

Rapid cooling of planetesimal core-mantle reaction zones from Mn-Cr isotopes in pallasites

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Abstract

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Pallasite meteorites, which consist of olivine-metal mixtures and accessory phosphates crystallised from silico-phosphate melts, are thought to represent core-mantle reaction zones of early differentiating planetesimals. Pallasite meteorites can be linked to five distinct planetesimals, indicating that they are default products of differentiation. However, their formation modes (deep, shallow, and impact environments) and age are still elusive. We have investigated the trace element and Mn-Cr isotopic signatures of Main-Group pallasite olivine, finding enhanced Mn, P and ⁵³Cr/⁵²Cr near crystal rims which indicates early ingrowth of radiogenic ⁵³Cr* in silico-phosphate melts. Mn-Cr isotopic data corroborate previous Hf-W isotopic data, indicating an early metal-silicate separation event but additionally that rapid cooling generated silico-phosphate eutectic melts with high Mn/Cr within ~2.5 to 4 Myr of Solar System formation. These melts formed before most known samples of planetesimal crusts (eucrite and angrite meteorites) and are among the earliest evolved planetary silicates. Additionally, Mn-rich phosphates in other, non-Main-Group pallasite meteorites suggest that core-mantle reaction zones are generic, datable features of differentiation.

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Introduction

The accumulated oxygen isotopic evidence for five distinct parent bodies of olivine and metal-rich pallasite meteorites (summarised in Boesenberg *et al.*, 2012) suggests that pallasitic material is the default end-product of planetesimal differentiation. Pallasites may represent samples of quiescent core-mantle boundaries (Boesenberg *et al.*, 2012), or violently formed mixtures of core and mantle materials (Yang *et al.*, 2010; Tarduno *et al.*, 2012) and are often discussed

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in terms of trapping of olivine in a liquid Fe-Ni metal groundmass progressively becoming saturated in chromite, troilite, schreibersite, and phosphate minerals during cooling (Boesenberg *et al.*, 2012). Despite this diverse mineralogy, the short-lived isotope chronologies of pallasites remain poorly understood due to depletion in crustal components (plagioclase and pyroxene; Nyquist *et al.*, 2009). The ⁵³Mn-⁵³Cr decay scheme ($t_{1/2}$ 3.7 Myr) would seem ideal for such meteorites due to the fractionation of parent and daughter between olivine (generally with high Mn/Cr) and chromite (low Mn/Cr); however, pallasite chronologies have stalled since pioneering Thermal Ionisation Mass Spectrometry (TIMS) studies (Birck and Allègre, 1988; Lugmair and Shukolyukov, 1998), with conflicting Secondary Ion Mass Spectrometry (SIMS) results having been later retracted (Huss *et al.*, 2011; Telus *et al.*, 2012). In this study, we re-investigate pallasite olivine trace elements and Mn-Cr isotopes using improved Laser-Ablation Inductively-Coupled-Plasma Mass-Spectrometry (LA-ICP-MS; Spandler and O'Neill, 2010) and SIMS (McKibbin *et al.*, 2013a) in two texturally different Main-Group pallasites: Brenham, with rounded olivines sharing equilibrated triple-junctions across a continuous network; and Brahin, with fragmental olivine of variable grain size (McKibbin *et al.*, 2013b).

Methods

Samples were cast in epoxy and polished for microbeam analysis. Trace element analyses of olivine were carried out following a previously developed LA-ICP-MS profiling method (Spandler and O'Neill, 2010). Sampling was undertaken with a 193 nm wavelength ArF Excimer laser coupled to a custom-built two-volume vortex ablation cell at RSES-ANU. An aperture was used to shape the laser beam into a rectangle, enabling high spatial resolution sampling parallel to crystal margins. Sampling of meteoritic olivine was bracketed by NIST610 and 612 glass standards, with the gas being analysed using an Agilent 7500s ICP-MS. Data were reduced according to established methods (Longerich *et al.*, 1996; Spandler and O'Neill, 2010) with NIST 612 as the primary external standard (Pearce *et al.*, 1997). For SIMS Mn-Cr analysis, we modified previous Sensitive High-mass Resolution Ion Micro Probe Reverse Geometry (SHRIMP-RG) methodology (McKibbin *et al.*, 2013a,c). Suitable areas of olivine ~30 µm in diameter were sputtered by a high current unfiltered primary ion beam (~16.9-56.6 nA mixed O⁻ and O₂⁻; McKibbin *et al.*, 2015). Ion beams of interest were directed sequentially to a single electron multiplier by cycling the magnet. For measurements in Brahin chromite (~4.0-5.5 nA filtered O₂⁻ primary ion beam), sequential collection of ⁵²Cr⁺, ⁵³Cr⁺, and ⁵⁵Mn⁺ was achieved with a single Faraday Cup. Data were reduced according to the 'first ratio estimator' method (Ogliore *et al.*, 2011) which we earlier referred to as 'ratio of total counts' (McKibbin *et al.*, 2013c). Instrumental mass fractionation was corrected by sample-standard bracketing with San Carlos olivine or in-house reference spinels. To convert ⁵⁵Mn⁺/⁵²Cr⁺ to ⁵⁵Mn/⁵²Cr, we used a Relative Sensitivity Factor (RSF) of 0.58 (±0.02) as a multiplier on olivine data. No multiplier was applied to chromite.



Results

LA-ICP-MS trace element profiles (Fig. 1 and Supplementary Information) indicate low Cr and high P and Mn concentrations near edges of pallasite olivine grains. Grain-to-grain and intra-grain variations in P and Cr are more pronounced in

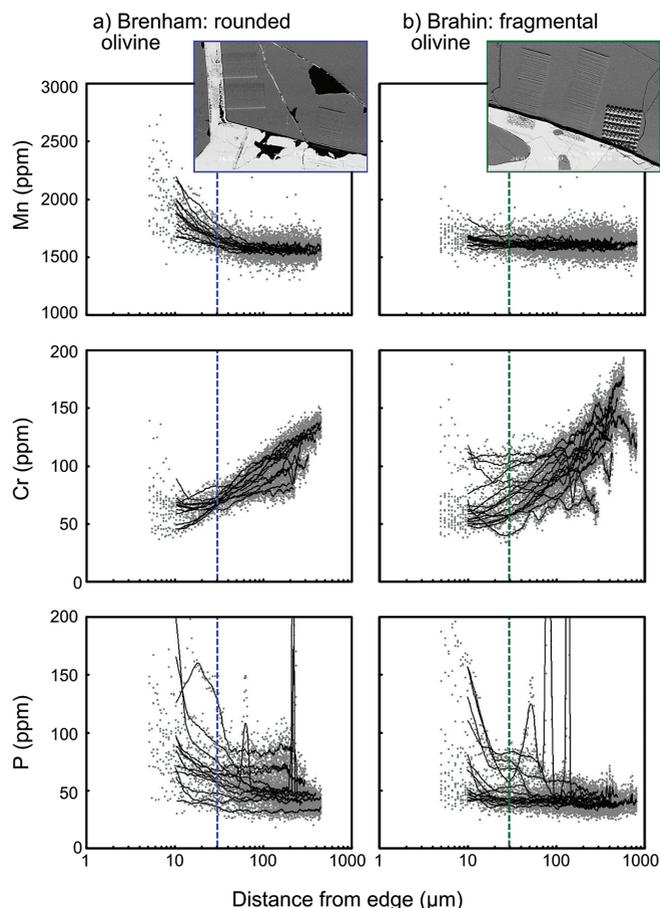


Figure 1 LA-ICP-MS trace element concentrations traverses in olivine for (a) Brenham (left panels) and (b) Brahin (right panels). Traverses were conducted from core to rim; concentrations are in parts per million by weight (ppm) and horizontal axes represent distances from olivine rims (μm). Data are represented by grey points and traverse averages are traced by solid lines. Vertical dashed lines (blue and green for Brenham and Brahin respectively) represent limit of SIMS spatial resolution ($\sim 30 \mu\text{m}$) when analysing near olivine margins. LA-ICP-MS tracks from this study and ablation pits from previous work (McKibbin *et al.*, 2013c).

rounded than in fragmental olivine, whereas Mn is very consistent. Mn and Cr variations range over a factor of ~ 2 -3 in olivine $^{55}\text{Mn}/^{52}\text{Cr}$ which ordinarily would be considered marginal for SIMS Mn-Cr dating. Nevertheless, this is well correlated with $^{53}\text{Cr}/^{52}\text{Cr}$ in the rounded olivines of Brenham (Fig. 2, blue data), while fragmental olivine exhibits more restricted $^{55}\text{Mn}/^{52}\text{Cr}$ and $^{53}\text{Cr}/^{52}\text{Cr}$ (Fig. 2, green data). Chromite has normal $^{53}\text{Cr}/^{52}\text{Cr}$ (Fig. 2 and Supplementary Information). $^{55}\text{Mn}/^{52}\text{Cr}$ and $^{53}\text{Cr}/^{52}\text{Cr}$ regression yields excessively high initial $^{53}\text{Mn}/^{55}\text{Mn}$ values, assuming *in situ* ^{53}Mn decay and that the system was closed to disturbance (Brenham: initial $^{53}\text{Mn}/^{55}\text{Mn}$ of $4.0 (\pm 1.2) \times 10^{-5}$ with sub-terrestrial initial $^{53}\text{Cr}/^{52}\text{Cr}$ at $0.11285 (\pm 0.00024)$ (2-sigma; MSWD = 0.63); Brahin: initial $^{53}\text{Mn}/^{55}\text{Mn}$ of $8.4 (\pm 4.5) \times 10^{-6}$ with initial $^{53}\text{Cr}/^{52}\text{Cr}$ of $0.11340 (\pm 0.00009)$ (2-sigma, MSWD = 0.49)).

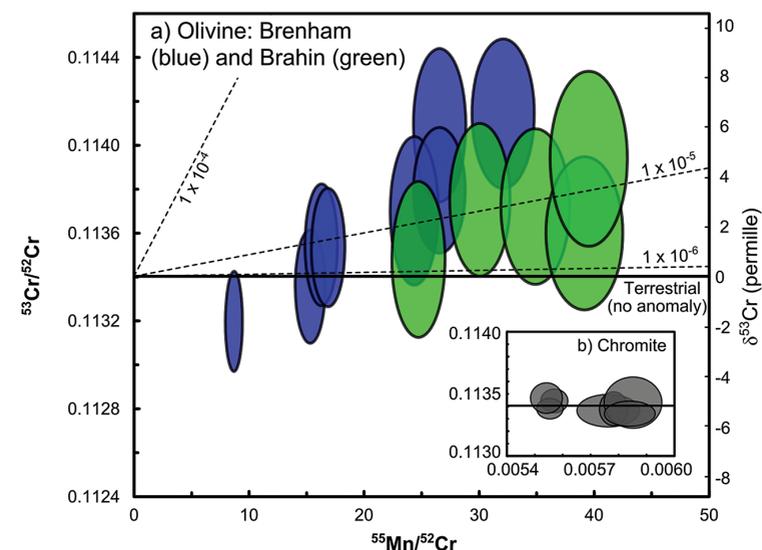


Figure 2 Mn-Cr isotopic composition of olivine and chromite from Brenham and Brahin pallasite meteorites. (a) SIMS Mn-Cr systematics for olivine from Brenham (blue ellipses) and Brahin (green ellipses) (errors are 2-sigma), and (b) Brahin chromite (data near the origin expanded in subfigure; 2-sigma errors in grey). The terrestrial Cr-isotopic composition (no anomaly) and increasing initial $^{53}\text{Mn}/^{55}\text{Mn}$ correlations are illustrated by an unbroken horizontal and inclined dashed lines respectively.

Discussion and Conclusions

The cooling history of pallasites is well recorded by late crystallising, P_2O_5 -rich accessory minerals, as well as our trace element and isotope results for olivine rims. Phosphoran olivine (with several wt. % P_2O_5) and Mg- and Si-phosphate



minerals crystallised from an unusual P₂O₅-rich silicate melt (Boesenberg *et al.*, 2012) which might ultimately be formed by oxidation of metallic P. High temperature merrillite and peritectic stanfieldite formed at or above ~1175 °C and have generally high rare earth element (REE) concentrations, while eutectic stanfieldite, farringtonite and silico-phosphate crystallised near the ~1120 °C eutectic after *in situ* fractional crystallisation (with generally lower REE concentrations; Ando, 1958; Davis and Olsen, 1991; Hsu, 2003). A parallel trend is recorded by olivine geochemistry: olivine cores exhibit variable Cr and P (Fig. 1) while divalent Mn varies over a shorter distance of several tens of micrometres, consistent with an overgrowth or rapid diffusion of divalent elements (Zhukova *et al.*, 2014a) and more slowly diffusing trivalent Cr (Ito and Ganguly, 2006) and pentavalent P (Spandler and O'Neill, 2010). However, the outermost ~30 µm of olivine crystal margins have very low Cr and steeply increasing P, recording crystallisation of olivine after cooling to the silico-phosphate eutectic (~1120–980 °C; crystallising farringtonite, stanfieldite, olivine, and probably iron and troilite as well). The occurrence of genuinely 'phosphoran' olivine rims in some pallasites, with several wt. % P₂O₅ (Boesenberg *et al.*, 2012) also indicates rapid cooling at this stage and eventual saturation of this metastable mineral.

The inferred initial ⁵³Mn/⁵⁵Mn of 4.0 (±1.2) × 10⁻⁵ for Brenham and 8.4 (±4.5) × 10⁻⁶ for Brahin are very high compared to other early Solar System materials (Birck and Allègre, 1988; Lugmair and Shukolyukov, 1998) and cannot represent fossil isochrons because they exceed or are close to the initial ⁵³Mn/⁵⁵Mn for the Solar System (9.1 (±1.7) × 10⁻⁶; Nyquist *et al.*, 2009). Small variations (~0.1 per mille) in ⁵³Cr/⁵²Cr are likely present in Brenham pallasite olivine, with slightly higher (~2 per mille) excesses in coexisting metal (Hsu, 2005; Qin *et al.*, 2010), due to cosmic ray exposure effects during transport to Earth. However, our ⁵³Cr/⁵²Cr in olivine rims are higher and inconsistent with the lower susceptibility of olivine to cosmogenic effects relative to metal (via lower Fe/Cr). Anomalies related to pre-solar, nucleosynthetic isotope components are even smaller and unlikely to survive planetary differentiation (Trinquier *et al.*, 2008; Qin *et al.*, 2010). We therefore conclude that ⁵³Cr excesses are radiogenic.

Although relatively low, ⁵⁵Mn/⁵²Cr (~10–40) implies that radiogenic Cr is unsupported by Mn, the elevated ⁵³Cr/⁵²Cr nevertheless implicates a reservoir with high Mn/Cr and indicates fractionation of Mn from Cr after significant decay, *i.e.* at least several million years after establishment of an early reservoir. The unsupported nature of Cr is inconsistent with *in situ* decay of ⁵³Mn followed by ⁵⁵Mn loss since elemental profiles indicate that, if Mn was mobile, then it migrated into olivine rather than out. Rather, association of ⁵³Cr/⁵²Cr with P suggests that ingrowth of ⁵³Cr* occurred in a high Mn/Cr silico-phosphate melt before crystallisation of olivine rims and phosphates.

High Mn/Cr in eutectic phosphates (~60–145 in Springwater and Eagle Station pallasites; Davis and Olsen 1991; Hutcheon and Olsen, 1991), probably due primarily to early chromite saturation which keeps available Cr concentrations low, indicates that the melt from which they crystallised is a good candidate

for the high Mn/Cr reservoir. Ingrowth of ⁵³Cr* in this melt requires several million years, *i.e.* an interval similar to or longer than the half-life of ⁵³Mn. Such a reservoir is modelled in Figure 3 as a function of ⁵⁵Mn/⁵²Cr and the timing of isolation from the parent body or nebula (Myr after Solar System formation) in order to find a model-dependent Mn-Cr date for this event. We assume a Solar System initial of ⁵³Mn/⁵⁵Mn of 9.1 × 10⁻⁶ (Nyquist *et al.*, 2009) and that ⁵³Mn decays completely, implying that the reservoir persists for ~10–20 Myr. The difficulties of a lower Solar System initial, such as in Trinquier *et al.* (2008), or incomplete decay of ⁵³Mn, are discussed below.

The ⁵⁵Mn/⁵²Cr of phosphates (~60–145; Davis and Olsen, 1991; Hutcheon and Olsen, 1991) and olivine rims (~25–40; this study) can be used to bracket the parental silico-phosphate melt (vertical lines in Fig. 3). Mn and Cr are generally considered to be fairly neutrally partitioned between olivine and melt (*e.g.*, Mallmann and O'Neill, 2013) although by comparison with other pallasites, Mn may have been more incompatible in olivine from the Brenham and Brahin

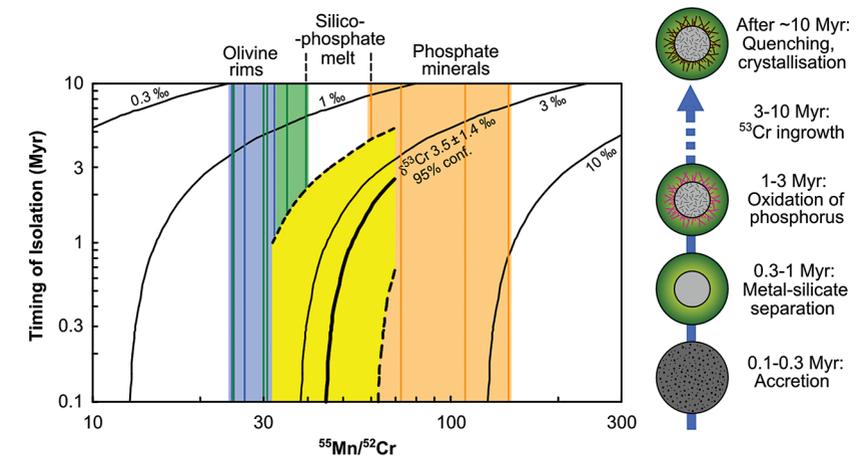


Figure 3 Model of the Mn-Cr evolution of a planetary (pallasite) reservoir as a function of ⁵⁵Mn/⁵²Cr and time of isolation from the Solar System. Hyperbolic lines indicate various ⁵³Cr/⁵²Cr compositions (in per mille). SIMS analyses for Brenham and Brahin olivine which yielded radiogenic Cr (in the ⁵⁵Mn/⁵²Cr range 20–40, blue and green respectively) and literature compositions for phosphate minerals (orange) are presented as vertical lines. A Solar System initial ⁵³Mn/⁵⁵Mn of 9.1 × 10⁻⁶ (Nyquist *et al.*, 2009), along with a conservatively estimated ⁵³Cr isotope enrichment in pallasite olivine rims of 3.5 ± 1.4 per mille and a bulk ⁵⁵Mn/⁵²Cr for late interstitial melts of 40–60 (bounded by olivine and high Mn/Cr phosphates) constrains the isolation of evolved silico-phosphate melt to before ~2.5 to 4 Myr (yellow field) followed by decay of ⁵³Mn to extinction (white field bound by olivine rims and phosphate minerals). The evolution of a planetesimal isolated from the nebula sufficiently early (*i.e.* with cooling and core-mantle redox-reactions occurring in the yellow region, before 2.5–4 Myr) is given on the right. Chronological constraints are from Mn-Cr (this study) and Hf-W data (Kruijjer *et al.*, 2014).



environment (Boesenberg *et al.*, 2012). However, Mn is compatible in phosphates, while Cr is probably incompatible (Davis and Olsen, 1991; Hutcheon and Olsen, 1991). Therefore, olivine and the various phosphates constrain their parental melt to $^{55}\text{Mn}/^{52}\text{Cr} \sim 40\text{--}60$. This melt may have occasionally been quenched to 'phosphoran olivine' under favourable conditions (Boesenberg *et al.*, 2012) in the terminal pallasite cooling event (Fowler-Gerace and Tait, 2015).

Because olivine $^{55}\text{Mn}/^{52}\text{Cr}$ is not high enough to generate detectable anomalies in-situ, Mn-Cr fractionation must occur after decay, as during crystallisation from such a silico-phosphate melt strongly enriched in Mn and hence eventually in $^{53}\text{Cr}^*$. A weighted mean of the $^{53}\text{Cr}/^{52}\text{Cr}$ for olivine rims (taking points with $^{55}\text{Mn}/^{52}\text{Cr} > 20$) gives a value of 0.11380 ± 0.00016 (95 % conf., Mean Square Weighted Deviation [MSWD] 2.4), or an enrichment of 3.5 ± 1.4 per mille. These data give a model-dependent Mn-Cr date for isolation at ~ 1 Myr after Solar System formation, with absolute upper limits of 2.5–4 Myr for a melt with $^{55}\text{Mn}/^{52}\text{Cr}$ in the range 40–60. This timescale confirms early accretion (0.1–0.3 Myr) and protracted core-mantle differentiation (to $\sim 1.1\text{--}1.3$ Myr) suggested by Hf-W chronologies for iron meteorite parent bodies (Kruijer *et al.*, 2014). Incomplete decay of ^{53}Mn , or low values of initial $^{53}\text{Mn}/^{55}\text{Mn}$ for the Solar System (Trinquier *et al.*, 2008), become difficult to accommodate. We therefore favour a higher Solar System initial $^{53}\text{Mn}/^{55}\text{Mn}$ (Nyquist *et al.*, 2009) and near complete decay of ^{53}Mn (~ 10 Myr at eutectic temperatures) for $^{55}\text{Mn}/^{52}\text{Cr}$ in the range 40–60. If isolation occurred earlier than indicated by Hf-W, then such constraints could be relaxed.

The history outlined above closely follows silicate-metal differentiation to form planetesimal cores at $\sim 1.1\text{--}1.3$ Myr after Solar System formation (Kruijer *et al.*, 2014). Elevated $^{53}\text{Cr}/^{52}\text{Cr}$ in Brenham olivine therefore indicates heating, core-mantle separation, and cooling-induced core-mantle back-reaction in the Main-Group pallasite parent body within ~ 2.5 to 4 Myr of Solar System formation. The latter requires cooling of olivine and liquid metal to the silico-phosphate and Fe-FeS eutectics around 1120–980 °C (Boesenberg *et al.*, 2012). Cooling to low-temperature eutectics therefore occurred rapidly. It suggests that even though cooling was initially fast, at perhaps $100\text{--}200 \text{ K Myr}^{-1}$, it slowed considerably at the phosphate eutectic (~ 1120 °C) and stayed near this temperature for at least several million years, allowing ingrowth of $^{53}\text{Cr}^*$ before quench-crystallisation. Trace element variations and clear charge-balancing relationships between Cr and slow-diffusing Al in olivine (McKibbin *et al.*, 2013b) indicates suppression of Cr diffusion. That Cr might move slower than divalent cations (Ito and Ganguly, 2006), and that low silica activity can suppress divalent (Zhukova *et al.*, 2014a) and trivalent cation diffusivity (Zhukova *et al.*, 2014b) suggests that in pallasites, trace element variations might not be erased at 1000 °C even over millions of years. This timescale, similar to or longer than the lifetime of ^{53}Mn , accommodates a cooling history comprising 1) rapid accretion, heating and core-mantle separation (Kruijer *et al.*, 2014); 2) rapid cooling to near-solidus temperatures followed by thermal buffering due to removal of crust, formation of regolith (Warren, 2011)

and, potentially, crystallisation reactions (Morse, 2011; Namur *et al.*, 2014); and 3) final quenching to preserve disequilibrium assemblages (Boesenberg *et al.*, 2012; Fowler-Gerace and Tait, 2015).

Isolation of late silico-phosphate melt before ~ 2.5 to 4 Myr after Solar System formation implies that it represents one of the earliest silicate differentiation products, potentially predating almost all basaltic eucrites and angrites (Wadhwa *et al.*, 2009; Schiller *et al.*, 2010; Brennecka and Wadhwa, 2012; McKibbin *et al.*, 2015; Schiller *et al.*, 2015). Early cooling of the Main-group pallasite parent body to near solidus temperatures provides further evidence for early accretion of iron meteorite-type parent bodies, distinct from later forming ureilite- and chondrite-type parent bodies (*e.g.*, Budde *et al.*, 2015). Additionally, this process appears to have been reproducible: the presence of high $^{55}\text{Mn}/^{52}\text{Cr}$ phosphate in the Eagle Station pallasite (Davis and Olsen, 1991), which originated in a different parent body in a different part of the Solar System (Clayton and Mayeda, 1996) indicates that coexisting silico-phosphate and metal-sulphide-phosphide melts could be a general feature of planetesimal differentiation. Such phosphates and associated olivine rims (potentially phosphoran) should lend themselves to dating using Mn-Cr, enabling broad-scale mapping of the ^{53}Mn extinct nuclide chronometer to other systems and constraining the timing of core-mantle separations in planetesimals.

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Additional Information

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Rapid cooling of planetesimal core-mantle reaction zones from Mn-Cr isotopes in pallasites

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Supplementary Information

The Supplementary Information includes:

- Supplementary Methods and Results
- Tables S-1 to S-5
- Figure S-1
- Supplementary Information References

Supplementary Methods and Results

The Brenham and Brahin stony-iron meteorites were selected because both have been assigned to the Main-Group of pallasites (Clayton and Mayeda, 1996) and show similar distinctive olivine trace element characteristics, belonging to a low-Mn subgroup (Boesenberg *et al.*, 2012). They likely sampled a single geological unit on the same parent body but exhibit different textural characteristics. Samples were cast into epoxy along with terrestrial reference materials and polished for *in situ* measurement of trace elements by LA-ICP-MS and Mn-Cr isotopic ratios by SIMS, the latter using Sensitive High-mass Resolution Ion MicroProbe Reverse Geometry (SHRIMP-RG).

Trace element analysis of olivine was conducted using the method developed by Spandler and O'Neill (2010). Sampling was undertaken with a 193 nm wavelength ArF Excimer laser using a second-generation custom-built 'HelEx' two-volume vortex ablation cell at RSES, ANU (Eggins *et al.*, 2003). An aperture

was used to shape the laser into a rectangle, which was aligned parallel to olivine rims for high spatial resolution sampling. The stage was driven at a rate of 1 $\mu\text{m s}^{-1}$ to enable continuous sampling across the grains, from core to rim. Sampling of meteoritic olivine was bracketed by NIST 610 and 612 standard silicate glasses. The laser was tuned to achieve energies of 50 mJ and repetition rate of 5 Hz, with ablation occurring in a He atmosphere with gas flow augmented by Ar at the ablation site and H outside the sample chamber. Spatial resolution was limited to $\sim 5 \mu\text{m}$ by the laser beam width and gas flow rates. The gas flow was directed to an Agilent 7500s ICP-MS. Various combinations of the isotopes ^7Li , ^{27}Al , ^{29}Si , ^{31}P , ^{43}Ca , ^{45}Sc , ^{47}Ti , ^{49}Ti , ^{51}V , ^{52}Cr , ^{53}Cr , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{69}Ga , ^{71}Ga were investigated in Brenham and Brahin olivine. Data were reduced according to Longerich *et al.* (1996), with ^{29}Si as the internal standard and NIST 612 as the primary external standard using the concentrations reported by Pearce *et al.* (1997). NIST 610 and BCR2g were analysed as secondary standards to check for accuracy. For Sc, we subtracted 0.2 ppm from nominal concentrations due to possible interference of $^{29}\text{Si}^{16}\text{O}^+$ on $^{45}\text{Sc}^+$ (De Hoog *et al.*, 2010). Secondary standard concentrations were reproducible to $\sim 5.2\%$ and $\sim 8.5\%$ or better for NIST 610 and BCR2g respectively, with absolute concentrations within 16% and 18% or better for all elements in each standard respectively (Table S-1). Of the investigated elements, we selected a subset for further processing and present ^{27}Al , ^{31}P , ^{45}Sc , ^{51}V , ^{53}Cr , ^{55}Mn , ^{59}Co , ^{60}Ni , and ^{71}Ga data for olivine from both meteorites (Tables S-2 and S-3 for Brenham and Brahin respectively). Each profile was smoothed using a 20-point moving average. LA-ICP-MS data for reference materials, Brenham and Brahin olivine are given in Table S-1, Table S-2, and Table S-3 respectively.

Table S-1 Secondary standard reference materials for LA-ICP-MS.

Standard	Al ₂ O ₃ (wt. %)	P	Sc	V	Cr	Mn	Co	Ni	Ga
BCR2g	14.23	1419	33.4	421.3	16.1	1523	37.6	14.0	21.3
s.d.	0.82	22	2.1	11.0	0.4	130	0.6	1.2	0.2
n	4								
GeoREM	13.4	1550	33.0	425.0	17.0	1550	38.0	13.0	23.0
s.d.	0.4	70	2.0	18.0	2.0	70	2.0	2.0	1.0
NIST 610	2.05	405.9	494.7	486.5	467.0	470.6	435.8	472.0	449.5
s.d.	0.04	6.4	25.8	18.7	1.1	23.5	9.9	1.7	1.7
n	4								
Pearce <i>et al.</i> (1997)	1.95	413	455	450	408	444	410	458.7	433

For isotopic analysis of olivine using SHRIMP-RG, we have modified our previous methodology. Rather than using a filtered primary ion beam to sputter the surface (McKibbin *et al.*, 2013a) and due to small expected Cr-isotope anomalies arising from relatively high Cr concentrations in the range ~ 50 -150 ppm (McKibbin *et al.*, 2013b), we have used a high current unfiltered primary ion beam

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Table S-2 LA-ICP-MS traverse data for Brenham olivine.

Distance (µm)	Traverse	Al27	P31	Sc45	V51	Cr53	Mn55	Co59	Ni60	Ga71	Mn/Cr
298.415	Bren-11	23.27	44.78	0.94	7.49	128.13	1572.23	4.75	13.32	0.40	12.27
297.916	Bren-11	23.84	51.62	0.92	6.78	136.28	1588.10	5.18	20.27	0.36	11.65
297.417	Bren-11	27.53	68.11	1.06	6.79	138.20	1622.51	5.16	20.47	0.29	11.74
296.918	Bren-11	26.97	71.07	1.20	6.98	131.74	1542.71	4.97	18.92	0.40	11.71
296.419	Bren-11	27.66	74.95	1.05	7.15	131.43	1552.57	5.37	16.52	0.37	11.81
295.92	Bren-11	29.42	69.03	1.22	7.23	131.78	1643.15	4.68	19.19	0.46	12.47
295.421	Bren-11	26.73	63.47	1.44	6.75	128.10	1550.99	4.95	17.85	0.42	12.11
294.922	Bren-11	26.59	65.83	0.98	6.32	130.15	1574.13	5.04	15.45	0.57	12.09
294.423	Bren-11	25.49	45.89	0.99	6.69	128.56	1577.77	5.30	13.42	0.28	12.27
293.924	Bren-11	25.28	50.78	1.07	6.85	124.17	1566.44	4.89	14.07	0.33	12.61
...											

Due to the length of this table, only the first few lines are displayed here. [Click here](#) to download the entire table in Excel.

Table S-3 LA-ICP-MS traverse data for Brahin olivine.

Distance (µm)	Traverse	Al27	P31	Sc45	V51	Cr53	Mn55	Co59	Ni60	Ga71	Mn/Cr
310.638	Brah-01	9.70	57.19	1.16	5.65	56.32	1626.22	4.53	9.54	0.18	28.87
310.067	Brah-01	10.03	58.46	1.02	5.28	58.99	1674.77	4.44	11.08	0.03	28.39
309.496	Brah-01	9.32	49.86	1.34	5.59	63.14	1702.03	4.18	11.65	0.03	26.95
308.925	Brah-01	10.10	51.03	1.11	5.32	60.87	1646.10	5.03	10.73	0.03	27.04
308.354	Brah-01	9.19	52.05	1.11	5.63	66.60	1652.35	3.93	10.07	0.14	24.81
307.783	Brah-01	9.12	42.97	1.30	5.31	57.66	1580.42	3.68	10.13	0.00	27.41
307.212	Brah-01	8.51	50.76	1.25	5.50	61.61	1626.94	3.71	11.65	0.08	26.41
306.641	Brah-01	10.26	45.27	1.12	5.46	67.95	1701.40	4.12	10.57	0.13	25.04
306.071	Brah-01	9.06	50.47	1.32	5.34	59.40	1588.54	4.46	9.31	0.03	26.74
305.499	Brah-01	9.62	53.26	1.20	5.57	62.15	1719.94	4.04	11.04	-0.03	27.68
...											

Due to the length of this table, only the first few lines are displayed here. [Click here](#) to download the entire table in Excel.

(~30 µm diameter; ~16.9-20.2 nA for Brenham and ~52.8-56.6 nA for Brahin; mixed O⁻ and O₂). Secondary ions produced during sputtering were extracted by a potential of ~10 kV and passed through narrow source and collector slits of 350 and 500 µm respectively, giving mass resolution (m/Δm, 10 % peak height) of ~6000. This mass resolution allowed separation of molecular interferences such as oxides and hydrides. Ion beams of interest were directed sequentially to a single electron multiplier by cycling the magnet. Data were first collected for ⁵²Cr⁺ and ⁵⁵Mn⁺ in 10 replicates (the first 2-3 minutes of sputtering, 2 and 1 seconds per cycle respectively) because temporal changes in observed ⁵⁵Mn⁺/⁵²Cr⁺ associated with downhole effects as sputtering proceeds can be significant (McKibbin *et al.*, 2013c). Measurements of ⁵²Cr⁺ and ⁵³Cr⁺ followed for each spot, for which 80 replicates were collected (the next ~35 minutes) and to achieve a similar number of total counts for each of these masses, we used integration times of 1 second and 10 seconds respectively. The count rate for ⁵⁵Mn⁺ was kept below ~1 Mcps to minimise wear on the electron multiplier. For SHRIMP-RG measurements in Brahin chromite, a ~4.0-5.5 nA filtered O₂⁻ primary ion beam was used to sputter the surface. Sequential collection of ⁵²Cr⁺, ⁵³Cr⁺, and ⁵⁵Mn⁺ was undertaken in 10 replicates by cycling the magnet to direct the beams into a Faraday Cup. All measurements on meteoritic and terrestrial reference materials were conducted at the same conditions. Raw terrestrial reference material ion count ratios are given in Table S-4.

Two previous studies on the Mn-Cr systematics of pallasites using small ion probes (Cameca IMS-3f) found elevated ⁵³Cr/⁵²Cr in phosphates and olivine (Hutcheon and Olsen, 1991; Hsu, 2005) and inferred initial ⁵³Mn/⁵⁵Mn values as high as 1-2 × 10⁻⁵. Huss *et al.* (2011) revised the values of Hsu (2005) using improved data reduction techniques, and did not resolve any radiogenic anomaly, although some pallasites were not well constrained and could be consistent with initial ⁵³Mn/⁵⁵Mn of ~1 × 10⁻⁵. New measurements with improved ion probes (Cameca IMS-6f and 1280) also failed to resolve ⁵³Cr* (Tomiyama *et al.*, 2007). For our measurements, SIMS data were reduced according to the 'First Ratio Estimator' method (Ogliore *et al.*, 2011) which we have earlier referred to as 'Ratio of Total Counts' (McKibbin *et al.*, 2013c). This involves summing all counts for each isotope within an analysis (⁵³Cr⁺, ⁵⁵Mn⁺), and dividing by the sum of corresponding data for the normalising isotope for that analysis (⁵²Cr⁺).

Instrumental mass fractionation (IMF) on Cr isotopes was corrected by sample-standard bracketing with San Carlos olivine (for Brenham and Brahin olivine) or in-house reference spinels (for Brahin chromite) using a two-isotope correction procedure (⁵³Cr/⁵²Cr), assuming a 'terrestrial' value of 0.1134 for the reference materials. In a previous study, we used the median of absolute deviations (MAD) from polynomial curves fit to our time-interpolated count data (McKibbin *et al.*, 2013c); this method somewhat underestimates the error and we now calculate internal spot-specific errors as the standard error on the mean of sub-ratios determined for each magnet cycle within a single analytical spot (Telus *et al.*, 2012; McKibbin *et al.*, 2015). The standard deviation of our terrestrial olivine or spinel ⁵³Cr⁺/⁵²Cr⁺ was propagated to meteoritic olivine and spinel



Table S-4 Cr-isotope data for San Carlos olivine and terrestrial spinel standards.

Analysis	PB nA	⁵² Cr+ kcps	⁵³ Cr+/ ⁵² Cr+	1-sigma
SC-3.08 (for Brenham olivine)	16.9	54.2	0.11193	0.00006
SC-3.10 (for Brenham olivine)	17.2	56.1	0.11177	0.00006
SC-3.13 (for Brenham olivine)	18	54.5	0.11186	0.00007
SC-3.15 (for Brenham olivine)	18.3	58.2	0.11190	0.00006
SC-3.16 (for Brenham olivine)	19.5	58.6	0.11180	0.00006
SC-3.17 (for Brenham olivine)	20.1	58.5	0.11174	0.00006
SC-3.18 (for Brenham olivine)	20.2	55.8	0.11188	0.00007
SC-10.04 (for Brahin olivine)	52.9	79.6	0.11182	0.00007
SC-6.06 (for Brahin olivine)	55.2	87.8	0.11171	0.00005
SC-6.07 (for Brahin olivine)	52.9	70.0	0.11171	0.00006
SC-6.08 (for Brahin olivine)	52.8	83.5	0.11170	0.00006
SC-10.05 (for Brahin olivine)	54.4	97.1	0.11151	0.00007
SC-7.06 (for Brahin olivine)	53.2	125.7	0.11173	0.00006
NewCaledonia-1.05 (for Brahin chromite)	4.9	-	0.11240	0.00004
NewCaledonia-1.06 (for Brahin chromite)	4.9	-	0.11260	0.00004
NewCaledonia-1.07 (for Brahin chromite)	4.6	-	0.11226	0.00005
NewCaledonia-1.12 (for Brahin chromite)	4.9	-	0.11255	0.00002
NewCaledonia-1.16 (for Brahin chromite)	4.7	-	0.11250	0.00013
NewCaledonia-1.20 (for Brahin chromite)	5.2	-	0.11240	0.00004
NewCaledonia-1.23 (for Brahin chromite)	4.8	-	0.11239	0.00003
NewCaledonia-1.25 (for Brahin chromite)	5	-	0.11255	0.00003
Tumut-1.08 (for Brahin chromite)	5	-	0.11266	0.00002
Tumut-1.10 (for Brahin chromite)	5.3	-	0.11251	0.00002
Tumut-1.14 (for Brahin chromite)	4.9	-	0.11259	0.00021
Tumut-1.18 (for Brahin chromite)	4.8	-	0.11261	0.00006
Tumut-1.22 (for Brahin chromite)	5.1	-	0.11269	0.00002
Tumut-1.24 (for Brahin chromite)	4.5	-	0.11245	0.00008
Tumut-1.26 (for Brahin chromite)	4.3	-	0.11247	0.00004

⁵³Cr/⁵²Cr ratios respectively. To convert the ion ratio ⁵⁵Mn+/⁵²Cr+ into the inter-element ratio ⁵⁵Mn/⁵²Cr, we use a Relative Sensitivity Factor (RSF) of 0.58 (±0.02) as a multiplier on olivine data (⁵⁵Mn/⁵²Cr = ⁵⁵Mn+/⁵²Cr+ × RSF). Olivine RSF is strongly dependent on composition; this value was determined using a range of ~Fo₉₀ olivines (McKibbin *et al.*, 2013a), which is close to that found in Main-group pallasites. We have carefully investigated whether variations in primary beam current could have induced variable instrumental mass fractionation, but lack of correlation between this instrumental parameter and our observed ⁵³Cr+/⁵²Cr+ (Fig. S-1a,c) does not indicate this to be the case. The isotopic ratio is, as perhaps expected, negatively correlated with mean ⁵²Cr+ count rate (Fig. S-1b,d).

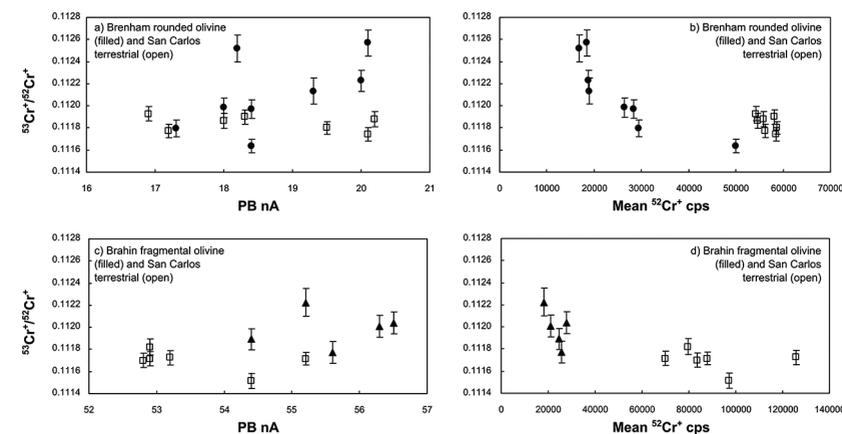


Figure S-1 Primary beam and mean ⁵²Cr+ counts per second against raw ⁵³Cr+/⁵²Cr+ ion count ratios, uncorrected for instrumental mass fractionation, for olivine from Brenham (a and b) and Brahin (c and d), with San Carlos terrestrial olivine measurements in each of their respective analytical sessions.

We did not apply an RSF to Brahin chromite and in this case took measured ⁵⁵Mn+/⁵²Cr+ to be the same as ⁵⁵Mn/⁵²Cr (RSF = 1) because chromite ⁵⁵Mn/⁵²Cr is very low and a small degree of systematic bias in this variable will not change geological interpretations. For our chromite analyses, which were run in parallel with in-house terrestrial chromites, we found that the analytical scatter for terrestrial chromites was larger than for Brahin chromite. This may be due to matrix effects associated by variable Cr, Al, Mg and Fe. However, perhaps because these compositions approximately bracketed our meteoritic chromite, the ⁵³Cr/⁵²Cr for Brahin was indistinguishable from the terrestrial ratio. Therefore, we do not propagate the excess scatter from terrestrial chromites to the Brahin chromite. It should be noted that whether or not we propagate this extra uncertainty, our geological conclusions remain the same. Reduced and fractionation corrected Mn-Cr-isotope data for meteoritic materials are given in Table S-5.



Table S-5 Cr-isotope data for meteoritic olivine and chromite.

Analysis	PB nA	⁵² Cr+ kcps	⁵⁵ Mn/ ⁵² Cr	1-sigma	⁵³ Cr/ ⁵² Cr	1-sigma
Brenham-1.31	17.3	29.5	15.47	0.53	0.11335	0.00011
Brenham-1.33	18.2	16.8	26.63	0.92	0.11409	0.00014
Brenham-1.34	18	26.5	16.42	0.57	0.11354	0.00011
Brenham-1.35	18.4	49.9	8.86	0.31	0.11320	0.00009
Brenham-1.37	18.4	28.3	17.01	0.59	0.11353	0.00011
Brenham-1.41	19.3	19.0	24.43	0.84	0.11370	0.00014
Brenham-1.42	20	18.8	26.59	0.92	0.11379	0.00012
Brenham-1.43	20.1	18.4	32.09	1.11	0.11414	0.00014
Brahin-3.01	60.5	27.7	30.10	1.07	0.11375	0.00014
Brahin-4.01	61.7	21.0	34.87	1.22	0.11372	0.00014
Brahin-4.03	60.8	25.6	24.80	0.93	0.11348	0.00014
Brahin-4.06	64.3	24.6	39.12	1.36	0.11360	0.00014
Brahin-4.07	64.6	18.4	39.48	1.37	0.11393	0.00016
BrahinChromite-1.09	5.4	-	0.00578	0.00002	0.11338	0.00006
BrahinChromite-1.11	4.8	-	0.00557	0.00002	0.11344	0.00004
BrahinChromite-1.13	5.2	-	0.00576	0.00005	0.11336	0.00005
BrahinChromite-1.15	5.2	-	0.00556	0.00002	0.11338	0.00003
BrahinChromite-1.17	5.1	-	0.00585	0.00004	0.11343	0.00008
BrahinChromite-1.19	4.4	-	0.00554	0.00002	0.11346	0.00005
BrahinChromite-1.21	4.8	-	0.00584	0.00004	0.11334	0.00004

LA-ICP-MS trace element profiles (Fig. 1 and Tables S-2, S-3) exhibit decreasing Cr and increasing P and Mn near crystal edges. P is strongly enriched in the outermost ~20-30 µm. Grain-to-grain and intra-grain variations in P and Mn are more pronounced in rounded than in fragmental olivine, whereas Cr is very consistent in the former. Olivine cores for both meteorites are characterised by Mn concentrations of ~1400-1800 ppm, increasing to ~1700-2600 at the edges of Brenham olivine but only slightly increased to ~1500-1800 for Brahin. Cr in Brenham olivine cores is ~70-150 ppm; Brahin exhibit a wider range of ~60-190 ppm. For both meteorites, Cr in olivine rims is mostly in the range ~40-80 ppm. From these LA-ICP-MS data, Mn/Cr for olivine cores varies within and between grains, at 11-22 for Brenham and 9-30 for Brahin. Both increase near edges to 25-50 and 15-40 respectively (Fig. 1). SIMS ⁵⁵Mn/⁵²Cr and ⁵³Cr/⁵²Cr are well

correlated in Brenham olivine over a range of ~9-32 and ~0.1132-0.1140 (~7 per mille variation) respectively, while for Brahin olivine they are more restricted at ~25-40 and ~0.1134-0.1139 (~4 per mille variation) respectively. Chromite was found to have low ⁵⁵Mn/⁵²Cr and normal ⁵³Cr/⁵²Cr (0.0055-0.0059 and 0.1134 ± 0.0001 respectively; 2 standard deviations; Fig. 2 and Supplementary Information). ⁵⁵Mn/⁵²Cr and ⁵³Cr/⁵²Cr regression yields excessively high initial ⁵³Mn/⁵⁵Mn values for each meteorite, assuming *in situ* ⁵³Mn decay and that the system was closed to disturbance. Brenham gives an initial ⁵³Mn/⁵⁵Mn of 4.0 (±1.2) × 10⁻⁵ with sub-terrestrial initial ⁵³Cr/⁵²Cr at 0.11285 (±0.00024) (2-sigma; MSWD 0.63). Brahin gives an initial ⁵³Mn/⁵⁵Mn of 8.4 (±4.5) × 10⁻⁶ with an initial ⁵³Cr/⁵²Cr of 0.11340 (±0.00009) (2-sigma, MSWD 0.49). SIMS Mn-Cr data are given in Table S-4. We do not regard these initial ⁵³Mn/⁵⁵Mn to be accurate because of their excessively high values and seemingly rotated isochron in the Brenham data; instead they reflect ingrowth in a different Mn-rich reservoir (a silico-phosphate melt) and subsequent crystallisation of ⁵³Cr*-rich olivine rims.

Supplementary Information References

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