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Towards consistent chronology in the early Solar System: high resolution ^{53}Mn - ^{53}Cr chronometry for chondrules.

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ABSTRACT

New high-precision ^{53}Mn - ^{53}Cr data obtained for chondrules extracted from a primitive ordinary chondrite, Chainpur (LL3.4), define an initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(5.1 \pm 1.6) \times 10^{-6}$. As a result of this downward revision from an earlier higher value of $(9.4 \pm 1.7) \times 10^{-6}$ for the same meteorite (Nyquist et al. 2001), together with an assessment of recent literature, we show that a consistent chronology with other chronometers such as the ^{26}Al - ^{26}Mg and ^{207}Pb - ^{206}Pb systems emerges in the early Solar System.

Subject headings: astrochemistry — minor, planets, asteroids — nuclear reactions, nucleosynthesis, abundances — planetary systems: protoplanetary disks — solar system: formation

1. Introduction

The use of short-lived radio-nuclides as robust high-resolution chronometers in the early solar system is based on the fundamental assumption that all these radio-nuclides were initially homogeneously distributed throughout the early solar nebula. This assumption can

be rigorously tested by cross calibrating the different chronometers through acquisition of high precision isotope data in a suite of early Solar System materials suitable for this purpose.

Classically, short-lived chronometers such as the ^{53}Mn - ^{53}Cr system ($t_{1/2} = 3.7\text{Ma}$) are anchored to the absolute Pb-Pb age of $4557.8 \pm 0.5\text{Ma}$ (Lugmair & Galer 1992) for angrites LEW 86010 (LEW) and Angra dos Reis (ADOR) with the $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(1.25 \pm 0.07) \times 10^{-6}$ (Lugmair & Shukolyukov 1998). A growing number of new high precision data suggests that short-lived relative chronometers such as the ^{26}Al - ^{26}Mg system ($t_{1/2} = 0.73\text{Ma}$) are broadly consistent with the high precision long-lived ^{207}Pb - ^{206}Pb chronometer (Sanders & Taylor 2005). It has been recognized for sometime however, that there are some inconsistencies in the ^{53}Mn - ^{53}Cr chronometry (c.f. McKeegan & Davis (2003)). For example, when using the angrite age anchor (Lugmair & Shukolyukov 1998) based on the $^{53}\text{Mn}/^{55}\text{Mn}$ ratios, the chondrules of ordinary chondrites (Nyquist et al. 2001) are older than that of Ca-Al-rich inclusions (CAIs) (Amelin et al. 2002), the oldest known solid objects of our Solar System. This is opposite to what one would conclude based on ^{26}Al - ^{26}Mg and U-Pb chronometers, where most chondrules appear to be $\approx 2\text{Ma}$ younger than the CAIs (c.f. Kita et al. (2005) for a recent review). Such results could be interpreted prematurely as an argument against a chronological interpretation for short-lived radioactivity in the early Solar System and instead as favoring arguments for production of ^{53}Mn within the solar nebula and/or heterogeneous distribution of ^{53}Mn and ^{26}Al within the early solar system. The importance of this problem prompted us to revisit this issue using MC-ICP-MS to obtain high precision ^{53}Mn - ^{53}Cr data in a suite of chondrules from a primitive ordinary chondrite, Chainpur (LL3.4).

2. Samples and analytical methods

Six individual chondrules extracted from a primitive ordinary chondrite, Chainpur (LL3.4), weighing between 20-30 mg were dissolved in a mixture of HF and HNO_3 in pressurized vessels. Subsequently, dissolution in aqua regia (concentrated HCl and HNO_3 mixture in 3:1 ratio) ensures complete digestion of fluoride complexes and Cr-rich refractory phases, such as spinel. The chemical purification used for our study is adapted and refined from procedures in Birck & Allegre (1984), Lugmair & Shukolyukov (1998), Nyquist et al. (2001) and Glavin et al. (2004). First, Cr was separated from the major elements with 1N HCl by elution through cationic-exchange resin. This step was repeated twice to completely eliminate traces of major elements. Cr was further purified from other elements, in particular Ti and V, on a cation exchange resin with $\text{HNO}_3/\text{HF}/\text{HCl}$. The total yield was $\geq 90\%$. The samples were analyzed by high-resolution multi-collector inductively-coupled plasma mass

spectrometry (Nu Plasma HR MC-ICP-MS) at the University of California, Davis. The samples were introduced to the mass spectrometer via a DSN-100 desolvating nebulizer. Isobaric interferences from argon carbides and nitrides such as $^{40}\text{Ar}^{12}\text{C}$, $^{40}\text{Ar}^{13}\text{C}$, and $^{40}\text{Ar}^{14}\text{N}$ were resolved from ^{52}Cr , ^{53}Cr , and ^{54}Cr using pseudo-high resolution mode. The $^{55}\text{Mn}/^{52}\text{Cr}$ ratios were measured directly on the Nu Plasma HR in multi-collection static mode from a small aliquot of the initial dissolution and corrected against a gravimetric standard of known $^{55}\text{Mn}/^{52}\text{Cr}$ ratio. An exponential law was used to correct for mass fractionation assuming $^{50}\text{Cr}/^{52}\text{Cr}=0.051859$ (Lugmair & Shukolyukov 1998). $^{53}\text{Cr}/^{52}\text{Cr}$ is expressed as parts per 10,000 deviations relative to the terrestrial standard SRM 979 ($\epsilon^{53}\text{Cr}^*$). The total blank of the chemistry is ≤ 1 ng, which represents less than 0.1 % of the total signal and is therefore negligible.

3. New results

Mn-Cr data are presented in Table 1. Our new results show that the initial $^{53}\text{Mn}/^{55}\text{Mn}$ in Chainpur chondrules is $(5.1 \pm 1.6) \times 10^{-6}$ (Fig. 1).

Including the Chainpur whole rock data point of Nyquist et al. (2001) (pink solid square in Fig. 2) with our new chondrule data, changes the regressed slope only imperceptibly (from 5.11×10^{-6} to 5.07×10^{-6}), with the same uncertainty of $\pm 1.59 \times 10^{-6}$.

Our initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio for Chainpur is similar to the new value for Semarkona (LL3.0) chondrules, $(5.8 \pm 1.9) \times 10^{-6}$, obtained at the Johnson Space Center (JSC) (see Kita et al. (2005)). If we regress only the chondrule data of Nyquist et al. (2001) for Chainpur, we obtain $^{53}\text{Mn}/^{55}\text{Mn} = (6.9 \pm 2.0) \times 10^{-6}$, consistent within error with our new data. However, the latter value for the initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio is substantially lower than that reported by Nyquist et al. (2001) for Chainpur chondrules (LL3.4), $^{53}\text{Mn}/^{55}\text{Mn} = (9.4 \pm 1.7) \times 10^{-6}$ and barely overlaps with that obtained for Bishunpur chondrules (LL3.1), $^{53}\text{Mn}/^{55}\text{Mn} = (9.5 \pm 3.1) \times 10^{-6}$.

4. Solution to the inconsistent $^{53}\text{Mn}/^{55}\text{Mn}$ ratios

We have closely re-examined the data in Nyquist et al. (2001) and found that the high initial $^{53}\text{Mn}/^{55}\text{Mn}$ value of $(9.4 \pm 1.7) \times 10^{-6}$ for Chainpur was obtained by regression of all the chondrule data together with data from five bulk chondrites, including one whole rock Chainpur chondrite and four additional ordinary chondrites (Forest Vale-H4, Dhajala-H3-4, Arapahoe L5 and Jilin, H5) (see Fig. 2). This is stated clearly on page 925 in Nyquist et

al. (2001), “A linear least-squares fit to the data for 11 Chainpur chondrules and 5 bulk chondrites using the Williamson (1968) program gives an isochron slope... corresponding to $^{53}\text{Mn}/^{55}\text{Mn}=(9.4\pm 1.7)\times 10^{-6}$ ”. The data for Bishunpur were treated by Nyquist et al. (2001) consistently, as stated on page 926: “A linear least-squares fit to the Bishunpur data gives an isochron slope... corresponding to $^{53}\text{Mn}/^{55}\text{Mn} = (9.5\pm 3.1)\times 10^{-6}$... well within error limits of the values for Chainpur. As for the Chainpur isochron, the bulk chondrites were included in the isochron fit”. We note that there are no Bishunpur whole rock data reported in Nyquist et al. (2001). Applying the Ludwig Isoplot 3 program to the Nyquist et al. (2001) data, we obtain $^{53}\text{Mn}/^{55}\text{Mn}=(9.08\pm 2.95)\times 10^{-6}$ for Chainpur, and $(9.53\pm 3.97)\times 10^{-6}$ for Bishunpur, respectively, consistent within error to the values obtained by Nyquist et al. (2001) using the Williamson program. This agreement precludes the different data reduction algorithms as being the cause of the differences in the regressed slopes. Thus, the differences between the initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratios in our study and that of Nyquist et al. (2001) are primarily due to the inclusion of data for four other whole rock ordinary chondrites. We suggest that the approach used here by including data only for one meteorite (Chainpur) provides a more accurate assessment of the initial abundance of ^{53}Mn during chondrule formation.

5. Comparative chronology in the early Solar System

We use two absolute age anchors in Fig. 3, the high precision Pb-Pb ages of CAIs (solid red circle = 4567.2 ± 0.6 Ma) (Amelin et al. 2002) and LEW86010 (solid dark blue square = 4557.8 ± 0.5 Ma) (Lugmair & Galer 1992), respectively; the offset between the two ages is 9.4 ± 0.8 Ma. If we use instead the recently updated LEW86010 Pb-Pb age of 4558.62 ± 0.18 Ma (Amelin 2007), the age difference between the two age anchors is 8.58 ± 0.63 Ma, identical within error to the previous value.

The line joining the two age-anchor points shall be called the *Early Solar System Equiline*. The ^{53}Mn - ^{53}Cr systematics in CAIs are not well established (Papanastassiou et al. 2002). The solar system’s initial abundance of ^{53}Mn is instead obtained from bulk carbonaceous chondrites, which give a $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(8.5\pm 1.5)\times 10^{-6}$ (Shukolyukov & Lugmair 2006). We have also obtained a similar result for carbonaceous chondrites $(8.5\pm 1.2)\times 10^{-6}$ (Moynier et al. 2007). Relative to this value, our Chainpur chondrules are calculated to be 2.73 Ma younger than the CAIs (solid yellow circle in Fig. 3). Relative to the LEW/ADOR age anchor with $^{53}\text{Mn}/^{55}\text{Mn}=(1.25\pm 0.07)\times 10^{-6}$ (Lugmair & Shukolyukov 1998), our Chainpur chondrules are 7.51 Ma older (solid green square). Because of the common Pb problem, there is no high-precision Pb-Pb age available for the Chainpur chondrules (Amelin, pers. comm.). Plotted instead on the x-axis in Fig. 3 is the widely accepted younger ^{26}Al - ^{26}Mg age

for chondrules (Kita et al. 2005), 2.5 ± 1.0 Ma, relative to the CAI age anchor at 4567.2 ± 0.6 Ma (Amelin et al. 2002). Our new Chainpur data plot on the *Equiline* within the analytical uncertainty. The new JSC Semarkona chondrule data with a $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(5.8 \pm 1.9) \times 10^{-6}$ give a ^{53}Mn - ^{53}Cr age of 7.5 ± 2.1 Ma older than the LEW/ADOR anchor, consistent with the $^{26}\text{Al}/^{26}\text{Mg}$ ages of chondrules (Kita et al. 2005). In contrast, the earlier Chainpur data (Nyquist et al. 2001) with an initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(9.4 \pm 1.7) \times 10^{-6}$ would correspond to an age of 10 Ma older than LEW86010 with an uncertainty of 1-2 Ma, very similar to the time of CAI formation, but inconsistent with the ^{26}Al - ^{26}Mg age of chondrules (Kita et al. 2005). Based on the collective ^{53}Mn - ^{53}Cr , ^{26}Al - ^{26}Mg and ^{207}Pb - ^{206}Pb systematics (Nyquist et al. 2003; Wadhwa et al. 2005), the Asuka 881394 eucrite also plots on the *Equiline*; the solid purple circle is an ^{26}Al - ^{26}Mg age relative to the CAI anchor, while the open square behind it is a ^{53}Mn - ^{53}Cr age relative to the LEW/ADOR anchor. Two quenched angrites (D’Orbigny and Asuka 881371) are also plotted in Fig. 3 based on literature data (Glavin et al. 2004; Spivak-Birndorf et al. 2005; Sugiura et al. 2005; Zartman et al. 2006).

Using the latest ^{207}Pb - ^{206}Pb age of 4564.65 ± 0.65 Ma (Amelin 2007) and $^{53}\text{Mn}/^{55}\text{Mn}$ initial ratio of $(3.40 \pm 0.14) \times 10^{-6}$ (Shukolyukov & Lugmair 2007), relative to the new ^{207}Pb - ^{206}Pb age anchor of 4558.62 ± 0.18 Ma (Amelin 2007) and respective $^{53}\text{Mn}/^{55}\text{Mn} = (1.25 \pm 0.07) \times 10^{-6}$ for LEW86010 (Lugmair & Shukolyukov 1998), the angrite Sahara 99555 also plots on the *Equiline*. The very old age of 4566.18 ± 0.14 Ma reported by Baker et al. (2005) for this angrite would plot off the *Equiline* significantly. However, this age has now been updated to a value of 4564.56 ± 0.20 Ma (Bizzarro, pers. comm.), consistent with the data of Amelin (2007).

6. Conclusion

High-precision ^{53}Mn - ^{53}Cr data obtained for Chainpur (LL3.4) chondrules refine the initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio to $(5.1 \pm 1.6) \times 10^{-6}$ at the time of chondrule formation. A major discrepancy in early solar system chronology has been resolved as a result of this new study and a consistent chronology with other chronometers such as ^{26}Al - ^{26}Mg and ^{207}Pb - ^{206}Pb is now starting to emerge. ^{53}Mn - ^{53}Cr chronometry appears to be a promising tool to establish chondrule formation timescales, particularly if applied to other suitable materials from other primitive chondrites.

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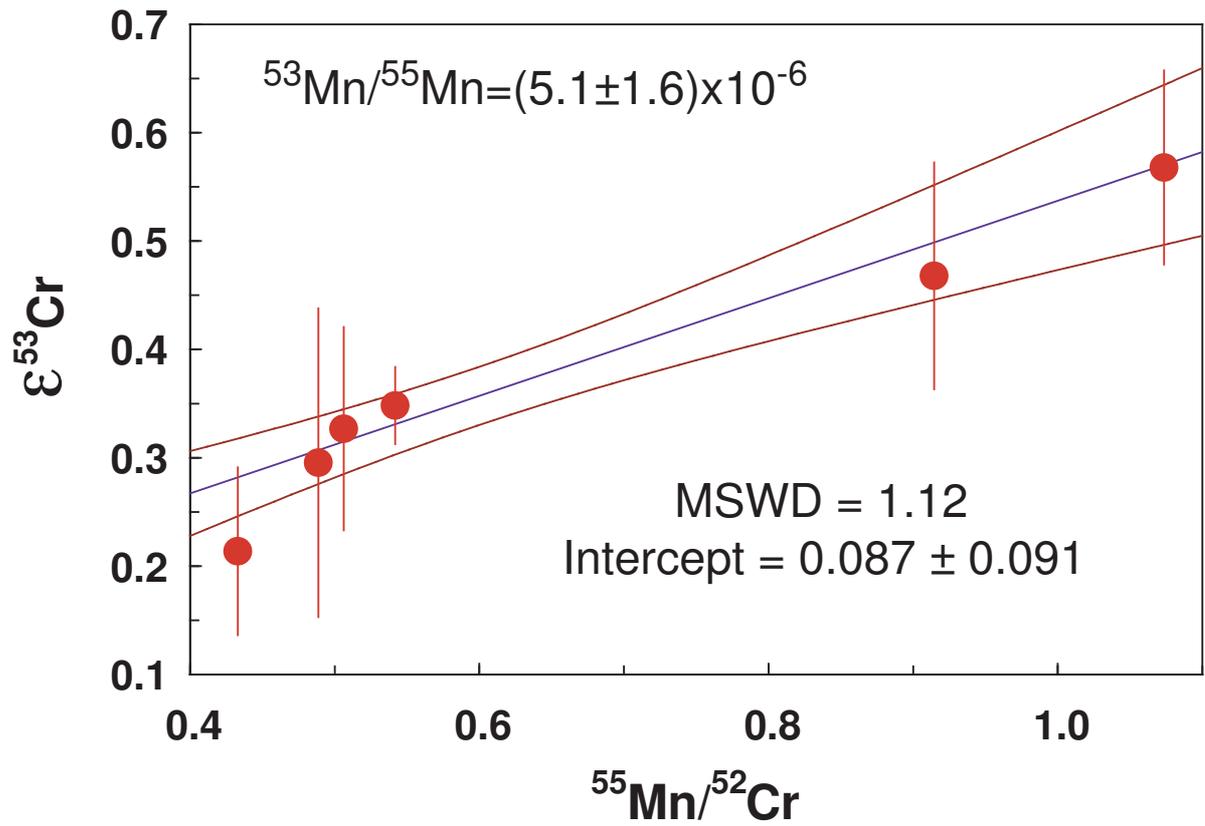


Fig. 1.— ^{53}Mn - ^{53}Cr isochron for six chondrules from the Chainpur (LL3.4) ordinary chondrites.

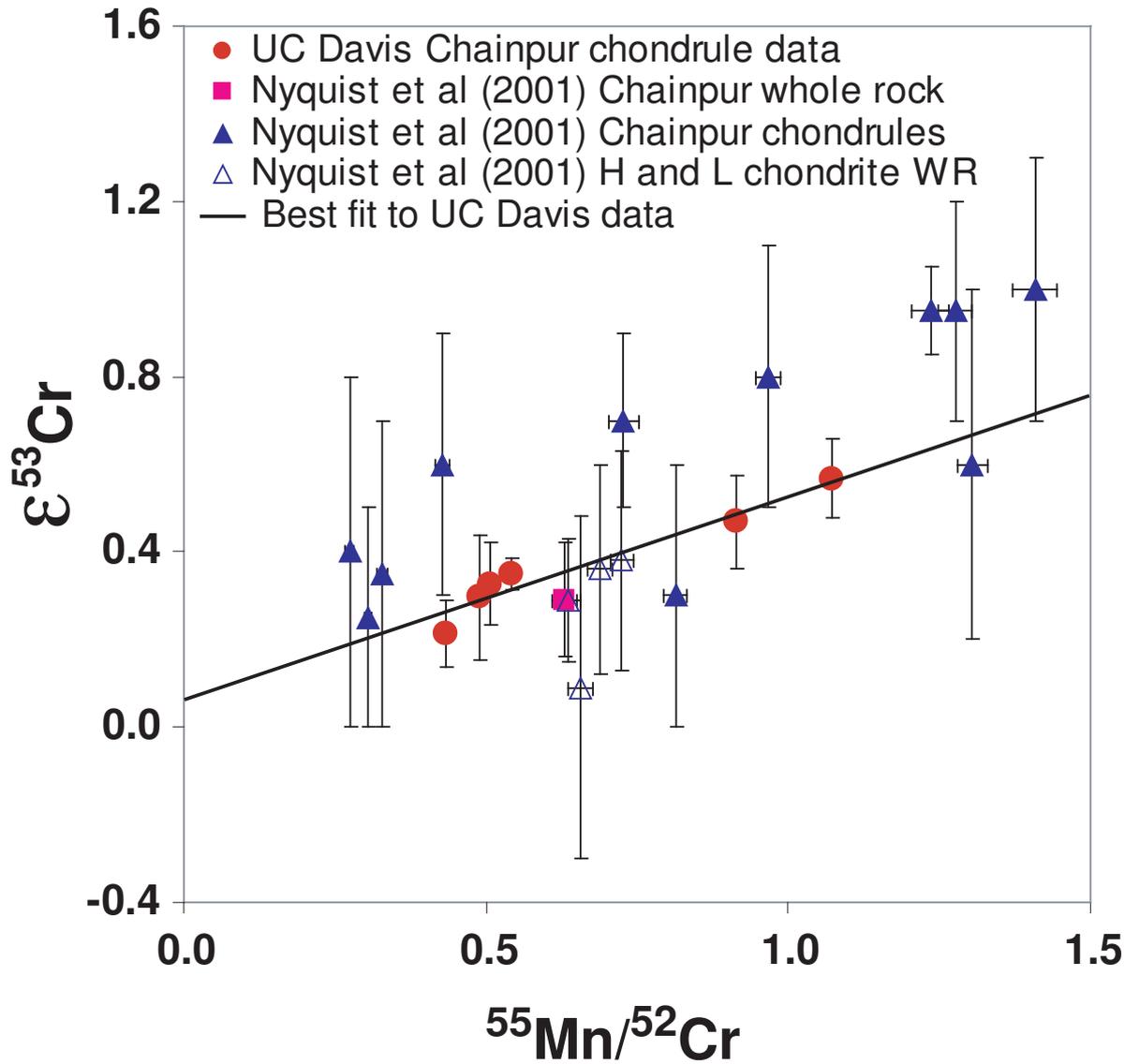


Fig. 2.— New ^{53}Mn - ^{53}Cr data from this study compared with the literature data (Nyquist et al. 2001) for Chainpur LL3.4 chondrules. Whole rock data for four bulk ordinary chondrites (open triangles) and for Chainpur (pink squares) are also shown.

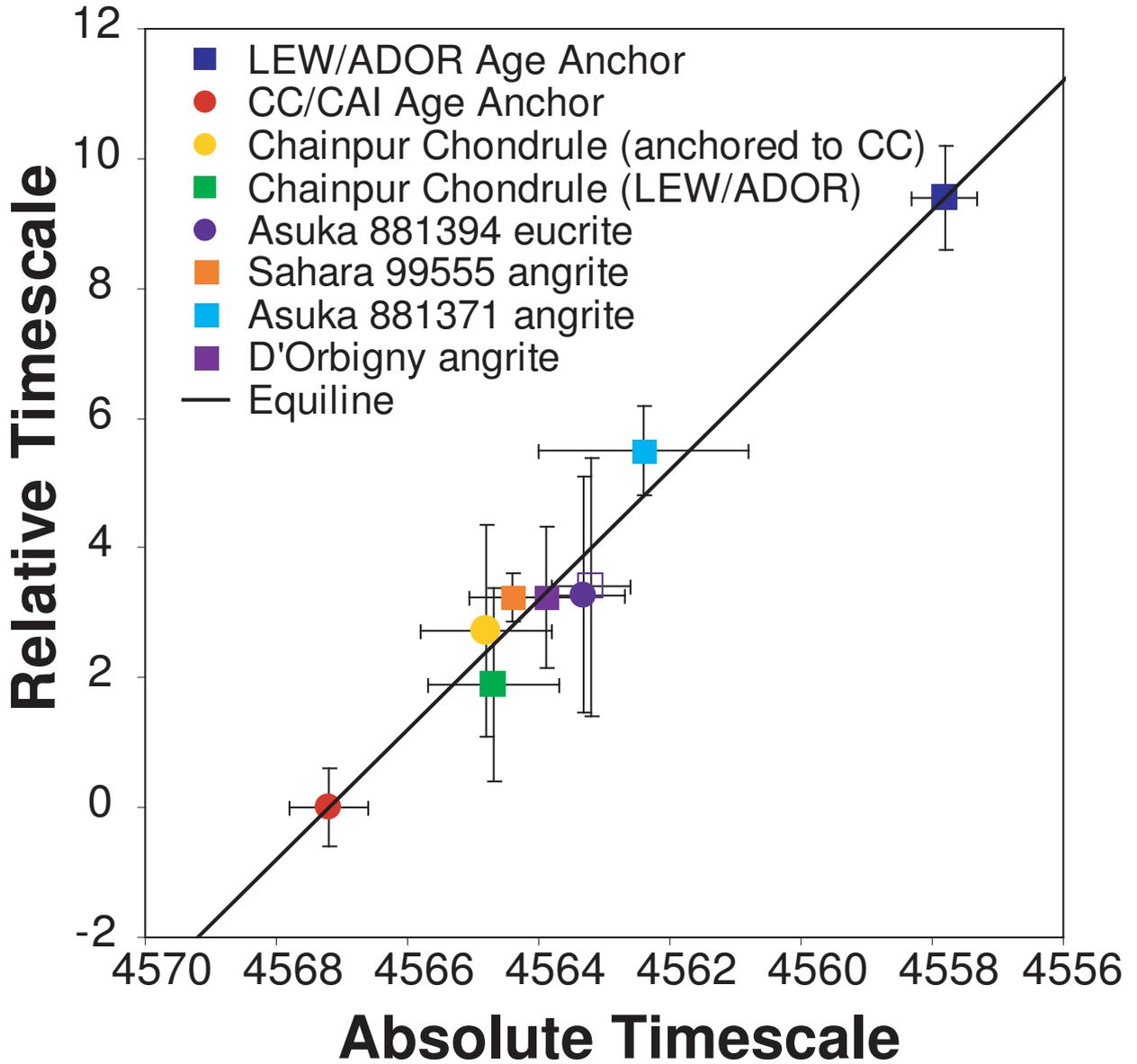


Fig. 3.— Consistent chronology of Chainpur chondrule plotting on the *Early Solar System Equiline*. The *Equiline* is drawn through the two age anchors commonly used in the early Solar System chronology (LEW86010 /Angra dos Reis and carbonaceous chondrite/CAIs). For relative ages on the y-axis, solid circles are relative to the CC/CAI anchor with $^{26}\text{Al}/^{27}\text{Al}=5 \times 10^{-5}$ or $^{53}\text{Mn}/^{55}\text{Mn} = (8.5 \pm 1.5) \times 10^{-6}$ (Shukolyukov & Lugmair 2006), solid and open squares are relative the LEW/ ADOR anchor with $^{53}\text{Mn}/^{55}\text{Mn}=(1.25 \pm 0.07) \times 10^{-6}$.

Table 1. Chainpur chondrule $^{55}\text{Mn}/^{52}\text{Cr}$ and $\epsilon^{53}\text{Cr}^*$ data.

Chainpur	$^{55}\text{Mn}/^{52}\text{Cr}$	2σ	$\epsilon^{53}\text{Cr}^*$	$2\sigma_{\text{m}}$	n^a
Chondrule 1	1.074	0.013	0.568	0.090	7
Chondrule 2	0.506	0.008	0.327	0.094	6
Chondrule 3	0.433	0.003	0.214	0.077	10
Chondrule 4	0.542	0.002	0.348	0.036	9
Chondrule 5	0.489	0.001	0.295	0.142	14
Chondrule 6	0.915	0.027	0.468	0.105	16

^a n = number of repeat measurements