Relict chondrules in primitive achondrites: Remnants from their precursor parent bodies

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ABSTRACT

We studied the petrography, analyzed the chemical compositions, constrained the closure temperatures (via geothermometry), and determined the oxidation states of relict chondrules in Campo del Cielo (IAB iron meteorite), Graves Nunataks (GRA) 98028 (acapulcoite), and Netschaëvo (IIE iron meteorite) to constrain their formation conditions and investigate links to known meteorite groups. Despite having been thermally metamorphosed, mineral phases within relict chondrules retain information about their precursor compositions. The sizes and textures of relict chondrules, and silicate and chromite compositions indicate that Campo del Cielo, GRA 98028, and Netschaëvo had distinct parent bodies that were similar to, but different from, known chondrite groups. To determine the utility of relict chondrule sizes in thermally metamorphosed meteorites, we determined the chondrule size distributions in the LL chondrites Semarkona (LL3.00), Soko-Banja (LL4), Siena (LL5), and Saint-Séverin (LL6), and the H chondrites Clovis (no. 1) (H3.6), Kesen (H4), Arbol Solo (H5), and Estacado (H6). As expected, mean chondrule diameters increase with degree of thermal metamorphism.

We find that Campo del Cielo and GRA 98028 were reduced during thermal metamorphism, consistent with previous studies, indicating that their precursors were initially more FeO-rich than their current compositions. In contrast to previous studies, we find no evidence for reduction of silicates in Netschaëvo. Normal zoning of olivine in Netschaëvo is consistent with crystallization and suggests its silicates are near their primary FeO-contents. The presence of elongated chromite grains along olivine grain boundaries in Netschaëvo indicates formation during thermal metamorphism under oxidizing conditions. Due to the absence of reduction and the composition of chromite being distinct from that of metamorphosed H chondrites, we conclude that Netschaëvo, and by extension the IIE iron meteorites, are not from the H chondrite parent body.

1. INTRODUCTION

Primitive achondrites and partially differentiated meteorites have been thermally modified since accretion, but did not melt completely. As a result, the study of primitive achondrites and partially differentiated meteorites, and their precursors, is paramount to understanding the earliest stages of asteroidal differentiation (e.g., McCoy et al., 1996; Bogard et al., 2000; Benedix et al., 2005). Relict chondrules in meteorites provide an invaluable opportunity to investigate both the range of thermal metamorphic processes that modified asteroids and the compositions of their precursors. Relict chondrules are chondrules that were subjected to thermal metamorphism that was extensive enough to modify their morphologies and compositions but not so extensive as to make them unrecognizable. In meteorite groups with both unequilibrated and equilibrated members, such as the ordinary chondrites, the initial precursor materials are preserved in unmetamorphosed samples, while relict chondrules are used as indicators of degree of thermal metamorphism in equilibrated members. However, in meteorite groups without unequilibrated members relict chondrules provide the best indication of the nature of their precursor material.

Relict chondrules have been observed in several primitive achondrite groups and silicate-bearing iron meteorites (e.g., Olsen and Jarosewich, 1971; Bild and Wasson, 1977; Yanai and Kojima, 1991; McCoy et al., 1996; Benedix et al., 1998; Rubin, 2006; Schrader et al., 2010; Gardner-Vandy, 2012; Van Roosbroek et al., 2012; 2013; 2015; 2016). While relict chondrules have been identified in the winonaites Dhofar 1222, Pontlyfni, Mount Morris, Northwest Africa (NWA) 725, NWA 1052, and NWA 1463 (Benedix et al., 1998; Rubin, 2006; 2007; Greenwood et al., 2012), none have been reported in the related IAB iron meteorites (e.g., Benedix et al., 2000; Tomkins et al., 2013; Ruzicka, 2014). Relict chondrule-bearing acapulcoites include Allan Hills (ALH) 77081, Graves Nunataks (GRA) 98028, Monument Draw, and Yamato (Y) 74063 (Schultz et al., 1982; Yanai and Kojima, 1991; McCoy et al., 1996; Rubin, 2007). Relict chondrules have also been noted in the IIE iron meteorites Netschaëvo (Olsen and Jarosewich, 1971; Bild and Wasson, 1977) and Mont Dieu (Van Roosbroek et al., 2012; 2013; 2015; 2016).

The parent asteroids of the winonaite–IAB iron meteorites, the acapulcoites, and the IIE iron meteorites have varied metamorphic histories. It has been proposed that the winonaite–IAB parent body underwent partial melting (Wlotzka and Jarosewich, 1977) and incomplete differentiation, during which it was catastrophically disrupted and re-accreted (Benedix et al., 2000). A study of winonaite and silicate-bearing IAB iron meteorites determined that while their two-pyroxene closure temperatures (900–1200°C) were higher than those determined via olivine-spinel geothermometry (590–700°C), the oxygen fugacity stayed relatively constant although modest reduction likely occurred during cooling (Benedix et al., 2005). Closure (i.e., equilibration) temperatures also varied between samples, indicating heterogeneous heating on the centimeter scale, which was attributed to the catastrophic breakup and reassembly of the winonaite–IAB parent asteroid (Benedix et al., 2005). The acapulcoites have been argued to form via internal thermal metamorphism and/or heating via impacts (McCoy et al., 1996; Rubin, 2007). The cause of the partial differentiation of the IIE parent body is also complex; it has been suggested that internal heating led to partial melting and differentiation ~4.5 Gyr ago, followed by localized impact heating ~3.6 Gyr ago (Bogard et al., 2000).

Chondrule formation conditions and precursors vary between chondrite groups (e.g., Rubin, 2010; Berlin et al., 2011; Jones, 2012). Depending on the degree of thermal metamorphism relict chondrules may retain indicators of their initial formation conditions and compositions. We conducted a study of a chondrule-bearing primitive achondrite (i.e., acapulcoite) and two silicate-bearing iron meteorites (IIE and IAB) to determine (1) any similarities with, and/or genetic links to, known chondrite groups, and (2) their oxidation histories during cooling.

2. ANALYTICAL PROCEDURE

2.1. Mineralogy and petrology

Thin sections of Campo del Cielo USNM 5615-2 (IAB iron meteorite), GRA 98028,1 (acapulcoite), and Netschaëvo USNM 494-1 (IIE iron meteorite) were initially characterized via optical microscopy to identify relict chondrules (Electronic Annex 1;

EA-1). Backscattered electron (BSE) image collection and mineral identification via energy dispersive X-ray spectroscopy (EDS) were conducted on an FEI Nova NanoSEM 600 scanning electron microscope (SEM) at the Smithsonian Institution (SI) National Museum of Natural History, Department of Mineral Sciences. Modal abundances of select mineral phases were measured within each thin section by pixel (i.e., point) counting (n.b., area % determined by point counting is equivalent to volume %; Eisenhour, 1996).

Chondrule diameters in thin sections and polished mounts were determined using Adobe Photoshop® by measuring chondrules in full section BSE images and X-ray element maps (Figure EA-2, Table 1 and EA-3). Chondrule diameters were measured in the following sections: Campo del Cielo USNM 5615-2, GRA 98028,1, Netschaëvo USNM 494-1, Semarkona USNM 1805-17 (LL3.00), Soko-Banja USNM 3078-1 (LL4), Siena USNM 3070-3 (LL5), Saint-Séverin USNM 2608-3 (LL6), Clovis (no. 1) ASU 168_A_2 (H3.6), Kesen ASU 362_C_1 (H4), Arbol Solo ASU 1046_C_1 (H5), and Estacado ASU 44_A_4 (H6). Sections of witnessed falls were selected when possible. BSE images and X-ray element maps were obtained with the SEM at SI (Campo del Cielo, GRA 98028, and Netschaëvo; LL chondrites from Schrader et al., 2016), and the Cameca SX-100 electron probe microanalyzer (EPMA) at the University of Arizona (UA) for the H chondrites. Mean chondrule diameters were determined by measuring both the major and minor axes of each chondrule, and group means, standard deviations (σ), and standard error of the mean (SE) were determined from these average diameters (Table 1).

The major element abundances within olivine, pyroxene, plagioclase, chromite, metal, and sulfide were measured with a JEOL 8900 Superprobe EPMA at SI. Additional silicate analyses of Campo del Cielo were obtained on the EPMA at UA. Polished and carbon-coated thin sections were analyzed with a focused beam by individual point and line-scan measurements (operating conditions: 15kV and 20 nA). A ZAF correction method (a Phi-Rho-Z correction technique; Armstrong, 1988) was used, and peak and background counting times were varied per element to optimize detection limits. Only stoichiometric silicate analyses with totals between 98.0–102.0 wt.%, chromite analyses with totals between 97.0–102.0 wt.%, and Fe,Ni-metal and sulfide analyses with totals

between 98.0–102.0 wt.% were retained; standards and detection limits are listed in Tables 2–4.

2.2. Thermodynamic calculations

Closure temperatures were calculated for relict chondrules and surrounding matrix using the olivine-spinel and two-pyroxene geothermometers for suitable mineral pairs (Table EA-4). Compositional analyses were performed via EPMA at the edges of mineral pairs to determine closure temperatures, although mineral grains used for these analyses were homogeneous. Olivine-spinel temperatures were determined from co-existing olivine-chromite pairs using an Excel version of the MELTS calculator (Sack and Ghiorso, 1991a; 1991b). Two-pyroxene temperatures were determined from co-existing low-calcium (LCP) and high-calcium pyroxene (HCP) mineral pairs using the QUILF program (Anderson et al., 1993). Each temperature was determined at a pressure estimate of 1 bar; which is a reasonable approximation for asteroids (e.g., Benedix et al., 2005; Gardner-Vandy et al., 2013). Pyroxene projections, including minor elements, were computed using QUILF using wt.% oxide data for each pyroxene pair (e.g., Lindsley, 1983). Temperature estimate uncertainties are approximately $\pm 50^{\circ}\text{C}$ (1 sigma, 1σ) for olivine-spinel temperatures (e.g., Benedix et al., 2005), and are determined for each mineral pair directly by QUILF for two-pyroxene temperatures (from $\pm 14^{\circ}\text{C}$ to $\pm 304^{\circ}\text{C}$, 1σ ; Tables 3, 4, and EA-4).

The corresponding oxygen fugacity ($f\text{O}_2$) was calculated at the appropriate closure temperature for each mineral pair. If multiple mineral pairs were present and their closure temperatures were within 2σ of each other, weighted mean temperatures were obtained to minimize uncertainties. The $f\text{O}_2$ for olivine-chromite pairs were determined from the quartz-iron-fayalite (QIFa) buffer reaction, while the $f\text{O}_2$ for two-pyroxene pairs were determined from the quartz-iron-ferrosilite buffer reaction (QIFs). In practice, the relevant reaction may be $\text{FeSiO}_3 + \text{Fe} + \frac{1}{2} \text{O}_2 = \text{Fe}_2\text{SiO}_4$, but is simplified here to calculate the $f\text{O}_2$ at each closure temperature. The reaction equations utilized are:

and

The $f\text{O}_2$ for each reaction is determined via the following equations (for simplicity, Fe_2SiO_4 is expressed as Fa and FeSiO_3 is expressed as Fs):

$$\log(f\text{O}_2) = \log(a_{\text{Fa}}) - \log K_1 - 2\log(a_{\text{Fe}}) - \log(a_{\text{SiO}_2}) \quad (3)$$

and

$$\log(f\text{O}_2) = 2\log(a_{\text{Fs}}) - \log K_2 - 2\log(a_{\text{Fe}}) - 2\log(a_{\text{SiO}_2}) \quad (4)$$

Equations 1 and 3 correspond to the QIFa buffer reaction, while equations 2 and 4 correspond to QIFs. The online MELTS calculator (<http://melts.ofm-research.org/CalcForms/index.html>) was used to obtain the activity of fayalite (a_{Fa}) and ferrosilite (a_{Fs}) (Sack and Ghiorso, 1989; Hirschmann, 1991). The Fe content of Fe,Ni-metal was used to obtain the Fe activity (a_{Fe}). Following Benedix et al. (2005), we assume a silica activity (a_{SiO_2}) of 0.9 for the three-component system metal-olivine-LCP. The HSC 7.0 Chemistry Reaction Equation module was used to obtain the temperature dependent equilibrium constant (K) for each reaction at 1 bar; the equilibrium constants (e.g., K_1 and K_2) can also be determined from equations given in Gardner-Vandy et al. (2013). Each $f\text{O}_2$ was then referenced to the iron-wüstite (IW) buffer, which was also determined using HSC Chemistry. While Fe,Ni-metal was not observed in the thin section of Campo del Cielo USNM 5612-2, Choi et al. (1995) reported the Fe,Ni-metal composition of silicate inclusions in Campo del Cielo to be ~7.13 wt.% Ni; allowing an estimate of the a_{Fe} to be ~0.93 in contrast to 0.91 used by Benedix et al. (2005). However, the resultant differences in $f\text{O}_2$ between using a_{Fe} of 0.93 or 0.91 are negligible.

3. RESULTS

Locating and identifying relict chondrules in equilibrated meteorites can be difficult, but is possible with petrographic techniques. Identifying relict chondrules from recrystallized matrix in a thermally metamorphosed meteorite based on chemical

composition of silicates alone is improbable. This is because even in unequilibrated chondrites, the major and minor element compositions of silicate grains in the matrix and in chondrules are indistinguishable (e.g., Frank et al., 2014; Schrader et al., 2015). Following thermal metamorphism and chemical equilibration, identifying major and minor element differences in recrystallized matrix and relict chondrules is even more unlikely. Typically, barred olivine (BO) and radial pyroxene (RP) chondrules are the most easily observed relict chondrules as they have textures distinct from recrystallized matrix (e.g., Benedix et al., 1998; Gardner-Vandy et al., 2013). However, only searching for these textural types imposes a bias, as porphyritic chondrules are the most abundant chondrite type. Porphyritic chondrules range in abundance from 84% in L chondrites to >99% in CK chondrites (Jones, 2012), and therefore should be the most abundant type of relict chondrule. In contrast, the abundance of BO chondrules is lowest in EH chondrites at 0.1%, and highest in the CV chondrites at 6% (Jones, 2012). Radial pyroxene chondrules range in abundance from 0.2% in CV chondrites to 13% in EH chondrites (Jones, 2012). The lower abundance of easily identifiable chondrule textures (i.e., BO and RP), is why we primarily identified relict chondrules discussed here using the distinct grain sizes of their silicates and their opaque mineral abundances compared to those of the surrounding matrix (e.g., Fig. 1; e.g., Benedix et al., 1998).

Relict chondrules were identified in all meteorites studied here. Approximately elliptical polymineralic objects resembling porphyritic relict chondrules were identified in half of the thin section of Campo del Cielo by this method (Figs. 1a,b and EA-1), and are considered here to be relict chondrules based on the criteria discussed above. Relict chondrules with characteristic chondrule textures are easily discernable throughout thin sections of both GRA 98028 and Netschaëvo (Figs. 1c–f and EA-1).

3.1. Campo del Cielo (IAB iron meteorite)

Campo del Cielo USNM 5615-2 is a thin section of a silicate-rich portion of the 2000 kg El Taco mass, part of the Campo del Cielo IAB iron meteorite (e.g., Wlotzka and Jarosewich, 1977). Despite originating from an iron meteorite, the opaque minerals (i.e., pyrrhotite $[(\text{Fe},\text{Ni},\text{Co},\text{Cr})_{1-x}\text{S}]$, schreibersite $[(\text{Fe},\text{Ni})_3\text{P}]$, and chromite $[\text{FeCr}_2\text{O}_4]$) account

for only ~1 vol.% of the whole thin section (Tables 2 and 4). The thin section consists of two distinct portions separated by a horizontal crack (Fig. EA-1). The portion above the crack is dominated by graphite and contains roughly circular polymineralic objects that are free of graphite and appear to be relict chondrules, whereas the surrounding matrix contains abundant graphite. The apparent diameters of the relict chondrules range from 0.39 to 1.34 mm (mean $\pm$ 2SE, 0.68 $\pm$ 0.10 mm, 20 relict chondrules; Table 1 and Figure EA-2). They consist of olivine, LCP, and HCP that form triple junctions (Fig. 2a), with albitic plagioclase and minor amounts of sulfide and chromite (Fig. 2b). In one instance, rutile (TiO₂) is associated with pyrrhotite (Fig. 1b). Texturally, all studied objects resemble porphyritic olivine pyroxene (POP) relict chondrules. The portion below the crack does not contain relict chondrules, is dominated by silicate minerals (olivine, pyroxene, and albitic plagioclase) with a larger grain size (single silicate mineral grains up to 0.63 mm), and also contains schreibersite.

Wlotzka and Jarosewich (1977) studied the same silicate inclusions in El Taco from which Campo del Cielo USNM 5615-2 was obtained, and concluded they were only partially melted. Distinct silicate inclusions from El Taco all have chondritic bulk and individual mineral (i.e., olivine, orthopyroxene, diopside, and albitic plagioclase) compositions (Mason, 1967; Wlotzka and Jarosewich, 1977). The presence of albitic plagioclase is unlike that of most achondrites (Wlotzka and Jarosewich, 1977), which typically contain anorthitic plagioclase (e.g., Weisberg et al., 2006). The Fa/Fs ratio in Campo del Cielo varies from 0.53–0.79 (Fa_{3.5–4.5} and Fs_{5.4–6.6}) across 10 different silicate inclusions (19 thin sections) studied by Wlotzka and Jarosewich (1977). The largest compositional variation between silicate inclusions is in Ca, Al, and alkali elements, which Wlotzka and Jarosewich (1977) concluded might have been due to the loss of plagioclase and/or diopside during partial melting at temperatures between 1120°C and 1390°C. Individual olivine grains are richer in FeO at their edges (by ~0.55 wt.% FeO) than their cores (i.e., reverse zoning), indicating reduction (Wlotzka and Jarosewich, 1977). In contrast, silicate crystallization from a melt results in normal zoning. The observations of chondritic bulk and individual mineral compositions of Campo del Cielo silicates indicate that the silicate inclusions were never fully melted, but only partially melted. Our observations are consistent with those of Wlotzka and Jarosewich (1977),

which leads us to the conclusion that the roughly elliptical objects are relict chondrules and were not rounded by melting.

The silicate compositions of the relict chondrules are $\text{Fa}_{4.1\pm0.1}$ ($\text{Fa}_{3.8-4.4}$; 37 analyses), LCP with $\text{Fs}_{5.4\pm0.4}$ and $\text{Wo}_{1.3\pm0.2}$ ($\text{Fs}_{4.7-6.4}$ and $\text{Wo}_{0.9-1.5}$; 23 analyses), and HCP with $\text{Fs}_{2.6\pm0.4}$ and $\text{Wo}_{45.4\pm1.0}$ ($\text{Fs}_{1.6-3.2}$ and $\text{Wo}_{43.8-47.3}$; 26 analyses; Fig. 3 and Tables 2, 3, and EA-3); with an Fa/Fs of 0.76. Olivine grains are relatively homogeneous, with the widest range in Fa content within a single grain being 0.2 (or 0.12 wt.% FeO). In multiple relict chondrules reverse zoning of olivine is present, with the grain edge being more FeO-poor than the core ($\text{Fa}_{4.0-4.2}$, $\text{Fa}_{4.1-4.3}$, and $\text{Fa}_{4.1-4.3}$ [$\text{Fa}_{\text{edge-core}}$] for Ch3, Ch7, and Ch8, respectively). The compositions of silicates in the coarser-grained silicate portion, are $\text{Fa}_{4.2\pm0.1}$ ($\text{Fa}_{4.1-4.3}$; 8 analyses), LCP with $\text{Fs}_{5.8\pm0.7}$ and $\text{Wo}_{1.5\pm0.2}$ ($\text{Fs}_{4.9-6.7}$ and $\text{Wo}_{1.2-1.7}$; 8 analyses), and HCP with $\text{Fs}_{2.6\pm0.3}$ and $\text{Wo}_{45.4\pm1.8}$ ($\text{Fs}_{2.0-3.0}$ and $\text{Wo}_{39.9-46.7}$; 12 analyses); with an Fa/Fs of 0.72.

Chromite grains within relict chondrules and the coarser-grained silicate portion are subhedral, and are typically associated with pyrrhotite (Fig. 2b). Except for Ch1, chromite grains within the relict chondrules are internally homogeneous in composition. Chromite compositions are distinct between different relict chondrules. In contrast, the chromite grains within the coarser-grained silicate portion are compositionally homogeneous (Fig. 4b). In relict chondrules, chromite $\text{Fe}/(\text{Fe}+\text{Mg})$ ranges from 0.48 to 0.57 and $\text{Cr}/(\text{Cr}+\text{Al})$ ranges from 0.91 to 0.99. In the coarser-grained silicate portion, chromite $\text{Fe}/(\text{Fe}+\text{Mg})$ ranges from 0.50 to 0.52 and $\text{Cr}/(\text{Cr}+\text{Al})$ ranges from 0.99 to 1.00. The relict chondrules and coarser-grained silicate portion also contain the sulfide pyrrhotite, with minor amounts of Ni (below detection limits [bdl] to 0.66 wt.%) and Cr (bdl–1.26 wt.%). No Fe,Ni-metal was observed in the Campo del Cielo thin section.

The calculated two-pyroxene closure temperatures for five relict chondrules range from $902\pm38^\circ\text{C}$ to $985\pm49^\circ\text{C}$, and are the same within 1σ uncertainty. A sixth chondrule has a two-pyroxene closure temperature with a higher 1σ uncertainty, $804\pm304^\circ\text{C}$. The weighted mean for all two pyroxene temperatures from the five relict chondrules ($937\pm12^\circ\text{C}$; 7 mineral pairs) is lower than, but within 1σ of the weighted mean temperature of the coarser-grained silicate portion ($965\pm17^\circ\text{C}$; 6 mineral pairs; Table EA-4). The calculated $f\text{O}_2$ s at two-pyroxene closure temperatures are IW–4.3 to IW–4.6 (Fig.

5 and EA-4). Olivine-spinel closure temperatures of three chondrules (from $531 \pm 50^\circ\text{C}$ to $551 \pm 50^\circ\text{C}$) are within 1σ uncertainty of a region of the coarser-grained silicate portion ($549 \pm 50^\circ\text{C}$ to $557 \pm 50^\circ\text{C}$; Tables 2, 3, and EA-4). The calculated $f\text{O}_2$ s at olivine-spinel closure temperatures are IW-3.1 to IW-3.2 (Fig. 5 and EA-4).

3.2. GRA 98028 (acapulcoite)

Relict chondrules are present throughout GRA 98028. The thin section is comprised of ~68 vol.% silicate minerals and ~20 vol.% opaque minerals (metal, sulfide, and chromite; Tables 2 and 4). The original opaque mineral abundance may have been closer to ~32 vol.%, as ~12 vol.% of the sample are Fe-oxides (presumably limonite; Rubin, 2007) likely from terrestrial weathering.

The apparent diameters of the relict chondrules studied range from 0.18 to 1.71 mm (mean $\pm$ 2SE, 0.60 ± 0.09 mm, 34 relict chondrules; Table 1 and Figure EA-2). Chondrules consist of olivine, LCP, HCP, albitic plagioclase, Fe,Ni-metal, sulfide, and occasionally contain minor amounts of chromite (Figs. 1c,d, 2c,d, and EA-1). All chondrules studied are either porphyritic pyroxene or POP (Table EA-3).

The silicate compositions of the relict chondrules are $\text{Fa}_{8.2 \pm 0.5}$ ($\text{Fa}_{7.5-10.4}$; 49 analyses), LCP with $\text{Fs}_{9.1 \pm 0.5}$ and $\text{Wo}_{1.4 \pm 0.3}$ ($\text{Fs}_{8.3-10.0}$ and $\text{Wo}_{0.6-1.8}$; 38 analyses), and HCP with $\text{Fs}_{4.0 \pm 0.3}$ and $\text{Wo}_{45.3 \pm 0.9}$ ($\text{Fs}_{3.2-4.6}$ and $\text{Wo}_{43.9-47.2}$; 38 analyses; Figs. 3 and EA-3, and Tables 2 and 3); with an Fa/Fs of 0.90. Generally, olivine grains within relict chondrules are homogeneous, with the widest range of Fa within a single grain typically ~0.2. Reverse zoning is present within an olivine grain of Ch12, which has a rim composition of $\text{Fa}_{8.2}$ and a core composition of $\text{Fa}_{10.4}$. The compositions of silicates in the matrix are LCP with $\text{Fs}_{8.8 \pm 0.3}$ and $\text{Wo}_{1.3 \pm 0.2}$ ($\text{Fs}_{8.5-9.5}$ and $\text{Wo}_{1.0-1.5}$; 8 analyses) and HCP with $\text{Fs}_{4.3 \pm 0.6}$ and $\text{Wo}_{44.8 \pm 0.3}$ ($\text{Fs}_{4.0-5.8}$ and $\text{Wo}_{44.4-45.3}$; 9 analyses), similar to pyroxene in relict chondrules.

Chromite grains within relict chondrules and the surrounding matrix are subhedral to anhedral (typically with a sinuous texture present between surrounding silicate grains) and are usually associated with Fe,Ni-metal and/or pyrrhotite (e.g., Figs. 2c,d). The chromite grains within individual relict chondrules are typically compositionally homogeneous, although some are heterogeneous (e.g., Ch2, Ch8, and Ch10). Chromite

grains within the matrix are internally homogeneous in composition but distinct from one another (Fig. 4c). In relict chondrules, chromite $\text{Fe}/(\text{Fe}+\text{Mg})$ ranges from 0.57 to 0.71 and $\text{Cr}/(\text{Cr}+\text{Al})$ ranges from 0.83 to 0.99. In the matrix, chromite $\text{Fe}/(\text{Fe}+\text{Mg})$ ranges from 0.56–0.67 and $\text{Cr}/(\text{Cr}+\text{Al})$ ranges from 0.88 to 0.95. The relict chondrules contain pyrrhotite, with a wide range in Ni content (bdl–11.1 wt.%) and minor amounts of Cr (bdl–0.41 wt.%). In chondrules, Ni-poor metal (<10 wt.% Ni) contains 4.33–9.94 wt.% Ni, bdl–0.16 wt.% P, bdl–0.76 wt.% Cr, and bdl–0.21 wt.% Co, while Si is bdl in all cases. Ni-rich metal (>10 wt.% Ni) contains 10.5–31.2 wt.% Ni, with bdl–0.11 wt.% P, bdl–0.70 wt.% Cr, with Co and Si bdl in all cases.

Two-pyroxene closure temperatures for nine relict chondrules range from $870\pm104^\circ\text{C}$ to $994\pm14^\circ\text{C}$ and are similar within 1σ uncertainty. Although, one chondrule appears to record a temperature distinctly lower than others (e.g., Ch1 [$845\pm27^\circ\text{C}$] vs. Ch14 [$967\pm20^\circ\text{C}$]). A weighted mean two-pyroxene temperature over all chondrules is $961\pm9^\circ\text{C}$. The calculated $f\text{O}_2$ s at two-pyroxene closure temperatures are IW–3.5 to IW–3.8 (Fig. 5 and EA-4). Olivine-spinel closure temperatures of nine relict chondrules range from $659\pm50^\circ\text{C}$ to $742\pm50^\circ\text{C}$ and are the same within 1σ uncertainty (Tables 2, 3, and EA-4). The calculated $f\text{O}_2$ s at olivine-spinel closure temperatures are IW–2.3 to IW–2.5 (Fig. 5 and EA-4).

3.3. Netschaëvo (IIE iron meteorite)

Netschaëvo USNM 494-1 (IIE silicate inclusion) is composed of ~85 vol.% silicate minerals (olivine, LCP, and albitic plagioclase) and ~15 vol.% opaque minerals (metal, sulfide, and chromite; Tables 2 and 4). The apparent diameters of the relict chondrules studied range from 0.24 to 2.88 mm (mean $\pm$ 2SE, 0.81 ± 0.15 mm, 34 relict chondrules; Table 1 and Figure EA-2). Chondrules consist of olivine, LCP, sulfide, Fe,Ni-metal, Ca-phosphate, chlorapatite, and minor abundances of chromite and schreibersite (Figs. 1e,f, 2e,f, and EA-1). No HCP was observed. Chondrule textural types studied include BO, POP, and transitional BO/POP.

The silicate compositions of the relict chondrules are $\text{Fa}_{14.0\pm0.5}$ ($\text{Fa}_{13.1-16.2}$; 57 analyses), and LCP with $\text{Fs}_{13.1\pm0.2}$ and $\text{Wo}_{0.9\pm0.3}$ ($\text{Fs}_{12.7-13.4}$ and $\text{Wo}_{0.3-1.6}$; 32 analyses; Figs.

3 and EA-3, and Table 2); with an Fa/Fs of 1.07. The maximum difference in Fa content between distinct olivine phenocrysts in chondrules is 2.8 (Ch8), although the difference is typically ~0.5 (e.g., Ch1). An olivine grain in Ch7 is normally zoned, with the edge composition at Fa_{13.8} and core at Fa_{13.6}. Matrix compositions are similar to relict chondrules, Fa_{14.5} (1 analysis) and LCP with Fs_{13.2±0.1} and Wo_{1.4±0.6} (Fs_{13.1–13.3} and Wo_{0.8–2.1}; 7 analyses).

Chromite grains within relict chondrules and matrix range in shape from subhedral to anhedral, typically within olivine grains and sometimes associated with pyrrhotite (Figs. 2e,f). In some cases thin (≤ 1 μm wide) elongated chromite grains appear distributed in discontinuous arcs and in linear alignments (Fig. 2e). Chromite grains within individual relict chondrules and matrix are compositionally distinct from one another and are either internally homogeneous or heterogeneous (Fig. 4d). In relict chondrules, chromite Fe/(Fe+Mg) ranges from 0.73 to 0.82 and Cr/(Cr+Al) ranges from 0.73 to 0.81. In the matrix, chromite Fe/(Fe+Mg) ranges from 0.74 to 0.79 and Cr/(Cr+Al) ranges from 0.79 to 0.81. Relict chondrules contain pyrrhotite with Ni contents between 0.19 and 2.51 wt.%, and minor amounts of Cr (bdl–0.47 wt.%) and Co (bdl–0.39 wt.%). In chondrules, Ni-poor metal contains 5.53–7.34 wt.% Ni, bdl–0.13 wt.% P, bdl–0.26 wt.% Cr, and bdl–0.09 wt.% Co, while Si is bdl in all cases; Ni-rich metal contains 32.2–39.4 wt.% Ni, with minor elements bdl in all cases. Metal in the matrix is Ni-poor, and contains 6.32–6.49 wt.% Ni, bdl–0.05 wt.% P, bdl–0.07 wt.% Co, while Cr and Si are bdl in all cases.

Calculated olivine-spinel closure temperatures of relict chondrules range from 624±50°C to 787±50°C (Tables 2 and EA-4), and are different within 1 σ uncertainty between some chondrules. The single olivine-spinel closure temperature determined for a mineral pair in the matrix is 734±50°C. The calculated $f\text{O}_2$ s at olivine-spinel closure temperatures are IW–1.8 to IW–2.1 (Fig. 5 and Table EA-4).

3.4. Chondrule diameters of ordinary chondrites across petrographic types

Apparent chondrule diameters were studied in H3–6 and LL3–6 chondrites to quantify if and how the mean sizes of chondrules change with increasing degree of thermal metamorphism (Table 1). These measurements were obtained to determine the

usefulness of chondrule size measurements of Campo del Cielo, GRA 98028, and Netschaëvo in comparison to known chondrite groups. The mean sizes of chondrules were found to increase in both the H (382 total chondrules measured) and LL (209 total chondrules measured) chondrites with progression of thermal metamorphism, as expected from the loss of the smallest chondrules (i.e., no longer being able to recognize them) during thermal metamorphism (Table 1 and Fig. 6). The difference in mean chondrule size between H3 (0.38 ± 0.04 mm, mean ± 2 SE) and H6 (0.72 ± 0.10 mm) is a factor 1.87, while the difference between LL3 (0.50 ± 0.16 mm) and LL6 (0.74 ± 0.14 mm) is a factor of 1.47. The mean size of chondrules in chondrites of similar petrographic type (e.g., 3 vs. 4; 4 vs. 5; 5 vs. 6), are within 2SE of one another (Fig. 6). The single exception is Siena (LL5; 0.44 ± 0.10 mm), which has a mean chondrule size below that of Semarkona (LL3.00); however the section was relatively small compared to the other equilibrated LL chondrites, yielding fewer chondrules to measure (26.6 mm^2 vs. 175.9 mm^2 ; Table 1). Histograms of all measured chondrules are given in Figure EA-2.

4. DISCUSSION

4.1. Precursor constraints: Relict chondrule petrology

Ordinary and carbonaceous chondrite groups have characteristic chondrule sizes and textures (e.g., Rubin, 2010; Jones, 2012; Friedrich et al., 2014). While thermal metamorphism likely obscured the boundaries of the smallest chondrules initially present and increased the mean size of chondrules (Fig. 6 and Table 1) in Campo del Cielo, GRA 98028, and Netschaëvo, chondrule measurements from these samples still provide useful insight into possible relationships with known chondrite groups.

4.1.1. Campo del Cielo (IAB iron meteorite)

It is widely accepted that the winonaites and IAB iron meteorites originated from a common parent body, termed the winonaite–IAB parent asteroid (e.g., Clayton and Mayeda, 1996; Benedix et al., 1998; 2000; 2005; Franchi, 2008). The O-isotope compositions of winonaites and silicate minerals from IAB iron meteorites are similar to

one another, and are distinct from all other chondrite groups. This suggests that additional samples from the winonaite–IAB parent asteroid are not present in the meteorite record (or are to date unstudied), such as unmetamorphosed precursor material.

While the apparent diameters of relict chondrules in Campo del Cielo (0.39 to 1.34 mm; 0.68 ± 0.10 mm, mean ± 2 SE) are similar to the average for the Renazzo-like carbonaceous (CR) (mean 0.7 mm) and LL (mean 0.55 mm) chondrites (e.g., Nelson and Rubin, 2002; Friedrich et al., 2014; Schrader et al., 2015), Campo del Cielo is not genetically related to these meteorites. The apparent size distribution of relict chondrules in Campo del Cielo is also similar to those of relict chondrules observed in the winonaite Pontlyfni (0.70–0.80 mm) by Benedix et al. (1998), consistent with the genetic link previously established via O-isotopes.

4.1.2. GRA 98028 (*acapulcoite*)

It has been suggested that acapulcoite precursor material was distinct from known chondrite groups (McCoy et al., 1996), but similar to the CR chondrite parent body in terms of major/minor element (Rubin, 2007) and O-isotope compositions (Greenwood et al., 2012). The apparent diameters of relict chondrules in GRA 98028 (0.18 to 1.71 mm; 0.60 ± 0.09 mm, mean ± 2 SE) are similar to the averages for the CR (mean 0.7 mm), LL (mean 0.55 mm), and L (mean 0.50 mm) chondrites (e.g., Nelson and Rubin, 2002; Rubin and Grossman, 1987; Teitler et al., 2010; Friedrich et al., 2014; Schrader et al., 2015). Since mean chondrule diameters increase with progression of thermal metamorphism (Fig. 6), and the thermally metamorphosed meteorite GRA 98028 has a mean chondrule size below that of unaltered CR chondrites, we conclude that the acapulcoites are not thermally metamorphosed CR chondrites. Therefore, while the acapulcoite precursor may have been similar to carbonaceous chondrites, there is currently no such sample recognized in the meteoritic record.

4.1.3. Netschaëvo (*IIE iron meteorite*)

Based on chemical and O-isotope compositional similarities between IIE iron meteorite silicate minerals and H chondrites, it has been suggested that Netschaëvo is similar to the ordinary chondrites (e.g., Rubin, 1990) and may be a reduced H chondrite

(e.g., Wasson et al., 1993). Similarly, the chemical and isotopic compositions of relict chondrules ($\text{Fa}_{15.7\pm0.4}$ and $\text{Fs}_{14.4\pm0.5}$) within the IIE iron meteorite Mont Dieu led Van Roosbroek et al. (2015) to conclude that Mont Dieu was once an H chondrite. However, it has also been suggested that the IIE iron meteorites and H chondrites are from distinct, but compositionally similar, parent bodies (Bogard et al., 2000), similar to other low-FeO ordinary chondrites (McCoy et al., 1994; Russell et al., 1998). Larger $\Delta^{17}\text{O}$ variations in IIE iron silicates than H chondrite silicates led McDermott et al. (2016) to conclude that IIE iron meteorites and H chondrites most likely originated on separate parent bodies. The apparent relict chondrule diameters in Netschaëvo (0.24 to 2.88 mm; mean $\pm$ 2SE, 0.81 ± 0.15 mm, 34 relict chondrules; Table 1 and Figure EA-2) are similar to those of CV (mean 0.9 mm) chondrites (Rubin, 2010; Friedrich et al., 2014), and the H6 and LL6 chondrites studied here (Fig. 6 and Table 1). The size distribution of relict chondrules in Netschaëvo (mean 0.81 ± 0.15 mm; this study) and Mont Dieu (0.40–1.5 mm, mean $\sim$ 1 mm; Van Roosbroek et al., 2015) are larger than those in unequilibrated H chondrites (0.45 mm; King and King, 1979; Kuebler et al., 1999; Teitler et al., 2010; Friedrich et al., 2014). However, the mean size of chondrules in Netschaëvo (0.81 ± 0.15 mm) is within 2SE of the H6 chondrite Estacado (0.72 ± 0.10 mm) and the LL6 chondrite Saint-Séverin (0.74 ± 0.14 mm; Fig. 6 and Table 1). Therefore, a mean chondrule size of $\sim$ 0.8 mm is not sufficient to link Netschaëvo to any particular chondrite group. The size of relict chondrules does not rule out, nor is it conclusive evidence of, a link between the IIE iron meteorites and H chondrites.

4.2. Precursor constraints: Chromite texture and composition

The morphology of a chromite grain is an indicator of the degree of thermal metamorphism it experienced; grains progress from euhedral (i.e., well-formed crystal faces) in unequilibrated chondrites to euhedral/subhedral (i.e., less-distinct crystal faces) and then anhedral (i.e., no crystal faces) in equilibrated chondrites (Johnson and Prinz, 1991; Davidson et al., 2011). Chromite textures in Campo del Cielo, GRA 98028, and Netschaëvo are consistent with thermal metamorphism (i.e., subhedral and anhedral; Figs. 2b-f).

In unequilibrated chondrites chromite grains have heterogeneous compositions (e.g., Johnson and Prinz, 1991; Davidson et al., 2011; Fig. 4a). Chromite grains in relict chondrules studied here display a wider compositional range than those in their matrix and Campo del Cielo's coarser-grained silicate portion, indicating that some chondrule chromite grains may have partially retained their primary compositions. Potentially metamorphic chromite grains found outside chondrules are compositionally homogeneous. Thermal metamorphism experiments under reducing conditions on the H6 chondrite Kernouvé determined that heating (between 950°C and 1200°C) alters the Fe/(Fe+Mg) ratio of chromite (higher temperatures result in lower Fe/(Fe+Mg)), while the Cr/(Cr+Al) ratio remains relatively unchanged from its primary composition (Ford et al., 2008). This is attributed to Fe-Mg diffusion being more rapid than Cr-Al diffusion in chromite (e.g., Kracher, 1985; Ford et al., 2008). Therefore, we infer that the Cr/(Cr+Al) ratios of chromite in Campo del Cielo, GRA 98028, and Netschaëvo are primary, while the Fe/(Fe+Mg) ratio may have been altered during thermal metamorphism.

In spite of thermal metamorphism, the Cr/(Cr+Al) ratio of chromite stays relatively constant but differs between some meteorite groups (e.g., Ford et al., 2008). A comparison of chromite ($\text{Cr}/(\text{Cr}+\text{Al}) > 0.8$) and Cr-rich spinel (i.e., $\text{Cr}/(\text{Cr}+\text{Al}) > 0.5$; Krot et al., 1993) in chondrules from a range of unequilibrated and equilibrated chondrites, primitive achondrites, achondrites, and iron meteorites (Fig. 4a) suggests it is not possible to use the Cr/(Cr+Al) composition of chromite to confidently determine a match to a known meteorite group due to the wide range of Cr/(Cr+Al) ratios. The compositions of chromite grains in the H, L, and LL chondrite groups also show significant overlap (e.g., Fig. 7 in Schmitz et al., 2001). Netschaëvo's silicate inclusions are thermally metamorphosed and have been considered to be petrographic type 6 (Bild and Wasson, 1977). Chromite from the metamorphosed H6 chondrites has a restricted compositional range that is distinct from chromite in Netschaëvo, indicating that they are not genetically related (Fig. 4a). Furthermore, the differences in Cr/(Cr+Al) ratio between Campo del Cielo, GRA 98028, and Netschaëvo suggest they are likely from distinct parent bodies (Fig. 4a).

In unequilibrated chondrites, chromite grains are only present in type II (FeO-rich) chondrules as their formation conditions were oxidizing enough to result in the formation

of chromite during chondrule cooling (e.g., Johnson and Prinz, 1991; Zanda et al., 1994; Davidson et al., 2011). In contrast, type I (FeO-poor) chondrule formation was too reducing for chromite to form. Therefore, since Campo del Cielo and GRA 98028 do not appear to have been oxidized on their parent bodies during metamorphism, we suggest that chromite-bearing relict chondrules were originally type II chondrules (e.g., Fa >10). The presence of chromite grains in relict chondrules of Netschaëvo suggests that either the chondrules were all initially FeO-rich enough to contain chromite, or that some chromite formed during parent body thermal metamorphism under oxidizing conditions. Some relict chondrules in Netschaëvo exhibit thin ($\leq 1 \mu\text{m}$ wide), elongated anhedral chromite grains that are distributed in discontinuous arcs and in linear alignments (e.g., Fig. 2e). These morphologies result from thermal metamorphism; they are consistent with Cr-mobilization to the edge of silicate phenocrysts during heating (e.g., Grossman and Brearley, 2005), indicating that the chromite grains likely formed along primary chondrule olivine grain boundaries. The apparent absence of chromite from some chondrules in Campo del Cielo (Ch4, 5, and 8) and GRA 98028 (Ch6, 7, 9, 12, and 13) may be a thin section artifact (i.e., the chondrule contained chromite, but not in the plane of the thin section) or indicate that these were initially type I chondrules (initial Fa contents <10). Type II chondrules are more abundant than type I chondrules in unequilibrated ordinary chondrites, but less abundant in carbonaceous and enstatite chondrites (e.g., Rubin, 2010; Jones, 2012; Schrader et al., 2015). Therefore, if we assume the presence of chromite grains relates to initial chondrule type, the ubiquitous chromite in Netschaëvo may suggest an ordinary chondrite-like precursor. In contrast, the higher number of inferred type I chondrules may indicate that both Campo del Cielo and GRA 98028 had precursors similar to carbonaceous chondrites.

4.3. Precursor constraints: Silicate compositions

The olivine and pyroxene compositions of the meteorites studied here are consistent with their individual classifications (Fig. 3) and provide information on parent body metamorphic processes.

574 4.3.1. *Campo del Cielo* (IAB iron meteorite)

575 The composition of olivine in Campo del Cielo indicates reduction. Olivine grains in
576 three Campo del Cielo relict chondrules show reverse zoning, which is direct evidence of
577 reduction (e.g., Wlotzka and Jarosewich, 1977; Benedix et al., 2005). This is consistent
578 with the reversed zoning of olivine (mean of 0.55 wt.% FeO greater in grain core than
579 rim) observed by Wlotzka and Jarosewich (1977). This suggests that the precursor
580 silicates of Campo del Cielo were initially more FeO-rich than ~Fa₄.

582 4.3.2. *GRA 98028* (acapulcoite)

583 Some olivine grains in relict chondrules of GRA 98028 have reverse zoning, which is
584 direct evidence for reduction (e.g., McCoy et al., 1996; Rubin, 2007). We infer that the
585 precursor material of the acapulcoites was more FeO-rich than ~Fa₁₀.

587 4.3.3. *Netschaëvo* (IIE iron meteorite)

588 The origin of the IIE iron meteorites is currently a matter of debate, having been
589 attributed to either formation on a distinct parent body or via reduction of an H chondrite
590 precursor. Based on chemical and morphological observations Netschaëvo was suggested
591 to have formed via the latter (e.g., Russell et al., 1998). Evidence for this includes
592 Netschaëvo's lower Fa/Fs ratio (1.04) and lower FeO content of its silicates than
593 equilibrated H chondrites, and the close contact between Netschaëvo's angular silicates
594 and metallic host (e.g., Russell et al., 1998). This relationship was considered to result
595 from reduction of H chondrite silicates with ~Fa_{16.9–20.1} and ~Fs_{15.7–18.1} (Russell et al.,
596 1998), resulting in lower FeO contents of silicates in Netschaëvo (mean Fa_{14.0} and Fs_{13.1};
597 Tables 2 and EA-3 and Fig. 3) and Mont Dieu (Fa_{15.7±0.4} and Fs_{14.4±0.5}, Van Roosbroek et
598 al., 2015).

599 However, our data shows a higher Fa/Fs ratio for Netschaëvo of 1.07, similar to that
600 of the relict chondrule bearing IIE iron meteorite Mont Dieu determined by Van
601 Roosbroek et al. (2015; Fa/Fs = 1.09). The Fa/Fs ratios of H chondrites (Fa/Fs = 1.08–
602 1.13), L chondrites (Fa/Fs = 1.13–1.21), and LL chondrites (Fa/Fs = 1.18–1.19) (Keil and
603 Fredriksson, 1964; Gomes and Keil, 1980; Russell et al., 1998) are higher than, but the H
604 chondrite range is similar to, that of Mont Dieu and our data for Netschaëvo. However,

despite the similar Fa/Fs ratio, due to the lower FeO content than in H chondrites and lack of evidence for reduction we find it more likely that Netschaëvo is not related to the H chondrites.

In addition, there is no compositional or textural evidence for reduction of Netschaëvo. For example: (1) At least one olivine grain in Netschaëvo exhibits normal zoning indicating normal crystallization. (2) The presence of elongated anhedral chromite grains indicates mobilization of Cr during metamorphism under oxidizing conditions (Section 4.2). (3) We do not find that close contact of angular silicates with a metallic host indicates reduction. Close contact between H chondrite silicate clasts and host metal are seen in the H6 chondrite Portales Valley (mean $Fa_{19.6}$ and $Fs_{17.2}$; Ruzicka et al., 2005) and the H4 clasts of Sacramento Wash 005 (mean $Fa_{18.9}$ and $Fs_{15.5}$; Schrader et al., 2010). Neither silicates in Portales Valley nor Sacramento Wash 005 experienced reduction relative to H chondrite values resulting in FeO-poor silicate compositions similar to those in Netschaëvo or Mont Dieu, showing that angular silicates in contact with metal does not imply that reduction occurred. Therefore, we conclude that the FeO content of Netschaëvo, and IIE iron meteorite silicates, cannot be explained via reduction from an H chondrite precursor and therefore they do not share a common parent body.

These observations support previous work that concluded that the IIE iron meteorite parent body was distinct from, and its silicates had a lower initial FeO content than, the H, L, or LL ordinary chondrites (Bild and Wasson, 1977; Bogard et al., 2000). This has implications for astronomical observations; asteroid 6 Hebe was identified as a probable parent body for both the H chondrites and the IIE iron meteorites (Gaffey and Gilbert, 1998) because its location in the asteroid belt adjacent to the ν_6 and 3:1 resonances makes it probable it has delivered material into Earth crossing orbits, and its surface is likely composed of H chondrite-like silicates and regions of Fe,Ni-metal. Asteroid (214869) 2007 PA8 has also been suggested to be similar to the H chondrites (Sanchez et al., 2015). If 6 Hebe is the parent body of the H chondrites, the Fe,Ni-metal regions inferred to be present (Gaffey and Gilbert, 1998) may be consistent with the Fe,Ni-metal melt veins observed in Portales Valley [H6] (e.g., Ruzicka et al., 2005) and Fe,Ni-metal blebs of Sacramento Wash 005 [H4 clast] (e.g., Schrader et al., 2010), not the metallic portions of IIE iron meteorites.

4.4. Thermodynamic constraints on alteration

4.4.1. Peak metamorphic and closure temperatures

Constraining the thermal history of a meteorite is vital to determining its formation history. The two-pyroxene and olivine-spinel closure temperatures calculated here, and the differences between the two (ΔT) vary between samples. Closure temperatures for two-pyroxene and olivine-spinel mineral pairs were determined for Campo del Cielo and GRA 98028 (Fig. 5 and Table EA-4). Since HCP was not located within Netschaëvo, two-pyroxene closure temperatures and corresponding fO_2 values (Section 4.4.2.) could not be determined. Similarly, chondrule-bearing IIE iron meteorites studied by Van Roosbroek et al. (2015) and McDermott et al. (2016) also lacked HCP.

The lowest temperature melt to form during thermal metamorphism is Fe,Ni-sulfide at $\sim 950^\circ\text{C}$ (Fe,Ni–FeS eutectic; Kullerud, 1963; McCoy et al., 2006). Since Fe,Ni-sulfide veins were not observed in sections of either GRA 98028 or Netschaëvo, the peak metamorphic temperature (PMT) for both GRA 98028 and Netschaëvo is inferred to be $< 950^\circ\text{C}$. Due to the suspected loss of plagioclase and/or diopside during partial melting, Wlotzka and Jarosewich (1977) concluded that Campo del Cielo silicates experienced PMTs between 1120°C and 1390°C . Since geothermometers record closure temperatures and not PMTs, we expect calculated two-pyroxene and olivine-spinel temperatures to be below the estimated PMTs of each sample. The highest mean closure temperatures in each sample are below these estimated PMTs within 2σ uncertainty: Campo del Cielo is $947 \pm 10^\circ\text{C}$ (two-pyroxene, $\pm 1\sigma$); GRA 98028 is $961 \pm 9^\circ\text{C}$ (two-pyroxene); and Netschaëvo is $681 \pm 15^\circ\text{C}$ (olivine-spinel; Table EA-4).

The two-pyroxene closure temperatures for Campo del Cielo are consistent with those of winonaites and IAB iron meteorites ($730\text{--}1200^\circ\text{C}$; Benedix et al., 1998; 2005). The olivine-spinel closure temperatures determined here for Campo del Cielo are $\sim 100^\circ\text{C}$ lower than those determined from other samples of Campo del Cielo ($634\text{--}688^\circ\text{C}$; Benedix et al., 2005). The relatively high ΔT between two-pyroxene and olivine-spinel closure temperatures suggests that silicates in Campo del Cielo USNM 5615-2

($\Delta T \sim 388 \pm 38^\circ\text{C}$ to $434 \pm 70^\circ\text{C}$, 1σ) may have cooled more slowly than other Campo del Cielo samples (USNM 5615-4 and 5615-6) studied by Benedix et al. (2005) ($\Delta T \sim 280^\circ\text{C}$), providing further evidence for the complex cooling history of the winonaite–IAB parent body discussed by Benedix et al. (2005).

Two-pyroxene temperatures determined here for GRA 98028 are generally lower than two-pyroxene temperatures for acapulcoites ($980\text{--}1170^\circ\text{C}$; McCoy et al., 1996 and references therein). The heating of GRA 98028 to lower temperatures than other acapulcoites is consistent with its abundant relict chondrules. The relatively low ΔT for GRA 98028 ($138 \pm 145^\circ\text{C}$ to $262 \pm 40^\circ\text{C}$, 1σ) suggests it cooled faster than Campo del Cielo USNM 5615-2, consistent with it containing abundant relict chondrules.

4.4.2. Oxidation history

Determining the $f\text{O}_2$ for meteorites at their two-pyroxene and olivine-spinel closure temperature constrains the oxidation history of the meteorites during cooling from their PMTs. Important differences between this study and Benedix et al. (2005) exist. While we found similar two-pyroxene closure temperatures for relict chondrules in Campo del Cielo compared to those in Benedix et al. (2005) for entire winonaite samples and silicate inclusions from IAB iron meteorites, our calculated $f\text{O}_2$ values are distinct. Benedix et al. (2005) found a constant $f\text{O}_2$ at both temperatures, and interpreted this as evidence that the winonaite and IAB iron meteorites did not undergo significant reduction during partial melting and therefore had a relatively reduced precursor. Their calculated values were for whole samples, and possible internal variations in temperatures and $f\text{O}_2$ s were considered. Once we recognized this discrepancy we attempted to reproduce the results of Benedix et al. (2005) from their raw data; we found the same olivine-spinel closure temperatures within uncertainty (using MELTS and QUILF) and the same corresponding $f\text{O}_2$ values using equation (3). However, while we found the same two-pyroxene closure temperatures within uncertainties we found distinct $f\text{O}_2$ values (lower by 2 log units) corresponding to the two-pyroxene closure temperatures calculated with equation (4) (recalculated data plotted in Table EA-4 and Fig. 5b). To verify our procedure we recalculated closure temperatures and $f\text{O}_2$ s from Gardner-Vandy et al. (2013) with

equations (3 and 4) and obtained consistent results. After this discrepancy was confirmed we determined, by personal communication with G. Benedix, that there was a factor of 2 error made the equation that was used to determine the $f\text{O}_2$ values at two-pyroxene temperatures in Benedix et al. (2005). Therefore we provide updated $f\text{O}_2$ values corresponding to two-pyroxene closure temperatures from data of Benedix et al. (2005) in Table EA-4 and Figure 5b. These new results suggest that both Campo del Cielo and GRA 98028 trended to higher $f\text{O}_2$ relative to the IW buffer as they cooled (Fig. 5a and Table EA-4); contrary to the results of Benedix et al. (2005) for Campo del Cielo.

We find that the $f\text{O}_2$ values at each closure temperature lay on distinct trends, with the $f\text{O}_2$ s at the two-pyroxene closure temperatures being lower relative to the IW buffer than those at the olivine-spinel closure temperatures (e.g., mean $\pm$ 1SE of IW -4.5 ± 0.1 vs. IW -3.2 ± 0.0 , respectively, for Campo del Cielo and IW -3.7 ± 0.1 vs. IW -2.4 ± 0.1 , respectively, for GRA 98028; Fig. 5a and Table EA-4). This may imply that Campo del Cielo and GRA 98028 became more oxidizing relative to the IW buffer during cooling. While the lack of observed HCP in Netschaëvo prohibits further investigation of its $f\text{O}_2$ at higher temperatures than those recorded by olivine-spinel geothermometry, the normal zoning in one of its relict chondrules suggests it did not undergo reduction, indicating that this olivine grain may be near its initial Fa value (i.e., $\sim\text{Fa}_{14}$; Table EA-3).

Numerous authors have argued that the winonaite-IAB iron meteorites (e.g., Campo del Cielo) and the acapulcoites (e.g., GRA 98028) were reduced (Wlotzka and Jarosewich, 1977; Prinz et al., 1983; Kallemeyn and Wasson, 1985; Kracher, 1985; McCoy et al., 1996; Benedix et al., 1998; 2005; Rubin, 2007). Direct evidence for reduction in Campo del Cielo and GRA 98028 is supported here by reverse zoning in relict chondrule olivine. The $f\text{O}_2$ s of Campo del Cielo and GRA 98028 are lower relative to the IW buffer at higher temperatures (Fig. 5). While this may appear to imply oxidation upon cooling, and thus reduction at peak temperature, it is equally possible that $f\text{O}_2$ was not buffered by IW but instead by another system.

(1) Perhaps during cooling Campo del Cielo and GRA 98028 were not buffered by the IW buffer, but instead the graphite-oxygen (C-CO) buffer at much higher temperatures than recorded here. Graphite reduction of metal is a high temperature process, typically achieved at temperatures $>1200^\circ\text{C}$ or possibly near 1050°C in an

asteroidal setting (e.g., Schmidt and Avery, 1978; Kracher, 1985; Walker and Grove, 1993). Reduction of olivine in olivine-silica-metal assemblages to lower Fa contents during heating from 1100°C to 1300°C has also been shown (Mueller, 1963; Speidel and Nafziger, 1968). Reduction by graphite near peak metamorphic temperature has previously been suggested for the IAB iron meteorites (Wlotzka and Jarosewich, 1977; Kracher, 1985). Two-pyroxene closure temperatures are not a record of the PMT, and those calculated here (Table 3) are not within the temperature ranges observed for reduction. The PMT of GRA 98028 was likely <950°C, and therefore graphite reduction is unlikely. However, the PMT range for Campo del Cielo of 1120°C to 1390°C suggested by Wlotzka and Jarosewich (1977) is within the temperature range for graphite reduction.

(2) Alternatively, the system may have been buffered by a more complex system than considered here, such as fayalite forming from the oxidation of metal and pyroxene. With our current data, given the obvious complexity of these primitive achondrites, additional studies of members of these groups (most of which are not chondrule bearing) will be required to resolve this issue.

CONCLUSIONS AND IMPLICATIONS

We used petrographic and compositional data to constrain closure temperatures, oxidation states, and the nature of precursor material of parent body thermal metamorphism for Campo del Cielo, GRA 98028, and Netschaëvo.

1. Mineral phases within relict chondrules in Campo del Cielo, GRA 98028, and Netschaëvo retain information about their precursor compositions. The sizes and textures, silicate compositions, and chromite Cr/(Cr+Al) ratios of relict chondrules are consistent with previous studies that Campo del Cielo, GRA 98028, and Netschaëvo had distinct parent bodies that were similar to, but different from, known chondrite groups. Chondrule sizes, silicate compositions, and the abundance of chromite-bearing relict chondrules indicate that the precursor of Netschaëvo was similar to ordinary chondrites, while the precursors of Campo del Cielo and GRA 98028 were similar to carbonaceous chondrites.

760

761 2. We show that, as expected, the mean diameters of chondrules in LL and H ordinary
762 chondrites increase with progression of thermal metamorphism. This data shows that
763 relict chondrule diameters in thermally metamorphosed meteorites are a useful parameter
764 to investigate links to known chondrite groups.

765

766 3. The precursors of Campo del Cielo and GRA 98028 were initially more FeO-rich than
767 their current compositions (i.e., $>Fa_{4.4}$ and $>Fa_{10.4}$, respectively). For Campo del Cielo
768 and GRA 98028, we find that the fO_2 values at each closure temperature lay on distinct
769 trends, with the fO_2 at the two-pyroxene closure temperature being lower relative to the
770 IW buffer than those at the olivine-spinel closure temperature.

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772 4. The lack of evidence for reduction indicates that Netschaëvo's silicates are near their
773 primary FeO-contents (i.e., $\sim Fa_{14}$). The similar lack of significant reduction of the H
774 chondrites in contact with metallic hosts (i.e., Portales Valley and Sacramento Wash 005),
775 and the distinct composition of chromite in Netschaëvo compared to that in H6
776 chondrites lead us to conclude that Netschaëvo, and by extension the IIE iron meteorites,
777 did not originate from the H chondrite parent body, but a compositionally similar asteroid.

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FIGURE CAPTIONS

Figure 1. BSE images of representative chondrules within: (a,b) Campo del Cielo, (c,d) GRA 98028, and (e,f) Netschaëvo. Ch = chondrule; ol = olivine, LCP = low-calcium pyroxene; HCP = high-calcium pyroxene; gr = graphite; chr = chromite; met = Fe,Ni-metal; Ni-met = Ni-rich Fe,Ni-metal; sf = sulfide; CaP = calcium-phosphate; pl = plagioclase; rut = rutile.

Figure 2. BSE images of selected regions of relict chondrules in (a,b) Campo del Cielo, (c,d) GRA 98028 Ch2, and (e,f) Netschaëvo. Ch = chondrule; ol = olivine, LCP = low-calcium pyroxene; HCP = high-calcium pyroxene; gr = graphite; chr = chromite; sf = sulfide; pl = plagioclase; ilm = ilmenite. Arc = arcs, anhedral grains, of chromite indicated by arrow.

Figure 3. Fayalite (Fa) versus ferrosilite (Fs) content of low-calcium pyroxene (LCP) in relict chondrules in Campo del Cielo, GRA 98928, and Netschaëvo. Compositional fields for winonaite and IAB iron meteorites (Benedix et al., 1998; 2005; Takeda et al., 2000), acapulcoites and lodranites (McCoy et al., 1996; 1997; and references therein), and equilibrated H and L chondrites (Gomes and Keil, 1980; Rubin, 1990) are plotted for reference. The mean compositional values for the H6 chondrite Portales Valley (Ruzicka et al., 2005), an H4 clast from Sacramento Wash 005 (SaW 005; Schrader et al., 2010), and silicate clasts from the IIE iron meteorite Mont Dieu (Van Roosbroek et al., 2015) are plotted for comparison.

Figure 4. Individual analyses of chromite grains within chondrules and surrounding matrix from (a) all samples of this study, (b) Campo del Cielo, (c) GRA 98028, and (d) Netschaëvo. Compositional fields in (a) for acapulcoites (Zipfel et al., 1995), IAB (Benedix et al., 2000) and IIE iron meteorites (Bunch et al., 1970), H6 chondrites (Bunch et al., 1967), and unequilibrated carbonaceous chondrites and ordinary chondrites (CCs and OCs; Bunch et al., 1967; Snetsinger et al., 1967; Smith et al., 1972; Ackerman and Raase, 1973; Fudali and Noonan, 1975; Jones, 1990; Johnson and Prinz, 1991; Brearley et al., 1991; McCoy et al., 1991; Kennedy and Hutcheon, 1992; Krot et al., 1993; Simon et al., 1994; Weinbrunch et al., 1994; Ruzicka et al., 1998; Ford et al., 2008; Schrader, 2012) are plotted for reference.

Figure 5. Logarithmic plot of oxygen fugacity (fO_2) versus temperature for (a) the mineral pairs of this study, and (b) the recalculated values for silicate inclusions from IAB iron meteorites and winonaite from ¹Benedix et al. (2005). The iron-wüstite (IW) buffer (including IW-1 to IW-5) and the graphite-oxygen (C-CO) buffer at 1 bar are given for reference. Where olv-sp = olivine-spinel, and two-pyx = two-pyroxene geothermometers.

Figure 6. Mean diameter of chondrules (mean±2SE, in mm) measured in Campo del Cielo USNM 5615-2 (IAB iron meteorite), GRA 98028,1 (acapulcoite), and Netschaëvo USNM 494-1 (IIE iron meteorite); Estacado ASU 44_A_4 (H6), Arbol Solo ASU 1046_C_1 (H5), Kesen ASU 362_C_1 (H4), and Clovis (no. 1) ASU 168_A_2 (H3.6);

and Saint-Séverin USNM 2608-3 (LL6), Siena USNM 3070-3 (LL5), Soko-Banja USNM 3078-1 (LL4), and Semarkona USNM 1805-17 (LL3.00).

ELECTRONIC ANNEX CAPTIONS

Figure EA-1. Full thin section backscattered electron images of (a) Campo del Cielo USNM 5612-2, (b) GRA 98028, and (c) Netschaëvo USNM 494-1. Chondrule numbers and letters on images correspond to EA-3 and EA-4.

Figure EA-2. Histograms of mean chondrule diameters.

Table EA-3. Table of relict chondrule petrology and silicate composition.

Table EA-4. Table of closure temperatures and oxidation states.

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Table 1. Mean chondrule diameters (mm).

Meteorite	Ch. mean diameter (mm)	1s	2SE	Count
Campo del Cielo USNM 5615-2 (IAB)	0.68	0.23	0.10	20
GRA 98028,1 (acapulcoite)	0.60	0.28	0.09	34
Netschaëvo USNM 494-1 (IIE-iron)	0.81	0.45	0.15	34
LL chondrites				
Semarkona USNM 1805-17 (LL3.00)	0.50	0.53	0.16	46
Soko-Banja USNM 3078-1 (LL4)	0.61	0.42	0.08	110
Siena USNM 3070-3 (LL5)	0.44	0.25	0.10	26
Saint-Séverin USNM 2608-3 (LL6)	0.74	0.36	0.14	27
H chondrites				
Clovis (no. 1) ASU 168_A_2 (H3.6)	0.38	0.26	0.04	200
Kesen ASU 362_C_1 (H4)	0.52	0.29	0.10	34
Arbol Solo ASU 1046_C_1 (H5)	0.59	0.28	0.06	100
Estacado ASU 44_A_4 (H6)	0.72	0.35	0.10	48

Ch. = chondrule. Section area = total thin section or polished mount surface

Table 2. Representative olivine-chromite mineral pairs.

	Campo del	Campo del	GRA 98028	GRA 98028	Netschaëvo	Netschaëvo
Meteorite	Cielo	Cielo				
Chondrule	Ch1	Ch1	Ch5	Ch5	Ch1	Ch1
Mineral	olivine	chromite	olivine	chromite	olivine	chromite
Analysis #	4	3	32	20	1	3
SiO ₂	40.7	bdl	40.4	bdl	40.3	bdl
TiO ₂	bdl	0.28	bdl	1.08	bdl	1.35
Al ₂ O ₃	bdl	0.89	0.03	5.06	bdl	9.52
Cr ₂ O ₃	bdl	66.7	bdl	62.7	0.16	54.9
V ₂ O ₃	nd	0.71	nd	0.72	nd	0.86
FeO	3.99	16.2	8.80	20.0	14.0	27.5
MnO	0.45	3.25	0.43	1.47	0.37	0.82
MgO	55.0	7.07	49.9	7.32	46.4	3.54
ZnO	nd	1.93	nd	nd	nd	0.24
Total	100.2	97.1	99.6	98.3	101.3	98.8
Fa	3.9		9.0		14.5	
Fe/Mn	9		20		37	
Closure						
temperature ^a	531±50°C		742±50°C		646±50°C	

a = olivine-spinel closure temperature determined using MELTS (Sack and Ghiorso, 1991a, 1991b), $\pm 1\sigma$.

bdl = below detection limit; nd = not determined.

Standards and detection limits (in wt.%) for silicates: forsterite for Mg (0.01),

VG-A99 USNM 113498 glass for Na (0.02), San Carlos olivine for Si (0.02), Kakanui hornblende for Al (0.01), Ti (0.04), K (0.01), Rockport fayalite for Fe (0.03), diopside for Ca (0.02), fluorapatite for P (0.02), rhodonite for Mn (0.03), and chromite for Cr (0.02).

Standards and detection limits (in wt.%) for chromite: diopside for Si (0.02),

chromite for Mg (0.01), Fe (0.05), and Cr (0.02), Kakanui hornblende for Al (0.02), rhodonite for Mn (0.05) and Zn (0.09), vanadium metal for V (0.05), and titanium metal for Ti (0.02).

Na₂O, CaO, K₂O, and P₂O₅ were bdl in each case here.

Table 3. Representative two-pyroxene mineral pairs (wt.%).

	Campo del	Campo del	Campo del	Campo del	GRA 98028	GRA 98028	GRA 98028	GRA 98028
Meteorite	Cielo	Cielo	Cielo	Cielo				
Chondrule	Ch1	Ch1	Ch7	Ch7	Ch5	Ch5	Ch14	Ch14
Mineral	LCP	HCP	LCP	HCP	LCP	HCP	LCP	HCP
Analysis #	1	3	126	125	24	23	110	109
SiO ₂	59.3	55.1	58.3	54.8	58.1	54.6	57.6	54.6
TiO ₂	0.19	0.54	0.17	0.66	0.32	0.63	0.25	0.59
Al ₂ O ₃	0.19	0.87	0.23	0.85	0.24	0.69	0.26	0.66
Cr ₂ O ₃	0.28	1.39	0.25	1.40	0.30	0.99	0.29	0.98
FeO	3.58	1.81	3.24	1.66	6.34	2.50	6.32	2.67
MnO	0.52	0.29	0.51	0.27	0.51	0.28	0.47	0.23
MgO	37.0	18.5	36.2	18.1	34.5	17.7	34.5	18.2
CaO	0.55	21.9	0.76	21.4	0.90	23.3	0.80	21.7
Na ₂ O	0.04	0.80	0.04	0.85	bdl	0.66	bdl	0.58
K ₂ O	bdl	0.02	bdl	bdl	bdl	bdl	bdl	bdl
Total	101.7	101.1	99.8	100.0	101.2	101.3	100.5	100.2
Fs	5.1	2.9	4.7	2.7	9.2	3.9	9.2	4.2
En	93.9	52.5	93.9	52.7	89.1	49.3	89.3	51.5
Wo	1.0	44.6	1.4	44.6	1.7	46.8	1.5	44.3
Closure								
temperature ^a	919±33 °C		985±49 °C		880±136 °C		967±20 °C	

a = two-pyroxene closure temperature determined by the QUILF program (Lindsley, 1983; Anderson et al., 1993), $\pm 1\sigma$. Standards and detection limits (in wt.%) for silicates: forsterite for Mg (0.01), VG-A99 USNM 113498 glass for Na (0.02), San Carlos olivine for Si (0.02), Kakanui hornblende for Al (0.01), Ti (0.04), K (0.01), Rockport fayalite for Fe (0.03), diopside for Ca (0.02), fluorapatite for P (0.02), rhodonite for Mn (0.03), and chromite for Cr (0.02). P₂O₅ is below detection limit (bdl) in each case here.

Table 4. Representative metal, sulfide, and schreibersite analyses (wt.%).

Meteorite Chondrule	Campo del Cielo Ch7	Campo del Cielo Ch1	GRA 98028 Ch5 Ni-poor metal	GRA 98028 Ch14 Ni-rich metal	GRA 98028 Ch6 sulfide	Netschaëvo Ch1 Ni-poor metal	Netschaëvo Ch1 Ni-rich metal	Netschaëvo Ch7 sulfide	Netschaëvo Ch7 sulfide	Netschaëvo Ch10 scheibersite
Mineral Analysis #	sulfide 35	scheibersite 13	metal 38	metal 116	sulfide 51	metal 13	Ni-rich metal 21	sulfide 95	sulfide 97	scheibersite 76
P	0.19	15.49	0.07	bdl	0.08	0.07	bdl	bdl	bdl	14.20
S	33.3	0.04	bdl	bdl	37.7	bdl	bdl	37.9	37.82	bdl
Cr	0.14	bdl	bdl	0.42	0.11	bdl	bdl	bdl	bdl	bdl
Fe	66.3	31.0	92.5	77.2	61.9	93.8	63.5	59.0	61.1	37.0
Co	bdl	bdl	0.08	bdl	bdl	bdl	bdl	0.39	bdl	bdl
Ni	0.56	54.1	6.71	22.7	0.21	6.07	36.0	2.51	0.30	48.6
Total	100.5	100.6	99.4	100.3	100.0	99.9	99.4	99.9	99.3	99.9

Standards and detection limits (in wt.%) for metals, sulfides, and phosphides: schreibersite or troilite for Fe (0.06), Fe,Ni-metal for Ni (0.05), schreibersite for P (0.03), troilite for S (0.02), chromium metal for Cr (0.02), cobalt metal for Co (0.06), silicon metal for Si (0.05), and aluminum metal for Al (0.02).

Si and Al are below detection limit (bdl) in each case shown.