Abstract—We used synchrotron X-ray microtomography to image in 3-dimensions (3D) eight whole chondrules in a ~1 cm³ piece of the Renazzo (CR) chondrite at ~17 µm per volume element (voxel) edge. We report the first volumetric (3D) measurement of metal/silicate ratios in chondrules and quantify indices of chondrule sphericity. Volumetric metal abundances in whole chondrules range from 1 to 37 volume % in 8 measured chondrules and by inspection in tomography data. We show that metal abundances and metal grain locations in individual chondrules cannot be reliably obtained from single random 2D sections. Samples were physically cut to intersect representative chondrules multiple times and to verify 3D data. Detailed 2D chemical analysis combined with 3D data yield highly variable whole-chondrule Mg/Si ratios with a supra-chondritic mean value, yet the chemically diverse, independently formed chondrules are mutually complementary in preserving chondritic (solar) Fe/Si ratios in the aggregate CR chondrite. These results are consistent with localized chondrule formation and rapid accretion resulting in chondrule + matrix aggregates (meteorite parent bodies) that preserve the bulk chondritic composition of source regions.

INTRODUCTION

The CR (Renazzo-type) chondrites are primitive meteorites that although hydrously altered did not suffer significant thermal metamorphism, so the properties of their chondrules are important records of chondrule formation (Mason and Wiik 1962, Wood 1962, 1963; Lee et al. 1992; Weisberg et al. 1992, 1993, 1995; Krot et al. 2002; DeGregorio et al. 2008). Renazzo is one of only two CR chondrite falls. In some Renazzo chondrules, metal occurs in two locations: as large interior metal grains, and as numerous smaller metal grains along the chondrule rim. In other chondrules, metal is in smaller grains and more evenly dispersed. Rare chondrules have multiple concentric silicate layers decorated by metal grains (Weisberg et al. 1993; Ebel and Rivers 2007, their DVD-Fig. 9). Interior metal generally has higher concentrations of the more refractory siderophile elements (e.g., Co, Ni; Re, Os, W, Ir, Ru, Mo, Pt) than rim metal, which tends to be enriched in more volatile elements (e.g., Fe, Cu, Au; Weisberg et al. 1993; Connolly et al. 2001; Humayun et al. 2002; Campbell et al. 2002a, 2002b).

One hypothesis (Zanda et al. 1994, 2002a,b; Kong and Palme 1999; Kong et al. 1999; Campbell et al. 2002a) calls for partial evaporation and rapid recondensation of metal to explain metal segregation, and textural, chemical and isotopic characteristics of chondrules, as reviewed by Campbell et al. (2005b). They argued that Ni and Co concentrations in the metal grains of the least circular (in thin section), finest-grained chondrules do not follow a condensation trend, and concluded that the relative amounts of Ni and Co in the interior grains were gradually established during multiple chondrule melting events, due to reduction of fayalitic (FeO-bearing) olivine and evaporation of S from sulfides. Repeated or extensive heating of some chondrules advanced this process, coarsened silicate grains, and promoted a spherical shape of the resulting chondrules. In their scenario, “primitive” chondrules are FeO-rich, probably also FeS-rich, with a mixture of many small metal and 16O-enriched silicate grains, in a non-spherical, convoluted morphology. More “evolved” chondrules have coarser silicate and metal grains, volatile-rich metal grains on their rims (Humayun et al. 2002), circular morphologies in 2D, less 16O-rich silicates (Varley et al. 2003), and well-established, volatility-correlated, core-
rim differences in metal composition, particularly higher Co and Ni concentrations in interior metal grains. To quantify the degree of melting of chondrules, Zanda et al. measured a chondrule convolution index (CVI) in thin section (Zanda et al. 2002a, 2002b; Varley et al. 2003; cf. Nettles et al. 2006). The CVI, minimum value 1.0, is defined as the ratio of the measured perimeter of the chondrule to the perimeter of a circle with the same area:

$$CVI = \frac{\text{chondrule perimeter}}{4\pi \times \text{chondrule area}}.$$  

Correlation of the CVI with chemical data led Zanda et al. (2002a) to suggest that the least evolved Renazzo chondrules formed “by aggregation of numerous droplets in a dust-rich environment.”

Other hypotheses for the metal segregation in CR chondrules include condensation of core metal at higher temperatures, suggesting accretionary growth of the chondrules as temperature decreased (Weisberg et al. 1992, 1993). Wood and McSween (1977, p. 368) concluded: “the concentric arrangement of metal in these objects suggests that they grew, with successive layers being added by accretion or condensation.” Alternatively, additional Fe was incorporated into the metal on the chondrule rims due to FeO reduction from adjoining silicates (Lee et al. 1992). Connolly et al. (2001) analyzed PGE distributions in CR chondrite metal and argued that some rim metal grains, rich in refractory siderophiles, are original to primary formation of the chondrules. They argued that other rim grains, rich in volatile siderophiles, were formed by recondensation from surrounding vapor derived from chondrule reduction and evaporation, and are therefore depleted in refractory siderophiles.

Previous studies of CR chondrules have been limited to two-dimensional (2D) polished thin or thick sections cut at random (e.g., Krot et al. 2002). Here, we use three-dimensional (3D) tomographic imaging (Ebel and Rivers 2007), to obtain sizes, shapes, and volumetric metal/silicate ratios of eight representative Renazzo chondrules. We combine 3D data with 2D petrology and mineral chemistry on surfaces cut through individual chondrules, informed by 3D images, to assess existing hypotheses for the formation of CR chondrules and the accretion history of the CR chondrite parent body or bodies. This is the first work combining 2D and 3D methods to obtain volumetric bulk metal/silicate ratios of chondrules. We argue that the huge range in metal/silicate ratio supports theories of chondrule formation in a local region with chondritic Fe/Si, and rapid “complementary” accretion of chondrules into parent bodies.

**METHODS**

**Tomography and Image Analysis**

Chondrule shape, ratios of metal to silicates, and metal grain distribution are well suited to 3D study by microtomography, due to the very high contrast in X-ray transmission between metal, matrix, and chondrule silicates. Metal grains frequently surround chondrules, setting them apart from matrix in CR chondrites. We used microtomography to study eight whole Renazzo chondrules in situ, then sliced and analyzed five of those in 2D sections.

Spatial resolution in tomographic images is described by the edge length of each cubic volume element (voxel). A single value for X-ray attenuation, a function of mean atomic number, is computed for each voxel (or pixel, in a single 2D virtual slice through the volume). Part of a fragment (~8 × 8 × 15 mm, 1.636 g.; Fig. 1a) of Renazzo (AMNH 588) was imaged at 17.11 micron/voxel edge, for a total tomography volume of $X = Y = 554, Z = 472$ voxels (Fig. 1). Methods of tomography and image handling are described in detail by Ebel and Rivers (2007). The technique allows discrimination between metal and silicate grains, but not between silicate phases at the chosen X-ray energy and spatial resolution. From a 3D tomographic volume describing the X-ray attenuation of every voxel, one can readily produce images of an infinite number of “virtual”, random sections in any orientation. We chose to examine stacks of sequential virtual images, or “slices,” perpendicular to the z-axis (vertical, Fig. 1a) of the tomographic volume.

Eight chondrules were chosen to be representative of the wide range of metal-silicate textures we observed by tomography (Figs. 1 and 2a). From the full data set (e.g., Fig. 2a), a data volume containing each chondrule was extracted, and each image slice was cropped manually using ImageJ (NIH-wwww 2008) to isolate the chondrule of interest in each slice where it appeared. Figure 2b shows number 44 of 99 cropped slices of chondrule 1, this one isolated from Fig. 2a. Representative sequential slices for all 8 chondrules are illustrated in Fig. 3. Each stack of slices was further edited to obtain a separate image stack, containing just the metal-rich rim of the chondrule exposed in each slice. Figure 2c illustrates this rim for slice 44 of chondrule 1. Widths of these “rim” areas were established as inside the penetration width of the largest metal grain that was clearly a “rim” grain. Metal/(metal + silicate) ratios in rim areas and in each entire chondrule are reported in Table 1 (columns 13 and 14).

The number of voxels in the perimeter and surface area were measured in each slice of each chondrule, and summed over all the slices of each chondrule to calculate chondrule volume and surface area (Table 1, columns 3–6). A CVI was calculated for each chondrule in each slice (Fig. 4; Table 1 columns 7–10). A three-dimensional CVI (3D-CVI) was also calculated for each chondrule (Hertz et al. 2003), defined as the ratio of the measured surface area to the surface area of a sphere with the same volume as that measured for the chondrule (Table 1, column 11).

Using identical thresholding techniques for each chondrule, the number of pixels contributing to metal in each slice was measured (Fig. 4), and summed to the volume fraction of metal in each chondrule (Table 1, column 12). To obtain the data in Table 1, no actual physical cutting was done on the
Shape, metal abundance, chemistry, and origin of chondrules in Renazzo

Table 1. Textural characteristics measured and calculated from 3D tomographic data for 8 Renazzo chondrules. The number of virtual slices \( n \) yields volume and surface area, from which the maximum, minimum, and standard deviation of CVI observed in all slices of each chondrule are calculated, and an average CVI weighted by chondrule size (area), and a 3D convolution index (3D-CVI). Metal/silicate ratios (as % metal) are for whole chondrule volumes and for portions identified as "rim."

<table>
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<tr>
<th>Chon</th>
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<th>Chondrule volume</th>
<th>Surface area</th>
<th>Convolution index (CVI)</th>
<th>Metal</th>
<th>Metal</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>( \text{mm}^3 )</td>
<td>( \text{mm}^2 )</td>
<td>Min</td>
<td>Max</td>
<td>( \sigma )</td>
</tr>
<tr>
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<td>98</td>
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<td>23037</td>
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<td>16798</td>
<td>6.02</td>
<td>1.02</td>
</tr>
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<td>20758</td>
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<td>27989</td>
<td>10.04</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Fig. 1. Renazzo sample. Only part of original rock (A) was imaged. Cross section (B) is tomography slice \( Z = 380 \) of 472, illustrating wire saw cuts and chondrule 1 in section B1. Orthogonal tomography slices \( Y = 300 \) of 554 in (C) and \( X = 180 \) of 554 in (D) illustrate the locations of chondrule 1 and slice \( Z = 380 \). Scale bars are in mm. Empty space in (B) has been cropped from the tomography image.
original Renazzo sample. Accuracy of 3D data analysis was verified by inspection of thin sections through the chondrules. The BSE image in Fig. 2D illustrates the sharp appearance of the chondrule-matrix boundary in polished section for most Renazzo chondrules. An accretionary rim surrounds both chondrule 1 and also a small attached chondrule, which has a very different metal texture and uniform metal grain compositions (c1x in Table 4). This attached chondrule was not counted as part of chondrule 1 (Fig. 3).

Chemical Analysis

Guided by tomographic analysis, we purposely cut the sample (Fig. 1) to expose equatorial surfaces of particular chondrules. The AMNH sections containing these slices are: ch1a = Ren1sB1-S2H (Fig. 2D), ch1b = Ren1sB1ps4a; ch2a = Ren1sB1ps7a; ch2b = Ren1sB3ps1A; ch3, 4, 5 = Ren1psA. All cuts were made with a 50 or 30 µm tungsten wire saw (Princeton Instruments) with boron carbide abrasive in machine oil slurry. Figure 2b illustrates the tomographic image of chondrule #1 that corresponds as closely as possible to the ~100 µm thick polished section (Fig. 2D). The axes of tomographic data are not exactly orthogonal to the cut and polished surfaces of the irregular prismatic sample (Fig. 1).

X-ray mapping, and analyses of silicates and metal grains were performed using the 5-spectrometer Cameca SX100 electron microprobe (EMP) at AMNH. Tables 3 and 4 report averages of n spot analyses, each normalized to 100 wt%, and the average analysis sum. X-ray intensity maps were used to calculate modal abundances of silicate phases in each chondrule (Table 2). Similar modal calculations were done on sub-portions of chondrules 2 (section a) and 3 to obtain modal silicate abundances in the ellipsoid roughly corresponding to the olivine-rich core, and in the ellipsoidal shell corresponding to the pyroxene-rich rim in these igneously layered chondrules (Fig. 5). Technical details are available from the corresponding author.

Laser-ablation ion-coupled plasma mass-spectrometry (LA-ICP-MS) analysis of metal grains was performed to confirm the systematic correlations of major and trace siderophile elements in metal grains (e.g., Humayun et al. 2002). LA-ICP-MS was accomplished on chondrule 1, section a (circled, 1–15, Fig. 2D) at the University of Chicago (Campbell et al. 2005a), and on chondrule 1 section b, and chondrules 2–5 on the single-collector Element 2 at the University of Maryland Plasma Mass Spectrometry Lab. No single grain was analyzed in both labs. Spot sizes were 15–50 µm depending on grain size. Concentration data for individual analyses and averaged values are reported in online supplemental Tables 1–3.

RESULTS

Chondrule Shape and Texture by Tomography

The entire imaged portion of Renazzo (Fig. 1) contained more than 90 entire chondrules greater than 520 µm in diameter. We measured eight chondrules in detail (Fig. 3). Measurements on each of the complete tomography sequences are plotted in Fig. 4. Tomographic datasets can be found in Ebel and Rivers (2007, on DVD). Both metal modal abundances and CVI, measured in 2D for any particular chondrule, depend strongly upon which slice is measured, as evident in Figs. 3 and 4, and the standard deviation in CVI (Table 1, column 9).
All of the chondrules studied are FeO-poor type I porphyritic chondrules, the dominant type in CR chondrites (Weisberg et al. 1995). These chondrules represent ranges of grain size, metal abundance, and shape that are typical of the chondrules in CR chondrites. For example, chondrule 1 is a porphyritic olivine chondrule with a 300 µm metal nugget in its core. On its rim are smaller metal grains that are 50–100 µm in size. Chondrules 2 and 3 are layered (Fig. 5), with forsteritic olivine + mesostasis-rich cores, including metal grains, surrounded by coarse-grained, low-Ca, pyroxene-rich igneous rims. Chondrule 2 is finer grained than 3, with a more irregular (convoluted) outline (Figs. 3 and 5). Chondrules 4 and 5 appear in tomography to be a classical compound chondrule pair, in which chondrule 5 was partially molten (Ebel and Rivers 2007, their DVD-Fig. 3B; Ebel-www 2008).

This kind of 3D analysis has never been done before in
Fig 4. Modal metal (triangles) and convolution index (CVI, squares) measured in sequential chondrule images. Average values for CVI (dotted) and %metal (dashed) are superposed.
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CR chondrites, and allows quantitatively comparison of 2D and 3D methods. The images in Fig. 3 suggest that the less (e.g., 2, 6, 8) or more coarsened, rounded nature (e.g., 1, 3–5, 7) of each chondrule can, in most cases, be qualitatively assessed from a single random section through its middle region. Quantitative results, however, show significant variations even in these central regions (Fig. 4). The variability in CVI (Table 1, column 9) is high enough that different random sets of cross-sections could produce a wide variation in rank order of “convolution” of these 8 chondrules. In particular, chondrule 1 contains the large high-Ni “core” metal grain, but has a CVI significantly above unity (i.e., it is rounded but not circular). The 3D-CVI are only weakly correlated (r² = 0.44) with the average 2D CVI, and even more weakly with metal abundance (r² = 0.29). Although the main variance in CVI is between core and rim areas, there is no way in a thin section to tell which area one is observing.

Volumetric Metal/Silicate Ratios by Tomography

We report here, after Hertz et al. (2003), the first direct volumetric (3D) measurements of metal abundances in chondrules. Two results are apparent: (1) both metal abundance and metal grain shape are highly variable among 2D slices of a single chondrule, and (2) there is a large variation in bulk metal abundance between the chondrules. These inter- and intra-chondrule variations would not be recognized using only standard 2D techniques. The representative slices in Fig. 3 illustrate, qualitatively, the problems inherent in 2D analysis of 3D objects that are not spherically symmetric in shape or metal distribution. Metal abundances tend to peak in initial and final virtual slices that intersect rims, where metal grains are concentrated. Even in the central portions of many of these chondrules, large variations are evident in both metal abundance (Fig. 4) and metal grain shape (Fig. 3). For example, slices 45 and 50 of chondrule 1 show a metal-rich chondrule core, whereas slices 30, 80 and 90 of the same chondrule show a metal-poor core (Fig. 3). Likewise, slices 30, 50 and 60 of chondrule 5 appear metal-rich, whereas slices 35, 40 and 70 appear metal-poor.

The high X-ray contrast between metal and silicates allows robust determination of whole chondrule metal/silicate ratios. Fractional metal abundances in the eight chondrules measured in 3D vary from ~1 vol.% to a remarkably high ~37% (Table 1, column 12). These bulk volumetric metal abundances (Table 1, column 12) generally differ from the apparent abundances acquired by 2-D section analysis (Table 2), and from the average value across each image stack (Fig. 4).
Modal abundances of silicates were only accessible by 2D methods (Table 2). The results of 2D modal calculation using custom-written software, output with pixels color-coded by mineralogy as determined by a rule-based algorithm from raw element maps, are indistinguishable from the Mg-Ca-Al mosaic composite X-ray maps shown in Fig. 5. Modal abundances of olivine, pyroxenes, glass, trace carbonate (verified by energy dispersive spectrometry), and unidentifiable pixels in five sectioned chondrules are given in Table 2.

Chondrules 2 and 3 are layered, with an inner region that appears to be nearly spherical, with coarser forsteritic olivine and large metal grains near its rim (Figs. 3 and 5). Because these two chondrules appear roughly symmetrical in 3D and 2D (Fig. 3), we approximated the effect of layering on modal calculations by fitting ellipsoids to an outer region (rim), and an inner region (core) for one section of each of these chondrules (Fig. 5). We start with the assumption that the olivine/pyroxene/glass ratios in Table 2, and phase compositions in Tables 3 and 4, are representative of rim and core regions each entire chondrule. This assumption is justified by the larger proportion of silicates, relative to metal, exposed in sections; lack of localized concentrations of a single silicate phase; smaller grain size of silicates compared to metal; observed chemical homogeneity of silicate phases; and the fact that we could not distinguish among silicates in 3D.

Bulk chemical compositions were calculated for each chondrule by modal recombination, using the silicate chemical compositions in Table 3. No systematic differences in major element contents between olivines or pyroxenes in Table 3. Silicate compositions (wt%). Data are average and standard deviation (parenthetical below) for n electron microprobe analyses. Mean values of oxide totals for n original analyses are also given. Low-Ca pyroxene is labeled “pyx,” and high-Ca grains “Ca-px.” Mineral structures were not determined. K2O, P2O5, and SO2 are below detection limits and omitted from totals. Only analyses with 96 < total < 102 wt% are included.
Fig. 5. X-ray composite maps of Renazzo chondrules 1–5. X-ray intensities of Mg, Ca, and Al are overlapped in, respectively, red, green, and blue channels of rgb images. Metal is black. Yellow curves outline inferred rim and core regions in chondrules 2 and 3.
Table 4. Metal grain compositions. Composition ‘c1x” is a small chondrule attached to chondrule 1 (Fig. 1). Data are mean and standard deviation for n electron microprobe analyses. ‘Xmetal” is the volume fraction of chondrule metal in rim and core grains in the whole chondrule (Table 1), except for chondrule 2 with homogeneous metal compositions.

<table>
<thead>
<tr>
<th>Chon</th>
<th>n</th>
<th>Fe (wt%)</th>
<th>Ni</th>
<th>P</th>
<th>Cr</th>
<th>Co</th>
<th>Sum</th>
<th>Xmetal</th>
<th>Co/Fe</th>
<th>Ni/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Core</td>
<td>124</td>
<td>90.87(0.28)</td>
<td>8.18 (0.15)</td>
<td>0.32 (0.15)</td>
<td>0.29 (0.05)</td>
<td>0.35 (0.02)</td>
<td>100.03 (0.42)</td>
<td>0.452 (0.02)</td>
<td>0.0039 (0.09)</td>
</tr>
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<td>0.42 (0.21)</td>
<td>0.21 (0.05)</td>
<td>0.24 (0.02)</td>
<td>100.38 (1.05)</td>
<td>0.548 (0.02)</td>
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</tr>
<tr>
<td>2</td>
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<td>200</td>
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<td>5.25 (0.92)</td>
<td>0.33 (0.19)</td>
<td>0.55 (0.2)</td>
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<td>0.0027 (0.05)</td>
</tr>
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</tr>
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<td>Core</td>
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chondrule interiors and chondrule rim regions were detected. A simple calculation based on 2D modal data yielded bulk chondrule SiO2, MgO, FeO, CaO, and Al2O3 (Table 6). Caveats apply to this kind of analysis (Hezel 2007). However, recent work shows that in many cases olivine/pyroxene ratios are sufficiently constant between serial sections that 2D modal measurements can be representative of the true 3D bulk chondrule composition (Hezel, personal communication). For layered chondrules 2 and 3, a second bulk composition calculation was made, modeling each as a combined inner ellipsoid (core) and an outer ellipsoidal shell (Fig. 5). These volumes were assumed to be represented by the silicate mineral modes (Table 2) measured in the core and rim areas shown in Fig. 5. Ratios MgO/SiO2(wt%) calculated this way for chondrule 2 illustrate sensitivity to Ca-pyroxene abundance, relative to the simpler 2D calculation. For chondrule 3, the second calculation brings the bulk MgO/SiO2 ratio to below solar, due to the thick pyroxene-rich rim. For comparison with chondritic (solar) ratios, the relative mass fractions of the oxides were calculated, preserving their solar proportions relative to the mean FeO of all eight chondrules. The composition of this “solar” chondrule differs from the mean of the measured chondrules in important ways. Recalculation of the mean chondrule oxides using these layered compositions for chondrules 2 and 3 brings the mean chondrule oxide values closer to the solar expectation.

Metal Analysis in Polished Section

Mean chemical compositions of rim and core metal grains are presented in Table 4. Both Cr/Fe and P/Fe are considerably sub-solar in all metal grains measured. Phosphorus is enriched in rim metal, with the ratio (P/Fe) 1.3× and 2.1× higher in rim than in core grains for chondrules 1 and 5, respectively. Results for Cr are ambiguous, but Cr is not as strictly siderophile as the other elements measured in metal. Detailed examination of metal grain microstructures reveals no subgrains or exsolution.

The absolute Fe, Ni and Co abundances in each chondrule were calculated using the relative abundances of rim and core metal grains observed in 3D (Table 1, column 13), and assuming that the chemical compositions of core and rim metal grains analyzed in 2D sections (Table 4) are representative of similarly located grains in the entire chondrule. We identify the high-Ni grains in chondrule 5 as “core,” although there are a few other grains not on the chondrule rim, but much nearer to it, that have low-Ni compositions typical of rim grains.

We normalized rim and core mean compositions to only Fe, Co, and Ni, because these elements dominate metal grain compositions (Table 4). We then calculated the bulk metal composition in each fractionated chondrule, using the tomographically measured rim/core metal abundances (Table 1, column 13), and also calculated the bulk Fe-Ni-Co composition of metal in unfractionated chondrule 2. These results are compared in Table 5 with solar abundances.

Part of our goal is to assess the evolution of metal in CR chondrules, and trace element chemistry is critical to this end. Metal grains were measured by LA-ICP-MS for two sections of chondrule 1 (Fig. 2D), and one each of chondrules 2, 3, and 5. Full results are available in an online supplement. Trace siderophile element compositions are highly variable within and between metal grains. Figure 6 illustrates average results for chondrules 1 (sections a and b), 2 and 3, normalized to 100 wt% total. Humayun et al. (2002) report Mo, Ru, W, Re, Os, Ir, Pt, Ni, Co, and sometimes Pd enriched in core metal, and depleted in rims, while Fe, Cu and sometimes Pd are enriched in rims, and Ga and Ge are not measurably core/rim fractionated (Campbell et al. 2002a). Here, results for Fe, Cu, Mo, Os, Ir, and Pt are similar, but Ni and Pd are always enriched in core metal grains: core/rim Pd/Fe are 2.33, 2.07, 2.04; in chondrules 1, 3, and 5 respectively. Rim metal grains are also enriched in As and Au.
PGEs and the volatile siderophiles. Palladium does not fractionate significantly from Fe during high-temperature vapor-solid interactions in the solar nebula (Campbell et al. 2001), but Pd is less readily oxidized and has a lower solubility in the silicate melt than Fe. Enrichment of core metal in Pd/Fe (by $\sim 2\times$) was observed by Humayun et al. (2002) in only one of 11 chondrules they studied. By contrast, we observe core Pd enrichment in all core/rim fractionated chondrules where Pd was measured (Figs. 6 and 7). Difference in oxidation and silicate solubility would also have affected the abundances of the other siderophile elements, but their much stronger fractionations (for refractory PGEs) and fractionations in the opposite direction (for volatile elements Cu, As, Au) reveal that volatility effects were more important than redox effects on these elements. Finally, we note that the Pd/Fe ratio in the rim grains is subchondritic, whereas it is superchondritic in the core metal. This relationship is consistent with a model in which volatilized Fe (and other volatile siderophiles, such as Cu and Au) recondensed onto rim grains (Conolly et al. 2000; Humayun et al. 2002; Campbell et al. 2005b).

**DISCUSSION**

**Petrology in 2D and 3D**

Assigning the perimeter of a chondrule for measurement of the CVI is a subjective exercise. All of our chondrules were virtually “cut” from matrix (Fig. 1) by one person, from data at a single spatial resolution and contrast, using consistent criteria. Yet most of our CVI measurements are below 1.45, while a majority of those by Zanda et al. (2002a) and Nettles et al. (2006) are higher. It is likely that perimeters drawn around high-resolution surface maps or photomicrographs are generally more convoluted (jagged or embayed) than those drawn around lower-resolution X-ray tomographic images. Nevertheless, our results allow robust textural comparison within a single dataset.

Our results confirm many of the observations of Nettles et al. (2006) concerning the use of the CVI as a single indicator of the degree of chondrule melting. A single CVI measurement in thin section is unreliable due to the large standard deviations in CVI (Table 1, column 9) and the range even among nearby slices (Fig. 4). Nettles et al. (2006) also noted that a single criterion like the CVI should be supplemented by metal grain size and distribution information. That is exactly the information which supplies the visual clues for qualitative assessment of chondrule melting (Fig. 3; Nettles et al. 2006; see also Ebel and Rivers 2007).

The sphericity of entire chondrules, measured by the 3D-CVI, is a more reliable texture indicator than single 2D measurements. The 3D-CVI correlate with the observed abundance and texture of metal grains, and are lowest in chondrules 4, 5, 1, 7 and 3, in which either the total abundance of metal is low (#4 and 7), or metal is concentrated in a few large grains (#1, 3, and 5). The 3D-CVI appears to be weakly correlated to total chondrule volume. As a chondrule’s surface area increases, it has more opportunity to have a large 3D-CVI, and surface convolution becomes easier to measure in larger chondrules. We do not observe any correlation between FeO in olivine (Table 3) and the 3D-CVI.

It has been suggested (Grossman and Wasson 1985; Tsuchiyama et al. 2000) that metal is driven to the rims of rapidly spinning, partially molten chondrules by centrifugal force. In this scenario, metal should be concentrated on the equatorial plane of a spinning chondrule (Uesugi and Sekiya 2006). Tomographic images in orthogonal directions do not reveal any preferred (equatorial) surface distribution of metal grains in the CR chondrites we studied. In experimental analogs of non-spinning chondrules, metal also migrates to outer surfaces (Connolly et al. 1994), apparently to minimize surface energy. Alternatively, metal grains could be accreted directly to the outer surfaces of earlier-formed chondrules. De-coupled accretion of high-temperature metal and silicate grains would explain the high variability in bulk metal/silicate volumetric ratios in chondrules (Table 1). Separate, sequential accretion of metal and silicates would also explain the existence of chondrules with multiple concentric layers: silicate/metal/silicate/metal.

**Chondrule Layering**

In 3D, we have observed a few chondrules in CR chondrites that have multiple metal-rich and metal-poor layers. One well-developed example is in sample Acfer 139-2 imaged by Ebel and Rivers (2007, their DVD-Fig. 9C; cf. Ebel-www 2008), and consists of a forsterite core decorated with metal, all rimmed by forsteritic silicate, then larger metal grains, then a thinner rind of silicate, with an outer rim of smaller metal grains. Imaging in 3D allowed us to precisely bisect chondrules to reveal, in 2D, not only the metal layering observed by tomography, but also the igneous layering sequence—olivine-rich core, Ca-poor pyroxene-rich rim (Fig. 7 inset; Fig. 5)—that is observed in some CR chondrules.
Our 3D data show that neither type of layering would be recognized in many 2D sections. Olivine-pyroxene layering is consistent with high-temperature equilibration with a solar gas, because olivine condenses at higher temperatures than pyroxene (Ebel and Grossman 2000; Ebel 2006).

The inner regions of layered chondrules appear to be nearly spherical, with coarser forsteritic olivine and large metal grains than the outer regions (e.g., Fig. 5B). Yet the interior metal grains are not always Ni- or Co-rich, for example in chondrule 2. The outer region (rim) of this chondrule is a more irregular, fine-grained layer (Fig. 5A) that gives the chondrule an over-all convoluted texture (Table 1, Figs. 3 and 4), and the metal grains in this rim are also ~solar in Ni/Fe and Co/Fe ratio (Table 4, Figs. 6 and 7). We have not found any layered CR chondrules with a convoluted, fine-grained core surrounded by a spherical, coarse-grained rim.

Metal grains in chondrule 3 (Table 4, Fig. 7) show a core-to-rim composition trend consistent with the high- to low-temperature trend predicted by condensation calculations (Fig. 7; Ebel and Grossman 2000, their Fig. 14). It is not at all clear how these compositional gradients would be predicted or explained by evaporation-recondensation models for bimodal metal compositions (e.g., Zanda et al. 1994; Kong and Palme 1999; Campbell et al. 2005b). Instead, these gradients suggest that the core region of chondrule 3 equilibrated with vapor at high temperatures, and that successive layers of silicate and metal were subsequently accreted and annealed, with only partial re-equilibration of the inner core minerals. The Pd/Fe ratios of interior and rim metal grains (Fig. 6) suggest the later influence of an oxidizing environment, which would preferentially remove Fe (Campbell et al. 2005b). Alternative thermodynamic conditions may exist, however, in which core grains could concentrate Pd at the same temperatures at which Ni and Co would be enriched (Fig. 7).

**Major Element Abundance and “Complementarity”**

For the 8 chondrules studied here, the standard deviation of metal abundance is >95% of its average value (Table 1, column 12; Fig. 3 by inspection). Each chondrule has a unique budget of siderophile elements (Table 5). Similarly, chondrule bulk silicate compositions show large variability in chondrule MgO/SiO$_2$ ratios (Table 6). It is clear, however, that bulk samples of CR chondrites (Lodders and Fegley 1998, their Table 16.10), and the Renazzo meteorite (Kellenseym and Wasson 1982; Weisberg et al. 1993) contain Mg, Si, Fe, Co, and Ni in solar proportions. The concept of “complementarity” can explain these observations.

The complementarity between the chemical compositions of matrix and chondrules (Palme et al. 1992) has been addressed in several studies (Kong and Palme 1999; Kong et al. 1999; Klerner and Palme 1999; Bland et al. 2005). Meteorites with chondritic (solar) ratios of major elements contain chondrules and matrix in varying ratios. Because
Shape, metal abundance, chemistry, and origin of chondrules in Renazzo

Chondrules and matrix differ in mean major element abundance, the chondrules must have formed, coexisting with the matrix grains, as a closed system in those elements, from a chondritic batch of material in the protoplanetary disk. It is less likely that complementarity would result from exotically formed chondrules (e.g., near the Sun), transported and mixed with matrix dust local to the region of later parent body accretion.

Table 6. Bulk silicate compositions of chondrules (wt%), calculated from Tables 2, 3, and 4, compared with solar expectation. Cr₂O₃, MnO, and NiO are omitted. Chondrules 2 and 3 are calculated using both simple modes (above), and the core + rim layer estimate of Table 2 (below). Oxide proportions expected for a solar complement of oxides for comparison (AG89: Anders and Grevesse 1989; L03: Lodders 2003).

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>MgO/SiO₂</th>
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<tbody>
<tr>
<td>ch1</td>
<td>54.99</td>
<td>0.14</td>
<td>2.41</td>
<td>1.62</td>
<td>38.85</td>
<td>1.93</td>
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<tr>
<td>ch2</td>
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<td>0.20</td>
<td>7.32</td>
<td>1.46</td>
<td>31.83</td>
<td>4.45</td>
<td>0.10</td>
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<tr>
<td>ch3</td>
<td>43.13</td>
<td>0.14</td>
<td>0.72</td>
<td>3.38</td>
<td>51.66</td>
<td>0.79</td>
<td>0.19</td>
</tr>
<tr>
<td>ch4</td>
<td>48.69</td>
<td>0.35</td>
<td>2.96</td>
<td>2.54</td>
<td>40.86</td>
<td>2.48</td>
<td>2.13</td>
</tr>
<tr>
<td>ch5</td>
<td>44.30</td>
<td>0.15</td>
<td>1.64</td>
<td>2.18</td>
<td>50.56</td>
<td>0.72</td>
<td>0.44</td>
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<tr>
<td>Mean:</td>
<td>49.08</td>
<td>0.20</td>
<td>3.01</td>
<td>2.24</td>
<td>42.82</td>
<td>2.07</td>
<td>0.58</td>
</tr>
</tbody>
</table>

By layers:

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>MgO/SiO₂</th>
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</thead>
<tbody>
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<td>1.49</td>
<td>32.57</td>
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<tr>
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<td>0.20</td>
<td>4.21</td>
<td>1.52</td>
<td>36.26</td>
<td>2.41</td>
<td>0.06</td>
</tr>
<tr>
<td>Mean:</td>
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<td>0.21</td>
<td>3.67</td>
<td>1.87</td>
<td>39.82</td>
<td>2.34</td>
<td>0.56</td>
</tr>
<tr>
<td>ch5</td>
<td>43.13</td>
<td>0.07</td>
<td>1.92</td>
<td>0.42</td>
<td>6.04</td>
<td>1.11</td>
<td>0.80</td>
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<tr>
<td>Solar:AG89</td>
<td>52.13</td>
<td>0.17</td>
<td>3.76</td>
<td>1.87</td>
<td>37.56</td>
<td>2.97</td>
<td>1.54</td>
</tr>
<tr>
<td>L03</td>
<td>53.13</td>
<td>0.17</td>
<td>3.79</td>
<td>1.87</td>
<td>36.35</td>
<td>3.12</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Fig. 7. Co and Ni compositions of rim and core metal grains. Mean core grain (c) compositions for chondrules 1, 4, and 5 are diamond, rectangle and triangle, respectively. Individual analyses of core grains from chondrule 3 are plotted (open circles) with reference to position in the chondrule (inset, BSE image). Rim grains from all chondrules cluster near the canonical solar composition (star, Anders and Grevesse 1989). Solar Co/Ni ratio (dotted) is provided without error estimates. Solid line shows predicted metal composition condensing from a gas of solar composition at a total pressure of 10⁻³ bar, and dashed line for a gas enriched 100× in CI dust at 10⁻⁴ bar (Ebel and Grossman 2000), approximately coincident with the path for a solar gas at 10⁻⁸ bar (Ebel 2006).
The variation observed here among chondrules themselves offers separate confirmation of this theory of complementarity. Renazzo chondrules were formed by a process that preserved the complementary relationship between silicate and metal fractions in the parent body. That is, all the Renazzo chondrules (and other CR chondrules) appear to have formed from a single chondritic (solar) batch of material that was processed (heated/cooled) selectively and locally. This produced chondrules with highly variable, non-chondritic metal/silicate volumetric ratios, as measured in just these eight chondrules, and observed qualitatively in 3D imagery of other chondrules. Yet the independently-formed chondrules are themselves “complementary” in that they combine with each other, and with matrix, to produce a chondritic (solar) bulk abundance of major elements in Renazzo. This complementarity is preserved even though metal and silicate appear to have been fractionated locally, one from another, before, during or following the chondrule formation process.

Klerner and Palme (1999) found that Renazzo matrix MgO/SiO₂ (wt%) = 0.496, compared to 0.703 in bulk Renazzo (Mason and Wiik 1962), and solar 0.684 (Lodders 2003) or 0.720 (Anders and Grevesse 1989). They concluded that chondrules must, in aggregate, have a high MgO/SiO₂ ratio. Our volumetric control on silicate phase abundances is less strong than for metal/silicate ratios. Nevertheless, our results (Table 2) illustrate a large spread in modal olivine content just from 2D polished sections, from 8% to 42%. Heterogeneous—and supra-chondritic—bulk chondrule silicate compositions are evident in calculated MgO/SiO₂ ratios (Table 6). These results support the hypothesis that the chondrules are complementary to each other (and to matrix), in the same sense established for metal.

Our data do not permit an assessment of whole chondrule Ni/Fe ratios at the level necessary to address chondrule/matrix ratios. Zolensky et al. (1993) report Ni/Fe = 0.0787, and Hezel (pers. comm.) 0.0586, very close to the solar values of 0.0576 (Anders and Grevesse 1989) or 0.0600 (Lodders 2003), and within probable error of bulk Renazzo. Our data do not rule out a sub-solar Ni/Fe for Renazzo chondrules, but require that such a signature be controlled by the more abundant, high variance rim grains (Fig. 6).

Origin of Chondrules in CR Chondrites

Some less spherical chondrules have fine-grained textures, with chondritic metal grains (~solar Ni/Fe and Co/Fe) similar to those on the rims of coarse-grained, rounded chondrules with Ni-, Co-rich interior metal grains. Rare multi-layered chondrules preserve multiple generations of metal grains, separated by silicates. A hypothesis that addresses both observations is that high-Ni, high-Co grains in chondrule cores formed at high temperature, able to chemically equilibrate with a vapor containing chondritic proportions of siderophile and lithophile elements (Fig. 6). These metal grains are preserved in discrete layers inside a few chondrules, but this texture was obliterated by melting in most chondrules, forming Ni, Co-rich core metal nuggets (e.g., ch3, Fig. 5C). A second generation of metal grains then formed at lower temperature, with metal grains having near-solar Ni/Fe and Co/Fe (Fig. 6), along with more SiO₂-rich silicate. These later metal grains and silicates adhered to the rims of pre-existing chondrules, or combined to make a next generation of chondrules. Perhaps we are observing in Renazzo two or more generations of chondrules. Multiple metal/silicate layers would then result from successive adherence of generations of metal and silicates onto a single first generation chondrule.

CONCLUSIONS

Computer-aided X-ray tomography can be used to quantify the bulk (volumetric) metal/silicate ratios of chondrules, and to quantify chondrule shape and size. This is particularly necessary in meteorites in which chondrules vary greatly in shape and metal abundance, and are not radially symmetric (e.g., CR chondrites). Tomography allows informed intersection of chondrules for obtaining 2D chemical data, for extrapolation to volumetric chemical analysis.

The convolution, modal abundances of metal, and olivine/pyroxene ratios observable in each CR chondrule vary significantly depending upon which random 2D slice of that chondrule is measured. While the 3D-CVI defined here offers an index that agrees with the eye’s intuition of the degree of chondrule melting, perimeter definition is a subjective exercise in application. Although they remain subjective, metrics including metal grain size and proximity to chondrule rims could be developed to evaluate textures on larger ensembles of chondrules. At least in CR chondrites, these textures can be quantified most accurately by 3D analysis.

We present the first 3D determinations of chondrule metal/silicate volumetric proportions in chondrules in any chondrite. Combined tomographic and chemical study strongly supports a complementary chemical relationship between the entire suite of metal-poor and metal-rich chondrules present in the whole Renazzo meteorite. This study also suggests a supra-chondritic Mg/Si ratio in the entire chondrule suite. These findings are consistent with the hypothesis of “complementarity” between components in meteorites (Palme et al. 1992; Klerner and Palme 1999; Bland et al. 2005; Hezel and Palme 2007). Although some separation of chondrule silicate from metal by thermal maturation of chondrules may have occurred, local metal-silicate fractionation may, alternatively, have occurred outside of chondrules, before or during chondrule formation. Local space could then contribute layers of pre-separated material to accumulate chondrules with layers of
different texture, and also metal grains with volatility- or $f_{O_2}$-controlled compositions. These processes would require repeated, very local heating events, and some physical mechanism for independent but local formation of metal and silicate grains, up to sizes of tens of microns. Magnetic phenomena, surface energetics, or nucleation and growth physics could be involved in such an early separation of metal from silicates.

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