to an absolute time scale. The only absolute chronometer capable of providing time resolution comparable to that of chronometers based on short-lived radionuclides, and thus providing an appropriate time anchor, is the U-Pb chronometer. A unique attribute of this chronometer is that it is based on the decay of two long-lived radioisotopes, i.e.,  $^{235}\text{U}$  that decays to  $^{207}\text{Pb}$  with a half-life 703.8 Myr and  $^{238}\text{U}$  that decays to  $^{206}\text{Pb}$  with a half-life 4469 Myr. The extraordinarily high precision afforded by the U-Pb chronometer compared to chronometers based on other long-lived radioisotopes results from the rapid evolution of the radiogenic Pb isotopic composition (i.e.,  $^{207}\text{Pb}/^{206}\text{Pb}$ ) due to the relatively short half-life of  $^{235}\text{U}$  and the occasionally very high U/Pb ratios in planetesimals and planets affected by volatile loss and/or core formation since Pb is both volatile and chalcophile, but U is neither.

## 2. INITIAL CONDITIONS

Prior to a discussion of the time scales of planetesimal differentiation, we briefly summarize our current understanding of the initial conditions prevalent in the solar nebula immediately prior to the formation of these planetesimals. More detailed discussions of nebular conditions and processes may be found elsewhere in this book (e.g., chapters in Section 3). We note that an

understanding of conditions and processes in the solar nebula (especially the degree to which it was homogenized) is particularly important with regard to the application of the high-resolution chronometers based on extinct radionuclides, since factors such as the abundance and distribution of the parent radionuclides are critical in determining the feasibility of age dating events in the early solar system.

TABLE 1. Selected short-lived radioisotopes utilized so far in constraining the time scales of planetesimal differentiation.

| Radioisotope (R*) | Half-life (Myr) | Daughter Isotope (D*) | Reference Isotope (R) | Solar System Initial Ratio (R*/R) <sub>0</sub> | Time Anchor* (if any)                                                                    |
|-------------------|-----------------|-----------------------|-----------------------|------------------------------------------------|------------------------------------------------------------------------------------------|
| <sup>26</sup> Al  | 0.73            | <sup>26</sup> Mg      | <sup>27</sup> Al      | $\sim 5 \times 10^{-5}$                        | CAIs<br>(R*/R) <sub>T</sub> = $5 \times 10^{-5}$ at 4.567 Ga                             |
| <sup>60</sup> Fe  | 1.5             | <sup>60</sup> Ni      | <sup>56</sup> Fe      | $\sim 3\text{-}10 \times 10^{-7}$              |                                                                                          |
| <sup>53</sup> Mn  | 3.7             | <sup>53</sup> Cr      | <sup>55</sup> Mn      | $\sim 10^{-5}$                                 | LEW 86010 Angrite<br>(R*/R) <sub>T</sub> = $1.25\text{-}1.44 \times 10^{-6}$ at 4.558 Ga |
| <sup>107</sup> Pd | 6.5             | <sup>107</sup> Ag     | <sup>108</sup> Pd     | $\sim 5 \times 10^{-5}$                        | Gibeon (IVA) Iron<br>(R*/R) <sub>T</sub> = $2.4 \times 10^{-5}$ at $\sim 4.56$ Ga        |
| <sup>182</sup> Hf | 9               | <sup>182</sup> W      | <sup>180</sup> Hf     | $1.0\text{-}1.6 \times 10^{-4}$                | Chondrites<br>(R*/R) <sub>T</sub> = $1 \times 10^{-4}$ at $\sim 4.56$ Ga                 |
| <sup>146</sup> Sm | 103             | <sup>142</sup> Nd     | <sup>144</sup> Sm     | $\sim 7 \times 10^{-3}$                        | Angrites<br>(R*/R) <sub>T</sub> = $7 \times 10^{-3}$ at 4.558 Ga                         |

\*Sources: <sup>26</sup>Al: Lee et al. (1976), Amelin et al. (2002), and references therein; <sup>60</sup>Fe: Tachibana and Huss (2003), Mostefaoui et al. (2004); <sup>53</sup>Mn: Lugmair and Galer (1992), Nyquist et al. (1994), Lugmair and Shukolyukov (1998); <sup>107</sup>Pd: Chen and Wasserburg (1996); <sup>182</sup>Hf: Kleine et al., (2002), Yin et al. (2002b), Quitté and Birck (2004); <sup>146</sup>Sm: Lugmair and Galer (1992) and references therein.

Table 1 provides a listing of selected short-lived radionuclides that have so far been applied towards constraining the time scales involved in planetesimal differentiation. This table includes current estimates of the solar system initial abundance ratios (R\*/R)<sub>0</sub>, which are estimates of the initial abundances of these radionuclides in the meteorite forming region of the solar nebula at the time of formation of the earliest condensates, the refractory calcium-aluminum-rich inclusions (CAIs) found in primitive chondrites, the most precise age estimate for which is currently  $4567.2 \pm 0.6$  Ma (Amelin et al., 2002).

In Table 1, the solar system initial abundance ratios (R\*/R)<sub>0</sub> of the radionuclides with half-lives  $\geq 10$  Myr (i.e., <sup>146</sup>Sm and <sup>182</sup>Hf), but perhaps also some shorter-lived radionuclides (such as <sup>107</sup>Pd and <sup>53</sup>Mn), may be accounted for by continuous galactic nucleosynthesis where a balance is reached between their production and decay (e.g., Meyer and Clayton, 2000). Radionuclides

whose abundances may be accounted for by this means are generally assumed to be homogeneously distributed in the solar nebula.

The initial abundance ratios of several of the radionuclides with half-lives  $\leq 10$  Myr (e.g.,  $^{26}\text{Al}$ ) are too high to be accounted for by continuous galactic nucleosynthesis alone. Alternatives for the predominant production sites of these shorter-lived radionuclides are either that (1) they were synthesized in a stellar (either a supernova or an AGB) environment and injected into the molecular cloud just prior to its collapse and solar nebula formation (e.g., Cameron et al., 1995; Cameron, 2001; Gallino et al., 2004) or (2) they were produced “locally” by mechanisms such as trapping of galactic cosmic rays in the molecular cloud as it collapsed (Clayton and Jin, 1995; Desch et al., 2004) or production by energetic particle irradiation within the nebula during an early active phase of the Sun (Shu et al., 1996; Gounelle et al., 2001; Leya et al., 2003). Whether the short-lived radioisotopes that may be produced in any of the above scenarios were effectively homogenized prior to the formation of solids in the nebula is presently unresolved. Numerical simulations of processes associated with molecular cloud core collapse triggered by a nearby explosive stellar event indicate that spatial heterogeneities in the distributions of shock wave injected short-lived radionuclides may survive on short time scales (Vanhala and Boss, 2002). Nevertheless, in the case of an external seeding source for these short-lived radionuclides, differential rotation and turbulence in the nebula is generally anticipated to result in radial and vertical mixing, perhaps on the time scale of a million years or less subsequent to initiation of collapse (which is assumed to occur immediately prior to formation of the first solids in the nebula). If, however, the short-lived radionuclides were predominantly produced by local irradiation within the early solar system, they are expected to be distributed heterogeneously within the nebular disk at least over the duration of the active phase of the early Sun (e.g., Gounelle et al., 2001).

Whether the solar nebula was isotopically homogeneous or not is a critical issue since an assumption in the application of any chronometer based on a short-lived radionuclide to meteorites and their components is that the initial abundance ratio of radioactive to stable isotope of the element, i.e.,  $(R^*/R)_0$ , be uniform in the meteorite forming region. In the specific case of determining the timing of planetesimal differentiation using such a chronometer, the scale at which the isotopic heterogeneity may be present is also important. Numerous studies have shown that large isotopic heterogeneities were present in the nebula on the small scale, i.e., on

the scale of micron-sized presolar grains and mm- to cm-sized inclusions (CAIs) within primitive meteorites (e.g., Loss et al., 1994; Zinner, 1996). However, there are only a few instances where isotopic heterogeneities have been documented on the planetesimal scale. Specifically, mass-independent variations in the isotopic compositions of oxygen (Clayton et al., 1973; Clayton, 1993) and chromium (Lugmair and Shukolyukov, 1998; Shukolyukov et al., 2003) have been documented in bulk samples of primitive and differentiated meteorites. Although disputed by some (Becker and Walker, 2003ab), such variations have also been noted for molybdenum (Dauphas et al., 2002; Yin et al., 2002a; Chen et al., 2004) and ruthenium (Chen et al., 2003; Papanastassiou et al., 2004). By and large, however, most other isotopic systems investigated so far in meteorites indicate homogeneity on the planetesimal scale at the level of precision achievable by current state-of-the-art instrumentation (e.g., Zhu et al., 2003; Dauphas et al., 2004ab).

### 3. TIME SCALES OF PLANETESIMAL DIFFERENTIATION

#### 3.1 Incipient Melting

Primitive achondrites, such as acapulcoites, lodranites, winonaites and brachinites, have igneous textures but their bulk compositions, although showing some variations, are relatively close to those of chondrites. Therefore, these meteorites are considered to be the products of the earliest stages of melting and igneous processing on planetesimals (Mittlefehldt et al., 1998, and references therein).

The acapulcoites and lodranites are thought to be the residual products of partial melting of chondritic precursors (Mittlefehldt et al., 1996; McCoy et al., 1997ab). Chronological constraints obtained so far indicate that these meteorites formed within ~10 Myr of the formation of the earliest solids in the nebula. Evidence for the presence of live  $^{244}\text{Pu}$  ( $t_{1/2} \sim 82$  Myr) in Acapulco phosphates supports early formation of this meteorite (Pellas et al. 1997).  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  systematics determined by Prinzhofer et al. (1992) for Acapulco gave a very old age ( $4.60 \pm 0.03$  Ga), which the authors interpreted as the time of recrystallization immediately following its formation event. Given this old  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  age, one would expect a  $^{146}\text{Sm}/^{144}\text{Sm}$  ratio significantly higher than in angrites at 4558 Ga (i.e., the time anchor for the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  system; Table 1). However, the  $^{146}\text{Sm}/^{144}\text{Sm}$  ratio of  $0.0067 \pm 0.0019$  determined for this sample (Prinzhofer et al., 1992), is within error of that in angrites at their time of formation. Moreover,

U-Pb systematics in phosphates from Acapulco give an age of  $4557 \pm 2$  Ma (Göpel et al., 1992, 1994), marginally younger, but much more precise, than the  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  age. The older  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  age is therefore questionable and could be due to disturbance during extensive later metamorphism experienced by this meteorite (McCoy et al., 1996). Furthermore, Acapulco has an inferred  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(7.5 \pm 1.4) \times 10^{-7}$ ; compared to the LEW 86010 angrite (the time anchor for the  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  system; Table 1), this translates to a  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  age of  $4555.1 \pm 1.2$  Ma (Zipfel et al., 1996), consistent with its Pb-Pb and  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  systematics.  $^{129}\text{I}$ - $^{129}\text{Xe}$  ( $t_{1/2} \sim 17$  Myr) systematics in Acapulco phosphates indicate Xe closure  $\sim 9$  Myr after the Bjurbole L4 chondrite, which also appears to be consistent with Pb-Pb systematics (Nichols et al., 1994; Brazzle et al., 1999).

Brachinites are olivine-rich primitive achondrites generally considered to be either partial melt residues (e.g., Nehru et al., 1983, 1992, 1996; Goodrich, 1998) or igneous cumulates (e.g., Warren and Kallemeyn, 1989). Although precise absolute formation ages for these primitive achondrites are not yet available, there are indications that they formed close to  $\sim 4.56$  Ga, soon after the beginning of the solar system. These include the presence of fission tracks from the decay of live  $^{244}\text{Pu}$  (Croaz and Pellas, 1983) and  $^{129}\text{Xe}$  excesses due to the decay of  $^{129}\text{I}$  (Bogard et al., 1983; Ott et al., 1987; Swindle et al., 1998). Wadhwa et al. (1998) reported a  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  isochron for Brachina that indicated a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(3.8 \pm 0.4) \times 10^{-6}$  at the time of last equilibration of Cr isotopes (Fig. 1). Comparison of this value with the  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(1.25 \pm 0.07) \times 10^{-6}$  in the angrite LEW 86010 at 4558 Ma (Table 1) implies a Mn-Cr age of  $4563.7 \pm 0.9$  Ma for this meteorite.

However, not all primitive achondrites investigated so far offer a general consistency between long- and short-lived radioisotope systematics. The Divnoe meteorite is an ultramafic primitive achondrite whose relationship to other primitive achondrite groups is as yet unclear (Petaev et al., 1994; Weigel et al., 1996). This meteorite is inferred to have an extremely high  $^{146}\text{Sm}/^{144}\text{Sm}$  ratio of  $0.0116 \pm 0.0016$  that in comparison to the  $^{146}\text{Sm}/^{144}\text{Sm}$  ratio of 0.007 in angrite LEW86010 (Table 1) provides an age of  $4.633 \pm 0.022$  Ga, consistent with its old  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  age of  $4.62 \pm 0.07$  Ga, although uncertainties are large (Bogdanovski and Jagoutz, 1996). These ages are problematic since they are older than the age inferred for CAI formation, which is generally assumed to reflect the time of formation of the first solids in the solar nebula.  $^{53}\text{Mn}$ -

$^{53}\text{Cr}$  systematics in this achondrite, on the other hand, indicate that Cr isotopes were equilibrated at  $\leq 4542$  Ma when the  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio was  $\leq 6 \times 10^{-8}$  (Bogdanovki et al., 1997).

Despite some discrepancies, the chronological constraints discussed above show clearly that, compared to the absolute age of CAI formation ( $4567.2 \pm 0.6$  Ma; Amelin et al., 2002), the onset of melting on some planetesimals began as early as  $\sim 2$  to 5 Myr after the formation of the first solids and possibly extended to  $\geq 10$  Myr on others.

### 3.2 Crust Formation

Primary crystallization ages, ideally from internal mineral isochrons of individual members of achondrite groups such as the angrites and noncumulate eucrites that represent basaltic rocks that formed in asteroidal near-surface environments, offer the best means of assessing the time scales of crust formation on planetesimals.

*Angrites.* Angrites are a small group of mineralogically unique basalts composed mostly of Ca-Al-Ti-rich pyroxenes (fassaite), olivine and anorthitic plagioclase (Mittlefehldt et al., 1998, and references therein). Early evidence for the presence of fission Xe (from the decay of  $^{244}\text{Pu}$ ;  $t_{1/2} \sim 82$  Myr) in Angra dos Reis, the type meteorite of the angrites, established its antiquity (Hohenberg, 1970; Lugmair and Marti, 1977; Wasserburg et al., 1977). Subsequently, evidence for the former presence of  $^{244}\text{Pu}$  has also been reported in two other angrites (Eugster et al., 1991; Hohenberg et al., 1991).  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  systematics in Angra dos Reis (ADOR) and LEW 86010 (LEW) are well behaved and give old crystallization ages between  $4.53 \pm 0.04$  and  $4.56 \pm 0.04$  Ga (Lugmair and Marti, 1977; Wasserburg et al., 1977; Jacobsen and Wasserburg, 1984; Lugmair and Galer, 1992; Nyquist et al., 1994).  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  systematics have also been determined in the more recently discovered angrite D'Orbigny, and, despite some disturbance evident in the plagioclase, possibly due to late metamorphism and/or terrestrial weathering, are generally consistent with earlier results for ADOR and LEW (Nyquist et al., 2003a; Tonui et al., 2003).  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  systematics in ADOR and LEW ( $^{146}\text{Sm}/^{144}\text{Sm} \sim 0.007$ ) are concordant with their  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  systematics, although preliminary data for D'Orbigny suggest disturbance of the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  system (Tonui et al., 2003).

The most precise estimate of the crystallization age of the angrites is offered by their Pb-Pb systematics. An internal Pb-Pb isochron defined by LEW minerals gives an age of  $4558.2 \pm 3.4$  Ma, concordant with the highly precise U-Pb model age of  $4557.8 \pm 0.5$  Ma obtained from the



extremely radiogenic Pb compositions in the pyroxenes of ADOR and LEW (Lugmair and Galer, 1992). Preliminary U-Pb model ages derived from D'Orbigny pyroxenes are in agreement with those derived from ADOR and LEW pyroxenes (Jagoutz et al., 2003). The highly precise Pb-Pb age of the angrites has made it possible to use the formation time of these samples as a precise time anchor for the application of chronometers based on short-lived radionuclides, particularly  $^{53}\text{Mn}$  ( $t_{1/2} \sim 3.7$  Myr) and  $^{146}\text{Sm}$  ( $t_{1/2} = 103$  Myr) (Table 1).

Evidence for the presence of live  $^{53}\text{Mn}$  at the time of their formation is found in ADOR and LEW, with the inferred  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio ranging from  $\sim 1.25 \times 10^{-6}$  (Lugmair and Shukolyukov, 1998) to  $\sim 1.44 \times 10^{-6}$  (Nyquist et al., 1994). No detectable evidence for the presence of live  $^{26}\text{Al}$  has been found in these samples ( $^{26}\text{Al}/^{27}\text{Al} < 2 \times 10^{-7}$ ; Lugmair and Galer, 1992). However, such a result is not unexpected given that, at the time these angrites formed (4558 Ma),  $\sim 12$  half-lives of  $^{26}\text{Al}$  had elapsed since the time of CAI formation (4567 Ma; Amelin et al., 2002) when the  $^{26}\text{Al}/^{27}\text{Al}$  ratio was  $\sim 5 \times 10^{-5}$ . Intriguingly, although the preliminary U-Pb model age for D'Orbigny is similar to that of ADOR and LEW, the  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio at the time of its formation ( $\sim 3 \times 10^{-6}$ ) is significantly higher (Nyquist et al., 2003a; Glavin et al., 2004) and implies that D'Orbigny formed  $\sim 4$  to 5 Myr prior to ADOR and LEW. There is also recent evidence that suggests the presence of live  $^{26}\text{Al}$  in the D'Orbigny and Sahara 99555 angrites ( $^{26}\text{Al}/^{27}\text{Al} \sim 2 \times 10^{-6}$ ; Nyquist et al., 2003a), which is consistent with the higher  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio in D'Orbigny. This indicates that Mn-Cr and Al-Mg systematics in D'Orbigny have remained unaltered since the time of last equilibration of Cr and Mg isotopes (and record the time of its original crystallization), but Pb-Pb systematics in this rock may have been disturbed subsequently.

*Eucrites.* Like the angrites, the noncumulate eucrites are pyroxene-plagioclase rocks. However, there are significantly greater numbers of known noncumulate eucrites than there are angrites. Recent high precision oxygen isotope data of Wiechert et al. (2004) demonstrate that most noncumulate eucrites (along with the cumulate eucrites, diogenites and howardites) lie on a single mass fractionation, consistent with their origin on a single parent body. Therefore, these basalts are the most numerous crustal rocks available from any single solar system body other than the Earth and the Moon. A handful of the noncumulate eucrites (in particular Ibitira, but possibly also Caldera, Pasamonte and ALHA 78132) have oxygen isotope compositions distinct from the others, implying either that these samples originated on different parent bodies or that

isotopic heterogeneity was preserved on the Howardite-Eucrite-Diogenite (HED) parent body (Wiechert et al., 2004).

Unlike angrites (which did not undergo any significant degree of recrystallization or metamorphism), the noncumulate eucrites appear to record a protracted history of extensive thermal processing on their parent body subsequent to their original crystallization. As a result, many of the long- and short-lived chronometers investigated in these samples appear to record secondary thermal events rather than their original formation event. Nevertheless, there are several lines of evidence that suggest that the original crystallization of these basalts in the crust of their parent body occurred very early in the history of the solar system. Although typically characterized by large uncertainties, several of these samples such as Chervony Kut ( $4580 \pm 30$  Ma; Wadhwa and Lugmair, 1995), Juvinas ( $4560 \pm 80$  Ma; Lugmair, 1974), Pasamonte ( $4580 \pm 120$  Ma; Unruh et al., 1977), Piplia Kalan ( $4570 \pm 23$  Ma; Kumar et al., 1999) and Yamato 792510 ( $4570 \pm 90$  Ma; Nyquist et al., 1997a) record  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  ages close to  $\sim 4.56$  Ga. In some cases where  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  systematics appear to be disturbed and record ages younger than  $\sim 4.56$  Ga, the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  systematics are relatively undisturbed and still provide evidence for early crystallization of basaltic eucrites such as Caldera ( $^{146}\text{Sm}/^{144}\text{Sm} = 0.0073 \pm 0.0011$ ; Wadhwa and Lugmair, 1996) and Ibitira ( $^{146}\text{Sm}/^{144}\text{Sm} \sim 0.009 \pm 0.001$ ; Prinzhofer et al., 1992). However, there is at least one instance (i.e., the basaltic eucrite EET 90020), where the  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  age ( $4430 \pm 30$  Ma) and  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  systematics ( $^{146}\text{Sm}/^{144}\text{Sm} = 0.0048 \pm 0.0020$ ) are indeed concordant, within rather large uncertainties. As will be discussed below, both the  $^{147}\text{Sm}$ - $^{144}\text{Nd}$  age and initial  $^{146}\text{Sm}/^{144}\text{Sm}$  ratio for EET90020 are very similar to values obtained for the Moore County and Moama cumulate eucrites (Jacobsen and Wasserburg, 1984; Tera et al., 1997). The young  $^{147,146}\text{Sm}$ - $^{143,142}\text{Nd}$  age for this noncumulate eucrite has been interpreted to possibly record late magmatism on the parent body (Nyquist et al., 1997b). Therefore, EET 90020 could be the crystallization product of a younger melting event that may also be responsible for the formation of the cumulate eucrites. However, the  $^{39}\text{Ar}$ - $^{40}\text{Ar}$  chronometer, which is more easily reset by shock reheating than the Sm-Nd system, records a slightly older age of  $\sim 4.48$ - $4.49$  Ga for EET 90020 (Bogard and Garrison, 1997). Therefore, it is possible that this basalt underwent a complex petrogenetic history as suggested by Yamaguchi et al. (2001), such that its Sm-Nd systematics may not necessarily record its primary igneous formation.

Although the Rb-Sr chronometer tends to be more susceptible to resetting than the Sm-Nd system, it also generally points to an ancient age of formation for the noncumulate eucrites (e.g., Allègre et al., 1975; Nyquist et al., 1986). The most precise of the absolute chronometers, i.e., the U-Pb system, mostly appears to have been affected by post-crystallization events and terrestrial Pb contamination in the noncumulate eucrites and records mineral isochron ages in the range of 4128 Ma to 4530 Ma (Tatsumoto et al., 1973; Unruh et al., 1977; Galer and Lugmair, 1996; Tera et al., 1997).

In recent years there has been increasing evidence for the presence of various short-lived radionuclides (particularly  $^{26}\text{Al}$ ,  $^{53}\text{Mn}$  and  $^{60}\text{Fe}$ ) in the noncumulate eucrites at their time of crystallization, which further supports the early formation of these crustal basalts. The first evidence for live  $^{26}\text{Al}$  in an achondrite was reported by Srinivasan et al. (1999). These authors demonstrated the presence of excess  $^{26}\text{Mg}$  from the decay of  $^{26}\text{Al}$  in plagioclase of the Piplia Kalan basaltic eucrite, from which a  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $(7.5 \pm 0.9) \times 10^{-7}$  was inferred in this sample at the time of its formation (Fig. 2). Compared to the canonical  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $\sim 5 \times 10^{-5}$  in CAIs, the  $^{26}\text{Al}/^{27}\text{Al}$  ratio inferred for Piplia Kalan suggests that crust formation on the parent planetesimal of this eucrite occurred within  $\sim 5$  Myr of the beginning of the solar system. Subsequently, evidence for the presence of live  $^{26}\text{Al}$  has been found in additional basaltic eucrites ( $^{26}\text{Al}/^{27}\text{Al}$  ratios in the range of  $\sim 6 \times 10^{-7}$  to  $\sim 2 \times 10^{-6}$ ; Srinivasan, 2002; Nyquist et al., 2003b; Wadhwa et al., 2004). Of these, the  $^{26}\text{Al}/^{27}\text{Al}$  ratio is most precisely determined in the Asuka 881394 eucrite (i.e.,  $(1.34 \pm 0.05) \times 10^{-6}$ ; Fig. 3), and translates to an Al-Mg age of  $4563.4 \pm 0.6$  Ma (compared to CAIs; Table 1). This indicates that crust formation on the eucrite parent planetesimal occurred within  $\sim 4$  Myr of the formation of the first solids in the solar system.

Evidence for the presence of live  $^{53}\text{Mn}$  at the time of eucrite formation has been documented in several noncumulate eucrites including Chervony Kut, Juvinas, Ibitira (Lugmair and Shukolyukov, 1998) and Asuka 881394 (Nyquist et al., 2003b). Compared to the LEW 86010 angrite (Table 1), Mn-Cr ages for these eucrites were determined to be  $4563.6 \pm 0.9$  Ma,  $4562.5 \pm 1.0$  Ma,  $4557 \pm 2/-4$  Ma, and  $4564 \pm 2$  Ma, respectively. These old ages indicate that crust formation on the parent planetesimal of these basalts occurred within  $\sim 4$  to 10 Myr of the formation of the first solids. Additionally, the Mn-Cr age for the Asuka 881394 eucrite is consistent with its Al-Mg age. Several other basaltic eucrites in which Mn-Cr systematics have been investigated do not show any evidence for live  $^{53}\text{Mn}$  (Lugmair and Shukolyukov, 1998;

Nyquist et al., 1996, 1997ab). In these cases, it is likely that secondary thermal events have resulted in later resetting of the Mn-Cr system, as appears to be the case for the U-Pb system in most noncumulate eucrites as well. Finally, there is unambiguous evidence for the former presence of live  $^{60}\text{Fe}$  in two noncumulate eucrites, Chervony Kut and Juvinas (Shukolyukov and Lugmair, 1993a,b), also attesting to an early formation age of these basalts. However, the inferred  $^{60}\text{Fe}/^{56}\text{Fe}$  ratios in these two samples translate to an age difference between them of  $\sim 5$  Myr, whereas Mn-Cr systematics indicate an age difference of only  $\sim 1$  Myr; this may be from disturbance of the Fe-Ni system in these samples (Lugmair and Shukolyukov, 1998).

Basaltic noncumulate eucrites thus show clear evidence of having formed close to  $\sim 4.56$  Ga in the crust of their parent planetesimal. In contrast, cumulate eucrites, which formed in the crust of the same parent planetesimal as the noncumulate eucrites (Clayton and Mayeda, 1996; Wiechert et al., 2004), have significantly younger concordant Sm-Nd and Pb-Pb ages, ranging from the oldest of  $4456 \pm 25$  Ma (Sm-Nd) and  $4484 \pm 19$  Ma (Pb-Pb) for Moore County (Tera et al., 1997) to the youngest of  $4410 \pm 20$  Ma (Sm-Nd, Lugmair et al., 1977) and  $4399 \pm 35$  Ma (Pb-Pb, Tera et al., 1997) for Serra de Magé. Thus, Sm-Nd and Pb-Pb systematics in the cumulate eucrites indicate that isotopic closure occurred up to  $\sim 150$  Myr after the noncumulate eucrites (Lugmair et al., 1977; Jacobsen and Wasserburg, 1984; Lugmair et al., 1991; Tera et al., 1997). The age difference between the noncumulate and cumulate eucrites may imply that active magmatism persisted on the eucrite parent body for a period of 40-150 Myr (Tera et al., 1997), an idea that possibly gains support from the  $4430 \pm 30$  Ma  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  age of the noncumulate eucrite EET 90020 (Nyquist et al., 1997b) and the overlapping initial  $^{146}\text{Sm}/^{144}\text{Sm}$  ratios of Moore County, Moama, and EET 90020 (Jacobsen and Wasserburg, 1984; Nyquist et al., 1997b; Tera et al., 1997). If this is so, it further implies that the process of crust formation on the eucrite parent body possibly extended to  $\sim 150$  Myr after solar system formation. Since, as discussed above, the oldest noncumulate eucrites formed within  $\sim 4$  Myr of CAI formation,  $^{26}\text{Al}$  and/or  $^{60}\text{Fe}$  are likely heat sources for this initial stage of planetesimal differentiation. Energy sources that can account for later igneous activity (i.e., tens of millions of years after CAI formation) on small planetesimals are not obvious unless the cumulate eucrites are the crystallization products of impact melting on the eucrite parent body. Alternatively (and perhaps more likely), since the cumulate eucrites are slowly cooled rocks that possibly formed deeper within the crust of their parent body than noncumulate eucrites, the long-lived chronometers could be recording the long

cooling times required to achieve subsolidus temperatures. This is supported by the recent modeling of Ghosh and McSween (1998), which shows that, assuming reasonable parameters, it is possible to maintain temperatures in excess of the melting point of basalt at a depth of ~100 km for over ~100 Myr in a Vesta-sized planetesimal.

### 3.3 Global Silicate (Mantle) Differentiation

*Whole rock isochrons.* While an internal mineral isochron can provide constraints on the timing of formation of an individual achondrite in the crust of a planetesimal, a whole rock isochron (based on a long- or a short-lived chronometer) of a particular achondrite group can provide limits on the timing of parent-daughter element fractionation in the source (mantle) reservoir of their parent planetesimal, which in turn is a reflection of the time scale involved in global silicate fractionation (possibly associated with crystallization of a magma ocean). Whole rock Rb-Sr isochrons for the basaltic eucrites established early on that Rb-Sr fractionation in the mantle source reservoir of these achondrites occurred close to ~4.6 Ga (Papanastassiou and Wasserburg, 1969; Birck and Allègre, 1978). Smoliar (1993) evaluated all available Rb-Sr data for the eucrites and obtained a whole rock isochron age of  $4.55 \pm 0.06$  Ga for the noncumulate eucrites.

Achondrite whole rock isochrons based on short-lived chronometers have the potential for more precisely constraining the timing of global silicate differentiation on planetesimals. Such isochrons have recently been reported for the  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  and the  $^{182}\text{Hf}$ - $^{182}\text{W}$  systems in the Howardite-Eucrite-Diogenite (HED) group of achondrites (Lugmair and Shukolyukov, 1998; Quitté et al., 2000). The HED whole rock  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  isochron corresponds to a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(4.7 \pm 0.5) \times 10^{-6}$  (Fig. 4; Lugmair and Shukolyukov, 1998). Comparison with the LEW 86010 angrite (Table 1) gives a Mn-Cr age of  $4564.8 \pm 0.9$  Ma for global silicate fractionation on the HED parent body, which is within ~3 to 4 Myr after the formation of CAIs at ~4567 Ma (Amelin et al., 2002). This age is, within error, similar to the Al-Mg and Mn-Cr ages of eucrite Asuka 881394 (Nyquist et al., 2003b; Wadhwa et al., 2004) and the Mn-Cr age of eucrite Chervony Kut (Lugmair and Shukolyukov, 1998). The near agreement of the ages provided by the whole-rock isochrons and internal isochrons of these eucrites indicates not only that planetesimal differentiation started soon after solar system formation, but that the duration of the initial HED crust-mantle differentiation may have been as short as ~2 Myr or less.

A whole rock  $^{182}\text{Hf}$ - $^{182}\text{W}$  isochron for the HEDs was reported by Quitté et al. (2000) and corresponds to a  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of  $(7.96 \pm 0.34) \times 10^{-5}$  (Fig. 5). Currently there is no consensus on the initial  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of the solar system, with proposed values ranging from  $1.0 \times 10^{-4}$  (Kleine et al., 2002; Yin et al., 2002b) to  $1.6 \times 10^{-4}$  (Quitté and Birck, 2004). An initial  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of  $1.0 \times 10^{-4}$  would imply that global Hf-W fractionation in the HED mantle source occurred  $\sim 3$  Myr after the beginning of the solar system, which is consistent with the HED whole rock  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics discussed above. However, if an initial  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of  $\sim 1.6 \times 10^{-4}$  is assumed, then global Hf-W fractionation occurred  $\sim 9$  Myr after the beginning of the solar system. This is inconsistent not only with the HED whole rock  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics but also with the recent evidence for live  $^{26}\text{Al}$  in several eucrites (Srinivasan et al., 1999; Srinivasan, 2002; Nyquist et al., 2003b; Wadhwa et al., 2004). In this regard, it is worth noting that the initial  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of  $1.6 \times 10^{-4}$  is based on the reanalysis of the W isotopic composition of the Tlacotepec (IVB) iron meteorite, which has an extremely low  $\epsilon^{182}\text{W}$  value, i.e.,  $^{182}\text{W}/^{184}\text{W}$  ratio relative to the terrestrial standard in part per  $10^4$ , of  $-4.5$  (Quitté and Birck, 2004); similarly low  $\epsilon^{182}\text{W}$  values (i.e., lower than  $\sim -3.5$ ) for several other iron meteorites have recently been called into question (Yin and Jacobsen, 2003). However, the proposed initial  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of  $1.0 \times 10^{-4}$  is based largely on the  $^{182}\text{Hf}$ - $^{182}\text{W}$  systematics in chondrites that have undergone different histories and have experienced at least some degree of equilibration. Therefore, although a value close to  $1.0 \times 10^{-4}$  appears to be more plausible at this time, the question regarding the initial  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio for the solar system remains to be resolved.

Recently, Wadhwa et al. (2003) reported a whole rock  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  isochron for eucritic and diagenetic clasts from the Vaca Muerta mesosiderite that corresponded to a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(3.3 \pm 0.6) \times 10^{-6}$  (Fig. 6). These authors concluded that the lower slope of the isochron defined by these clasts implies that these materials originated on a parent planetesimal distinct from that of the HEDs, and which underwent global (mantle) differentiation  $\sim 2$  Myr after the HED parent body (or within  $\sim 5$  to  $6$  Myr after CAI formation).

*Initial Sr isotopic composition.* The antiquity of the highly volatile-depleted parent planetesimals of the angrites and the eucrites can also be inferred from their initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Assuming that the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio at the beginning of the solar system is represented by the average initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio measured in Allende CAIs (Gray et al., 1973; Podosek et al., 1991), and that subsequent evolution of radiogenic Sr occurred in an environment with solar

Rb/Sr ratios, the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the angrites (Lugmair and Galer, 1992; Nyquist et al., 1994, 2003a; Tonui et al., 2003) translate to an age difference of  $\sim 4$  Myr between CAI formation and the timing of Rb/Sr depletion event that established the angrite source characteristics.

The very low initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the eucrites similarly indicate that the volatile-depletion characterizing the eucrite parent body may have occurred early in the history of the solar system (Carlson and Lugmair, 2000, and references therein). A reevaluation of the Sr isotope data for the eucrites by Smoliar (1993) shows that whole rock Rb-Sr isochrons for the noncumulate and the cumulate eucrites define slightly, but resolvably, different initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (that are both distinctly lower than the eucrite initial, BABI, previously defined by Papanastassiou and Wasserburg, 1969). In fact, the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for the cumulate eucrites proposed by Smoliar (1993) is, within errors, similar to that for the angrites (e.g., Lugmair and Galer, 1992), suggesting that the volatile-depletion in their sources was established at similar times (possibly  $\sim 4$  Myr after CAI formation; see above). This time scale for the fractionation event that established the low Rb/Sr source characteristics of the cumulate eucrites is essentially consistent with the timing of global mantle differentiation defined by the HED whole rock  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  isochron. However, the slighter higher initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio defined by the noncumulate eucrites is potentially problematic since the simplest interpretation would be that their source evolved with a chondritic Rb/Sr ratio for  $\sim 4$  Myr longer (and is thus younger) than that of the cumulate eucrites, further implying that these two types of eucrites originated on distinct parent bodies (Smoliar, 1993). This is inconsistent with recent high precision oxygen isotope data (Wiechert et al., 2004) that suggest that the cumulate and noncumulate eucrites (with the possible exception of Ibitira) originated on a common parent planetesimal. As discussed by Carlson and Lugmair (2000), a possible explanation could be that the severe volatile-depletion on the eucrite parent body did not occur in a single step process, but rather took place over the course of its accretionary and early differentiation history. Subsequently, the process of magma ocean crystallization may have resulted in a slighter higher Rb/Sr ratio in the source of the noncumulate eucrites compared to that of the cumulate eucrites, thereby resulting in the higher initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio indicated by the whole rock isochron for the noncumulate eucrites.

### **3.4 Metal Segregation and Core Crystallization**

Limits on the time scales involved in metal segregation and core crystallization on planetesimals may be obtained from chronological investigations of iron-rich meteorites, such as magmatic irons (that represent the metallic cores of differentiated asteroidal bodies) and pallasites (considered to have formed near the core-mantle boundary). Depending on the geochemical affinities of the parent and daughter elements, different chronometers applied to such meteorite types can provide constraints on either the process of metal segregation (e.g., the  $^{182}\text{Hf}$ - $^{182}\text{W}$  chronometer, where Hf is lithophile and W is siderophile such that major fractionation occurs during separation of the metallic melt from silicates) or of core crystallization (e.g.,  $^{187}\text{Re}$ - $^{187}\text{Os}$ ,  $^{107}\text{Pd}$ - $^{107}\text{Ag}$  and  $^{53}\text{Mn}$ - $^{53}\text{Cr}$ , where the parent-daughter elements are fractionated during crystallization of Fe-Ni phases, sulfides and phosphates from the metallic melt).

*Metal segregation.* The W isotopic compositions of a variety of magmatic and nonmagmatic iron meteorites have been reported within the last decade (e.g., Lee and Halliday, 1995, 1996; Horan et al., 1998) and have the lowest  $^{182}\text{W}/^{184}\text{W}$  ratios of any solar system material, with  $\epsilon^{182}\text{W}$  values ranging from  $\sim -3$  to  $-5$  (with most values between  $-3.5$  and  $-4.1$ ). As emphasized by Horan et al. (1998), these  $\epsilon^{182}\text{W}$  values suggest that metal segregation on different planetesimals occurred within a period of  $\sim 5$  Myr in the early history of the solar system. As mentioned earlier, however, Yin and Jacobsen (2003) have called into question the lower end of the range of  $\epsilon^{182}\text{W}$  values in the iron meteorites, since such values have the improbable implication that some iron meteorites predate chondrites. These authors measured the W isotopic compositions of several iron meteorites, including some of those previously analyzed by Lee and Halliday (1996) and Horan et al. (1998), and reported that none had  $\epsilon^{182}\text{W}$  values lower than the chondritic initial value of  $-3.45 \pm 0.25$ . Recently, Quitté and Birck (2004) reanalyzed the W isotopic compositions of two iron meteorites, Duel Hill (IVA) and Tlacotepec (IVB), which were reported by Horan et al. (1998) to have among the lowest  $\epsilon^{182}\text{W}$  values. These authors reported an  $\epsilon^{182}\text{W}$  value of  $-3.5 \pm 0.3$  for Duel Hill, significantly higher than that previously reported for this meteorite by Horan et al. (1998) (i.e.,  $-5.1 \pm 1.1$ ). However, for Tlacotepec, they obtained an  $\epsilon^{182}\text{W}$  value of  $-4.4 \pm 0.3$ , which agrees well with the previous value ( $-4.5 \pm 0.4$ ; Horan et al., 1998). Therefore, it appears that the W isotopic composition of the iron meteorites ranges down to at least this value. However, only 4 out of 28 iron meteorites measured by Lee and Halliday (1996) and Horan et al. (1998) have  $\epsilon^{182}\text{W}$  values below the



chondritic initial value, outside of uncertainty, and the mean  $\epsilon^{182}\text{W}$  value for all these samples is  $-3.8 \pm 0.5$  ( $1\sigma$ ). Therefore, the results from these studies are consistent with most iron meteorites having  $\epsilon^{182}\text{W}$  values that are not resolvably below the initial chondritic value. As to the  $\epsilon^{182}\text{W}$  values of some iron meteorites lying below the initial chondritic value, one possibility is that the W isotopic compositions of the components (mainly metal and silicates) of the chondrites analyzed so far, and used to defined the initial chondritic  $\epsilon^{182}\text{W}$  value, may have been equilibrated to some degree. This possibility has implications for the initial  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of the solar system, but remains to be rigorously evaluated.

As noted by Quitté and Birck (2004), since the revision of the chondritic W isotopic composition from  $\epsilon^{182}\text{W} \sim 0$  (Lee and Halliday, 1995) to  $-1.9$  (Kleine et al., 2002; Yin et al., 2002), the initial W isotopic composition of the differentiated mantle of the HED parent body (Quitté et al., 2000) lies significantly above the chondritic evolution line (Fig. 7). Assuming that the HED parent body had a bulk chondritic Hf/W composition and that core formation resulted in a Hf/W ratio in the HED mantle of at least  $\sim 39$  (i.e., equal to the highest Hf/W ratio measured in eucrites that are the products of partial melting of this mantle), Quitté and Birck (2004) estimated that metal segregation (core formation) on the HED parent planetesimal occurred  $\sim 0.6$  Myr prior to global mantle (silicate) differentiation. Interestingly, the preferred model of Wadhwa et al. (2003) to explain the fact that the whole rock  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  isochrons defined by the HEDs and silicate clasts from the Vaca Muerta mesosiderite passed above the chondritic point (Fig. 6) indicated that the silicate differentiation event that established the HED mantle source reservoirs occurred  $\sim 0.6$  Myr after a prior Mn/Cr fractionation event (most likely similar in its timing, if not coincident, with core formation). This model implied that the first Mn/Cr fractionation event, likely coincident with core formation, occurred simultaneously (at  $\sim 4565.6$  Ma) on both parent bodies, but that the end of silicate differentiation for each planetesimal occurred at different times (i.e., at  $\sim 4565$  Ma and  $\sim 4563$  Ma for the parent bodies of the HEDs and Vaca Muerta silicate clasts, respectively).

*Core crystallization.* Once the metal has segregated into the core of a planetesimal, the time scales involved in the crystallization of this metal may be constrained by isochrons derived from bulk samples and mineral phases of magmatic iron meteorites and pallasites. In recent years, precise Re-Os isochrons have been obtained for various groups of the iron meteorites. Most iron meteorite groups give relatively old Re-Os ages that range from  $4557 \pm 12$  Ma (IIIAB magmatic

irons) to  $4526 \pm 27$  Ma (IVB magmatic irons) (Shen et al., 1996; Smoliar et al., 1996; Horan et al., 1998; Cook et al., 2004). There is a discrepancy, however, in the Re-Os systematics in the IVA magmatic irons. While Shen et al. (1996) report a Re-Os age for the IVA irons that is  $60 \pm 45$  Myr older than for other iron meteorite groups, the data of Smoliar et al. (1996) give an age of  $4456 \pm 25$  Ma, significantly younger than other iron meteorite groups, which these authors attributed to later disturbance of the Re-Os system. Horan et al. (1998) subsequently reported the Re-Os isotopic compositions of several IVA irons and showed that while some lie on the  $4456 \pm 25$  Ma isochron of Smoliar et al. (1996), others were consistent with an older age. This suggests that the Re-Os isotope systematics in the IVA are indeed disturbed, perhaps by processes such as breakup and reassembly of the parent planetesimal, which have been invoked to explain the range of metallographic cooling rates of the IVA irons (e.g., Haack et al., 1996).

Re-Os ages reported so far use a  $^{187}\text{Re}$  decay constant that was determined by assuming that the IIIAB isochron should give the same age as the U-Pb age of the angrites (Smoliar et al., 1996), so the accuracy of these ages is only as good as the validity of this assumption. Nevertheless, the age range indicated by Re-Os isochrons is independent of the half-life, so the results for various iron meteorite groups, with the exception of the IVA irons, suggest that core crystallization (or more specifically, Re-Os isotopic closure) in planetesimals spanned a period of up to  $\sim 20\text{--}30$  Myr. Re-Os systematics in pallasites indicate that they may be younger than iron meteorites by  $\sim 60$  Myr; however, this apparently young age may be due to later reequilibration of the Re-Os system (Chen et al., 2002). Cook et al. (2004) recently reported the first high-precision  $^{190}\text{Pt}\text{--}^{186}\text{Os}$  isochrons for the IIAB and IIIAB magmatic irons, and estimated ages for these meteorite groups of  $4323 \pm 80$  Ma and  $4325 \pm 26$  Ma, respectively. These ages are significantly younger than Re-Os ages for iron meteorites, and these authors suggested that this discrepancy could reflect an error in the decay constant for  $^{190}\text{Pt}$ .

In contrast to the more leisurely pace of core crystallization suggested by Re-Os systematics, evidence for the former presence of live  $^{107}\text{Pd}$  in a variety of metal-rich meteorites, including irons and pallasites, indicates that this process occurred rapidly, well within the lifetime of this short-lived radionuclide. For most iron meteorites, closure of the  $^{107}\text{Pd}\text{--}^{107}\text{Ag}$  isotope system occurred within a narrow time interval of only  $\sim 4$  Myr. The highest inferred  $^{107}\text{Pd}/^{108}\text{Pd}$  ratio of  $\sim 2.4 \times 10^{-5}$  is in samples such as Gibeon (IVA) and Canyon Diablo (IA), for which well-defined  $^{107}\text{Pd}\text{--}^{107}\text{Ag}$  isochrons have been obtained (Chen and Wasserburg, 1996; Carlson and Hauri,

2001). Pallasites have somewhat younger Pd-Ag ages, most of which indicate isotopic closure  $\leq 10$  Myr after Gibeon and Canyon Diablo. Of the pallasites investigated so far, Brenham has the highest  $^{107}\text{Pd}/^{108}\text{Pd}$  ratio of  $(1.65 \pm 0.05) \times 10^{-5}$ , defined by a four-point internal isochron comprised of silicates and metal (Carlson and Hauri, 2001). This more precisely defined value is only marginally higher than the  $^{107}\text{Pd}/^{108}\text{Pd}$  ratio of  $\sim 1.1 \times 10^{-5}$  inferred from a single bulk data point (Chen and Papanastassiou, 1996; Chen et al., 2002), and indicates that closure of the Pd-Ag system occurred  $\sim 3.5$  Myr after Gibeon and Canyon Diablo. The recently acquired high precision Pd-Ag isotope data for the Canyon Diablo (IA) and Grant (IIIB) iron meteorites and the Brenham pallasite have additionally demonstrated that  $\epsilon$ -level differences in the initial Ag isotopic compositions of these meteorites can be resolved, and this have important implications for their formation histories (Carlson and Hauri, 2001). The initial Ag isotopic composition of Brenham indicates that during the 3.5 Myr time interval between closure of its Pd-Ag system and that of Canyon Diablo, the parent planetesimal of Brenham evolved with a nearly chondritic Pd/Ag ratio, unlike the high Pd/Ag ratio characterizing the bulk composition of this pallasite. This may suggest that metal-silicate separation on the Brenham parent body did not occur until shortly before its crystallization (Carlson and Hauri, 2001). This result is distinct from that of the IIIB iron Grant. Grant has a similar inferred initial  $^{107}\text{Pd}/^{108}\text{Pd}$  as does Brenham, but a more radiogenic initial Ag isotopic composition, which indicates that the high bulk Pd/Ag of Grant was a characteristic of its source (Carlson and Hauri, 2001). With the exception of the disturbed Re-Os systematics in the IVA irons, the Re-Os and Pd-Ag ages provide a broadly similar sequence of formation of the iron meteorites and pallasites, although the total time interval indicated by the Re-Os ages is considerably longer than that indicated by Pd-Ag ages.

$^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics in IIIAB magmatic irons and pallasites also indicate early fractionation and closure of the Mn-Cr system in these metal-rich meteorites. The first evidence of live  $^{53}\text{Mn}$  in IIIAB irons was provided by ion microprobe (SIMS) studies of phosphates that showed a wide range of  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios from  $\sim 1 \times 10^{-6}$  to  $\sim 2 \times 10^{-5}$  (Davis and Olsen, 1991; Hutcheon and Olsen, 1991; Hutcheon et al., 1992). Taken at face value, this range of  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios translates to a time interval of  $\sim 16$  Myr, which is inconsistent with the Pd-Ag systematics that indicate that most of these meteorites formed contemporaneously. A more recent SIMS study of  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics in phosphates in several IIIAB iron meteorites has demonstrated that the Mn-Cr ages based on inferred  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios are different for the different phosphate

minerals, most likely due to the slow cooling rate of the IIIAB iron meteorites combined with the difference in the diffusion behaviors of Mn and Cr in the different phosphates (Sugiura and Hoshino, 2003); the apparently wide range of inferred  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios in the previous studies of IIIAB irons may be similarly explained. Sugiura and Hoshino (2003) also showed that one of the phosphates (i.e., the Fe-Mn phosphate sarcopside) consistently recorded the same  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $\sim 3.4 \times 10^{-6}$  in all the IIIAB iron meteorites they investigated. These authors reasoned that the closure temperature of the Pd-Ag system in iron meteorites may be similar to that of the Mn-Cr system in sarcopside, and that the  $^{107}\text{Pd}/^{108}\text{Pd}$  ratio of  $\sim 2 \times 10^{-5}$  in these meteorites corresponds to a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $\sim 3.4 \times 10^{-6}$ . This would imply that, compared to the  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $\sim 1.25 \times 10^{-6}$  in the angrite LEW 86010 (Lugmair and Shukolyukov, 1998), isotope closure of the Mn-Cr (and Pd-Ag) systems in the IIIAB irons occurred  $\sim 5$  Myr before angrite crystallization (i.e., at  $\sim 4563$  Ma). Furthermore, it was suggested by these authors that in pallasites, the  $^{107}\text{Pd}/^{108}\text{Pd}$  ratio of  $\sim 1 \times 10^{-5}$  (inferred from Glorieta Mountain and Brenham pallasites; Chen and Wasserburg, 1996; Carlson and Hauri, 2001; Chen et al., 2002) corresponded to a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $\sim 1 \times 10^{-6}$  (based on data for the Omolon pallasite; Lugmair and Shukolyukov, 1998), implying broad consistency between Pd-Ag and Mn-Cr systematics (both reflecting a time interval of  $\sim 7$  Myr) between the iron meteorites and pallasite.

However, when all the available data for Pd-Ag and Mn-Cr systematics in various iron meteorites and pallasites are examined in detail, there are evident discrepancies between these two systems. For example, the Eagle Station pallasite has an inferred  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $\sim 2.3 \times 10^{-6}$  (Birck and Allègre, 1988), but there is no detectable evidence of live  $^{107}\text{Pd}$  in this meteorite (i.e.,  $^{107}\text{Pd}/^{108}\text{Pd} < \sim 7 \times 10^{-6}$ ; Chen and Wasserburg, 1996). Eagle Station is an anomalous pallasite not belonging to the “main-group” (Mittlefehldt et al., 1998, and references therein) and, as discussed by Lugmair and Shukolyukov (1998), has a Cr isotopic composition with an anomalously high  $^{54}\text{Cr}/^{52}\text{Cr}$  ratio of  $\sim +1.5 \epsilon$ . Therefore, this meteorite may contain an anomalous (most likely of presolar nucleosynthetic origin) Cr component that could complicate Mn-Cr systematics such that the  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio inferred from the measured  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios would not reflect the true value. Among the main-group pallasites, a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(1.4 \pm 0.4) \times 10^{-5}$  has been inferred from a SIMS study of Springwater (Hutcheon and Olsen, 1991); this value was since confirmed by another ion microprobe study (Hsu et al., 1997). However, based on thermal ionization mass spectrometry (TIMS) analysis of a separated olivine fraction from

Springwater, Lugmair and Shukolyukov (1998) inferred a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio for this pallasite more than an order of magnitude lower ( $\sim 1 \times 10^{-6}$ ). While TIMS studies of Eagle Station, Omolon and Springwater (Birck and Allègre, 1988; Lugmair and Shukolyukov, 1998) have yielded  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios of  $\sim 1\text{-}2 \times 10^{-6}$ , the SIMS investigations of Albin, Brenham and Springwater (Hutcheon and Olsen, 1991; Hsu et al., 1997) all give values of  $\sim 1\text{-}4 \times 10^{-5}$ . The fact that analyses of olivine from the same pallasite sample (i.e., Springwater) by bulk (TIMS) or microanalytical (SIMS) techniques yield such different inferred  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios could be indicative of redistribution of Mn and/or Cr within these olivines. If this is the case, then the bulk technique (which would “average” over any redistribution of the Mn and/or Cr) would be expected to be more reliable in terms of yielding the true  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio. As such, given the above discussion, the suggestion of Sugiura and Hoshino (2003) that pallasites (at least those belonging to the “main-group”) are characterized by a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $\sim 1 \times 10^{-6}$  may be a reasonable one. Nevertheless, some outstanding problems with the consistency of the Mn-Cr and Pd-Ag ages in pallasites remain.

#### 4. SUMMARY AND CONCLUSIONS

Based on the constraints available from long- and short-lived chronometers, differentiation of planetesimals in the early history of the solar system occurred very rapidly. Melting was initiated on some of the planetesimals, which were subsequently arrested in this state and did not differentiate fully. On some of these bodies, such incipient melting began as early as  $\sim 2$  to 5 Myr after the formation of the first solids in the solar nebula (i.e., CAIs), but possibly extended to more than  $\sim 10$  Myr on others. Other planetesimals underwent more extensive melting and differentiation and acquired the layered structure comprised of a silicate crust and mantle and a metallic core.

Crystallization ages of the basaltic angrites and noncumulate eucrites provide the best means of constraining the timing of crust formation. Most of the chronological evidence for these achondrites suggests that the earliest basalts were emplaced (and formed the crusts of planetesimals) within  $\sim 4$  Myr of the formation of CAIs. Primary basalt formation is likely to have continued till  $\sim 10$  Myr after CAI formation.

Global silicate differentiation (i.e., the process that established the mantle source reservoirs of the crustal materials) on the parent planetesimals of the angrites and eucrites is likely to have

occurred contemporaneously, within  $\sim 3$  to 4 Myr of CAI formation. However, this process occurred  $\sim 2$  Myr later on the parent body of the HED-like clasts from the Vaca Muerta mesosiderite. Therefore, the process of global mantle differentiation of planetesimals began early but possibly extended over a time interval of a few million years for different parent bodies.

Metal segregation on different planetesimals, represented by different groups of iron meteorites, is likely to have occurred over a short time interval of  $\sim 5$  Myr or so (and possibly even shorter). In the particular case of the HED parent body, metal segregation may have occurred  $\sim 0.6$  Myr prior to the global mantle differentiation as reflected in the Hf-W (and possibly also the Mn-Cr) systematics of the HEDs. Subsequent core crystallization is thought to have occurred over a longer period of time. Re-Os systematics suggest that core crystallization could have continued for  $\sim 20$  to 30 Myr, but short-lived chronometers (Pd-Ag and Mn-Cr) in most iron meteorites and pallasites indicate that core crystallization on their parent planetesimals spanned a shorter time interval of  $\leq 10$  Myr.

The various chronometers (long- and short-lived) applied towards obtaining the time scales discussed here are not always consistent with each other. In some cases, this is to be expected since these chronometers may be dating different events owing to differences in their closure temperatures. However, in other cases, discrepancies may result from disturbance of isotope systematics by secondary events. In the specific case of chronometers based on the short-lived radionuclides (particularly those with half-lives  $\leq 10$  Myr), there is the additional assumption of homogeneous distribution in the meteorite-forming region of the early solar system. This assumption still remains to be rigorously evaluated for several of the short-lived chronometers considered here. Nevertheless, the apparent convergence of the relative time scales indicated by Al-Mg and Mn-Cr with the absolute time scales provided by U-Pb dating suggests that these systems can indeed provide a robust chronology for early solar system events.

The main challenge for future studies seeking to better clarify the reasons for discrepancies between various radiogenic isotope systematics will be to extend chronological investigations to a greater variety of meteoritic materials, such that there are many more instances than there are at present of multiple chronometers being applied to the same objects. Such studies have been inhibited in the past by the limited fractionation in meteoritic materials of various parent-daughter element pairs, such that it has been difficult to apply multiple chronometers to a

particular meteorite. These types of investigations should become increasingly feasible with future advancements in analytical capabilities that will allow high precision isotopic analyses on meteoritic components having relatively low parent/daughter ratios.

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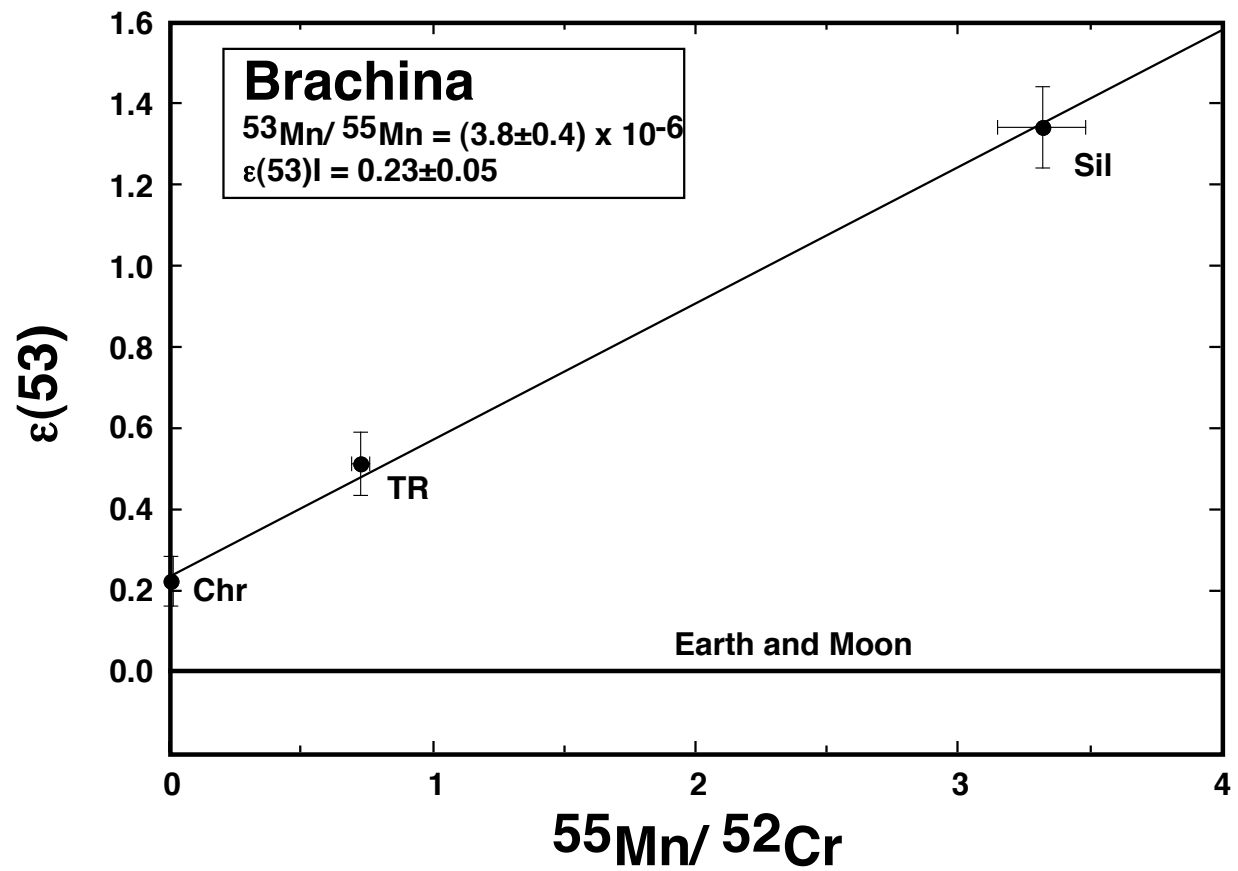


Figure 1.  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics in the primitive achondrite Brachina (Chr = chromite; TR = whole rock; Sil = silicates). Data from Wadhwa et al. (1998).

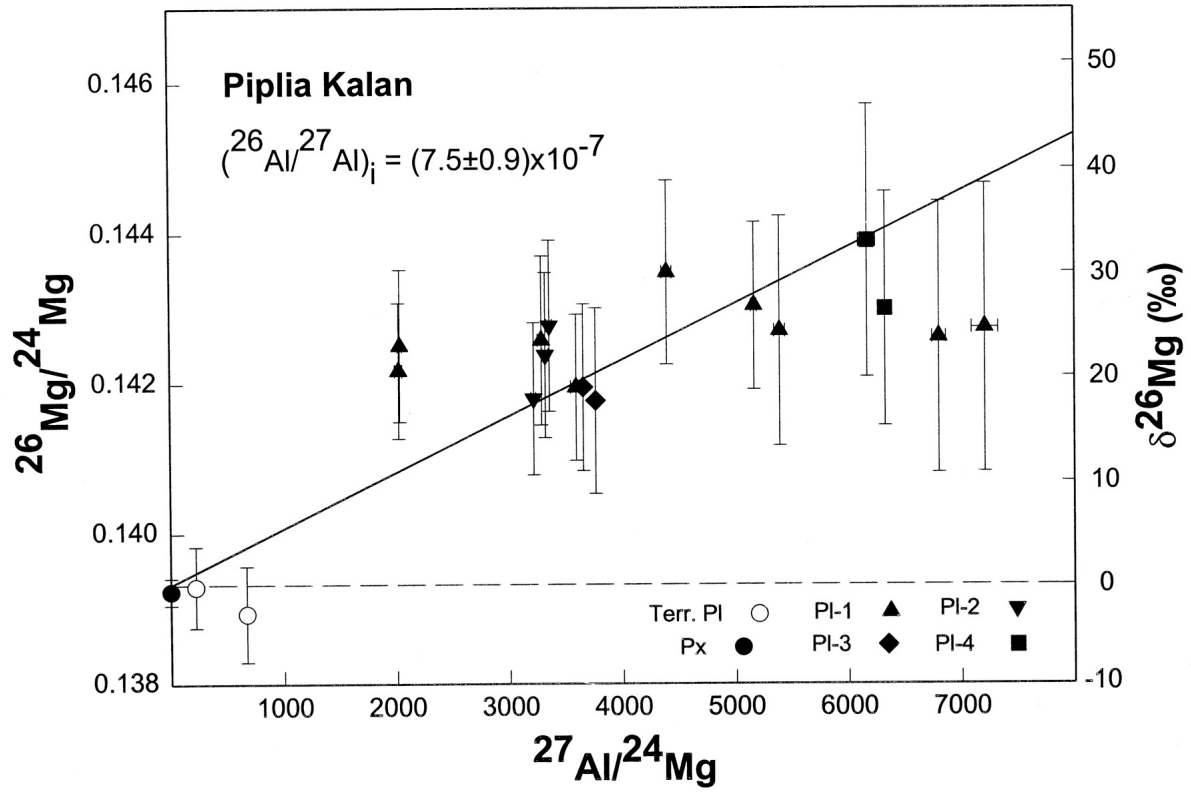


Figure 2.  $^{26}\text{Al}$ - $^{26}\text{Mg}$  systematics in the noncumulate eucrite Piplia Kalan (Px = pyroxene; Pl = plagioclase). Figure from Srinivasan et al. (1999).

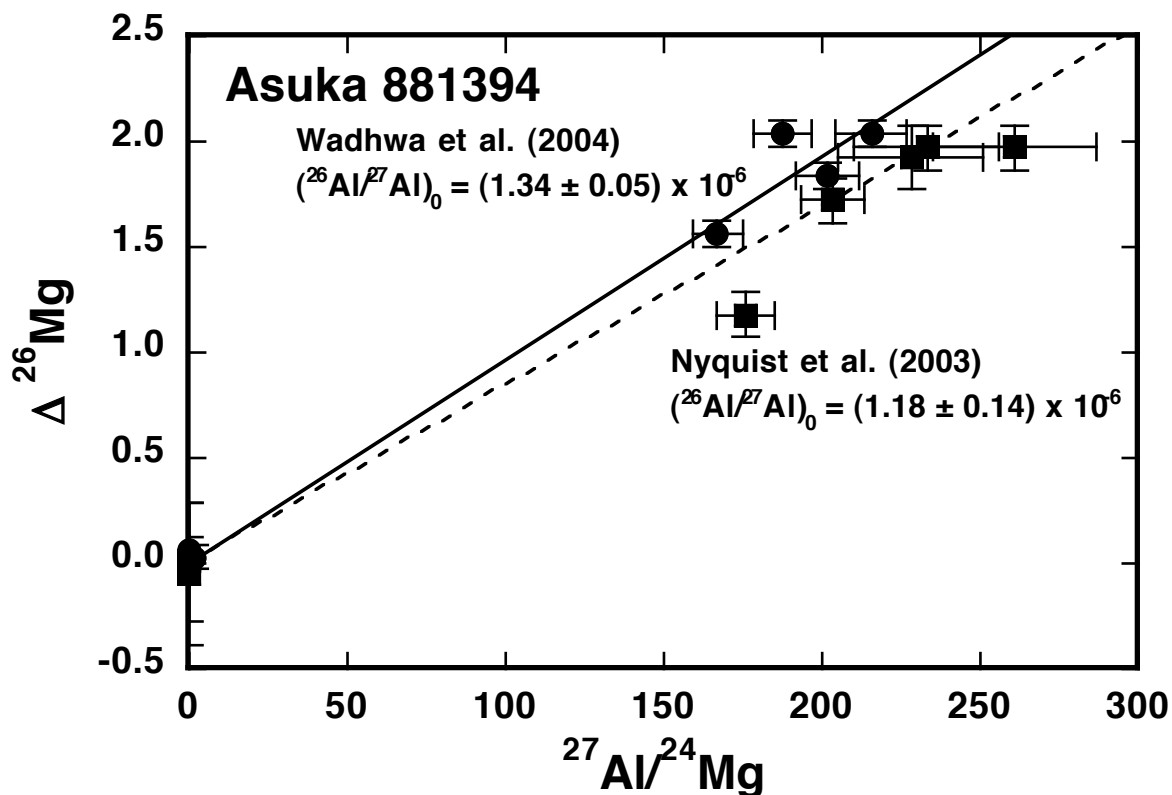


Figure 3.  $^{26}\text{Al}$ - $^{26}\text{Mg}$  systematics in the Asuka 881394 eucrite. Solid circles show the data of Wadhwa et al. (2004) and the solid line is the isochron defined by these data, slope of which corresponds to a  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $(1.34 \pm 0.05) \times 10^{-6}$ ; low Al/Mg data points near the origin are for pyroxene and whole rock, and high Al/Mg data points are for plagioclase. Solid squares are the data of Nyquist et al. (2003b) and the dashed line is the isochron defined by these data, slope of which corresponds to a  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $(1.18 \pm 0.14) \times 10^{-6}$ ; low Al/Mg data points near the origin are for pyroxene, and high Al/Mg data points are for plagioclase.

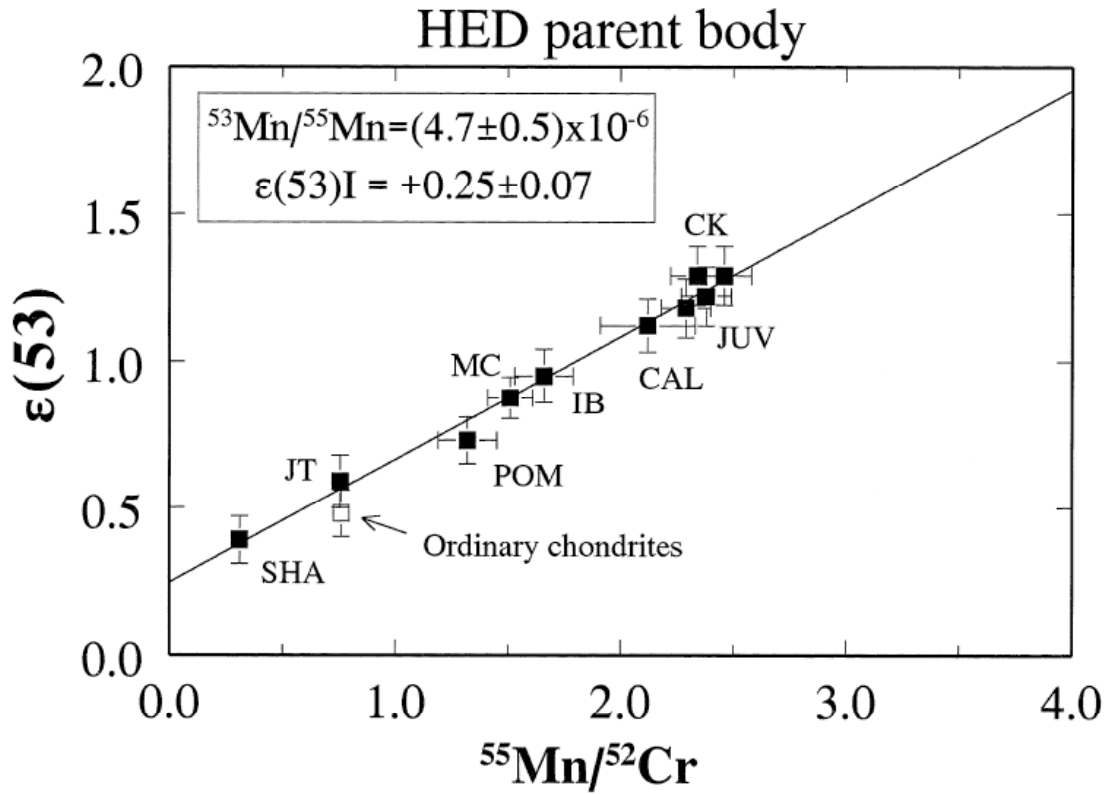


Figure 4.  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics in the Howardite-Eucrite-Diogenite (HED) parent body. Data points are whole rocks of noncumulate eucrites (CAL = Caldera; CK = Chervony Kut; IB = Ibitira; JUV = Juvinas; POM = Pomozdino), cumulate eucrites (MC = Moore County; SM = Serra de Magé) and diogenites (JT = Johnstown; SHA = Shalka). The slope of the HED whole rock isochron corresponds to a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(4.7 \pm 0.5) \times 10^{-6}$ . Figure from Lugmair and Shukolyukov (1998).

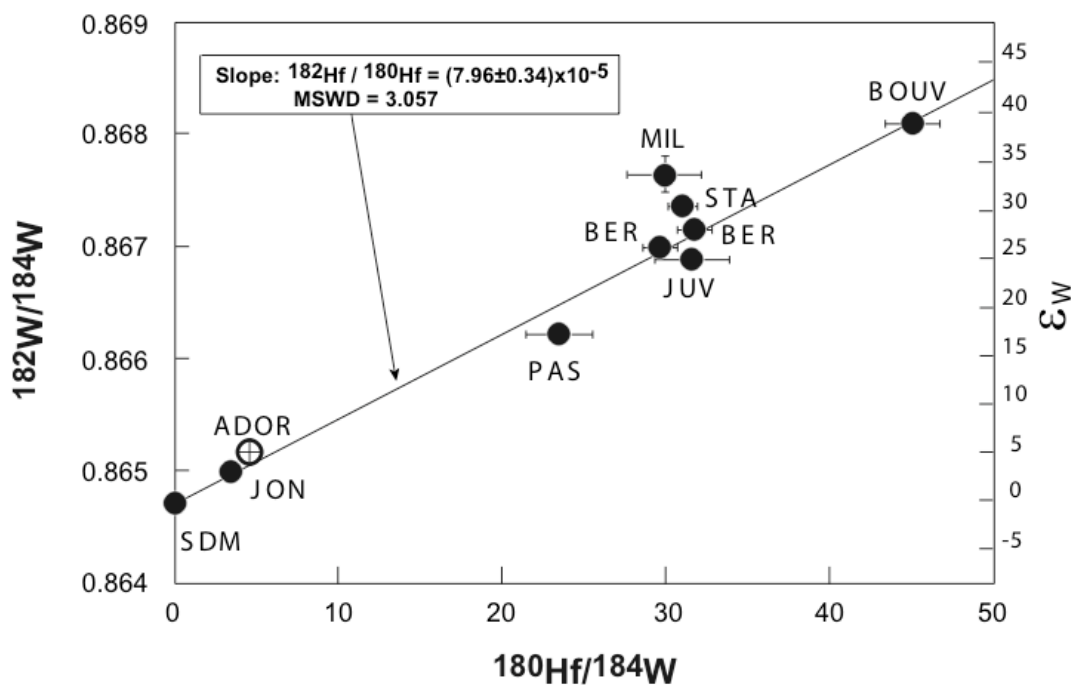


Figure 5.  $^{182}\text{Hf}$ - $^{182}\text{W}$  systematics in the Howardite-Eucrite-Diogenite (HED) parent body. Data points are whole rocks of several noncumulate eucrites (BER = Bereba; BOUV = Bouvante; JUV = Juvinas; JON = Jonzac; MIL = Millbillillie; PAS = Pasamonte; STA = Stannern) and a cumulate eucrite (SDM = Serra de Magé). Also shown is a data point for the angrite Angra dos Reis (ADOR). The slope of the HED whole rock isochron corresponds to a  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of  $(7.96 \pm 0.34) \times 10^{-5}$ . Figure from Quitté et al. (2000).

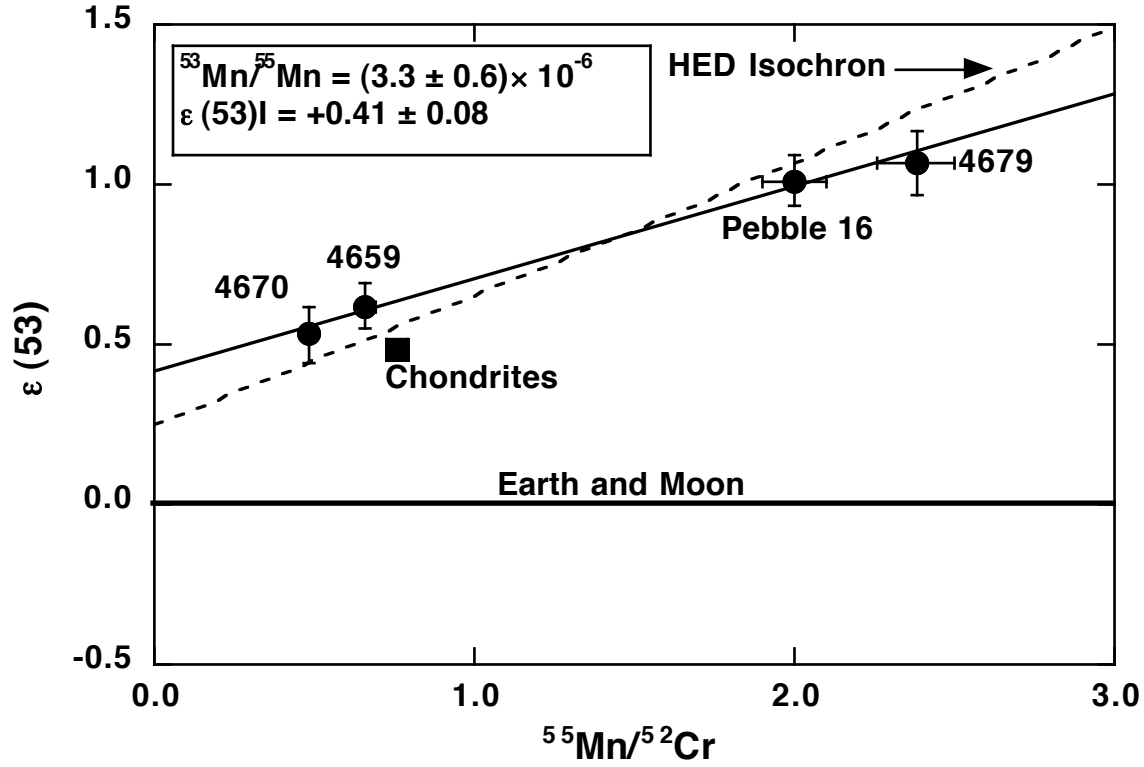


Figure 6.  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics in the parent body of the Vaca Muerta silicate clasts. Data points are whole rock fractions of two basaltic clasts (Pebble 16 and 4679) and two diagenetic clasts (4659 and 4670). For comparison, the HED bulk isochron corresponding to a  $^{55}\text{Mn}/^{53}\text{Mn}$  ratio of  $(4.7 \pm 0.5) \times 10^{-6}$  and initial  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio of 0.25  $\epsilon$  (Lugmair and Shukolyukov, 1998) is shown as the dashed line. As seen here, the data points for the VM clasts define a single isochron that has a distinctly lower slope and higher initial than the HED bulk isochron. Note that the HED and VM bulk isochrons pass marginally above the chondritic data point. Figure from Wadhwa et al. (2003).

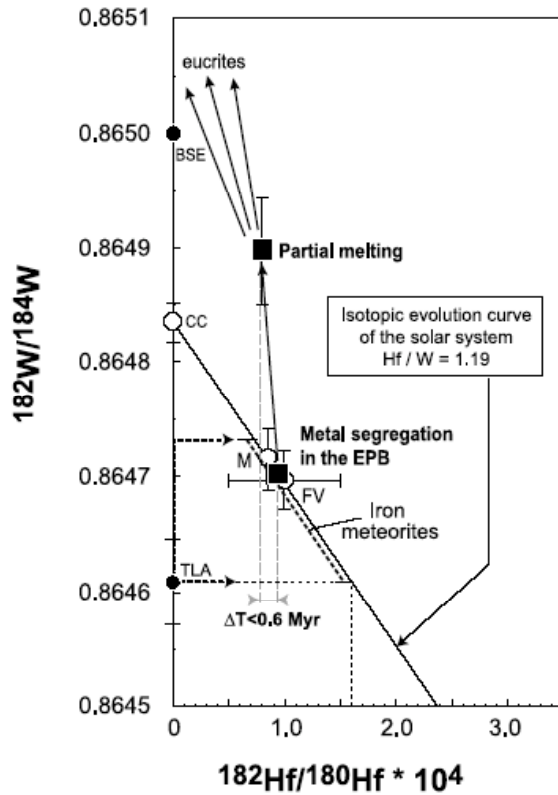


Figure 7.  $^{182}\text{Hf}$ - $^{182}\text{W}$  isotopic evolution in the HED parent body (solid arrows and black squares); early metal segregation occurs  $\sim 0.6$  Myr before global silicate differentiation. Data for chondrites are shown as the open circles (M = St. Marguerite; FV = Forest Vale); CC = carbonaceous chondrites, which are depleted by  $\sim 2$   $\epsilon$  units relative to bulk silicate earth (BSE). Dashed arrows and dashed line shows the range of W isotopic compositions of the iron meteorites, with the lowest value currently defined by the Tlacotepec (TLA) IVB iron meteorite. All W isotopic data have been renormalized relative to a terrestrial  $^{182}\text{W}/^{184}\text{W}$  standard value of 0.865000. Figure from Quitté and Birck (2004).