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DOI:

[10.1111/maps.12921](https://doi.org/10.1111/maps.12921)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Srinivasan, P., Jones, R. H., & Brearley, A. J. (2017). Compositions and microstructures of CB sulfides: Implications for the thermal history of the CB chondrite parent body. *Meteoritics and Planetary Science*. <https://doi.org/10.1111/maps.12921>

Published in:

Meteoritics and Planetary Science

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Compositions and Microstructures of CB Sulfides: Implications for the Thermal History of the CB Chondrite Parent Body

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Keywords: CB chondrites; sulfides; impact processing; exsolution

ABSTRACT

We studied textures and compositions of sulfide inclusions in unzoned Fe,Ni metal particles within CBa Gujba, CBa Weatherford, CBb HH 237, and CBb QUE 94411 in order to constrain formation conditions and secondary thermal histories on the CB parent body. Unzoned metal particles in all four chondrites have very similar metal and sulfide compositions. Metal particles contain different types of sulfides, which we categorize as: homogeneous low-Cr sulfides composed of troilite, troilite containing exsolved daubreelite lamellae, arcuate sulfides that occur along metal grain boundaries, and shock-melted sulfides composed of a mixture of troilite and Fe,Ni metal. Our model for formation proposes that the unzoned metal particles were initially metal droplets that formed from splashing by a partially molten impacting body. Sulfide inclusions later formed as a result of precipitation of excess S from solid metal at low temperatures, either during single stage cooling or during a reheating event by impacts. Sulfides containing exsolution lamellae record temperatures of $\ll 600^\circ\text{C}$, and irregular Fe-FeS intergrowth textures suggest localized shock melting, both of which are indicative of heterogeneous heating by impact processes on the CB parent body. Our study shows that CBa and CBb chondrites formed in a similar environment, and also experienced similar secondary impact processing.

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1. Introduction

The CB chondrites are an unusual group of carbonaceous chondrites rich in Fe,Ni metal. CBs are similar to other carbonaceous chondrites in terms of oxygen isotopic compositions, whole-rock chemistry, and they have normalized refractory lithophile abundances that are ~solar (e.g. see Weisberg et al., 1995). However, CBs also have a high abundance of metal (>40 vol.%), low abundance of matrix (<5 vol.%) that is dominated by impact melt, atypical cryptocrystalline and barred-olivine chondrules, calcium-aluminum-rich inclusions, low carbon content, and a high depletion in moderately volatile lithophile elements (Ramdohr, 1973; Kallemeyn et al., 1978; Newsom & Drake, 1979; Weisberg et al., 1990; 2001; Meibom et al., 2000; Krot et al., 2001; 2002; Rubin et al., 2003). CB chondrites are subdivided into types CBa and CBb, which are mainly differentiated by grain size (Weisberg et al., 1990; 2001; Krot et al., 2002). Oxygen isotopes indicate that CBa and CBb chondrites have similar origins, and are also closely related to the metal-rich CR and CH chondrites (Clayton and Mayeda, 1999; Weisberg et al., 1995; 2001; Krot et al., 2002).

The most accepted model for formation of CB chondrites is post-nebular condensation in an impact-generated vapor plume (Kallemeyn et al., 1978; Meibom et al., 1999; Petaev et al., 2001; 2003; Campbell et al., 2002; 2005; Rubin et al., 2003; Goldstein et al., 2011; Fedkin et al., 2015). CB chondrites contain unzoned metal grains, and CBb chondrites additionally contain zoned metal grains (Weisberg et al., 2001). Calculations on zoned metal grains in CBb chondrites show that elemental and isotopic zoning can be produced through equilibrium fractional condensation (Meibom et al., 1999; Petaev et al., 2001; 2003). Calculations on unzoned metal grains show that correlations between various siderophile elements can be produced by condensation from a post-impact vapor plume if the partial pressures of siderophiles were 10^7 x greater than a gas of solar composition at 10^{-4} bar (Campbell et al., 2002). U-Pb and Pb-Pb dating on chondrules in CBa Gujba give ages of 4562.7 ± 0.5 Ma (Amelin et al., 2002; Krot et al., 2004; 2005), ~5 Myr after formation of CAIs in CV chondrites. The CB formation age possibly postdates the lifetime of the solar nebula (Krot et al., 2005), supporting the impact plume model. However, CBs have experienced multiple post-accretion impact and shock events, so this chondrule formation age may have been reset.

CB chondrites contain some chondrules and impact-melt glass with even younger ages. Some chondrules in CBa Gujba have U-Pb ages of 4545.4 ± 3.9 Ma (Krot et al., 2004). Impact melt from CBa Weatherford gives Ar-Ar ages of 3.6 Ga (Kelly and Turner, 1987), and glass from CBa Bencubbin gives Ar-Ar ages of 4.20 ± 0.05 Ga (Marty et al., 2010). These young ages provide evidence of multiple resetting events after initial formation of individual components. Late impact events have caused chemical and textural changes in material on the surface of the CB parent body. Deformed chondrules and high-pressure phases have been described by Weisberg et al. (2001) and Weisberg and Kimura (2010), veins of impact melt have been observed both interstitial to chondrules and protruding chondrule interiors (Kelly and Turner, 1987; Weisberg and Kimura, 2010), and flattening and preferred alignment of metal have been noted in CBa Bencubbin (Meibom et al., 2005). All of these features indicate post-accretion shock on the CB parent body.

It is important to recognize the overprint of impact-related processes in order to interpret the initial formation conditions of individual components.

CB chondrites have a high abundance of Fe,Ni metal particles, and many unzoned metal grains contain inclusions of sulfides. Sulfides are Cr-bearing troilite (Fe,Cr)S, and occur as arcuate textures along metal grain boundaries, and also as inclusions within metal grains. These sulfides are thought to have precipitated from the metal in the solid state (Newsom and Drake, 1979; Weisberg et al., 2001; Krot et al., 2002; Rubin et al., 2003; Campbell et al., 2005b). The presence of sulfides in unzoned metal means that excess sulfur must have been present in solidified metal to allow sulfides to precipitate at lower temperatures. This is a problem for the formation of the solid metal by condensation because it is unlikely that a sufficient amount of sulfur would have dissolved in metal at high temperatures to allow precipitation of sulfides at lower temperatures (Rubin et al., 2003; Campbell et al., 2005b). An alternative model is that S-rich liquid could have condensed from gas due to higher pressures in the CB impact plume, with metal grains solidifying from this liquid (Rubin et al., 2003).

Regardless of the origins of sulfur in CB metal, sulfide inclusions in these meteorites can potentially provide evidence that can help to interpret the secondary impact history on the CB parent body. Most sulfide inclusions in metal grains are homogeneous, but some Cr-rich sulfide inclusions display exsolution textures with fine lamellae of daubreelite (FeCr₂S₄) (Ramdohr, 1973; Newsom & Drake, 1979; Weisberg et al., 2001; Rubin et al., 2003). Exsolution could have occurred during single-stage cooling, or during late-stage reheating episodes on the CB parent body.

We have carried out an extensive study of sulfides in CB chondrites with an emphasis on interpreting exsolution textures in Cr-bearing sulfides. We examined textures and compositions of homogeneous sulfides and sulfides containing exsolution lamellae in unzoned metal grains from CBa Gujba and Weatherford and CBb Queen Alexandra Range (QUE) 94411 and Hammadah al Hamra (HH) 237. Sulfide inclusions have not been found in zoned metal grains in this study or in previous studies (e.g. Campbell et al., 2005). Although the four chondrites we studied are very different in appearance, in terms of size, shape, and distribution of metal and silicate particles, we found similar textures and compositions of sulfide inclusions in all of them. This indicates that they all record a similar formation process as well as secondary thermal history. Using the Fe-Cr-S ternary phase diagram, we can place constraints on the temperatures recorded by sulfides displaying exsolution textures. We use properties of sulfides to further our understanding of impact processes on the CB parent body.

2. Samples and Analytical Methods

2.1. Samples

We analyzed samples of four CB chondrites. For CBa Gujba, we studied the following samples: 1) polished thick section UNM-Cr34.2, ~ 2 cm in diameter, 2) Gujba 7-0, a large polished sample set in epoxide, 2.5 x 4 cm in size, and 3) a 2.5 x 1.5 cm section set in epoxide. For CBa Weatherford we studied a 1.5 x 2 cm thin section of UNM-259. For CBb QUE 94411 we studied a 1 x 1.5 cm thin section of QUE 94411.8, loaned from the Smithsonian Institution, and for CBb HH 237 we studied a polished thick section 1 x 1.2 cm in size. Sections were documented using reflected light microscopy and scanning electron microscopy (SEM), and analyzed using electron microprobe (EPMA) and transmission electron microscope (TEM) techniques at the University of New Mexico.

2.2. Scanning electron microscopy

The SEM was used to examine textures and identify sulfide inclusions in the metal grains. We used a JEOL 5800LV SEM to acquire backscattered electron (BSE) images with a 20 kV accelerating voltage and 1 nA beam current. We also used a FEI Quanta 3D FEG SEM, equipped with an EDAX silicon drift (SD) energy dispersive X-ray spectrometer (EDS) and a focused ion beam (FIB). The accelerating voltage was 30 kV and the beam current was 32 nA. We obtained high-resolution BSE images, and from these created BSE mosaics for Gujba (section UNM Cr34.2), Weatherford, QUE 94411, and HH 237. We then used ImageJ (Schneider et al., 2012) to determine abundances of metal grains and sulfide inclusions from the mosaics.

2.3. Electron microprobe

A JEOL 8200 electron microprobe (EPMA), equipped with five wavelength-dispersive X-ray spectrometers (WDS) and an energy-dispersive X-ray spectrometer (EDS), was used for quantitative mineral analyses and mapping. Silicon, P, S, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn were measured by WDS in sulfides and metal grains. Standards used were Si metal, apatite (Wilberforce), pyrite, V metal, Cr metal, spessartine, Fe metal, Co metal, Ni metal, chalcopyrite, and sphalerite, respectively. The detection limits are as follows: 0.09% for Zn, 0.08% for Cu, 0.02% for Si, Ni, Co, Fe, Mn, and V, 0.01% for S and Cr. Peak overlap corrections were implemented using Probe for Windows software, for Ni-Co, Co-Fe, Mn-Cr, and V-Cr, to account for peak interferences between the transition metal elements. Mineral compositions were determined using a 20 kV accelerating voltage, 20 nA beam current, and 1 μ m spot size. Count times ranged between 20-40 seconds, depending on the concentration of the element in the phase. Combined WDS/EDS X-ray maps were obtained on sulfide inclusions and surrounding metal grains to identify elemental distributions.

2.4. Transmission electron microscopy

We selected one representative sulfide inclusion, ‘Sulfide 5’ from CBa Gujba, for transmission electron microscopy (TEM). A focused ion beam (FIB) section was prepared with the FEI Quanta 3D FEG SEM/FIB instrument. A platinum protective layer (2 μ m thickness) was deposited in a strip across the area of interest prior to FIB sample preparation to minimize ion beam damage. We cut a section of the inclusion ~20 μ m in length with gallium ion milling, which was performed with an ion beam voltage of 30 kV and beam currents from 3 nA down to 10 pA. The sample was removed from the thin section by the *in situ* lift out technique using an Omniprobe 200 micromanipulator and was transferred to a Cu TEM half grid. Final ion milling to electron transparency was carried out with the samples attached to the TEM grid.

TEM studies were performed using a JEOL JEM-2010 high-resolution TEM, equipped with an Oxford INCA EDS system and a Gatan Orius CCD imaging system, and a JEOL 2010F FASTEM TEM/STEM, equipped with a GATAN GIF 2000 imaging filtering system and Oxford INCA/ISIS EDS system, both operating at 200 kV. We obtained bright-field and dark-field STEM images to document the microstructures of the lamellae in the sulfide inclusion. Compositional data were obtained using the Oxford INCA X-ray analysis system using theoretical k-factors.

3. Results

3.1. Metal Grains and Sulfide Inclusions: Textural Observations

CB chondrites are metal-rich and contain >40 vol% kamacite (Fe,Ni) grains. Individual kamacite grains are commonly grouped together to form larger metal particles (Newsom and Drake, 1979; Weisberg et al., 2001; Krot et al., 2002). The terminology for metal particles in CBs is unclear in the literature; common terms used for the same objects are: clasts (Newsom & Drake, 1979; Weisberg et al., 2001; Campbell et al., 2002), aggregates (Weisberg et al., 1990; Krot et al., 2002; Campbell et al., 2002), fragments (Weisberg et al., 2001), metal chondrules (Weisberg et

al., 2002), and globules (Rubin et al., 2003). These terms imply processes such as accretion, breakup, or a size/shape parameter that do not necessarily apply to all the CBs. For this study, we use the term “particles” to describe the groupings of individual kamacite grains because it does not imply any specific formation process. CBa chondrites mostly contain mm-to-cm-sized metal particles, with a low abundance of μm -to-mm-sized particles. In our ~2 cm-sized sample of Gujba (UNM-Cr34.2), there are 30+ clearly defined metal particles that are mainly ellipsoidal and circular in shape, and, with a few elongated exceptions, their edges are round and smooth (Fig. 1a). In contrast, the ~2 cm sample of Weatherford contains ~30 metal particles that are mainly elongated and irregular in shape, and appear to be highly deformed; edges of the particles are irregular and the boundaries of individual particles are less well defined than those in Gujba (Fig. 1b). CBb chondrites mostly contain μm -to-mm-sized metal particles. In addition, our ~1 cm sample of HH 237 contains ~5 large metal particles that are ellipsoidal in shape; however, unlike in Gujba, they appear cracked and have irregular outlines (Fig. 1c). Our ~1.5 cm sample of QUE 94411 does not contain any cm-sized metal particles. All of the metal particles in this section are μm -to-mm-sized and irregular in shape (Fig. 1d). Metal particles in all four CB chondrites can be composed of homogeneous (unzoned) kamacite grains, homogeneous (unzoned) kamacite grains containing sulfide inclusions and/or silicate inclusions, or (in CBb only) zoned kamacite grains (Weisberg et al., 2001). Since sulfide inclusions do not occur in zoned metal grains, we focus exclusively on unzoned metal grains.

Some metal particles contain arcuate (‘bow-shaped’) sulfide textures along kamacite grain boundaries (Fig. 2a-e), which have been described for CBa Gujba by Rubin et al. (2003). Arcuate sulfides define the boundaries of each metal grain within the particle. Arcuate sulfide textures are common in both CBa chondrites, and are rare in the CBb chondrites. Figure 2b shows possible arcuate textures in CBb HH 237. However, arcuate sulfides in this grain could also be interpreted as infilling within cracks in the metal particle.

Sulfide inclusions, microns to hundreds of microns in size, occur in many homogeneous (unzoned) kamacite grains. Quantitative modal abundances of metal and sulfide inclusions are discussed below. Figures 2 and 3 show textures of sulfide inclusions in metal particles. Our qualitative estimate is that >80% of metal grains in CBa’s contain sulfide inclusions; this estimate includes only unzoned metal, since CBa chondrites do not contain zoned metal. In CBb HH 237 and QUE 94411, sulfide-bearing metal grains represent ~50% of the total metal, including unzoned and zoned metal.

We define two types of sulfide inclusions: homogeneous sulfides, which consist of Cr-bearing troilite (Fig. 2), and troilite inclusions containing exsolved daubreelite (Fig. 3). Both types of sulfides may or may not contain sub-micrometer metal blebs (Figs. 2f, 3e). Many of the sulfide textures shown here were also identified by Weisberg et al. (2001). Small inclusions, which typically occur in dense clusters within a kamacite grain (Fig. 2c), tend to only consist of the same type of sulfide in individual kamacite grains (i.e. homogeneous only or exsolved only). However, homogeneous sulfides and sulfides containing exsolution lamellae can coexist in the same metal particle. Weisberg et al. (2001) showed that a thin, sub-micrometer rim of high Ni is found around most sulfide inclusions. We observe a similar feature as a higher Z rim at the sulfide-metal interface in some grains in BSE images (Figs. 2f, 3a-e). This may also be associated with the isotopically heavy N that Suguira et al. (2000) observed at sulfide-metal interfaces.

The majority of sulfide inclusions in the four CB chondrites are homogeneous and composed of a Cr-bearing troilite (Fe,Cr)S. These sulfide inclusions are heterogeneously dispersed throughout their individual host kamacite grains. Inclusions range from small, circular,

micrometer-sized inclusions ($\leq 5 \mu\text{m}$) found in densely populated clusters (Figs. 2c, d), to larger, elongate inclusions ($\geq 15 \mu\text{m}$) that have greater distances between neighboring inclusions (Fig. 2e). These larger inclusions may in fact be arcuate sulfides or at least grain boundary sulfides. Some metal particles contain a few homogeneous sulfide inclusions, while others contain hundreds (Fig. 2e). Inclusions between 5-15 μm in size are both circular and elongated in shape in all four meteorites.

Clusters of small metal blebs are observed in some homogeneous sulfide inclusions, as documented by Weisberg et al. (2001). These blebs tend to be on a scale of tens of nanometers, but some can be on the sub-micrometer-scale. Metal blebs are typically concentrated towards the centers of homogeneous sulfide inclusions (Fig. 2f).

We observed troilite inclusions containing exsolved daubreelite in approximately 20% of metal particles in Gujba, no more than 20% in Weatherford and HH 237, and no more than 2% in QUE 94411. In all four chondrites, inclusions that show exsolution are typically 3-50 μm in diameter. Similar to homogeneous sulfides, larger inclusions containing daubreelite are irregular in shape, and smaller inclusions tend to be circular or elliptical (Fig. 3). Most sulfides with exsolution features consist of linear, parallel lamellae, typically of daubreelite (FeCr_2S_4) in a troilite host (Fig. 3a,b). The size of the lamellae, as well as the distance between lamellae, is variable among sulfide inclusions (Figs. 3a-d). A few sulfides in Gujba and Weatherford contain blocky daubreelite, in contrast to the typical linear lamellae (Fig. 3d). The constituents of the blocky texture have the same composition as the linear texture. We observed some inclusions that appear to consist of three phases based on differences in greyscale in BSE images; however, due to the small size of the second set of exsolved lamellae, it was not possible to resolve the compositions of individual phases using EPMA techniques alone. The grain in Fig. 3d also has a region with a very fine-grained sulfide texture at the sulfide/metal interface. As we observed for homogeneous sulfides, clusters of metal blebs are also observed in some sulfides displaying exsolution textures (Fig. 3e), and while most tend to be located within the centers of inclusions, we observed a few examples where blebs are located in the outer regions as well. Metal blebs in sulfides with daubreelite exsolution are always at the tens of nanometer-scale, and we did not observe any larger ones like those found in some homogeneous inclusions. Arcuate sulfides are mostly homogeneous, but a few contain areas that might possibly be a blocky exsolution texture (Fig. 3f). However, none of the arcuate textures contain linear lamellae of daubreelite.

X-ray maps were obtained from the electron microprobe to investigate elemental distributions in sulfide inclusions and surrounding metal. Figure 4 shows elemental maps from a metal grain in Gujba that contained a sulfide inclusion with exsolved daubreelite. The Cr map shows differences between the Cr-rich phase (daubreelite) and the Cr-poor phase (troilite). For the grain illustrated in Figure 4, and several other sulfide inclusions, X-ray maps show the common presence of sub-micrometer inclusions of phosphides at the interface between the sulfide and the surrounding metal. These phosphide inclusions are difficult to observe in BSE images. The P-rich inclusion in the P X-ray map does not correlate with Ca or Mg maps, so we excluded the possibility that this inclusion is a phosphate. Mg-rich silicate inclusions are also present at the interface between sulfides and the surrounding metal (Fig. 4). In addition to sulfide inclusions, some metal grains contain clusters of small silicate particles. Silicate inclusions are typically 1-50 μm in diameter, and can be circular or elongated in shape. Qualitative EDS analyses show that silicate inclusions are Mg-rich and contain minor Al and Ca.

A few metal particles show deformation features, and these features also occur in the sulfide inclusions. Some metal particles are elongated and show signs of plastic deformation, as described

by Weisberg et al. (2001). Deformed metal particles can be sulfide-free, but others have sulfide inclusions that are deformed in the same manner, indicating deformation occurred after the sulfides crystallized (Fig. 5a). Deformation of metal particles is seen in all four meteorites, but is rare in Gujba, which is consistent with the rounded shape of most of its metal particles. Deformation is also apparent in daubreelite lamellae of some sulfides, which are slightly curved and irregular in shape (Fig. 5b), indicating deformation after exsolution occurred. Most of the deformed sulfides are large in size (~20-50 μm) and elongated.

Irregular Fe-FeS textures displaying a “fizzed” texture are observed close to the edges of some metal particles (Chappell et al., 2011) as shown in Figure 6. These shock-melted sulfides are composed of a mixture of troilite and kamacite metal. They seem to be more common in the CBa chondrites, especially in Weatherford which shows the greatest amount of deformation. A few metal particles in the CBb chondrites exhibit these textures as well.

3.2. Modal Abundances of Metal and Sulfides

Using mosaics of high-resolution BSE images for each meteorite (Fig. 1) and the data processing program, ImageJ, we determined quantitative overall abundances of metal in the four CB chondrites (Table 1). Metal comprises ~50 vol% in Gujba, QUE 94411, and HH 237. Weatherford is slightly lower at ~40 vol%. Previous studies have reported metal volume to be between 60-80 vol% (Weisberg et al., 2001; Krot et al., 2002; Campbell et al., 2005b), which is much higher than our samples. We recognize that our data are obtained on relatively limited areas of sample surfaces, which could result in large errors especially for the coarse-grained CB chondrites. However, our values are similar to Rubin et al. (2003), who found the metal volume to be ~41% in Gujba.

Based on visual inspection of the high-resolution BSE mosaics, we observe that a high proportion (>80%) of large metal particles in CBa Gujba and Weatherford contain sulfide inclusions. Quantitative measurements on CBb chondrites are difficult due to the small size of the metal particles. We estimate approximately 50% of metal particles in the two CBb chondrites contain sulfides. Gujba has the highest abundance of metal particles containing sulfides with exsolution features, approximately 16%, whereas in QUE 94411 we only observed exsolution in two metal particles (roughly 2%). In all four meteorites, nanometer-to-micrometer-sized metal blebs are present in less than 5% of sulfide inclusions.

We also used ImageJ to determine abundances of sulfide inclusions in selected metal particles, in order to estimate initial S contents of the metal. Figure 7 compares two similarly sized metal particles in CBa Weatherford, which have significantly different sizes and distributions of sulfide inclusions. The calculated sulfide modal abundance for both is ~2%: large sulfides separated by greater distances (Fig. 7a) constitute roughly the same area as do the small sulfides found in densely populated clusters (Fig. 7b). In other words, the size of the sulfide inclusions does not appear to relate to the modal abundance of sulfides. We measured sulfide abundances in 36 grains in this way. Our analysis shows that modal abundances of sulfides in individual metal particles in CBa and CBb chondrites are ~0.4 to 5.2% and 0.5 to 7.7%, respectively (Fig. 7c, Table 1). Because ImageJ calculates modal abundances by means of pixel sizes, there is a potentially significant error due to the small sizes of some of the sulfide inclusions. Nevertheless, the modal abundances of sulfides in individual metal particles are generally very similar in both groups, although there is a weak trend of higher sulfide abundance in CBb grains.

3.3. Metal Compositions Obtained by EPMA

Compositions of homogeneous (unzoned) metal determined by EPMA are given in Table 2. All metal grains are kamacite (Fe,Ni). The average Fe content is ~93 wt% and Ni is ~6 wt%. The

range for Ni in CBa chondrites is 5.2-7.2 wt% and CBb is 4.8-9.2 wt%. This is comparable to Weisberg et al. (2001), who found Ni contents of 4.8 – 8.2 wt% in CBa and 4.1-14.8 wt% in CBb chondrites. Most metal compositions in the four CB chondrites have Co/Ni ratios close to or slightly above the solar ratio, slope of ~0.045, which is the calculated condensation path of solar abundances (Grossman and Olsen, 1974; Newsom and Drake, 1979; Meibom et al., 1999). Because this study primarily focuses on sulfide inclusions, and since zoned metal particles do not contain sulfide inclusions (Campbell et al., 2005), we only analyzed homogeneous (unzoned) metal grains. Our data are consistent with Weisberg et al. (2001), because high Ni contents are only observed in zoned metal in the CBb chondrites. Unzoned metal grains also contain minor amounts of P (0.1-1.6 wt%), Co (0.2-0.4 wt%), and Cr (b.d. to 0.4 wt%). Weisberg et al. (2001) reported similar ranges of P (0.1-0.7 wt%), Co (0.1-0.5 wt%), and Cr (b.d. to 0.6 wt%). A few metal grains in CBa Bencubbin have previously been shown to contain ~2 wt% Si (Newsom & Drake, 1979; Weisberg et al., 1990), but we did not observe any Si-rich metal in our study. Tables of individual metal analyses are given in the Supplementary Material.

We analyzed a limited number of metal blebs in sulfide inclusions. However, because most blebs are on the sub-micrometer-scale, they are difficult to analyze with EPMA techniques. The average composition of four larger metal blebs in homogeneous sulfides from Gujba and HH 237 is included in Table 2, with individual analyses given in the Supplementary Material. The composition of the blebs differs slightly from the surrounding kamacite grains; Ni is higher (~6.5 wt%) and Co is lower (~0.25 wt%). Consequently, the four metal bleb analyses do not have solar Co/Ni ratios: the three analyses from Gujba have a lower Co/Ni ratio (~0.03), and the one analysis from HH 237 is slightly higher (~0.06).

3.4. Sulfide Compositions Obtained by EPMA

Compositions of sulfides determined by EPMA are given in Table 3. Most homogeneous sulfides contain less than 4 wt% Cr and are composed of Cr-bearing troilite (Fe,Cr)S. Table 3 gives the sum of cations based on 1 sulfur anion for this phase. The range in the sum of cations is between 0.953-1.010. The cation sum obtained with TEM analyses (discussed in section 3.6, and given in Table 3) is 0.954-0.965, depending on the vanadium content.

The Cr-rich phase in some of the troilite grains is exsolved daubreelite, FeCr_2S_4 . EPMA analyses do not give the end-member compositions of the daubreelite lamellae and the troilite host because the widths of the lamellae are smaller than the analysis volume, so most analyses are mixtures of the two phases. Table 3 gives representative EPMA analyses that lie at the extremes of the range of mixed compositions. Tables of individual sulfide analyses are given in the Supplementary Material.

3.5. Metal and Sulfide compositions in the Fe-Cr-S Ternary

Individual sulfide analyses are shown on a Fe-Cr-S ternary diagram for each meteorite in Figure 8. Compositions of metal grains and metal blebs are also plotted, but are hard to distinguish as they overlap at the Fe end of the ternary. The compositions of stoichiometric daubreelite (44.5 wt% S, 36.1 wt% Cr, 19.4 wt% Fe) and troilite are indicated in each diagram. EPMA analyses are differentiated by type of sulfide: homogeneous, homogeneous with metal blebs, and sulfides displaying exsolved lamellae. The main difference between homogeneous sulfides and those containing daubreelite lamellae is the bulk chromium content. Homogeneous sulfides in Gujba, Weatherford and HH 237 have low Cr content, and cluster closer to the Fe-S join (Figs. 8a,b,c), whereas homogeneous sulfides in QUE 94411 have slightly higher Cr contents, up to 11 wt% Cr (Fig. 8d). This higher Cr content in homogeneous sulfides may be an effect of nanometer-sized Cr-rich lamellae that we could not observe in BSE images. If the homogeneous sulfides contain

metal blebs, EPMA analyses lie between troilite and metal (Fe,Ni,Cr), and plot on the Fe,Cr join in the diagram. EPMA analyses of sulfides with daubreelite lamellae lie between troilite and daubreelite, as well as scattering towards the Fe apex when metal blebs are present. We were not able to obtain stoichiometric daubreelite analyses from EPMA techniques because of the small size of the lamellae; however, some analyses in Gujba and HH 237 come close to this end-member composition. For inclusions with μm -sized phases, each EPMA analysis is a mixture of phases. The bulk compositions of the sulfides with daubreelite exsolution lie within the two- or three-phase region defined by the component minerals: bulk compositions of these sulfides are more Cr-rich than bulk compositions of homogeneous grains. Endmember compositions (daubreelite, troilite, and metal) are traced in a black triangle on each diagram to show the field of coexisting phases. The triangle on Gujba is defined by TEM data and the triangles on Weatherford and HH 237 are defined by EPMA data. The black triangles are very similar for Gujba, Weatherford, and HH 237. We do not have any analyses of daubreelite for QUE 94411, but we note that the homogeneous inclusions with higher Cr content show a trend towards the daubreelite point (Fig. 8d).

Figure 8e is a compilation of data for all four meteorites. CBa and CBb chondrites show almost the same trends in their sulfide and metal compositions. Fe-Cr-S phase relations at 600°C (El Goresy & Kullerud, 1969) are superimposed on this figure. Grey areas represent monosulfide solid solution fields (MSS_1 with low Cr and MSS_2 with high Cr), and the grey triangle shows the three-phase region between daubreelite, troilite, and Fe metal at this temperature. The three-phase triangle defined by our Gujba TEM data (dashed lines) is slightly shifted towards the right of the grey triangle, indicating a higher Cr content in the host troilite grains.

3.6. An EPMA and TEM Study of Gujba 5

We selected a relatively large, 30 μm long, irregularly-shaped troilite grain with exsolved daubreelite from Gujba (Sulfide 5) for a detailed EPMA and TEM study. We chose this particular inclusion because it was one of the largest sulfide inclusions observed, and it contained representative linear, parallel lamellae of daubreelite, seen in all CB chondrites. Figure 9a is a BSE image of Sulfide 5 showing its parallel daubreelite lamellae within a troilite host. The widths of lamellae are variable. Daubreelite lamellae extend further into the metal phase than the troilite phase. The inclusion is surrounded by kamacite metal. EPMA X-ray maps were obtained for this inclusion to show elemental distributions. The Cr map illustrates differences between the high-Cr daubreelite and Cr-bearing troilite (Fig. 9b). The location of a 12 μm line array of EPMA analyses is shown as a white line in Figure 9a: Fe, Cr, S, Mn, and V contents are shown in Figure 9c. High Cr (>25 wt%) and low Fe (<30 wt%) correspond to daubreelite (labeled “D”), whereas low Cr (~10 wt%) and high Fe (~50 wt%) correspond to troilite. The thin widths of most of the lamellae cause mixing in all analyses, particularly between 7 – 10 μm in the line array. As discussed below, lamellae are inclined relative to the surface. This accentuates the overlap between the lamellae in the excitation volume for the EPMA analyses. Vanadium and manganese are correlated with chromium content: daubreelite has higher V and Mn contents than troilite.

We used TEM techniques to obtain accurate endmember analyses on the individual lamellae. We cut a ~20 μm wide section of Sulfide 5 from Gujba with the focused ion beam (FIB) technique to use for TEM analysis, as indicated by the black line in Figure 9a. The lamellae in the FIB section were inclined at an angle of 47°, relative to the surface. TEM images show individual lamellae of daubreelite in SEM images actually consist of even finer-scaled intergrowths of daubreelite and troilite (Fig. 10), which explains why it is difficult to obtain stoichiometric daubreelite analyses with EPMA. Table 3 gives representative analyses of troilite and daubreelite obtained with the

TEM. Our analysis of daubreelite have an atomic Fe:Cr:S ratio of 1.19:2.05:4.0, which is close to the 1:2:4 stoichiometric ratio of daubreelite. Chromium content is ~36 wt%, Fe is ~22 wt%, and S is ~43 wt%. We also found compositional variation within troilite, and therefore separate it into two categories: low V and high V (which range from ~0.5-2.5 wt%, and are discussed further in section 3.7).

Dark-field STEM images from Sulfide 5 are shown in Figure 10. These show a second generation of troilite lamellae within the daubreelite lamellae, subparallel to the length of daubreelite (Fig. 10a). Although we could not obtain analyses of this phase, we suggest that it is likely a later growth of troilite from daubreelite. If this is the case, the initial daubreelite composition would have been slightly Fe-enriched instead of strictly stoichiometric. Daubreelite would exsolve troilite to get rid of its excess iron. A great deal of strain was also observed in individual lamellae, which is especially apparent in the mottled texture of troilite (Figs. 10b, c). Nanometer-sized precipitates were observed within troilite in high resolution TEM images, based on the contrast in the image (Fig. 10b). We were unable to resolve the composition of these precipitates, but they likely formed at very low temperatures because of their small size (~15 nm). Nanometer-sized voids are scattered throughout some of the troilite lamellae, but voids are not seen in the daubreelite lamellae (Figs. 10a, c).

STEM X-ray maps of the area in Fig. 10c are shown in Figs. 10d-f. Troilite has higher vanadium and nickel contents than daubreelite. The V X-ray map shows differences in intensities within troilite, with a high V phase and a low V phase. High V tends to occur around the edges of the lamellae (Fig. 10e). Nanometer-sized Ni-rich blebs are seen in the Ni X-ray map (Fig. 10f), and these are only found within troilite lamellae.

3.7. Mn, V, and Cr Relationships in Sulfides

Manganese, vanadium, and chromium contents of sulfide inclusions are shown in Figure 11. Vanadium and Cr contents were determined by both EPMA and TEM techniques. Manganese data could not be obtained using TEM because the Mn K α peak overlaps the Cr K β peak in the EDS spectrum. Since Cr has much higher concentrations than Mn in most of the sulfides analyzed, we are not able to deconvolve Mn peaks through the EDS software.

Homogeneous sulfides and sulfides with daubreelite lamellae show different trends on the Mn vs. Cr plot (Fig. 11a). Homogeneous sulfides have lower Cr contents than sulfides containing daubreelite, ~1-11 wt%, but mostly <5 wt%, and high Mn/Cr ratios. Manganese contents go up to 1.4 wt% in the most Cr-rich homogeneous sulfides. CBb chondrites, QUE 94411 and HH 237, tend to have higher Mn and Cr contents in their homogeneous sulfides than the CBa chondrites. This may be due to very fine grain (nanometer-scale) daubreelite lamellae that we could not observe in BSE images. EPMA analyses of sulfides with daubreelite exsolution are a mixture of troilite and daubreelite, and therefore show a larger spread in chromium. These sulfides have a lower Mn/Cr ratio than homogeneous sulfides, with manganese contents being slightly higher in daubreelite (~0.3 wt%) than in troilite (~0.1 wt%).

Vanadium and Cr contents are shown in Figure 11b. Based on EPMA analyses alone, it appears that homogeneous sulfides have low V, while sulfides with daubreelite lamellae have higher V content. Vanadium appears to be correlated with chromium in sulfides with daubreelite exsolution (Fig. 11b). However, TEM analyses for Gujba Sulfide 5 show V decreasing with increasing chromium. Daubreelite (~36 wt% Cr) has low V (<0.35 wt%), while troilite has up to ~2.5 wt% V. The differences between the analytical results from these two techniques are attributable to the spatial resolution of the analyses. Back-scattered electron images obtained with the SEM show daubreelite lamellae are homogeneous in composition (Fig. 9a), but dark-field STEM images

obtained with the TEM show daubreelite lamellae contain a second generation of troilite lamellae (Fig. 10a). STEM V X-ray maps show high V content is found at the daubreelite-troilite interface (Fig. 10e), likely associated with the second generation of troilite exsolution. EPMA analyses (spot size = 1 μm) on daubreelite are therefore including this second generation of troilite with high V content, giving the apparent increasing trend seen in Fig. 11b. Contrastingly, the TEM is measuring individual lamellae within each sulfide since the spatial resolution is much higher than with EPMA techniques. Our data indicate that low V troilite has higher Cr content (~6 wt%) and high V troilite has lower Cr content (~4 wt%). Although the textural appearance of Sulfide 5 indicates that this grain is representative of all sulfides showing linear exsolution, the vanadium content seems to be higher than in most other sulfide inclusions. Some Other sulfides displaying daubreelite exsolution might actually show a real positive correlation between V and Cr. It is hard to decipher the difference through EPMA, but further TEM analyses on other sulfide inclusions might be able to distinguish this.

4. Discussion

In the following discussion we first examine textural and compositional variations between the CBa and CBb chondrites to address the similarities and differences between the samples studied. We then discuss the origins of CB metal and sulfides, the validity of the vapor plume scenario from our sulfide compositions, and the interpretation of sulfide textures in the context of impact-generated reheating and shock events that occurred later on the CB parent body.

4.1. Textural and Compositional Comparison of CB Chondrites

It is well known that CBa and CBb chondrites are texturally different from one another (e.g. Weisberg et al., 2001). The essential characteristics of the two groups, as well as properties specific to the samples we studied, are illustrated in Fig. 1. CBa chondrites have large, mm-to-cm-sized metal particles and silicate chondrules. Gujba metal particles are primarily circular and elliptical in shape with smooth outlines, suggesting that they formed from melt droplets. In contrast, Weatherford metal particles are irregular and elongated, have ragged outlines, and appear to be plastically deformed (Fig. 1b). CBa chondrites have appreciable amounts of impact melt interstitial to their metal and chondrule particles: this is especially apparent in our Weatherford sample. CBb chondrites are mainly composed of μm -to-mm-sized metal particles and chondrules. In the section we examined, HH 237 contains a few larger metal particles similar to the shapes and sizes in CBa Gujba, however, they are fragmented (Fig. 1c). Our section of QUE 94411 only contains small, μm -to-mm metal particles (Fig. 1d). In terms of shape and size parameters, HH 237 is a combination of both Gujba-like and QUE 94411-like metal particles.

Despite the apparent large-scale textural differences, all four meteorites contain a high modal abundance of metal (40-50%, Table 1), similar modal abundance of sulfides (0.5-7.7%, Table 1), chemically similar metal particles and sulfides (Tables 2-3), and contain similar inclusions (Figs. 2-6). Arcuate sulfides and shock-melted sulfides are observed in both CBa and CBb, but are more abundant in CBa. All four chondrites also contain kamacite grains with homogeneous sulfide inclusions composed of Cr-bearing troilite, sulfides with exsolved daubreelite lamellae, silicate inclusions, and metal blebs within sulfide inclusions. The similarities between these four meteorites suggest that they not only have a related origin, but they also experienced similar secondary processes.

4.2. Origin of Metal Particles in CB Chondrites

The current leading model for CB formation is that individual components condensed from a post-nebular, impact-generated vapor plume. In the vapor plume model, a collision between a

metal-rich body and a silicate-rich body could produce a dense vapor plume highly enriched in siderophile elements (Wasson and Kallemeyn, 1990; Campbell et al., 2002; Rubin et al., 2003; Fedkin et al., 2015). Equilibrium condensation models show that the high abundance of metal (>40 vol%) can only be explained if condensation occurred from a highly metal-enriched gas, and siderophile elements were enriched by a factor of $\sim 10^7$ relative to solar nebular gas (Wasson and Kallemeyn, 1990; Campbell et al., 2000; 2002; 2005; Krot et al., 2002; Petaev, 2006). The high abundance of metal and low FeO contents in silicates suggest that the plume was a reduced environment (< IW), but less reduced than enstatite chondrites ($\sim$ IW-5) (Ebel, 2006; Fedkin and Grossman, 2006).

Based on the textures of CB components, metal could have formed in various ways in the plume scenario. The large impact that formed the vapor plume would have caused high enough temperatures for metal to melt and evaporate. Metal could have condensed directly from the metal-enriched vapor as liquid condensates (unzoned metal) and solid condensates (zoned metal) (Campbell et al., 2002; Rubin et al., 2003; Krot et al., 2005; Davidson et al., 2010; Fedkin et al., 2015). Metal droplets could also have formed from splashing of impactor/target material that was melted either prior to or during the plume-forming collision (Krot et al., 2005). Formation of unzoned metal particles must have involved molten metal in order to account for the rounded shapes we observe in some CB meteorites, especially CBa Gujba. Each particle would be considered as an individual melt droplet, later crystallizing as a metal grain, and arcuate sulfide textures would solidify along grain boundaries.

If both metal and silicate (e.g. chondrules) components formed in the vapor plume, temperatures and pressures in the plume must have been heterogeneous. CBa chondrites only contain unzoned metal particles, whereas CBb contain both zoned and unzoned. It is therefore likely that both types of meteorites formed in separate regions of the plume (Rubin et al., 2003; Fedkin et al., 2015). Fedkin et al. (2015) modeled the vapor plume scenario and suggested that for unzoned metal to form by gas-liquid or gas-solid condensation, the pressure required is 10^{-2} – 10^{-3} bar, with the vapor reaching temperatures ≥ 1900 K to nucleate metal that is homogeneous in composition. The presence of zoned metal in CBb chondrites implies formation in a different region of the vapor plume as gas-solid condensates (Krot et al., 2005; Rubin et al., 2003). Zoning patterns in zoned metal would require rapid cooling (50 K/yr) in a cooler environment, 1740 K for metal nucleation, a less dense environment, and lower pressures ranging from 10^{-5} – 10^{-8} bar (Fedkin et al., 2015). These constraints suggest that zoned metal particles form either towards the outer regions of the plume or in an isolated area within the plume.

Particle size differences between CBa and CBb chondrites suggest that particles in the two groups were deposited differently. Rubin et al. (2003) suggested that metal particles and chondrules were sorted during deposition based on settling velocities and density of grains. Coarser-grained CBa material might represent an earlier depositional component than fine-grained CBb material, resulting in a structure similar to a graded bedding sequence (Rubin et al., 2003). This would be consistent with CBa and CBb material forming in different regions of the plume. Our sample of HH 237 is an example of a possible intermediate region, since it contains some large, CBa-like metal particles, as well as small, CBb-like metal particles. In the alternative scenario, unzoned metal formed from surficial splashing of melt droplets on the parent body, and zoned metal represents gas-solid condensates from the plume. Size-sorting of unzoned metal is depositional and small unzoned particles may become mixed with (uniformly small) zoned metal particles during transport.

Although there are many merits to the impact plume hypothesis, we also note that there are many characteristics of CB chondrites that cannot be explained well by a post-nebula impact scenario. For example, CAIs have been observed in CB chondrites (Krot et al., 2001). The occurrence of refractory inclusions indicates formation by high temperature processes in the solar nebula, which is inconsistent with an impact origin. CB chondrites also have Mg-normalized refractory lithophile ratios ≥ 1 (Weisberg et al., 2001). This observation is consistent with other carbonaceous chondrites and indicates a primitive nebular signature. The origin of CB chondrites is complex. The high abundance and composition of metal seems to require a vapor plume scenario, yet the bulk chemistry indicates nebular origins. The coexistence of the various CB components perhaps requires more than one formation mechanism in the early Solar System.

4.3. *Formation of Sulfide, Phosphide and Silicate Inclusions in Metal Particles*

A few ideas have been proposed to explain the presence of sulfides in unzoned metal particles. Weisberg et al. (2001) suggested sulfide formation could occur if metal particles reacted with surrounding H_2S gas at lower temperatures to form troilite. However, studies on primitive ordinary chondrites by Lauretta et al., (1996) show that this process would have resulted in two concentric layers of sulfides of different compositions surrounding the metal grain. Neither the texture nor the relevant sulfide compositions are seen in CB chondrites (Lauretta et al., 1996; 2001; Campbell et al., 2005b), however, these meteorites have experienced multiple episodes of reheating which could have homogenized initially layered sulfides. Rubin et al. (2003) suggested that after supercooling of a S-bearing melt, some crystallizing kamacite grains grew fast enough to incorporate S, which later formed sulfide inclusions. Another possibility suggested by these authors was that metal formed as evaporative residues that melted and boiled. Crystallized metal that was removed from heat rapidly would contain higher concentrations of S, later allowing sulfide inclusions to precipitate (Rubin et al., 2003).

From our observations, we suggest that unzoned sulfides that occur in CBs likely formed as a result of crystallization and subsequent processing of what was initially a sulfur-bearing Fe,Ni metal melt. Arcuate textures provide clear evidence that the melt was S-bearing. As metal grains crystallize, S partitions into the melt phase and the residual melt becomes more S-rich. As the system cools further, sulfur from the residual melt crystallizes along metal grain boundaries as arcuate sulfide textures. Arcuate sulfides must have crystallized from the metal melt before the particles fell back onto the CB parent body: the particles must have been solid when they landed in order for their rounded shapes to be preserved. This is especially apparent in arcuate textures from CBa Gujba, where metal grains are mainly rounded (Figs. 1a, 2a). Deformation of metal particles in Weatherford (e.g. Fig. 1b) appears to be associated with emplacement of impact melt matrix, and does not appear to be related to accretion of molten or plastic material.

There are essentially two possibilities for the formation of S-bearing metal: splashing or as a liquid condensate. It is difficult to argue for formation of S-bearing metal as a liquid condensate, since S condenses at a much lower temperature than Fe. Rubin et al. (2003) suggested that sulfur condensed from the gas phase into metallic liquids as melt droplets cooled. Fedkin et al. (2015) provide a comprehensive model for formation of unzoned as well as zoned metal by condensation. Although their model accounts for many observations, they did not consider S in their calculations and it is not clear how S behaves in such a scenario. Based on our observations, we argue that S and Cr were likely present in the partially molten metallic core of the impacting planetesimal, which was splashed as liquid droplets during the impact. We therefore must provide an explanation for how sufficient sulfur can be incorporated in liquid metal to form the sulfide abundances observed. Sulfur has low solubility in solid metal, and as a result, will be excluded from the solid

phase during metal crystallization and concentrated in the residual metallic liquid (Chabot, 2004). Ma et al. (1998) conducted an experimental study on Fe-Ni-S melts and showed that ~0.1 wt% S can be dissolved in Fe,Ni metal at 900 °C. Chabot (2004) modelled fractional crystallization trends in magmatic iron meteorites and estimated that the parental cores of IIIAB, IIAB, and IVB irons had between 1-17 wt% initial S content. Our calculations on modal abundances indicate that sulfide inclusions comprise 0.5 to 7.7 vol% of metal particles (Fig. 7c). From these data, we estimate initial (bulk) S contents in metal are between ~0.14-3.3 wt% (Table 4). We suggest that S-bearing metal particles formed as a result of splashed material during the impact between a partially molten planetesimal core and a silicate body. The heterogeneous distribution of S in the metal particles may be due to variable volatilization of initial sulfur content, or the heterogeneity may be related to the timing of sulfide growth.

From our textural observations (e.g. Fig. 2), there are two types of sulfide inclusions based on size differences. Large sulfide inclusions are typically observed spread apart from other neighboring sulfides (Fig. 2d), and they may have crystallized out of the melt phase. Tiny sulfide inclusions are either observed clustered close to metal grain boundaries (Fig. 2c) or clustered towards the centers of metal grains (Figs. 2d, 3a), and may have precipitated out of metal in the solid state. However, there is no quantifiable difference in composition between these two types of sulfides, so the differences in sizes may be due to growth rates and cooling histories. If the initial cooling of the S-bearing metal melt was slow, sulfides would have enough time to crystallize out of the melt. If the initial cooling of the S-bearing metal melt was rapid, excess S would have been trapped within the metal phase, and sulfides would have precipitated out during later reheating events (discussed further in section 4.4). For example, for metal grains in Gujba that contain ~0.5 vol% sulfides and a typical homogeneous sulfide composition of $\text{Fe}_{60}\text{Cr}_5\text{S}_{35}$, the initial metal would require a minimum of 0.01 wt% Cr and 0.17 wt% S (Table 4). For metal grains in Gujba that contain ~0.5 vol% sulfides and typical sulfides displaying daubreelite ($\text{Fe}_{19}\text{Cr}_{36}\text{S}_{45}$) exsolution, the initial metal would require a minimum of 0.03 wt% Cr and 0.14 wt% S. Overall, an estimated range of 0.01-2.29 wt% Cr^0 is required in the solidified metal to account for the range of sulfides observed in all four CB chondrites. The estimated upper limit for Cr^0 is quite high, and implies that the impacting planetesimal that splashed metallic material must have also contained a significantly high Cr content in the melt. The initial metal melt would also require 0-0.11 wt% Mn and 0-0.06 wt% V (Table 4). A disproportionation reaction is required for this scenario to occur: S^0 , Fe^0 , Cr^0 , Mn^0 , and V^0 in the metal phase change valences and precipitate as S^{2-} , Fe^{2+} , Cr^{2+} , Mn^{2+} , and V^{2+} in the sulfides. This scenario does not require a change in oxygen fugacity in the system.

In addition to sulfides, we observed micrometer-sized silicate and phosphide inclusions at the metal-sulfide interface near many sulfide inclusions (Fig. 4), as well as a high-Z rim around sulfide inclusions (Figs. 3b,d-e). Suguira et al. (2000) showed that nitrogen carrier phases are nucleated at the boundary between sulfide inclusions and the metal host. They inferred that the presence of isotopically heavy N may have resulted from shock heating by one of the target asteroids that generated the impact plume, and subsequently incorporated N into metal at high temperatures. Phosphorus may have initially been dissolved in metal as well and precipitated as phosphides during the growth of sulfides. Similarly, Si could have been dissolved in metal if conditions were sufficiently reducing when metal formed. However, it is unlikely that Mg was dissolved in metal. This suggests an alternative mechanism for formation of silicate inclusions. These silicate inclusions may have formed when droplets of silicate melt became incorporated into molten metal, and they were later trapped as immiscible melt pockets when the metal solidified. The interface

between metal and silicate inclusions could have acted as a heterogeneous nucleation site for the nucleation of sulfides. In support of this suggestion, we also observed Mg-rich silicate inclusions occurring in densely-populated clusters. These may have formed from the collision of two molten particles, one metal and one silicate, and subsequent dispersion of immiscible silicate droplets within the molten metal.

4.4. Interpretation of Sulfide Textures

Phase diagrams for the Fe-Cr-S ternary system (El Goresy and Kullerud, 1969) can help to constrain the equilibration temperature recorded by sulfides containing exsolved daubreelite and metal blebs. The recorded temperature could either describe the maximum reheating temperature from impact heating, or the temperature from which the system was rapidly cooled during single-stage cooling. El Goresy and Kullerud (1969) showed that at 700 °C, daubreelite does not coexist with Fe metal. At 600 °C, there is a stability field for the three-phase assemblage MSS_1 (troilite) + daubreelite + Fe metal, which is the assemblage we observe in CB sulfide inclusions. Figure 8e shows our sulfide and metal data superimposed on the 600 °C Fe-Cr-S phase diagram from El Goresy and Kullerud (1969). Even though the assemblage is the same, the composition of troilite that we observe has much lower Cr content, indicating that our data are inconsistent with 600 °C phase relationships. The MSS_1 field likely has lower maximum solubility of Cr as temperature decreases, as evidenced by a decrease in the field size between 700 °C and 600 °C. We therefore infer that sulfides containing daubreelite record temperatures $\ll 600$ °C. Compositions of homogeneous sulfides that did not exsolve daubreelite cluster tightly on the Fe-Cr-S diagram (Fig. 8). In most cases, low Cr contents of homogeneous sulfides are consistent with similar closure temperatures recorded by the grains that show exsolution, $\ll 600$ °C. In other words, all inclusions record a similar temperature, and daubreelite exsolution occurs only in those inclusions which have a high enough bulk Cr content so that they lie in the three-phase field at this temperature. However, CBb QUE 94411 contains homogeneous sulfides with higher Cr content than the other three CBs, up to 11 wt% (Fig. 8d). This elevated Cr content may be due to nanometer-sized lamellae of a high-Cr component, or it could indicate that these inclusions record higher temperatures than homogeneous sulfides in the other CBs. These temperatures could still be < 600 °C, but since QUE 94411 contains only rare sulfides with exsolution for which we have not been able to measure troilite compositions, we cannot make any further inferences about the closure temperature. Some homogeneous sulfides and sulfides with exsolved daubreelite contain a large number of sub-micrometer metal blebs (Figs. 2f, 3e). At high temperatures, sulfide compositions were likely in a one-phase region, and as they cooled, they entered a two-phase region when daubreelite began exsolving, and a three-phase region when metal blebs began precipitating. Metal blebs must have formed after exsolution of daubreelite because they crosscut daubreelite lamellae.

Sulfide textures and microstructures could have either formed in a single-stage formation process, or in multiple heating stages, i.e. as a result of an extended impact history. We discuss these different scenarios below. First, we consider to what extent textural features of sulfides in CBs could be related to the secondary impact history of the CB parent body after accretion. Multiple observations from CB components provide evidence of thermal episodes that are likely caused by impact. For example, the presence of melt matrix is due to melting during impact events (Ramdohr, 1973; Newsom & Drake, 1979; Weisberg et al., 2001). Glass from impact melt areas in CBa Bencubbin has Ar-Ar ages of 4.20 ± 0.05 Ga (Marty et al., 2010), and glass from CBa Weatherford has Ar-Ar ages of 3.6 Ga (Kelly & Turner, 1987). This difference in age indicates that multiple impact events occurred after initial accretion of CB material. CBs also have some metal grains with two-phase microstructures of taenite and kamacite, which indicate heating to

~675 °C, and subsequent cooling to ~550 °C in a month or less (Goldstein et al., 2011). Additional evidence for secondary shock effects in CBs includes the observation of high-pressure phases, such as majorite garnet and wadsleyite (Weisberg and Kimura, 2010). Our observations from sulfide textures also indicate impact and shock-related events occurred on the CB parent body. Fe-FeS shock-melted sulfides (Fig. 6) were observed in all four CB chondrites. These sulfides were typically found near impact melt areas, and were especially common in the highly deformed CBa Weatherford sample. These textures do not display the same distinguishing features or compositions that would result from complete melting at the Fe-Ni-S eutectic (>950 °C; Scott, 1982). Instead, they indicate highly localized shock melting, and formed as a result of incomplete melting of Fe,Ni and rapid solidification of an Fe-Ni-S melt. It is possible that these sulfides once had exsolved daubreelite and the high-Cr lamellae were lost during shock melting. However, daubreelite is more refractory than troilite, making it less likely to melt during shock heating (e.g. Raghavan, 1998; Breen et al., 2016). Similar shock-melted sulfides have been described in the Tishomingo and IIIIE iron meteorites (Buchwald, 1975; Yang et al., 2014; Breen et al., 2016). Troilite and metal intergrowths in Tishomingo indicate quenching at $\sim 10^4$ - 10^5 °C/sec (Breen et al., 2016), which is likely comparable to the cooling rate of shock-melted sulfides in CBs.

Several papers have discussed deformation as a result of secondary, later impact events and shock (Weisberg et al., 2002; 2004; Weisberg and Kimura, 2010; Meibom et al., 2005), for example deformation of barred olivine chondrules in CBa Gujba (Weisberg et al., 2002). All four chondrites we studied also show plastic deformation in some of their sulfide inclusions and metal particles. CBa Weatherford appears to have undergone the greatest degree of deformation, with very irregularly-shaped metal grains, the edges of which are partially melted and entrained in impact melt matrix (Fig. 1b). In all four CB chondrites, some of the metal particles as well as the sulfides within them show plastic deformation (Fig. 5). For grains such as the one illustrated in Fig. 5a, deformation must have occurred after the sulfide inclusions formed, because sulfide inclusions are deformed in the same manner as the host metal grain. Deformation must have also occurred following exsolution of daubreelite in the sulfides (Fig. 5b).

In the cartoon in Figure 12, we compare two extreme models for the thermal histories of CB chondrites recorded by sulfide inclusions: a multiple-stage impact model (solid line), and a model in which sulfide formation takes place during single-stage continuous cooling (dashed line). In both models, metal particles are assumed to begin as S-bearing liquids at high temperatures. S-rich melt accumulates on grain boundaries and solidifies to form arcuate sulfides, and possibly some larger sulfide inclusions. Both models also require that some S was still retained in the metal after the melt solidified. In the multi-stage model, the S-bearing metal melt rapidly cools and crystallizes into polycrystalline metal grains. Reheating events cause sulfide inclusions to precipitate out of the solid S-bearing metal. Exsolution within Cr-rich sulfides could represent a different heating event, or may be from gradual cooling of high-Cr homogeneous sulfides. For this model, the <600 °C temperature recorded by the exsolved phases would likely correspond to the maximum reheating temperature. At this peak temperature, diffusion is fast enough to allow exsolution to occur, and subsequent cooling must be rapid enough to stop diffusion from continuing. Highly localized shock melting caused incomplete melting of Fe,Ni, forming the Fe-FeS shock-melted sulfides which then rapidly cool. Plastic deformation of metal and sulfides from shock follows exsolution of daubreelite and metal blebs. This could occur in a separate heating event, or in a different region on the parent body, since shock effects are likely to be heterogeneous. In the single-stage cooling model (Fig. 12, dashed line), reheating events are not required to form either sulfide inclusions or exsolution textures. Instead, sulfides with exsolution textures form from high-

Cr homogeneous sulfides during gradual cooling. However, the preservation of daubreelite lamellae under these slow cooling rates is difficult to explain. For this model, the temperature recorded by sulfides with exsolved daubreelite, $\ll 600^\circ\text{C}$, would be interpreted as the closure temperature of the system. Similar to the multiple-stage impact model, shock features like the Fe-FeS shock-melted sulfides and plastic deformation of daubreelite must postdate the cooling history of the sulfides. It is possible that a combination of both these two models is represented within CB sulfides.

Irrespective of which model occurred, it is clear that CB sulfides must have at least cooled rapidly following daubreelite exsolution to preserve their textures. Daubreelite lamellae are very fine in scale, and range between a few hundred nanometers to $\sim 2\ \mu\text{m}$ in width (Figs. 3, 10). TEM analysis also shows a second generation of troilite lamellae within the daubreelite lamellae (Fig. 10a), nanometer-sized Ni-rich particles (Fig. 10f), as well as an unknown nanometer-size phase (Fig. 10b) in the troilite lamellae. The presence of these extremely fine-scale features indicates rapid cooling after a low temperature heating event. We suggest that this is consistent with heating and cooling resulting from an impact.

5. Summary

It has been proposed previously that individual components of CB chondrites formed in an impact event that generated a vapor plume. We interpret our observations in the framework of this model, and assume that the differences in sizes of metal and silicate (chondrule) components between CBa and CBb chondrites indicate they formed in different regions of the vapor plume, and/or they fell back onto distinct regions on the parent body. HH 237, which contains both large and small metal particles, is a mixture of CBa and CBb material. In our study, we did not examine zoned metal grains in CBb chondrites, for which evidence has been presented previously arguing that they formed as gas-solid condensates. Our study focused on unzoned metal grains, many of which contain sulfide inclusions. Although they are texturally different, all four CB chondrites we studied have very similar unzoned metal and sulfide compositions, indicating that they share similar origins. Our understanding of unzoned metal grains is that they formed from S-bearing Fe-Ni melt droplets, with average Ni contents $\sim 6\ \text{wt}\%$ and Co/Ni close to the solar ratio. The metal droplets must have initially contained $\sim 0.09\text{--}3.35\ \text{wt}\%$ S and $\sim 0.01\text{--}2.29\ \text{wt}\%$ Cr in the melt. The presence of significant amounts of S argues for an origin as splashed melt droplets, rather than gas-liquid condensates. We suggest that the splashed melt could be derived from partially molten material on one of the impacting pair of bodies. Arcuate sulfide textures, mostly observed in the large metal particles in CBa chondrites, represent residual S-rich melt following crystallization of metal. Metal particles containing arcuate sulfide textures must have solidified before falling onto the parent body in order to preserve the elliptical/rounded morphologies of the metal particles in Gujba. Sulfide inclusions, consisting of Cr-bearing troilite, formed when excess S in the solid metal phase precipitated as the metal cooled. All four meteorites also contain troilite inclusions with exsolved daubreelite, and some sulfide inclusions contain sub-micrometer-sized metal blebs. Similarities in textures and compositions of sulfides among all four CB chondrites indicate that they all experienced similar formation and secondary heating processes. Sulfides with daubreelite lamellae record temperatures $\ll 600^\circ\text{C}$, which can be interpreted as either reheating temperatures during impact events that postdate accretion of the CB parent body, or closure temperatures during single-stage cooling. The fine-grained nature of inclusions and exsolution lamellae indicate that sulfide inclusions must have cooled rapidly. TEM analysis of a sulfide with exsolved phases from CBa Gujba shows multiple stages of exsolution as the grains cooled. Additional evidence for

impact events includes observations of shock-melted sulfides that postdate formation of sulfide inclusions. We also observe shock-induced deformation of sulfide-bearing metal grains that postdates both formation of sulfide inclusions and exsolution. Overall, we conclude that sulfides in CB chondrites preserve a record of prolonged impact and shock histories that postdate accretion following the impact plume event, consistent with the young, reset ages seen from impact melt matrix.

Acknowledgements.

We are indebted to J. I. Goldstein, who sadly passed away in 2015, for many constructive discussions on the interpretation of metal and sulfide textures. We thank M. Spilde and E. Dobrica for their assistance with EPMA and TEM methodology, as well as C. K. Shearer and F. M. McCubbin for their helpful reviews and suggestions. We are grateful to the Institute of Meteoritics at UNM and the Smithsonian Institution for the loan of meteorite samples used in this study. Electron microprobe, SEM and TEM work was carried out in the Electron Microbeam Analysis Facility, Department of Earth and Planetary Sciences and Institute of Meteoritics, University of New Mexico. This manuscript was significantly improved by the insightful reviews of E. R. D. Scott, M. Kimura, and M. K. Weisberg. This research was partially funded by NASA Cosmochemistry grant NNX12AH61G (R. H. Jones).

Editorial Handling: E. R. D. Scott

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FIGURE CAPTIONS

Figure 1. Backscattered electron mosaics of four CB chondrite samples. The contrast is enhanced so that metal grains and particles are white, chondrules are black, and matrix (impact melt) is dark grey/black interstitial to the metal and silicate material. [a] Metal in CBa Gujba consists mostly of mm-to-cm-sized metal particles that are circular to ellipsoidal in shape. [b] Metal in CBa Weatherford consists mostly of mm-to-cm-sized metal particles that are highly deformed; metal is elongated and irregular in shape. [c] Metal in CBb HH 237 mostly consists of μm -to-mm-sized metal particles, as well as a few metal particles that are comparable in size to those in Gujba and Weatherford. [d] Metal in CBb QUE 94411 mostly consists of μm -to-mm-sized metal particles, and unlike the other CBs, it does not contain any large metal particles.

Figure 2. Backscattered electron images of metal particles and homogeneous sulfides in CB chondrites. [a] Metal particle with arcuate sulfide textures along kamacite grain boundaries in CBa Gujba. [b] Metal particle in CBb HH 237. Sulfides occur along grain boundaries in what are possibly arcuate textures. [c] Arcuate sulfide textures and small, rounded sulfide inclusions in a metal particle from Gujba. Sulfide inclusions occur in densely concentrated clusters, mostly near grain boundaries. [d] Metal particle in CBa Weatherford containing small, circular sulfide inclusions in dense clusters, and large, elongate sulfide inclusions that are spread hundreds of microns apart. [e] Two adjacent metal particles in CBa Gujba that have significantly different abundances of sulfide inclusions. Top metal particle contains hundreds of small, circular sulfides. Bottom metal particle contains a few tens of larger, elongated sulfides. [f] Metal blebs in a homogeneous troilite sulfide inclusion. Blebs are mainly concentrated away from the edges of the inclusion.

Figure 3. Backscattered electron images of metal particles and sulfides with daubreelite exsolution in CB chondrites. [a] Cluster of small, circular exsolved inclusions in Weatherford. [b] Typical sulfide exsolution texture showing tens of thin, linear, parallel lamellae of daubreelite in a troilite host. [c] Sulfide inclusion with blocky troilite and daubreelite surrounded by a dark rim of an unidentified phase. [d] Sulfide inclusion with regions of blocky daubreelite, as well as linear daubreelite lamellae in a troilite host. A very fine-grained sulfide occurs at the metal/sulfide interface (top left). [e] Metal blebs in a sulfide inclusion with daubreelite lamellae. Metal blebs are concentrated towards the center of the inclusion. [f] Arcuate sulfide showing possible daubreelite exsolution.

Figure 4. Backscattered electron image and EPMA X-ray maps of a sulfide displaying exsolution lamellae in CBa Gujba. Daubreelite lamellae show plastic deformation. The Cr map shows daubreelite lamellae (red) in a troilite host (green). The sulfide inclusion is located in a kamacite grain, and contains a $\sim 5\ \mu\text{m}$ -size metal bleb (Fe, Ni maps). Small silicates (Si, Mg maps) and phosphide inclusions (P map) are located at the interface between the sulfide inclusion and the surrounding kamacite metal. The Al map shows a region of high Al at the sulfide-metal interface – we have not identified this phase.

Figure 5. Backscattered electron images of deformed metal particles and sulfide inclusions in CB chondrites. [a] Deformed metal particle in QUE 94411. Deformation in the metal is highlighted by sulfide inclusions, which curve in the same trend. [b] Deformed daubreelite lamellae in a sulfide inclusion in CBa Gujba.

Figure 6. Backscattered electron image of an irregularly shaped shock-melted sulfide composed of a mixture of troilite and kamacite metal.

Figure 7. Sulfide abundances in metal grains, determined from high-resolution BSE mosaics and processed with ImageJ software. [a-b] Examples of maps of sulfide inclusions extracted from BSE images using ImageJ. [a] Metal particle 17 from CBa Weatherford containing large, homogeneous sulfide inclusions distributed throughout the particle. Modal abundance of sulfides is ~2%. [b] Metal particle 16 from CBa Weatherford containing small, densely-clustered homogeneous sulfides and sulfides with exsolved lamellae. Modal abundance of sulfides is ~2%. [c] Plot of modal abundance of sulfides (%) vs. area of metal (μm^2) for metal particles with sulfide inclusions in CB chondrites.

Figure 8. Fe-Cr-S ternary diagrams (wt%) showing compositions of homogeneous sulfides, homogeneous sulfides with metal blebs, sulfides with daubreelite exsolution, and metal, obtained with EPMA, for each CB chondrite. Stoichiometric daubreelite (D) and troilite (T) are indicated with a circle on each figure, and extreme compositions of the sulfides with exsolved phases are represented with a black, dotted triangle. [a] CBa Gujba. TEM analyses for Sulfide 5 are also included. [b] CBb Weatherford. [c] CBb HH 237. [d] CBb QUE 94411. [e] Combined data for the four meteorites. Grey areas and grey lines show monosulfide solution (MSS) fields and phase relations at 600°C from El Goresy & Kullerud (1969). Black, dotted triangle shows the three-phase assemblage present in CB chondrites, based on TEM analyses of troilite from Gujba Sulfide 5 and stoichiometric daubreelite.

Figure 9. [a] Backscattered electron image of Sulfide 5 in CBa Gujba, consisting of a two-phase assemblage of daubreelite (dark grey) and troilite (light grey). Locations of an EPMA line array (white line) and a FIB section (black line) are indicated. [b] EPMA Cr X-ray map of Sulfide 5. Daubreelite has high Cr content (red) and troilite has low Cr content (blue). Yellow and green colors show mixtures of the two phases due to the thin width of the lamellae, and the observation from TEM that the lamellae are inclined at an angle of 47° to the plane of the section. [c] EPMA line array for Fe, S, Cr, V and Mn across Sulfide 5. Daubreelite (D) has high Cr and low Fe, as well as higher V and Mn than troilite.

Figure 10. Dark-field STEM [a, c], high-resolution TEM [b] images and STEM X-ray maps [d-f] of daubreelite exsolution lamellae in Sulfide 5 from CBa Gujba. Daubreelite lamellae are more complicated than they appear in BSE images (Fig. 9a). [a] Daubreelite lamellae showing a second generation of parallel lamellae, presumed to be troilite. [b] Unidentified nanometer-sized particles in troilite lamellae. [c] Strain in sulfides observed as mottled contrast. Troilite lamellae show a greater amount of strain than daubreelite lamellae, and also contain nanometer-sized voids. [d] Cr X-ray map of [c]. [e] V X-ray map of [c] showing higher V in troilite. Troilite also contains high V and lower V regions. [f] Ni X-ray map of [c] showing nanometer-sized Ni-rich blebs that mostly occur within troilite.

Figure 11. EPMA and TEM compositional data for sulfides in CB chondrites. [a] Mn vs. Cr (EPMA data only) graph shows different trends for homogeneous sulfides and sulfides with daubreelite exsolution. Homogeneous sulfides in CBb chondrites spread to higher Mn contents than those in CBa chondrites. [b] V vs. Cr graph showing analyses obtained with EPMA and TEM. Homogeneous sulfides contain little V. Gujba Sulfide 5 analyses from the TEM show two types

of troilite: high V and low V. Most of the V is within the troilite phase, and not within daubreelite. EPMA analyses are a mixture between troilite and daubreelite.

Figure 12. Cartoon showing possible thermal histories for metal grains in CB chondrites. We consider two models: a multi-stage heating model of repeated impact events (solid line) and a model with an initial single-stage cooling history (dashed line). In both models, metal particles are assumed to begin as S-bearing liquids at high temperatures. As the particles cool initially, solid metal crystallizes as individual kamacite grains. S-rich melt accumulates on grain boundaries and solidifies to form an arcuate sulfide texture. In the multi-stage model (solid line), solidification of metal particles is followed by rapid cooling. Secondary reheating events cause large sulfide inclusions ($>40\ \mu\text{m}$) to precipitate out of a metastable S-bearing metal melt, and tiny sulfide inclusions ($<40\ \mu\text{m}$) to later precipitate out of the solid S-bearing metal. Exsolution occurs within the sulfide inclusions, depending on temperature and Cr content, either during a further reheating event, or during cooling. In the single-stage cooling model (dashed line), homogeneous sulfides and those displaying daubreelite exsolution form during continuous cooling. In both scenarios, highly localized shock melting caused incomplete melting of Fe,Ni, forming the Fe-FeS shock-melted sulfides which then rapidly cooled. Plastic deformation of metal and sulfides from shock follows exsolution of daubreelite and metal blebs.

Supplementary Material. Electron microprobe analyses from metal and sulfides in CBa Gujba, CBa Weatherford, CBb HH 237, and CBb QUE 94411.

Figure 1.

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Figure 11.

Figure 12.

Table 1. Metal and sulfide abundances obtained from BSE mosaics and processed with ImageJ.

CB Mosaic				Metal Particles				Sulfide Inclusions				Description of Sulfides	
	<u>Map Area</u> (mm ²)	<u>Metal Area</u> (mm ²)	<u>Metal %</u>	<u>Particle</u> #	<u>Length</u> (μm)	<u>Width</u> (μm)	<u>Aspect</u> <u>Ratio</u>	<u>Area</u> (mm ²)	<u>Area</u> (mm ²)	<u>Av. Area</u> (μm ²)	<u>Av. Dia.</u> (μm)	<u>% Area</u>	
<u>Guiba</u>	347.4	170.3	49.0	12	1805	2988	1.66	4.24	0.03	9	3	0.71	Homogeneous, Small sulfides
				13	1733	2103	1.21	2.86	0.11	104	9	3.87	Homogeneous, Large sulfides
				16	1822	2553	1.40	3.65	0.05	19	4	1.26	Homogeneous, Large sulfides
				14	2891	3281	1.13	7.45	0.30	98	9	3.98	Homogeneous, Small & large sulfides
				15	693	1326	1.91	0.72	0.04	31	5	5.19	Eutectic textures only
				5	2235	2747	1.23	4.82	0.05	26	5	1.14	Exsolved
				7	1050	2254	2.15	1.86	0.01	10	3	0.39	Exsolved
				3	3622	4640	1.28	13.20	0.25	46	7	1.90	Exsolved
				17	3718	5110	1.37	14.92	0.67	58	7	4.49	Exsolved
<u>Weatherford</u>	217.4	88.0	40.5	18	637	1976	3.10	0.99	0.03	6	3	2.78	Homogeneous, Small sulfides
				17	1170	1246	1.06	1.14	0.03	43	8	2.31	Homogeneous, Large sulfides
				7	4132	5066	1.23	16.44	0.17	44	6	1.05	Homogeneous, Large sulfides
				19	2695	3254	1.21	5.50	0.18	31	6	3.33	Homogeneous, Small & large sulfides
				2	1270	3152	2.48	3.14	0.07	35	4	2.14	Homogeneous, Small & large sulfides
				20	327	424	1.29	0.11	0.00	22	6	3.65	Eutectic textures only
				8	1594	2246	1.41	2.81	0.06	9	3	2.30	Exsolved
				16	819	1242	1.52	0.80	0.02	4	2	1.99	Exsolved
				6	729	2688	3.69	1.54	0.02	11	3	1.52	Exsolved
<u>QUE 94411</u>	136.5	67.6	49.5	12	535	1258	2.35	0.53	0.02	13	4	4.13	Homogeneous, Small sulfides
				13	530	766	1.45	0.32	0.01	8	3	2.26	Homogeneous, Small sulfides
				24	392	566	1.45	0.17	0.01	9	3	5.31	Homogeneous, Small sulfides
				16	537	899	1.67	0.38	0.02	9	3	5.03	Homogeneous, Large sulfides
				25	186	215	1.15	0.03	0.00	30	5	4.33	Homogeneous, Large sulfides
				22	686	973	1.42	0.52	0.04	22	4	7.70	Homogeneous, Small & large sulfides
				23	382	547	1.43	0.16	0.01	8	3	3.46	Homogeneous, Small & large sulfides
				21	130	244	1.87	0.02	0.00	17	4	3.71	Exsolved

<u>HH 237</u>	102.1	51.5	50.4	15	260	464	1.78	0.09	0.00	10	3	4.79	Exsolved
				7	393	838	2.13	0.26	0.02	17	5	6.68	Homogeneous, Small sulfides
				29	496	579	1.17	0.23	0.01	7	3	4.18	Homogeneous, Small sulfides
				6	343	428	1.25	0.12	0.00	31	6	3.95	Homogeneous, Large sulfides
				16	1975	2864	1.45	4.44	0.02	5	2	0.51	Homogeneous, Large sulfides
				17	397	1298	3.27	0.41	0.02	22	4	4.85	Homogeneous, Large sulfides
				23	1344	1658	1.23	1.75	0.04	9	3	2.22	Homogeneous, Small & large sulfides
				24	836	998	1.19	0.66	0.02	9	3	2.69	Homogeneous, Small & large sulfides
				8	180	287	1.59	0.04	0.00	10	3	2.07	Exsolved
				19	574	754	1.31	0.34	0.01	22	6	2.15	Exsolved

Aspect Ratio: Particle width/length.

Table 2. Average compositions of metal in CBa and CBb chondrites determined by EPMA.

Average Metal Composition (Weight %)					
	<u>QUE 94411</u>	<u>HH 237</u>	<u>Weatherford</u>	<u>Gujba</u>	<u>Metal Blebs</u>
n	21	30	32	56	4
Si	b.d.	0.03 (0.02)	b.d.	b.d.	b.d.
P	0.50 (0.47)	0.32 (0.06)	0.34 (0.03)	0.32 (0.04)	0.21 (0.15)
S	0.02 (0.06)	b.d.	0.07 (0.14)	b.d.	0.19 (0.10)
V	b.d.	b.d.	b.d.	b.d.	b.d.
Cr	0.12 (0.04)	0.19 (0.10)	0.22 (0.09)	0.24 (0.10)	0.50 (0.08)
Mn	b.d.	b.d.	b.d.	b.d.	b.d.
Fe	94.4 (1.31)	94.3 (0.69)	93.2 (0.57)	93.1 (0.91)	92.9 (3.52)
Co	0.29 (0.04)	0.29 (0.02)	0.29 (0.01)	0.31 (0.03)	0.25 (0.10)
Ni	6.08 (0.96)	5.87 (0.43)	5.85 (0.36)	6.23 (0.65)	6.56 (2.89)
Cu	b.d.	b.d.	b.d.	b.d.	b.d.
Zn	b.d.	b.d.	b.d.	b.d.	b.d.
Total	101.4 (0.25)	101.0 (0.38)	100.0 (0.40)	100.3 (0.51)	100.6 (0.65)
Average Metal Composition (Atomic)					
Si	--	--	--	--	--
P	0.01	0.01	0.01	0.01	
S	--	--	--	--	--
V	--	--	--	--	--
Cr	0.00	0.00	0.00	0.00	0.01
Mn	--	--	--	--	--
Fe	0.93	0.93	0.93	0.93	0.92
Co	--	--	--	--	--
Ni	0.06	0.06	0.06	0.06	0.06
Cu	--	--	--	--	--
Zn	--	--	--	--	--
Total	1.00	1.00	1.00	1.00	1.00

b.d. = below detection.

Standard deviations given in parentheses.

n = Number of analyses included in average.

Table 3. Representative EPMA and TEM-EDS analyses of sulfides in CBa and CBb chondrites.

Sulfide Composition (Weight %)													
Grain	QUE		HH 237		Weatherford			Gujba					
								EPMA			TEM-EDS		
	Homog.	Homog.	Ex-Tro	Ex-Daub	Homog.	Ex-Tro	Ex-Daub	Homog.	Ex-Tro	Ex-Daub	L-V Tro	H-V Tro	Daub
	G5_S1	G17_S2	G19_S4	G19_S5	G5_S3	G9_S3	G8_S7	G11_S1	G9_S2	G6_S2	Spec 11	Spec 12	Spec 51
Si	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	n.a.	n.a.	n.a.
P	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.06	b.d.	b.d.	b.d.	n.a.	n.a.	n.a.
S	36.6	37.2	36.5	41.7	36.7	37.2	36.5	36.9	37.5	38.4	37.5	37.8	42.6
V	0.02	0.06	0.37	0.62	b.d.	b.d.	0.38	b.d.	0.29	0.27	0.38	1.88	0.05
Cr	2.07	2.37	7.56	24.2	2.67	6.41	15.5	2.29	6.76	15.6	6.02	4.23	35.3
Mn	0.02	0.06	0.11	0.24	0.03	0.32	0.09	0.04	0.26	0.18	n.a.	n.a.	n.a.
Fe	61.0	60.7	54.7	32.6	59.5	54.3	45.1	60.1	54.8	44.3	56.0	56.2	22.0
Co	b.d.	0.02	b.d.	b.d.	b.d.	b.d.	0.02	0.03	b.d.	b.d.	n.a.	n.a.	n.a.
Ni	0.26	0.19	0.86	0.11	0.20	0.25	0.69	0.21	0.14	0.20	0.12	b.d.	b.d.
Cu	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.10	b.d.	b.d.	0.14	n.a.	n.a.	n.a.
Zn	0.02	b.d.	b.d.	0.24	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	n.a.	n.a.	n.a.
Total	100.02	100.58	100.03	99.61	99.05	98.50	98.38	99.50	99.72	99.05	100.00	100.01	100.00
Sulfide Composition (Atomic)													
Si	--	--	--	--	--	--	--	--	--	--	--	--	--
P	--	--	--	--	--	--	--	--	--	--	--	--	--
S	1.000	1.000	1.000	4.000	1.000	1.000	4.000	1.000	1.000	4.000	1.000	1.000	4.000
V	--	0.001	0.006	0.038	--	--	0.026	--	0.005	0.017	0.006	0.031	0.003
Cr	0.035	0.039	0.128	1.430	0.045	0.106	1.049	0.038	0.111	0.999	0.099	0.069	2.046
Mn	--	0.001	0.002	0.013	0.001	0.005	0.006	0.001	0.004	0.011	--	--	--
Fe	0.956	0.938	0.861	1.794	0.931	0.838	2.840	0.935	0.839	2.650	0.858	0.854	1.189
Co	--	--	--	--	--	--	--	--	--	--	--	--	--
Ni	0.004	0.003	0.013	0.006	0.003	0.004	0.041	0.003	0.002	0.011	0.002	0.000	0.000

Cu	--	--	--	--	--	--	0.005	--	--	0.008	--	--	--
Zn	--	--	--	0.011	--	--	--	--	--	--	--	--	--
Cations	0.995	0.982	1.010	3.292	0.980	0.953	3.967	0.977	0.961	3.696	0.965	0.954	3.238

Table 4. ImageJ calculations for abundances of elements within sulfides and within the initial (bulk) metal melt.

<i>Wt% of element in sulfides (EPMA):</i>																
	<u>Gujba</u>				<u>Weatherford</u>				<u>HH 237</u>				<u>QUE 94411</u>			
	Homogeneous		Exsolved		Homogeneous		Exsolved		Homogeneous		Exsolved		Homogeneous		Exsolved	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Fe	55.072	61.637	25.209	59.202	58.935	59.474	35.977	59.815	52.413	62.194	24.746	54.682	47.441	76.633	n.a.	n.a.
Ni	0.115	0.309	0.039	1.502	0.202	0.224	0.088	1.848	0.195	0.960	0.090	2.441	0.182	3.545	n.a.	n.a.
S	33.891	36.915	27.573	41.666	36.671	36.834	27.421	39.950	35.891	37.149	29.313	43.527	17.902	38.690	n.a.	n.a.
Cr	1.303	6.410	6.071	29.027	2.568	2.956	2.568	20.391	1.960	8.312	7.559	29.787	1.107	11.931	n.a.	n.a.
Mn	0.014	0.120	0.040	0.281	0.021	0.050	0.021	0.334	0.002	0.673	0.071	1.431	0.006	1.203	n.a.	n.a.
V	0.015	0.165	0.116	0.792	0.046	0.064	0.046	0.455	0.081	0.133	0.213	0.834	0.000	0.161	n.a.	n.a.

<i>Wt% of element calculated in metal melt:</i>																
	<u>Gujba</u>				<u>Weatherford</u>				<u>HH 237</u>				<u>QUE 94411</u>			
	Homogeneous		Exsolved		Homogeneous		Exsolved		Homogeneous		Exsolved		Homogeneous		Exsolved	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Fe	0.275	4.746	0.126	4.559	0.295	4.580	0.180	4.606	0.262	4.789	0.124	4.211	0.237	5.901	n.a.	n.a.
Ni	0.001	0.024	0.000	0.116	0.001	0.017	0.000	0.142	0.001	0.074	0.000	0.188	0.001	0.273	n.a.	n.a.
S	0.169	2.769	0.138	3.125	0.183	2.763	0.137	2.996	0.179	2.786	0.147	3.265	0.090	2.902	n.a.	n.a.
Cr	0.007	0.481	0.030	2.177	0.013	0.222	0.013	1.529	0.010	0.623	0.038	2.234	0.006	0.895	n.a.	n.a.
Mn	0.000	0.009	0.000	0.021	0.000	0.004	0.000	0.025	0.000	0.050	0.000	0.107	0.000	0.090	n.a.	n.a.
V	0.000	0.012	0.001	0.059	0.000	0.005	0.000	0.034	0.000	0.010	0.001	0.063	0.000	0.012	n.a.	n.a.

n.a. = not analyzed

Wt% of element in metal was calculated using a minimum and maximum of 0.5 vol% and 7.5 vol% sulfides, respectively, in metal.