Constraints on mechanisms of chondrule formation from chondrule precursors and chronology of transient heating events in the protoplanetary disk

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The mineralogy, petrography, and oxygen-isotope compositions of porphyritic chondrules—dominant chondrule type in most chondrite groups—suggest formation by incomplete melting of isotopically diverse precursors during localized transient heating events in dust-rich regions of the protoplanetary disk characterized by $^{18}$O-poor compositions ($\Delta^{17}O_{\text{dust+gas}} \sim -7\%$ to $+4\%$) relative to the inferred Sun’s value ($\Delta^{17}O \sim -28 \pm 2\%$). The chondrule precursors included Ca,Al-rich inclusions (CAIs), amoeboid olivine aggregates (AOAs), chondrules of earlier generations, fine-grained matrix-like material, and possibly fragments of pre-existing planetesimals. Like porphyritic chondrules, igneous CAIs formed by melting of isotopically diverse precursors during transient heating events, but in an isotopically distinct, solar-like reservoir of the protoplanetary disk ($\Delta^{17}O_{\text{dust+gas}} \sim -24\%$), probably near the protoSun. Based on a narrow range of the initial $^{26}$Al/$^{27}$Al ratios inferred from the internal Al-Mg isochrons in igneous CAIs, their melting started at the very beginning of Solar System formation ($t_0$), defined by the CV CAIs with U-corrected Pb-Pb age of 4567.3 ± 0.16 Ma and the canonical $^{26}$Al/$^{27}$Al ratio of $(5.25 \pm 0.02) \times 10^{-5}$, and lasted at least 0.3 Ma. The U-corrected Pb-Pb absolute and $^{26}$Al-$^{26}$Mg relative ages of porphyritic chondrules from type 3 ordinary, CO, CV, and CR carbonaceous chondrites (assuming uniform distribution of $^{26}$Al in the disk at the canonical level) suggest chondrule formation started at $t_0$ and lasted for about $4$ Ma. These observations may preclude formation of the majority of porphyritic chondrules by splashing of differentiated planetesimals and by collisions between planetesimals; instead, they are consistent with melting of dust balls by bow shocks or magnetized turbulence in the disk.

Some porphyritic chondrules in equilibrated (petrologic type 4–6) ordinary chondrites contain relict fragments of coarse-grained chromite, ilmenite, phosphates, and albitic plagioclase. The similar mineral assemblage is commonly observed in type 4–6 ordinary chondrites, but is absent in type 3 chondrites, suggesting these chondrules formed by incomplete melting of thermally metamorphosed ordinary chondrite material, possibly by impacts.

The CB metal-rich carbonaceous chondrites contain exclusively magnesian non-porphyritic chondrules crystallized from complete melts. These chondrules formed in a gas-melt plume generated by a hypervelocity ($\geq 20$ km/s) collision between planetesimals ~4.8 Ma after $t_0$ in a transition or a debris disk. One of the colliding bodies was probably differentiated.

The CH metal-rich carbonaceous chondrites contain chondrules formed by different mechanisms. The magnesian non-porphyritic chondrules formed in the CB impact plume ~4.8 Ma after $t_0$. The chemically diverse (magnesian, ferroan, and Al-rich) porphyritic chondrules formed by incomplete melting of isotopically diverse precursors in the protoplanetary disk, most likely prior the CB impact plume event.

We conclude that there are multiple mechanisms of chondrule formation that operated over the entire life-time of the disk.

Keywords: chondrules, refractory inclusions, chondrule precursors, transient heating

INTRODUCTION

Chondrules are defined as molten or partially molten silicate ± Fe,Ni-metal ± sulfide droplets once freely floating in space before being accreted to their parent bodies. We note that igneous Ca,Al-rich inclusions (CAIs) (Type A, B, C, and forsterite-bearing Type B (for classification of CAIs see MacPherson, 2014)) also satisfy this definition, and, as we argue below, provide important constraints on the earliest transient heating events that melted solids in the protoplanetary disk. Chondrule formation is one of the most important but poorly understood processes that operated in the early Solar System. Among the currently discussed mechanisms of chondrule formation are shock waves of different scale and nature (e.g., Desch et al., 2010; Morris et al., 2012), magnetized turbulence

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in the protoplanetary disk (McNally et al., 2013), and collisions between primitive or differentiated planetesimals (e.g., Krot et al., 2005a; Asphaug et al., 2011; Johnson et al., 2014; Oulton et al., 2016).

Chondrules, together with refractory inclusions (CAIs and AOAs) and fine-grained matrix, are the major components in most chondritic meteorites (Scott and Krot, 2014). The important exceptions are CI chondrites that consist almost entirely of hydrated matrix and apparently never contained significant amount of chondrules (rare chondrule fragments and a CAI were reported in CI chondrites, Leshin et al., 1997; Zolensky and Frank, 2014), and CB and CH metal-rich carbonaceous chondrites that lack matrix (Krot et al., 2002).

In unmetamorphosed chondrites, chondrules and refractory inclusions have uniform, but different oxygen-isotope compositions (Fig. 1). These differences suggest that chondrules and refractory inclusions (hereafter CAIs) originated in the isotopically and probably spatially distinct disk regions, $^{16}$O-poor planetary-like and $^{16}$O-rich solar-like, respectively. It is inferred that CAIs formed in a disk region that was exposed to irradiation by solar energetic particles, had high ambient temperature (at or above condensation temperature of forsterite, $>1300$K) and approximately solar dust/gas ratio (1/100), most likely near the protoSun (McKeegan et al., 2000a; Scott and Krot, 2014 and references therein). They were subsequently transported radially away to the accretion regions of the chondritic and cometary planetesimals (e.g., Brownlee et al., 2006; Ciesla, 2010). In contrast, chondrules are thought to have formed in relatively cold ($<1000$ K) dust-rich ($10^2$–$10^5$ × solar) regions of the protoplanetary disk (e.g., Cuzzi and Alexander, 2006; Alexander et al., 2008; Alexander and Ebel, 2012). It is not known whether chondrule formation occurred only in the inner Solar System (inside Jupiter’s orbit) or took place in the outer disk (outside Jupiter’s orbit) as well (e.g., Walsh et al., 2011; van Kooten et al., 2016).

Fine-grained matrices and chondrules appear to be chemically and isotopically complementary, suggesting their close genetic relationship—formation in the same disk region (e.g., Bland et al., 2005; Hezel and Palme, 2008, 2010; Palme et al., 2014, 2015; Ebel et al., 2016; Becker et al., 2015; Budde et al., 2016a, b). In contrast, the lack of chondrule-matrix complementarity and the origin of chondrules and matrices in different disk regions were advocated by Zanda et al. (2012). According to this hypothesis, chondrules formed near the proto-Sun, were transported over large radial distances and mixed with thermally unprocessed, primitive matrix in colder regions of the disk.

In this paper, we focus on the nature of chondrule precursor materials and the chronology of transient heating events in the protoplanetary disk. We argue that (i) chondrules formed by multiple mechanisms; (ii) chondrule formation may have started contemporaneously with CAIs and lasted the entire life-time of the protoplanetary disk; (iii) most chondrites, except CB metal-rich carbonaceous chondrites, contain multiple generations of chondrules; (iv) chondrules in CB chondrites formed in a gas-melt impact plume resulted from a collision between planetesimals ~4.8 Ma after $t_0$; (v) CH chondrites contain multiple generations of chondrules formed by different mechanisms—by crystallization of complete melts produced in the CB impact plume ~4.8 Ma after $t_0$ and by melting of isotopically diverse precursors in the disk, most likely prior to the CB plume event.

**Precursor Materials of Porphyritic Chondrules**

Coarse-grained and fine-grained chondrule precursors

In typical (not metal-rich) chondrites, most chondrules have porphyritic textures and show large variations in
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chemical compositions, allowing to distinguish magnesian (Fa or Fs < 10 mol%; type I), ferroan (Fa or Fs > 10 mol%; type II), and aluminum-rich (bulk Al₂O₃ > 10 wt%) chondrules. Porphyritic chondrules are thought to have formed by incomplete melting of solid precursors resulting in preservation of several nuclei in the chondrule melt. Porphyritic chondrules commonly contain relict grains which did not crystallize from a host chondrule melt, and, therefore, provide important constraints on the nature of chondrule precursor materials (e.g., Scott and Krot, 2014 and references therein). Relict grains in chondrules can be distinguished based on their textures, mineralogy, chemical and oxygen isotopic compositions. Based on these characteristics, coarse-grained relics (>10–100 μm) identified in porphyritic chondrules include CAIs, AOAs, fragments of chondrules of earlier generations (Figs. 2a and b), and, possibly fragments of thermally processed planetesimals (Figs. 2c and d). Most relics ferromagnesian olivine and pyroxene grains have oxygen-isotope compositions that differ from those of the host chondrule phenocrysts and mesostasis. However, oxygen-isotope compositions of most relics olivine and pyroxene grains are generally similar to those of typical chondrules suggesting their close genetic relationship: these relics grains

Fig. 2. BSE images of (a, b, d) and Mg Kα X-ray elemental map (c) of (a) ferroan porphyritic chondrule (Type II) from Y-81020 (CO), (b–d) magnesian porphyritic chondrules (Type I) from Acfer 214 (CH) and Vigarano (CV). Region outlined in “c” is shown in detail in “d”. Type II chondrule in Y-81020 consists of ferroan olivine (ol), high-Ca pyroxene (cpx), plagioclase (pl), and Fe-sulfide (sf); it contains relict magnesian olivine grains (relict ol) and an amoeboid olivine aggregate (AOA). Type I chondrule in Acfer 214 consists of low-Ca pyroxene (lpx), olivine, Fe,Ni-metal nodules (met), and fine-grained mesostasis (mes); it contains a relict CAI composed of spinel (sp), hibonite (hib) and perovskite (pv). Type I chondrule in Vigarano contains a coarse-grained olivine ± Fe,Ni-metal fragment. Olivine grains in the fragment show triple junctions with interfacial angles of ~120° (yellow arrows in “d”), indicative of granoblastic equilibrium textures. Such textures cannot be produced by crystallization from chondrule melts and require prolonged thermal annealing, most likely in an asteroidal setting (from Libourel and Krot, 2006).
are most likely fragments of chondrules of earlier generations (e.g., Jones et al., 2004; Krot et al., 2005b; Russell et al., 2005; Kita et al., 2010; Rudraswami et al., 2011; Schrader et al., 2014; Tenner et al., 2015).

Because of high dissolution rates of olivine in chondrule melts (Soulié et al., 2012), several micron-sized relict grains could have survived only in chondrules that experienced a very small degree of melting. Chondrules in CV, CR and ordinary chondrites are often surrounded by ferromagnesian silicate igneous rims, which are typically finer grained than the host chondrules (Krot and Wasson, 1995; Rubin and Krot, 1996; Krot et al., 2004a).

Oxidation states of igneous rims (Fa or Fs contents in their olivines and pyroxenes) are generally similar to those of the host chondrules, suggesting formation under similar redox conditions. These rims appear to have formed by melting of relatively fine-grained solids (<10 μm) that accreted on the surface of previously solidified chondrules (Krot and Wasson, 1995). Therefore, igneous chondrule rims provide important constraints on the nature of fine-grained chondrule precursors; they also show that individual chondrules experienced repeatable melting events to different degrees.

Nagashima et al. (2013, 2014a, 2016) described the mineralogy and oxygen-isotope compositions of ferroan igneous rims around magnesian porphyritic (type I) chondrules in Acfer 094 (ungrouped), CO, and CR carbonaceous chondrites. These rims are mineralogically and chemically similar to type II chondrules and composed mainly of ferroan olivines, sodium-rich mesostasis, and sulfides (Figs. 2a and 3). A similar ferroan igneous rim was also described around an AOA in a CO chondrite, suggesting not only type I chondrules but also AOAs were reprocessed during type II chondrule-forming events (Nagashima et al., 2015a). Ion probe (SIMS) measurements of the ferroan igneous rims around the type I chondrules in Acfer 094 revealed the presence of abundant micron-sized relict 16O-rich olivine grains, isotopically similar to those in CAIs and AOAs (Figs. 1 and 3). These observations indicate that (i) fine-grained chondrule pre-
cursors, like coarse-grained ones, were isotopically heterogeneous, and (ii) some type I chondrules were among type II chondrule precursors and, therefore, were melted under the redox conditions recorded by type II chondrules. Note that Grossman et al. (2012) predicted theoretically and Villeneuve et al. (2015) demonstrated experimentally that melting of magnesian silicates plus metal under oxidizing conditions results in formation of ferroan silicate melts, suggesting that some type I chondrules could have been transformed into type II chondrules during chondrule melting.

Relationship between fine-grained chondrule precursors and chondrite matrices

Chondrule-matrix chemical (Bland et al., 2005; Hezel and Palme, 2008, 2010; Palme et al., 2014, 2015) and isotopic (Budde et al., 2016a, b) complementarity suggests that chondrules and matrix of a chondrite group formed in the same nebular region, and as a result must have been thermally processed together.

Nagashima et al. (2015b) described the mineralogy and oxygen-isotope compositions of chondrules, a chondrule igneous rim, and matrix in the ungrouped chondrite Kakangari (Fig. 4). They found that (i) matrix olivines and low-Ca pyroxenes show a bi-modal distribution of oxygen-isotope compositions: 16O-rich solar-like and 16O-poor planetary-like (Fig. 4c). The 16O-rich matrix olivines and low-Ca pyroxenes are similar to those of low-Ca pyroxene-bearing AOAs (Krot et al., 2004b, 2005c) and most likely originated in the CAI/OA-forming region. (ii) Chondrule olivines and low-Ca pyroxenes have predominantly 16O-poor compositions, similar to the 16O-poor matrix olivines and low-Ca pyroxenes (Fig. 4b). (iii) Like Kakangari matrix, the chondrule igneous rim shows a bio-modal distribution of oxygen-isotope compositions: several micron-sized 16O-rich olivine grains are overgrown by 16O-poor olivines and pyroxenes (Figs. 4d–g). Based on these observations, Nagashima et al. (2015b) suggested that (1) the Kakangari chondrules and 16O-poor matrix olivines and low-Ca pyroxenes originated in the same reservoir, and (2) Kakangari matrix was probably one of the chondrule precursors.

Due to a fine-grained (micron-sized) nature of primitive chondrite matrices, relatively low evaporation temperatures of silicates (<1300 K at total pressure of 10⁻⁴ bar; Ebel and Grossman, 2000), and high liquidus temperatures of chondrules (~1500–2000 K), the matrix-like materials are expected to be largely vaporized and re-condensed during chondrule formation (e.g., Wasson and Rubin, 2009). Matrices in primitive carbonaceous chondrites, e.g., Acfer 094 (ungrouped) and ALH 77307 (CO3.0) are composed mainly of amorphous ferromagnesian silicates and micron-sized crystalline magnesian olivines, pyroxenes, Fe,Ni-metal and sulfides, and are interpreted to be largely products of evaporation-condensation during chondrule formation (e.g., Brearley, 1996; Greshake, 1997; Abreu and Brearley, 2010; Howard et al., 2015). However, the presence of presolar grains in primitive chondrite matrices (e.g., Floss and Stadermann, 2009; Nguyen et al., 2010; Leitner et al., 2016) indicates that not all matrix materials experienced evaporation-condensation processes. There is no agreement on the fraction of matrix materials reprocessed during chondrule formation (e.g., Huss et al., 2005 and references therein). Due to a very low abundance of presolar grains in chondrite matrices (generally less than few hundred ppm, e.g., Nguyen et al., 2010), and their efficient destruction during even mild thermal metamorphism and aqueous alteration on chondrite parent bodies (e.g., Huss and Lewis, 1995; Haenecour et al., 2015), the abundance of matrix presolar grains is difficult to use for this purpose.

If fine-grained precursors of chondrule igneous rims (Nagashima et al., 2013, 2014a, 2016) were similar to the precursors of chondrite matrices, the abundance of 16O-rich micron-sized matrix grains can be used instead. Nagashima et al. (2016) estimated that the abundance of 16O-rich grains in precursors of CR chondrules and their igneous rims was several percent. The abundances of 16O-rich grains, including CAI minerals such as spinel and fassaite, have been estimated to ~1% and ~5% in CV (Kunihiro et al., 2005) and Acfer 094 matrices (Yurimoto et al., 2008), generally consistent with those estimated from CR chondrules. The abundance of 16O-rich grains in the CR and CO matrices, however, has not been measured yet. More work on isotopic compositions of primitive chondrite matrices is needed to quantify the effects of chondrule formation on chondrite matrices.

Presence of planetesimal fragments among precursors of porphyritic chondrules

Libourel and Krot (2006) described coarse-grained olivine-metal clasts inside porphyritic chondrules from the CV chondrite Vigarano (Figs. 2c and d). Olivine grains in these clasts show triple junctions with interfacial angles of ~120⁰, indicative of granoblastic equilibrium textures requiring prolonged thermal annealing at high temperature. Since such textures cannot be produced by crystallization from chondrule melts or by thermal annealing in a chondrule-forming region characterized by a relatively low ambient temperature, Libourel and Krot (2006) concluded that these clasts represent fragments of thermally processed planetesimals that experienced either strong thermal metamorphism or igneous differentiation. Subsequently, these fragments were incorporated into chondrule precursors and experienced melting and dissolution-crystallization in chondrule melts resulting in formation of porphyritic textures. Whattam et al. (2008) experimentally reproduced porphyritic textures by melt-
Fig. 4.
Precursors of igneous CAIs

Igneous CAIs, like porphyritic chondrules, show mineralogical and isotopic evidence for formation by multistage melting of chemically and isotopically diverse dust balls during transient heating events (e.g., MacPherson, 2014 and references therein). However, in contrast to porphyritic chondrules, the precursors of these CAIs appear to have consisted only of refractory grains and inclusions of earlier generations. For example, Bullock et al. (2012) concluded that forsterite-bearing Type B (FoB) CAIs in CV chondrites formed by melting of CAIs surrounded by $^{16}$O-rich forsterite condensates. Ivanova et al. (2012) and Krot et al. (2015a) described the presence of $^{16}$O-depleted relict ultrarefractory CAIs inside $^{16}$O-rich FoB CAIs. Ivanova et al. (2015) reported the presence of ~25 relict CAIs inside a FoB CAI from a CV chondrite (Fig. 5). These observations indicate that igneous CAIs, like chondrules, recorded multiple transient heating events in the protoplanetary disk, and therefore provide important constraints on the mechanism(s) and chronology of these events.
CHRONOLOGY OF TRANSIENT HEATING EVENTS IN THE PROTOPLANETARY DISK

U-corrected Pb-Pb absolute ages of igneous CAIs and chondrules

It was recently demonstrated that CAIs show significant variations in $^{238}\text{U}/^{235}\text{U}$ ratio (Brennecka et al., 2010). Therefore, absolute dating of extraterrestrial materials with $^{207}\text{Pb}-^{206}\text{Pb}$ chronology requires measurements of their U-isotope compositions. Due to small sizes of CAIs and chondrules, these remain to be a major obstacle for their absolute dating: both U and Pb isotopes have been measured so far only in 4 CV CAIs and 1 CV chondrule (Amelin et al., 2010; Connelly et al., 2012; Huyskens et al., 2016). However, since it was found that $^{238}\text{U}/^{235}\text{U}$ ratio is only variable among CAIs and uniform in other Solar System solids (137.786 ± 0.016; Connelly et al., 2012; Brennecka et al., 2015), the absolute dating of typical chondrules (excluding chondrules with relict CAIs) requires only the measurements of lead isotopes.

The U-corrected Pb-Pb ages of 4 CAIs and 16 chondrules reported in the literature are summarized in Fig. 6a. The CV CAIs are the oldest Solar System solids dated with an age of 4567.3 ± 0.16 Ma (Connelly et al., 2012). Chondrules show a range of absolute ages, from 4567.3 ± 0.4 to 4562.5 ± 0.4 Ma (Bollard et al., 2014, 2015; Huyskens et al., 2016), suggesting that chondrule formation started nearly contemporaneously with CAIs and lasted for ~5 Myr. The early formation of chondrules is consistent with early melting events recorded by igneous CAIs. The youngest absolute age of chondrules measured is recorded by magnesian non-porphyritic chondrules from the CB chondrite Gujba. These chondrules appear to have formed in an impact-generated plume of melt and gas, possibly in a transition or a debris disk (see below). Excluding the CB chondrules, the inferred duration of chondrule formation is ~4 Myr. Since the majority of chondrules formed in the accretionary disk, 4 Myr may correspond to its life-time.

$^{26}\text{Al}-^{26}\text{Mg}$ relative ages of igneous CAIs and chondrules

$^{26}\text{Al}$ is a short-lived radionuclide that decays to $^{26}\text{Mg}$ with a half-life of ~0.707 Myr (Norris et al., 1983). The distribution of $^{26}\text{Al}$ in the protoplanetary disk, homogenous vs. heterogeneous, remains controversial (e.g.,...
Fig. 6. (a) The U-corrected Pb-Pb absolute ages of igneous CAIs and chondrules. Data from Amelin et al. (2010), Connelly et al. (2012), Bollard et al. (2014, 2015), and Huyskens et al. (2016). (b) The inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios in igneous CAIs (FUN and non-FUN) and chondrules in the least metamorphosed ordinary and carbonaceous chondrites. The $^{26}\text{Al}-^{26}\text{Mg}$ relative ages of chondrules and igneous non-FUN CAI are calculated assuming uniform distribution of $^{26}\text{Al}$ in the protoplanetary disk at the canonical level. Data from Hutchison and Hutchison (1989), Kita et al. (2000, 2012, 2013), McKeeagan et al. (2006), Kunihira et al. (2004), Jacobsen et al. (2008), Rudraswami et al. (2008), Makide et al. (2009), Larsen et al. (2011), Larsen et al. (2012), MacPherson et al. (2012), Williams et al. (2012), Holst et al. (2013), Olsen et al. (2013), Ushikubo et al. (2013), Krot et al. (2014a), Nagashima et al. (2014b, 2015c), Schrader et al. (2015), and Park et al. (2016). Two lithologies in CAI F4 have different ($^{26}\text{Al}/^{27}\text{Al}$)$_0$. Model accretion ages of LL, CO, CV and CR chondrite parent asteroids from Sugiura and Fujita (2014).
chondrites define a model isochron corresponding to \((26\text{Al}^{27}\text{Al})_0\) of \(-5.2 \times 10^{-5}\), called the canonical (Jacobsen et al., 2008; Larsen et al., 2011). The slopes of the internal Al-Mg isochrons in most CAIs from different chondrite groups (CH and CB chondrites are important exceptions) are generally consistent with the canonical value, suggesting efficient homogenization of \(26\text{Al}\) in the CAI-forming region (e.g., MacPherson et al., 2011; Kita et al., 2013; MacPherson, 2014 and reference therein). If \(26\text{Al}\) was homogenized in the protoplanetary disk at the canonical level during the CAI-forming epoch, the \(26\text{Al} - 26\text{Mg}\) systematics can be used for dating objects that formed after this homogenization, including non-FUN igneous CAI and chondrules.

In Fig. 6b, we plotted \((26\text{Al}^{27}\text{Al})_0\) inferred from the internal Al-Mg isochrons in CV and CR igneous CAIs, including FUN and non-FUN inclusions, and chondrules from the least metamorphosed ordinary (LL) and carbonaceous (Acfer 094, CR, CO, CV, CH, and CB) chondrites. The non-FUN igneous CAIs in CV and CR chondrites show a narrow range of \((26\text{Al}^{27}\text{Al})_0\) \((-4.5 \times 10^{-5})\), suggesting melting of their precursors lasted for \(\lesssim 0.3\) Myr (e.g., Kita et al., 2013). In contrast, to these “canonical” CAIs, the FUN CAIs, which are all igneous objects (Krot et al., 2014b), show a large range in \((26\text{Al}^{27}\text{Al})_0\) from \(-5 \times 10^{-5}\) to \(-5 \times 10^{-5}\). Since these variations are most likely due to \(26\text{Al}\) heterogeneity (Holst et al., 2013; Park et al., 2016), the Al-Mg isotope systematics of FUN CAIs cannot be used for their dating. We infer that melting of CAIs in the CAI-forming region started very early, possibly prior to addition of \(26\text{Al}\) to the protoplanetary disk, and lasted \(-0.3\) Myr after the canonical \(26\text{Al}/27\text{Al}\) was reached in the CAI-forming region.

All porphyritic chondrules in Semarkona (LL3.0), Y-81020 (CO3.0), Kaba (CV3.1), and Acfer 094 have resolvable excesses of radiogenic \(26\text{Mg}^{26}(26\text{Mg}^*)\) (Fig. 6b). Assuming uniform distribution of \(26\text{Al}\) in the disk at the canonical level, the inferred \((26\text{Al}^{27}\text{Al})_0\) correspond to an age difference of \(-1.5 - 3\) Myr after the canonical CAIs. In most, porphyritic chondrules in CR2-3 and CH3.0 chondrules show no resolvable excess of \(26\text{Mg}^*\), suggesting formation \(-3\) Myr after canonical CAIs. Based on the statistical analysis of the inferred \((26\text{Al}^{27}\text{Al})_0\) of several populations (generations) of porphyritic chondrules in Acfer 094, LL, CO and CR chondrites can be recognized; chondrules with the lowest \((26\text{Al}^{27}\text{Al})_0\) appear to be dominant in Acfer 094 and CR chondrites (Schrader et al., 2015).

When did formation of chondrules start, contemporaneously with CAIs as inferred from U-Pb absolute chronology (Fig. 6a) or \(-1.5\) Myr later as inferred from \(26\text{Al} - 26\text{Mg}\) relative chronology (Fig. 6b)? There is still no answer to this question. Some igneous CAIs experienced re-melting in the chondrule-forming regions (e.g., Itoh and Yurimoto, 2003; Krot et al., 2005b; MacPherson et al., 2012; Kawasaki et al., 2015). MacPherson et al. (2012) described a coarse-grained igneous CAI F4 composed of three igneous lithologies, compact Type A, Type B and Type C, from the CV carbonaceous chondrite Vigarano (see their figure 2). The inferred \((26\text{Al}^{27}\text{Al})_0\) in Type A + B and Type C lithologies are \((4.77 \pm 0.31) \times 10^{-5}\) and \((2.77 \pm 0.77) \times 10^{-5}\), respectively (Fig. 6b). The Type C lithology located in 2014 is characterized by the presence of igneous CAIs, supporting nearly contemporaneous formation of igneous CAIs and chondrules. We note, however, that no chondrules with internal Al-Mg isochrons corresponding to the canonical \(26\text{Al}/27\text{Al}\) have been described yet. As a result, it remains unclear whether this reflects the lower abundance of \(26\text{Al}\) in the chondrule-forming regions (e.g., Larsen et al., 2011; van Kooten et al., 2016) or the potential problems with Pb-Pb ages of chondrules (Kita et al., 2015).

**Accretion of Chondrite Parent Bodies and 26Al Abundance in Chondrules**

If \(26\text{Al}\) was uniformly distributed in the protoplanetary disk at the canonical level and was the major heat source of planetesimals, the initial abundances of \(26\text{Al}\) in chondrite parent bodies, and therefore, their accretion ages, can be constrained using the estimated peak metamorphic temperatures reached by these bodies (e.g., Sugiuira and Fujiya, 2014). The peak metamorphic temperatures of the ordinary, CO, CV and CR parent bodies are \(-950\text{°C}, -500-600\text{°C}, -500-600\text{°C}, \text{and} -100\text{°C}\), respectively (e.g., Huss et al., 2006 and references therein; Cody et al., 2008; Jilly et al., 2014). In Fig. 6b, we plotted the model accretion ages of LL, CO, CV and CR parent asteroids reported by Sugiuira and Fujiya (2014). A comparison between these ages and the \(26\text{Al}/26\text{Mg}\) ages of the LL, CO, CV and CR chondrules suggests that these asteroids accreted rapidly after formation of the youngest generation of chondrules. This conclusion is consistent with theoretical models of accretion through turbulent concentration (Cuazzo et al., 2010; Chambers, 2010) and streaming and gravitational instability in a dusty mid-plane (Youdin and Shu, 2002; Johansen and Klar, 2011), and the high dust/gas ratios inferred for the regions where chondrules formed (e.g., Alexander et al., 2008). It may also explain the unique chemical, isotopic, and mineralogical characteristics of known chondrite groups (e.g., Krot et al., 2014c) and the isotopic complementarity of chondrules and matrix in Allende (Budde et al., 2016b).
Transient heating events in the protoplanetary disk

CHONDRALES IN CB CHONDrites: Formation in a Gas-Melt Impact Plume

In contrast to typical carbonaceous chondrites containing predominantly porphyritic chondrules, abundant interchondrule matrix, and common CAIs, the CB metal-rich carbonaceous chondrites contain almost exclusively non-porphyritic chondrules with skeletal olivine and cryptocrystalline textures, abundant Fe,Ni-metal (sulfide nodules and irregularly-shaped, chemically zoned grains), rare CAIs, and no interchondrule matrix (Figs. 7 and 8). The CB chondrules and CAIs are texturally, mineralogically, and isotopically unique, i.e., virtually absent in other chondrite groups. Skeletal olivine chondrules are Ca- and Al-rich, and consist of forsteritic olivine, Al-rich high-Ca and low-Ca pyroxenes, and anorthitic mesostasis. Cryptocrystalline chondrules are Ca- and Al-poor, and have olivine-pyroxene-normative compositions. Both types of chondrules are magmas, but virtually Fe,Ni-metal-free (Krot et al., 2010); they have a narrow range of oxygen-isotope compositions (\( \Delta^{18}O \sim -2 \pm 1\%\); Fig. 9) and the youngest U-corrected Pb-Pb age of 4562.5 ± 0.4 Myr (Bollard et al., 2015). The majority of CB CAIs are igneous (Figs. 8c and d), isotopically uniform and \(^{16}O\)-depleted relative to CAIs in other chondrite groups (Fig. 9), and lack resolvable excess of \(^{26}Mg\)\(^*\) (Gounelle et al., 2007).

The unique characteristics of the CB chondrites and their components are best explained by an impact plume hypothesis (Campbell et al., 2001, 2002; Rubin et al., 2003; Krot et al., 2005a, 2010, 2012b, 2016a, 2016b; Dwyer et al., 2015; Fedkin et al., 2015; Oulton et al., 2015).
According to this hypothesis, hypervelocity collision (≥20 km/s) between planetesimals, possibly initiated by Jupiter’s migration (Johnson et al., 2016), produced an impact plume of melt and gas. Skeletal olivine chondrules, igneous CAIs, and Fe,Ni-metal ± sulfide nodules represent the melt fraction of the plume; zoned Fe,Ni-metal grains and cryptocrystalline chondrules condensed from the plume gas as solid and liquid condensates, respectively. The uniformly 16O-depleted igneous CAIs resulted from complete melting of possibly initially 16O-rich CAIs, followed by gas-melt interaction and oxygen-isotope exchange to a various degree in the CB impact plume (Krot et al., 2016a).

Late-stage generation of the CB impact plume suggests that the collision must have occurred between solid bodies; however, the nature of these bodies is not known. Based on the bulk chemical compositions of chondrules and metal grains in CB chondrites (Oulton et al., 2016) and thermodynamic modeling (Fedkin et al., 2015), it has been concluded that the collided bodies were a metallic asteroid and a differentiated silicate-rich body. This model, however, does not explain the whole-rock 15N-enrichment (Weisberg et al., 2001) and the presence of CAIs in CB chondrites (Krot et al., 2012b). Both seem to require involvement of a chondritic or a cometary body in the collision (e.g., Bonal et al., 2010; Krot et al., 2001, 2012b; van Kooten et al., 2016).

Accretion of the CB impact plume produced components is also poorly understood. Morris et al. (2015) suggested that they accreted on the surface of an impactor rather than forming a separate body.

Fig. 8. (a, c) Combined X-ray elemental maps in Mg (red), Ca (green) and Al (blue), (d) X-ray elemental map in Ti, and (b) BSE image of (a) skeletal olivine (SO) chondrule from Gujba, (b) cryptocrystalline (CC) chondrule from MAC 02675, and (c, d) igneous CAI from HH 237. cpx = Al,Ti-diopside; fo = forsterite; mel = melilitie; sp = spinel.
Transient heating events in the protoplanetary disk

The typical chondritic components include magnesian, ferroan and Al-rich porphyritic chondrules (Figs. 10e and f) and uniformly $^{16}$O-rich CAIs (Figs. 11c, 11d, and 12a). The CH porphyritic chondrules, like those in other carbonaceous chondrite groups, contain relict grains, including CAIs and chondrules of earlier generations. Aluminum-magnesium isotope systematics of CH porphyritic chondrules are similar to those in CR chondrules: most of them lack resolvable excess of $^{26}$Mg* (Fig. 6). In contrast to CR chondrules, the CH porphyritic chondrules are smaller and rarely surrounded by silica-bearing igneous rims, commonly observed around CR chondrules (Krot et al., 2004b). There are also some differences in O-isotope compositions of the CR and CH porphyritic chondrules (Figs. 1 and 12b). Finally, the CH porphyritic chondrules contain mineralogically and isotopically unique $^{26}$Al-poor grossite and/or hibonite-rich inclusions (Figs. 13a and b), which are and virtually absent in CR chondrites (Krot et al., 2015b; for more details, see the next section). The observations that some CH porphyritic chondrules show resolvable excess of $^{26}$Mg* suggest the presence of several generations of CH porphyritic chondrules; some of them may have predated the CB impact plume event (assuming that $^{26}$Al was uniformly distributed in the disk after the CAI-forming).

Based on the mineralogical, petrologic and isotopic characteristics of CH porphyritic chondrules, we infer that they were melted during multistage transient heating events of isotopically diverse precursors in a distinct disk region. Therefore, the CH chondrites and Isheyevo contain multiple generations of chondrules formed by different mechanisms; one of the generations resulted from the CB impact plume event.

Refractory Inclusions Melted during Formation of Porphyritic Chondrules: Evidence for a Localized Nature of Chondrule-Forming Events

The facts that relict CAIs and AOAs are found in porphyritic chondrules (Krot et al., 2006b) and that some CAIs and AOAs are surrounded by chondrule-like igneous rims (Krot et al., 2005b, 2016a, 2016b; Nagashima et al., 2015a), indicate that these refractory inclusions were thermally processed together with other chondrule precursors in the chondrule-forming regions. There are some mineralogical and isotopic differences between refractory inclusions in different chondrite groups: e.g., (i) large AOAs and coarse-grained igneous CAIs are found almost exclusively in CV chondrites (e.g., MacPherson, 2014); (ii) platy hibonite crystals (PLACs) and spinel-hibonite inclusions (SHIBs) are common only in CM chondrites (Ireland, 1988; Ireland and Compston, 1987;
Fig. 10. (a) Combined X-ray elemental map in Mg (red), Ca (green) and Al (blue) and (b) X-ray elemental map in Ni of Isheyevo (CH/CB). (c–f) BSE images of different chondrule types in Acfer 214 (CH). CH chondrites and Isheyevo contain the CB-like magnesian non-porphyritic chondrules with skeletal olivine (SO) and cryptocrystalline (CC) textures, as well as ferroan, magnesian and Al-rich porphyritic chondrules. cpx = high-Ca pyroxene; px = low-Ca pyroxene; mes = mesostasis; met = Fe,Ni-metal; ol = olivine; pl = plagioclase.
Liu et al., 2009; Kööp et al., 2016a, b); (iii) CAIs in CH chondrites are mineralogically and isotopically unique: they are very refractory (dominated by grossite, hibonite, perovskite, gehlenitic melilite, and Al-rich pyroxenes), have isotopically uniform oxygen compositions with a large range of $\Delta^{17}O$ among individual CAIs, from $\sim 35\%$ to $\sim 5\%$, and a bi-modal distribution of $^{26}\text{Al}/^{27}\text{Al}$, $\sim 5 \times 10^{-3}$ and $<5 \times 10^{-6}$ (Kimura et al., 1993; Weber et al., 1995; Krot et al., 2008). These differences can potentially allow to study the effects of chondrule formation on CAIs within a chondrite group. However, because CAIs are a minor chondritic component (Hezel et al., 2008), it is difficult to search for these effects in a large number of CAIs within a typical carbonaceous chondrite group. In contrast, the CH carbonaceous chondrites characterized by small sizes of chondrules and CAIs; as a result, each $cm^2$ sized polished section of a CH chondrite contains many CAIs that can be investigated for possible effects of chondrule melting.

Krot et al. (2015b, 2016a, 2016b) reported on the mineralogical and isotopic studies of CH CAIs, including relict CAIs in porphyritic chondrules. They found that (i) most relict CAIs in CH porphyritic chondrules are mineralogically similar to the CH CAIs showing no evidence for being affected by chondrule melting events, e.g., CAIs having uniform O-isotope compositions and surrounded by Wark-Lovering rims (Figs. 11c, 11d, 13a, and 13b). (ii) The CH CAIs unaffected by chondrule melting and the unmelted minerals in relict CAIs in CH porphyritic chondrules have similar oxygen-isotope compositions.

Fig. 11. BSE images of CAIs in CH chondrite Acfer 214. (a, b) Uniformly $^{16}O$-depleted ($\Delta^{17}O \sim 7\%$ to $\sim 5\%$) igneous CAIs surrounded igneous rims composed of Al,Ti-diopside and Ca-rich forsterite. (c, d) Uniformly $^{18}O$-rich ($\Delta^{17}O \sim 24\%$) grossite-rich CAIs surrounded by Wark-Lovering rims composed of spinel, $\pm$ hibonite, gehlenitic melilite, $\pm$ perovskite, and Al,Ti-diopside.
cpx = Al,Ti-diopside; fo = Ca-rich forsterite; grs = grossite; hib = hibonite; mel = melilite; pv = perovskite; sp = spinel.
These observations and the fact that liquidus temperatures of CAIs are lower than those of magnesian porphyritic chondrules indicate that CH CAIs were present in a region where CH porphyritic chondrules formed, but only a small fraction (~5–10%) were melted, suggesting a localized nature of the porphyritic chondrule-forming event(s).

Some relict CAIs inside CH porphyritic chondrules are texturally (igneous, spinel-rich) and isotopically (uniformly $^{16}$O-depleted) similar to the CB-like CAIs in CH chondrites (Figs. 11a, 12a, 12c, 13c, and 13d). If the uniformly $^{16}$O-depleted igneous CAIs in CHs recorded melting and isotope exchange in the CB impact plume (Krot et al., 2016a), then the CH porphyritic chondrules with the CB-like relict CAIs either postdated the impact plume event or formed during this event.

(Figs. 12a and c) and lack resolvable excess of $^{26}$Mg*. These observations and the fact that liquidus temperatures of CAIs are lower than those of magnesian porphyritic chondrules indicate that CH CAIs were present in a region where CH porphyritic chondrules formed, but only a small fraction of them (~5–10%) were melted, suggesting a localized nature of the porphyritic chondrule-forming event(s). Some relict CAIs inside CH porphyritic chondrules are texturally (igneous, spinel-rich) and isotopically (uniformly $^{16}$O-depleted) similar to the CB-like CAIs in CH chondrites (Figs. 11a, 12a, 12c, 13c, and 13d). If the uniformly $^{16}$O-depleted igneous CAIs in CHs recorded melting and isotope exchange in the CB impact plume (Krot et al., 2016a), then the CH porphyritic chondrules with the CB-like relict CAIs either postdated the impact plume event or formed during this event.

Fig. 12. Oxygen-isotope compositions of refractory inclusions and chondrules in CH chondrites. (a) There are two kinds of CH CAIs—uniformly $^{16}$O-rich surrounded by Wark-Lovering rims and the CB-like uniformly $^{16}$O-poor surrounded by igneous Al-diopside + Ca-rich forsterite rims. (b) There are two kinds of CH chondrules—the magnesian, ferroan and Al-rich porphyritic chondrules and the CB-like magnesian non-porphyritic, cryptocrystalline (CC) and skeletal olivine (SO) chondrules. The CB-like chondrules have much narrower ranges of $\delta^{17}$O values than the porphyritic chondrules. (c) Oxygen-isotope compositions of relict CAIs in CH porphyritic chondrules are similar to those of the rimmed CH CAIs showing no evidence for being melted during formation of porphyritic chondrules. (d) Oxygen-isotope compositions of CAI-bearing CH porphyritic chondrules are similar to those of CH porphyritic chondrules without relict CAIs. Data from Krot et al. (2010, 2012b, 2016a, 2016b).
Some chondrules in equilibrated ordinary chondrites (EOCs) of petrologic types 4–6 contain high abundance (up to 50 vol%) of chromite and/or Cr-spinel grains associated with albitic plagioclase (Ramdohr, 1967; Krot et al., 1993). These chondrules have Al-rich (>10 wt% Al₂O₃) bulk chemical compositions and very high Cr/Mg ratios, (180–750) × solar. Equilibrium thermodynamic calculations indicate that high Cr/Mg ratios observed in chromite-rich chondrules cannot be produced in the solar nebula and require unusual precursors (Krot et al., 1993). This is supported by the observations that no Cr-rich chondrules are known in UOCs of petrologic type 3; only small and rare chromite grains occur in type II chondrules. At the same time, chromite is a typical metamorphic mineral in EOCs, where it commonly associates with other metamorphic minerals, such as albitic plagioclase, phosphates, and ilmenite (Bunch et al., 1967; Snetsinger and Keil, 1969; Wlotzka, 2005).

The origin of chromite-rich chondrules is controversial. Wlotzka (2005) suggested chromite-rich chondrules resulted from enrichment of primary igneous spinel, commonly observed in Al-rich chondrules (Russell et al., 2000), in iron and chromium during thermal metamor-

**Fig. 13. BSE images of the (a, b) ¹⁸O-rich and (c, d) ¹⁸O-depleted relict CAIs in porphyritic chondrules in Acfer 214 (CH) and Isheyevo (CH/CB).** The relict CAIs are texturally, mineralogically, and isotopically similar to the CH CAIs surrounded by either Wark-Lovering or Al-diopside + Ca-rich forsterite igneous rims (Fig. 11) and apparently unaffected by melting during formation of porphyritic chondrules. cpx = Al,Ti-diopside; grs = grossite; hib = hibonite; mel = melilite; mes = mesostasis; met = Fe,Ni-metal; ol = olivine; pl = plagioclase; pv = perovskite; px = low-Ca pyroxene; sp = spinel.
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Phosphorus. Krot and Rubin (1993) and Rubin (2003) suggested that chromite-rich chondrules formed by impact melting of metamorphic chromite-rich precursors. The second hypothesis appears to be consistent with (i) the common presence of fine-grained chromite-plagioclase-phosphate regions in heavily shocked ordinary chondrites (Rubin, 2003), and (ii) the presence of a relict fragment composed of anhedral chromite (chr), ilmenite (ilm), troilite (tr), kamacite (km), phosphate (ph), and albitic plagioclase (pl). The mineralogy and mineral chemistry of minerals in the fragment are similar to those in metamorphosed ordinary chondrites.

Spinel in the Al-rich chondrules from OCs is often enriched in 16O relative to normal ferromagnesian porphyritic chondrules, most likely due to incorporation of CAI materials into the Al-rich chondrule precursors (Russell et al., 2000; Kita et al., 2010). If Cr-spinels in chromite-rich chondrules resulted from metamorphic Al+Mg ↔ Fe+Cr interdiffusion (Wlotzka, 2005), these spinels may have preserved 16O-rich compositions. In contrast, if chromite-rich chondrules formed by melting of EOC precursors (Krot and Rubin, 1993; Rubin, 2003), the Cr-spinels are expected to have δ18O values similar to those of bulk EOCs (Clayton et al., 1991). Oxygen-isotope measurements of Cr-spinel in chromite-rich chondrules can potentially provide a test of both hypotheses.

CONCLUSIONS

1. The mineralogy, petrography, and oxygen-isotope compositions of porphyritic chondrules suggest formation by melting, often incomplete, of isotopically diverse precursors during localized transient heating events in dust-rich regions of the protoplanetary disk characterized by 16O-poor compositions (δ17O_dust+gas ~ –7‰ to +4‰) relative to the inferred Sun’s value (δ17O ~ –28 ± 2‰). The chondrule precursors included CAIs, AOAs, fragments of chondrules of earlier generations, fine-grained matrix-like material, and, possibly, fragments of pre-existing planetesimals. The U-corrected Pb-Pb absolute and 26Al-26Mg relative ages of porphyritic chondrules from type 3 ordinary, CO, CV, CR and CH chondrites suggest chondrule formation started nearly contemporaneously with CAIs and lasted for about 4 Myr. Each chondrite group, except CB chondrites, contains multiple generations of chondrules. These observations appear to preclude formation of most porphyritic chondrules by splashing of differentiated planetesimals or by collisions between planetesimals; instead, they are consistent with melting of dust balls by bow shocks or magnetized turbulence in the protoplanetary disk.

2. In contrast to typical carbonaceous chondrites, the CB metal-rich carbonaceous chondrites contain exclusively magnesian non-porphyritic chondrules with skeletal olivine and cryptocrystalline textures. These chondrules formed in an impact generated gas-melt plume ~4.8 Ma after CV CAIs, possibly in the transition or the debris disk. The plume resulted from a hypervelocity (≥ 20 km/s) collision between planetesimals, possibly initiated by Jupiter’s migration. One of the colliding bodies was probably differentiated.

3. The CH metal-rich carbonaceous chondrites contain chondrules formed by different mechanism. The magnesian non-porphyritic skeletal olivine and cryptocrystalline chondrules having a narrow range of oxygen isotopic compositions formed in the CB impact plume.
–4.8 Ma after CV CAIs. The chemically and isotopically diverse (magnesian, ferroan, and Al-rich) porphyritic chondrules formed by incomplete melting of isotopically diverse precursors in the protoplanetary disk, most likely prior to the CB impact plume event.

4. Chromite-rich chondrules in equilibrated ordinary chondrites might have formed by melting of metamorphosed ordinary chondrite material, possibly by impacts.

5. We conclude that there are multiple mechanisms of chondrule formation that operated during the accretionary, transition, and, possibly, degrad stages of the protoplanetary disk evolution.

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