

Origin and Thermal History of Fe-Ni Metal in Primitive Chondrites

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Abstract. Recent work on the high temperature origins of chondritic Fe-Ni metal is reviewed. Emphasis is placed on the interplay between metal and silicate during chondrule formation, and on the chemical processes most responsible for metal formation, including volatilization/condensation, redox reactions with silicate, and desulfurization of FeS and other sulfides. Four specific chondrite metal settings are considered in depth: CR chondrites, in which the metal-chondrule interaction is most easily observed; ordinary chondrites, whose metal is also chondrule-processed but more metamorphosed than that of the CRs; CH and CB chondrites, whose metal appears to be largely produced by condensation; and CAI metal, which is highly enriched in refractory siderophile elements and records extremely high temperature processing.

1. Introduction

Metal comprises an important fraction of many chondrite groups (see Table 1 in Scott and Krot, this volume). In the H, EH, and CH chondrites, as well as in acapulcoites, it is a more important reservoir of Fe than the silicates and sulfides combined (Fig. 1). The total abundance of Fe, as well as its redox state, clearly defines the chondrite groups, as shown by the classic diagram of Urey & Craig (1953) and also by Figure 1, which indicates that each of these classes is a unique association of Fe-bearing minerals. Metal is thus likely to have played a major role in the fractionation of Fe and siderophile elements from Si and lithophile elements, generating the different chemical reservoirs from which these chondrite groups and planets as different as the Earth, Mercury and the Moon were made (e.g. Larimer & Wasson 1988).

Unravelling the origin of chondritic metal and its relationship with the associated silicates appears critical to our understanding of the processes at play in the protoplanetary

disks that generated chondrites, including chondrule formation. Iron comprises up to 95% of chondritic metal, so the origin of metal is largely regarded as that of its Fe, which happens to be the most difficult element to classify geochemically as it is an important lithophile, chalcophile and siderophile element (Larimer 1988) as well as a moderately volatile one. Metallic Fe could consequently have various origins such as condensation from the nebular gas (along with Ni at 1300 to 1400 K (Grossman 1972)), reduction from FeO in silicates, or devolatilization of FeS. It is however important to note that many of the siderophile elements found in metal are more noble than Fe (Larimer 1988) and could not have been hosted by silicates, although some of them could be found within sulfides.

In this paper, we will show that condensation, reduction and FeS devolatilization have probably all played a role in the genesis of chondritic metal. The paper will be divided into sections discussing the major types of metal in various chondrite classes. Section 2 will be devoted to CR chondrites, in which the relationship between silicates and metal appears the most obvious, in part because their metal is very abundant and the metamorphic over-print limited, but mostly because their chondrules have preserved an original textural relationship with their metal. Section 3 will be devoted to chondrule metal in other carbonaceous chondrites and metal in ordinary chondrites, which the CR case will help understand. Enstatite chondrite metal will not be treated here, because very primitive objects are rare in this class, and their metal has not yet been studied in a systematic way. Finally, in Sections 4 and 5 we will review two instances in which condensation is likely to have played a major role: metal from the unusually metal-rich CH and CB chondrites, and metal in calcium-aluminum-rich inclusions (CAIs).

This selective review will emphasize the important developments that have enhanced our understanding of early solar system processes within the last decade. A key element to this development has been the improvement in micro-analytical techniques that are sensitive to siderophile elements at trace abundance levels. Laser ablation inductively coupled plasma mass spectrometry (ICP-MS) has been particularly successful in this regard. This technique has been used to provide trace siderophile element analyses at spatial scales down to $\sim 15 \mu\text{m}$, which allows useful trace element distributions to be obtained from within heterogeneous metal grains as small as 80-100 μm . These distributions reveal a wealth of information about the thermal history of primitive chondrite metal as the trace siderophile elements span a wide range of chemical behaviors (Table 1), so that analysis of an appropriate suite of siderophiles often can be employed to confirm or discard hypotheses regarding the origin of a category of metal grains.

We will also take advantage of new insights gained from the enormous increase in the number of chondrite specimens that has resulted from systematic searches for meteorites, especially in Antarctica and the Sahara desert. These have greatly increased our recognition of the diversity of extraterrestrial materials, which now include several primitive and/or metal-rich chondrite groups: CR, CH, and CB. The increase in the numbers and variety of these metal-rich meteorites has yielded a wealth of new and important information such as the presence of a type of zoned metal grains that, in their elemental distributions, seem to have recorded a history of thermal and chemical processing in the solar nebula.

2. The Relationship Between Metal and Chondrules in CR Chondrites

The CR chondrites, typified by Renazzo, are of petrologic type 2, which means that they escaped thermal metamorphism and experienced moderate aqueous alteration. Their chondrule silicates are magnesium-rich (Weisberg et al. 1993) and they contain abundant metal (11 wt% in the case of Renazzo), which is typically associated with chondrules (Fig. 2). Metal is either found within chondrules, at chondrule edges or as large isolated grains within

the matrix, separated from chondrules. These properties make CR chondrites ideal specimens for examining the relationship between silicate and metal processing during chondrule formation.

Early studies suggested that the metal in Renazzo chondrules might be nebular condensate material, based on the abundances of Ni, Cr and P dissolved within this metal (Wood 1967; Grossman & Olsen 1974) and the fact that its Ni and Co abundances appear to follow a condensation trend (e.g. Weisberg et al. 1993). However, Lee et al. (1992) and Zanda et al. (1994) interpreted the metal compositions in terms of oxidation/reduction reactions rather than condensation/volatilization. Lee et al. (1992) described the role of Fe reduction in producing Ni and Co gradients within metal on chondrule rims in CR chondrites. Zanda et al. (1994) demonstrated that the metal grains within a given chondrule contain similar amounts of the dissolved minor elements, while there are chondrule to chondrule differences and metal in each chondrule appears to be in redox equilibrium with its silicates (see Section 3). They also showed that the large isolated grains within the matrix contained similar amounts of those minor elements, and suggested that in both types of metal grains, Si, when present, was not in dissolved form but as spherical silica glass (sometimes cristobalite) droplets exsolved at high temperature from the metallic melt during chondrule cooling (Fig. 3). These results implied that metal, if present within the chondrule precursors, had lost its original chemical composition as a result of chondrule formation, at least for the more lithophile elements such as Si, Cr and Fe itself, while the Ni and Co relationship could be interpreted in terms of Fe oxidation/reduction as the condensation curve simply follows the solar ratio of these two elements (Zanda et al. 1993). They also indicated that large grains now isolated in the matrix must have fallen from chondrules after the segregation of the metallic and silicate melts, as seen both in experiments (McCoy et al. 1999) and in some Renazzo chondrules (Fig. 2). Recent trace element analyses in the metal have provided further insight into the processing of metal during chondrule formation.

Zanda et al. (2002a) described the chondrules in Renazzo as following a distribution from irregular, slightly melted, fine-grained, objects to well-rounded, extensively melted chondrules with coarse grain sizes (Fig. 4) similar to the textural progression in the experimental charges of McCoy et al. (1999). The least melted objects show fine-grained silicate and metal distributed uniformly throughout the chondrule. As the degree of melting progresses, the outline of the chondrule becomes smoother while the metal begins to coalesce inside it into a smaller number of larger grains and a metallic rim begins to develop on the outer boundary of the chondrule. The silicate grain size is correlated with the degree of melting, because the destruction of seeds reduces the number of silicate grains that grow during subsequent cooling. The most extensively melted chondrules are nearly spherical, and usually have a well-developed rim of metal (Fig. 2b). Little metal remains interspersed within the silicates in these chondrules, but a small number of large, rounded metal grains sometimes has formed in the chondrule interior (Zanda et al. 2002a; Fig. 4) or on the chondrule surface (Figs. 2, 4). A correlation exists between chondrule morphology and metal and silicate composition in Renazzo, with olivine forsterite content and metal Ni and P contents increasing as the chondrules show greater degrees of melting and increase roundedness. This has been interpreted as evidence of combined Fe oxidation out of metal and FeO evaporation from the silicates, associated with the high temperature event that caused melting (Zanda et al. 2002a, 2002b). In addition, Zanda et al. (1993) argued that the correlation between Co and Ni in the metal grains, sometimes interpreted as a condensation signature (e.g. Weisberg et al. 1993), gradually establishes itself along the same sequence as a result of Fe exchange with the silicates and with the gas surrounding the chondrules. In the least melted chondrules, Ni and Co spread over a large range and do not correlate along the cosmic ratio; in more melted objects the concentrations still exhibit some scatter, but fall on the cosmic correlation, and in the more melted objects, the grains fall into two well defined categories with very different Ni

and Co: the outer grains with low Ni and Co concentrations and the inner ones with up to ~15 wt% Ni and ~0.6 wt% Co.

Measurements of platinum group elements (PGEs) and other trace siderophiles in CR chondrites, by ion microprobe (Connolly et al. 2001) and by laser ablation ICP-MS (Humayun et al. 2002; Campbell et al. 2002b), tell a consistent story; chondrule rim metal is depleted in refractory siderophiles, and less depleted in volatile siderophiles than chondrule interior metal. Connolly et al. (2001) used a recently developed ion microprobe technique (Hsu et al. 2000) to measure Os, Ir, Pt, and Au in the metal of three CR chondrites, paying particular attention to the metal grain location (chondrule interior, chondrule rim, or matrix). They noted that Au, a moderately volatile siderophile element, was depleted in all metal relative to chondritic (CI) values, but less so in the rim metal. Furthermore, the refractory elements Os, Ir, and Pt were noticeably depleted in many of the rim metal grains surrounding chondrules. Connolly et al. (2001) interpreted these trace element patterns in the rim metal to indicate that metal had been lost from the chondrules by volatilization, and then recondensed onto the chondrule surfaces, producing the refractory-poor, volatile-enriched metal observed, similar to the conclusions of Kong & Palme (1999) based on INAA of separated chondrules and matrix from Renazzo. Connolly et al. (2001) also reported that matrix metal in CR chondrites had Os, Ir, Pt, and Au compositions that were similar to those of the other two groups, and may represent material that had been expelled from chondrules while in the molten state.

Similar patterns in other trace siderophile element abundances were observed by Humayun et al. (2002). Their measurements of 18 siderophile elements, in 70 metal grains in Renazzo, were shown to eliminate the possibility that the metal in CR chondrites may have formed directly by nebular condensation. The distribution of volatile siderophile elements, including Cu, Pd, and Au, observed by Humayun et al. (2002) strongly supported the proposal of Connolly et al. (2001) that some metal had been volatilized and then recondensed onto the chondrule surfaces, forming the prominent metallic rims observed around CR chondrules. We note that the Ni and Co zoning reported by Lee et al. (1992) in chondrule rim metal is also qualitatively consistent with recondensation onto these grains. Humayun et al. (2002) also noted the strong influence of redox behavior affecting the relative compositions of chondrule interior metal vs. chondrule rim metal, especially in extensively melted, well-rounded chondrules; devolatilization of metal inside the chondrules was necessarily influenced by the solubility of each element in the silicate through which it must diffuse toward the chondrule surface. For example, small metal beads totally enclosed in high-MgO silicate grains contain extremely high correlated concentrations of Ni (up to about 11 wt%) and P (up to 1.8 wt%) while their Fe and Cr concentrations are low (down to 89 wt % and 0.1 wt% respectively). Such grain compositions can be explained by redox processes; Fe and Cr are more able than Ni and P to oxidize into the surrounding silicates to travel toward the chondrule surface and evaporate. This mechanism also explains the coupled Pd-Ni enrichment observed in some cases by Humayun et al. (2002).

According to the scenario presented above, CR chondrules began as fine-grained mixtures of silicate, and possibly metal, that underwent heating, melting, and evaporation. It is even possible that dust grains or small aggregates were melted individually and coalesced together in the melted state. The specific nature of the precursor materials remains uncertain. It may have been approximately chondritic in composition or depleted in volatile elements, including sulfur. Connolly et al. (1994) promote the inclusion of carbon into the chondrule precursors, as a reductant for metal formation from FeO-rich silicates during melting. Zanda et al. (1997) and Hewins et al. (1997) propose that the metal formed instead by decomposition of precursor Ni-bearing sulfides, at least in the case of ordinary chondrites (see below). It is also possible that most of the metal was simply incorporated into the proto-chondrules as metal, as it must be the case for the least easily oxidized elements; the nearly unfractionated proportions of refractory siderophiles such as Ru, Re, Os, Ir, and Pt reported by Connolly et

al. (2001) and Humayun et al. (2002), as well as their absolute abundances, suggest that these elements were not reduced from pre-existing sulfides or silicates in the manner proposed for Fe. The refractory siderophile elements (RSEs) must instead have been carried into the proto-chondrules in the metallic phase; this might have been simply Fe-Ni metal, with approximately solar RSE/Fe values, or it could plausibly have been in the form of tiny refractory-rich grains such as those that have been postulated in CAI formation (see below). This latter hypothesis is necessary to those models that call for the production of metal via desulfurization or silicate reduction, because these processes could only have played a significant role if Fe-Ni metal was not widely present before chondrule melting.

A lingering difficulty with the metal devolatilization/recondensation scenario advocated by Connolly et al. (2001) and Humayun et al. (2002) is the unlikelihood that siderophile elements such as Au and Cu would succeed in leaving metal grains under such reducing conditions, despite their volatile nature. The insolubility of Au and Cu in the silicate melt would prevent their rapid transmittal from an enclosed interior metal grain to the chondrule surface for volatilization. One might appeal to a model in which the volatile siderophiles were lost from the fine metal grains during the early stages of chondrule heating, before the metal was completely encased in silicate, which appears possible if the precursor consisted of tiny isolated droplets as discussed above. However, this model is not far from an alternative hypothesis, in which these volatile siderophile elements were never present in the chondrule precursors, but later condensed into the rim metal that had been expelled from the chondrule interiors.

These recent studies on trace element distributions in CR chondrite metal have succeeded in eliminating some proposals (such as direct condensation) for the origin of this metal, while also revealing processes that had not previously been recognized (such as the existence of a redox control for the volatilization of silicate-enclosed metal grains, and the recondensation of metal onto the chondrule rims). Metal formation in the CRs is strongly linked to chondrule formation, and as discussed in the following section, many facts relevant to CR metal also apply to other chondrite types.

3. Other Carbonaceous Chondrites and Ordinary Chondrites

While Fe-Ni metal is a well-recognized characteristic of ordinary chondrites, carbonaceous chondrites have the general reputation of being devoid of metal. This is strictly true, however, only for the CIs and related meteorites (i.e. less than a dozen meteorites) and practically also for the CKs. Admittedly, metal is rare in CMs and oxidized CVs, but it is a far from negligible component of COs and reduced CVs (up to 5-6 wt% in both groups; (McSween 1977a, 1977b)), not to mention the CRs, already treated above, and the very metal-rich CHs and CBs, described below.

Metal in the most primitive CO, reduced CV, and ordinary chondrites shares a number of properties with that in CR chondrites. Aside from metal in dusty olivines, which is minor in terms of volume and clearly a product of reduction during chondrule formation (Connolly et al., 1994; Leroux et al., 2003), metal in primitive chondrites occurs essentially in three settings: i) in FeO-poor chondrules, where it generally has the shape of rounded droplets, obvious remains of a mixture of immiscible metal and silicate liquids; ii) around chondrules, making partial or total rims, often associated with troilite, and probably originating from a combination of near-escape from the chondrule interiors, re-accretion after ejection, and re-condensation after vaporization following the scenario discussed above for CR chondrites; iii) outside of chondrules, as large, often rounded grains, generally associated with troilite. In ordinary chondrites, the latter grains, sometimes called metallic chondrules

(Bevan & Axon 1980) represent by far the largest fraction of metal, contrary to CR chondrites.

Metal in these chondrites has been first thought of as a means to retrace the thermal metamorphic history of their parent bodies (Wood 1967). The idea that it could have recorded nebular processes arose from the discovery of an enrichment in Cr, P and/or Si in metal grains, first, paradoxically, from the metal-poor CM2 chondrites (Olsen et al. 1973; Grossman & Olsen 1974; Grossman et al. 1979) and also from CR2s (Grossman & Olsen 1974), then of little metamorphosed ordinary chondrites (Bevan & Axon 1980; Rambaldi et al. 1980; Taylor et al. 1981; Rambaldi & Wasson 1981, 1984). Similar enrichments have been found in CV3 and CO3 chondrites (McSween 1977; Fuchs & Olsen 1973; Scott & Jones 1990). The generally accepted explanation, supported by equilibrium condensation calculations (Grossman & Olsen 1974; Grossman et al. 1979; Rambaldi et al. 1980), was that this metal has been formed by condensation in the nebula and has since kept its composition unchanged. However, observations, similar to those made on Renazzo, that metal composition varies much more from chondrule to chondrule than within chondrules, and that in chondrules metal and silicate compositions are more or less equilibrated, led Zanda et al. (1994) to hypothesize that metal composition was instead established during chondrule melting in all of these chondrites. This also applies to the large grains outside of chondrules, whose composition is similar to that of chondrule metal, and which were probably ejected from chondrules during melting as discussed above for the case of Renazzo. The three sets of values of the oxygen fugacity calculated by Zanda et al. (1994) from the partition of Si and Cr between metal and silicates and from the FeO content of olivine for individual chondrules of several carbonaceous and ordinary chondrites, assuming a temperature of 1873 K, agree well with each other, giving some support to the above hypothesis. This range of oxygen fugacities (10^{-9} to 10^{-12} bar) is also in good agreement with those calculated by Lauretta et al. (2001) for type I chondrules from Bishunpur, on the basis of the Si content in the matrix metal.

Kong & Ebihara (1996, 1997) measured siderophile elements in bulk metal fractions of unequilibrated ordinary chondrites by neutron activation. They conclude that their results are inconsistent with an origin of the metal by condensation in the nebula, but that the partition coefficients of 8 elements (W, Mo, Ga, Co, Fe, Cr, Mn, V) between metal and the non-magnetic fraction agree with the results of melting experiments at 1573 K and oxygen fugacities between 10^{-12} and 10^{-11} bar. These fO_2 values are not far from those calculated by Zanda et al. (1994) at 1873 K.

The chemical form under which Si, P and Cr appear in metal varies between chondrites (Zanda et al. 1994). While they are in solid solution in CMs and CRs (except for Si in CRs, Fig. 3), they form tiny ($\leq 1 \mu\text{m}$) inclusions interspersed in the metal volume (Fig. 5) in all other chondrites. A further difference occurs between Semarkona (LL3.0), where inclusions are chemically reduced (silicide, phosphide, sulfide), and all the others, where inclusions are oxidized (silica, phosphates, chromite). These inclusions most likely formed by precipitation, in the solid state, of dissolved Si, P and Cr. While this precipitation could have occurred at any time after metal solidification in chondrules, the gradation from CMs and CRs to Semarkona to others suggests that this happened during metamorphism in the parent bodies. In addition, rarer but larger inclusions of similar chemical forms are found in the metal of more metamorphosed chondrites (higher types 3, types 4 and 5) and are virtually absent from type 6 chondrites, indicating that incorporation of Si, P and Cr in metal has been a general process, whose outcome has progressively evolved and has finally been erased by metamorphism. An alternative view, voiced by Lauretta et al. (2001) and Lauretta & Buseck (2003), is that the oxidized forms of Si, P, and Cr formed in the metal during high temperature corrosion, either within the chondrule during the end stages of melting or after expulsion of the metal from the molten silicate.

The nature of the inclusions, although mostly characteristic of metamorphism, is not completely irrelevant to the redox processes of chondrule formation. In particular, the round silica inclusions, which are the only form of Si in CR metal and clearly formed by oxidation of Si while metal was still liquid, are rare or absent in the other chondrites. They have been found in Semarkona and Bishunpur (Zanda et al. 1994), but much more rarely than the more common tiny silica inclusions formed in the solid state. This means that only in CR chondrules was the oxygen fugacity always high enough when the metal was molten for Si to be oxidized. In the other chondrites Si, when present in metal, was generally still in solid solution when metal solidified, pointing to systematic differences in the chondrule formation conditions for different chondrite groups.

That Si, P and Cr were reduced into metal during chondrule formation does not indicate whether metal already existed in the precursors or not. Grossman & Wasson (1985) analyzed siderophile elements in 31 Semarkona chondrules by neutron activation. They found large variations of element abundances between chondrules and concluded that most chondrule metal was already present in the precursors in two components, refractory-rich and refractory-poor, and that some siderophiles (Co, Au, Ge) were, in part, in the silicates.

Spatially resolved measurements by ion microprobe (Hsu et al. 1998) and by laser ablation ICP-MS (Campbell & Humayun 2003) revealed large grain-to-grain variations in the abundances of highly siderophile elements in ordinary chondrite metal. Hsu et al. (1998) reported variations of ~300X in Os, Ir, and Pt abundances among metal grains in Tieschitz (H/L3). Campbell & Humayun (2003) noted similarly large, correlated variations in Ru, Re, Os, Ir, and Pt in unequilibrated ordinary chondrites, although less refractory siderophiles such as Pd and Au did not correlate with the refractory elements. The wide trace element abundance range observed, coupled with the lack of strong fractionations between refractory elements, suggests the incomplete homogenization of refractory siderophile carriers into ordinary chondrite metal (Campbell & Humayun 2003). This interpretation is supported by earlier neutron activation studies that showed elevated Ir/Ni ratios in nonmagnetic chondrite separates (Chou et al. 1973; Rambaldi et al. 1978). The link between chondrule formation and chondrite metal grain formation described in this chapter further implies that these refractory siderophile element carriers were incorporated heterogeneously into the chondrule precursors and were incompletely homogenized in the metal during chondrule formation. This scenario explains the inter-chondrule variability in siderophile element abundances noted in Semarkona by Grossman & Wasson (1985).

The presence of refractory siderophile carriers in the chondrule precursors does not preclude the formation of some Fe-Ni metal during chondrule formation. Experiments by Connolly et al. (1994) suggest that at least some metal could be produced by reduction of FeO in the silicates by carbon during chondrule heating. Indeed, carbon inclusions are found in the metal of many unequilibrated chondrites (Mostefaoui et al. 2000). Moreover, in Bishunpur, Mostefaoui et al. (1994) found that the presence of carbon inclusions in metal grains is correlated with high Co and low Cr concentrations, which they interpreted as resulting from reduction of Fe and Cr by C; in the grains where C has been entirely consumed, reduction has progressed to incorporate large amounts of Cr into metal and reduced enough Fe to noticeably dilute Co. The reverse is true when some carbon is left in the metal. Hanon et al. (1998) find that the carbon contents they measure in silicates of type I chondrules of Semarkona and Bishunpur by ion microprobe indicate that C was present in the precursors in amounts sufficient to account for the reduced silicates and the presence of metal. Under sufficiently reducing conditions, Fe reduction from fayalitic olivine might also have occurred even in the absence of carbon; experiments reported by Leroux et al. (2003) have indicated that this could occur at temperatures and timescales comparable to those of chondrule formation.

An additional, or alternate, possibility advocated by Hewins et al. (1997) and Zanda et al. (2005) is that most of the metal in ordinary chondrites was produced from FeS

devolatilization, as observed in some experiments (McCoy et al. 1999; Cohen et al. 2004). These authors argue that the intensity of the greatest melting event experienced by a chondrule can be estimated based on the size of its crystals, a hypothesis supported by the experiments of Nettles et al. (2004). This facilitates the ranking of chondrules in increasing order of melting (Fig. 6). Along this sequence, the bulk composition of the objects vary; the least melted ones are the most volatile-rich, whereas the most melted objects exhibit typical volatile-depleted type I chondrule compositions (Hewins et al. 1997). As in the experimental charges of McCoy et al. (1999) and Cohen et al. (2004), Fe-Ni metal is not present in the starting material, but it becomes more abundant along the sequence, at the expense of sulfides and magnetite, and becomes the only opaque phase in the more melted objects (Fig. 6). In even coarser, more melted objects, metal physically separates from the silicates to form large grains usually on the chondrule surface, as described above for the case of CR chondrites. On the basis of this trend, Zanda et al. (2005) maintain that the precursors of type I chondrules in ordinary chondrites resembled metal-free CI-like material and that, as the bulk of the metal of ordinary chondrites appears to have been processed in chondrules, it formed from the devolatilization of FeS, possibly in addition to reduction from magnetite. Note that this sequence differs slightly from the one described above for CR chondrites; the least melted objects in CR chondrites contain no sulfides and have textures that differ very significantly from the ones in OCs. The latter appear as an aggregate of fine grained crystals with minimal amount of melting, whereas the former look more like the coalescence of fine droplets and dust.

4. Metal in CH and CB Chondrites

The CH and CB chondrites are groups of metal-rich and highly primitive meteorites (Bischoff et al. 1993; Weisberg et al. 2001; Krot et al. 2002). The CH chondrites are typified by ALH 85085, and contain approximately 20% metal by volume, the remainder being principally chondrules and chondrule fragments (Scott 1988; Grossman et al. 1988; Weisberg et al. 1988). The grain size of both metal and silicate is small in CH chondrites, reaching a maximum of ~200 μm . The CB chondrites have even more metal, 50 to 70% by volume, and much larger grain sizes, with mm-sized objects not uncommon (Weisberg et al. 2001). Based on significant textural differences, Weisberg et al. (2001) further sub-divided the CB chondrites into two small groupings. In group CB_a, metal occurs as large, up to ~1 cm in size, kamacite (Fe-Ni with <7% Ni and a body-centered cubic unit cell) grains containing various amounts of Cr-rich troilite, with a texture corresponding to the solidification of an S-poor metal-sulfide liquid (Weisberg et al. 2001; Krot et al. 2002; Rubin et al. 2003). There is an emerging consensus that the CB_a meteorites may be the product of an impact plume or other non-nebular event, and do not reflect typical high-temperature processing of chondrite material (Kallemeyn et al. 2001; Campbell et al. 2002; Rubin et al. 2003). Similar interpretations regarding the CH chondrites (Wasson & Kallemeyn 1990) have not been as widely accepted. Of principal interest here is group CB_b, which includes the meteorites QUE 94411 (Fig. 7) and HH 237 and is characterized by the presence of metal-free chondrules, having mostly cryptocrystalline or barred textures, and three kinds of metal: metastable and chemically zoned grains in which the Ni content is greatest in the grain cores and decreases gradually toward the rims; unzoned grains, with uniform Ni distributions but variable Ni concentrations; and large metal-sulfide aggregates, which can reach several mm in diameter (Weisberg et al. 2001).

In the group CB_b meteorites, a pervasive shock-melted mixture of silicate and metal fills the space between metal and silicate grains (Meibom et al. 2005). However, cooling of this liquid appears to have been extremely fast, so that the temperature of the surviving metal

grains was not significantly raised as indicated, in particular, by the presence of martensite instead of exsolution into kamacite and taenite (high-Ni metal with a face-centered cubic unit cell) in the central regions of the zoned grains, whose Ni content exceeds the higher limit of kamacite stability (Weisberg et al. 2001; Meibom et al. 1999, 2000). This can also be taken to indicate that the metal in these meteorites has experienced very little thermal metamorphism, which may be associated with accretion after ^{26}Al decay (cf. Amelin & Krot, 2005). Because of the minimal extent of low-temperature parent body metamorphism, it has been possible to extract more information regarding the high-temperature thermal and chemical history of these metal grains than is usually possible in meteorites that have undergone substantial thermal alteration. Another manifestation of the pristine nature of these grains is the Ni-Co correlation, which is positive and has a slope that is very close the solar Ni/Co ratio (Meibom et al. 1999; Petaev et al. 2001; Weisberg et al. 1988, 2001) although, as discussed above for the case of CR metal, this can also result from Fe gain or loss during redox processes.

Some, but not all, of the metal in both the CH and the CB_b chondrites is compositionally zoned, with Ni and Co maxima in the grain cores, decreasing to the rims (Fig. 7). Minor and trace element compositions in these grains are correlated with Ni in a manner that strongly indicates that the elemental distributions are controlled by the volatility of each element, and not by redox behavior, metal/liquid partitioning, or any other recognizable chemical property (Meibom et al. 1999; Campbell et al. 2001). Refractory siderophile elements, including not only Ni but also Ru, Rh, Re, Os, Ir, and Pt, are enriched in the zoned grain cores, while volatile elements, including P, Cr, Cu, Ga, Ge, and Au, are depleted in the zoned grain cores relative to CI chondrite abundances (Campbell et al. 2001, 2005; Campbell & Humayun 2004). The micro-distribution of Pd in the zoned metal in CH and CB_b chondrites has been particularly diagnostic. Palladium, like other platinum group elements, is highly siderophile but has a volatility under solar nebula conditions that is very similar to that of Fe (Palme & Wlotzka 1976; Campbell et al. 2001). The recognition that Pd/Fe ratios are nearly chondritic throughout the zoned metal grains provides a strong indication of a volatility-controlled formation process. These observations have led to the conclusion that the observed zoning is a product of metal condensation in a gas of solar siderophile element composition, usually assumed to be the solar nebula (Meibom et al. 1999, 2000; Campbell et al. 2001, 2005; Campbell & Humayun 2004; Petaev et al. 2001, 2003; Weisberg et al. 2001). The nebular origin of CB_b metal is further supported by its hydrogen content (Lauretta et al. 2005).

More detailed interpretations of the formation of zoned metal from CH and CB_b chondrites have been based on a comparison of the observed element-element trends with those predicted to occur during condensation of a gas of solar composition (Campbell et al. 2001; Petaev et al. 2001, 2003). Important information on the nature of the environment in which the grains formed can be obtained in this manner, including the thermal history, timescales, and oxygen fugacity of the gas. In general, there is good agreement between the observed inter-element trends and those predicted by equilibrium condensation sequences. (The metal-gas equilibrium calculations do not distinguish between condensation and evaporation, but the direction of zoning suggests condensation during cooling. This is also supported by Fe and Ni isotopic measurements (Alexander & Hewins 2004).) However, as Campbell et al. (2001) noted, a simple fractional condensation model, in which all of the metal that would condense at high temperatures is sequestered into the cores of the growing grains, would completely deplete the gas in highly refractory components (such as Ru, Re, Os, Ir, Pt), thereby leaving none of these elements available for later, lower temperature, condensation into the outer regions of the grain. These models are therefore unable to reproduce the observed distributions, and other scenarios must be considered. Inefficient fractional condensation, in which only a small portion of the condensable fraction of the gas

actually condenses at a given temperature, appears to be required (Campbell et al. 2001; Petaev et al. 2001, 2003; Petaev & Wood, this volume).

Regardless of the details of the sequestering of metal into the cores of zoned grains, the timescales of condensation are best determined by the kinetic theory of gases; these calculations depend on the assumed gas density, but for a typical pressure of 10 Pa (10^{-4} bar), several studies place the timescale of growth of a ~ 200 μm grain to be on the order of several weeks (Meibom et al. 2000; Campbell et al. 2001; Petaev et al. 2003; Petaev & Wood, this volume). The temperature range over which most of a zoned metal grain condensed can be constrained by comparison between the compositional range spanned by the metal zoning and the calculated condensation sequence. Maximum temperatures are on the order of 1360 K (again assuming a nominal P_{tot} of 10 Pa), and condensation of Fe-Ni alloy is essentially complete by ~ 1250 K. Mean cooling rates are thereby $\sim 10^{-3}$ to 10^{-2} K/min, depending on the particular assumptions used in the modeling. Early efforts to constrain the cooling rate assumed a constant rate, but Petaev et al. (2003) found that in their model the growth of zoned metal in CH chondrites was best fit using a thermal history in which the cooling rate increases with decreasing temperature.

Timescales of Fe-Ni inter-diffusion in this temperature range are a little slower than the condensation timescales mentioned above, but similar enough that diffusion plays a significant role in the establishment of the zoning profiles in CH and CB_b metal (Campbell et al. 2001). Petaev et al. (2003) incorporated diffusion explicitly into their models of fractional condensation of metal, and found that its effect was significant on the elements considered in that study (Cr, Co, Ni). The effect of diffusion may be more important, and more informative, in the case of refractory siderophile element profiles, because of the strong association of these elemental distributions with the fractional condensation process. Better experimental determinations of the rates of diffusion of these elements will surely lead to better understanding of the conditions in which the CH and CB metal formed. In response to this need, new experimental data are becoming available (Watson & Watson 2004; Righter et al. 2004). One model that needs to be explored further with such diffusion data is that in which a refractory metal core interdiffuses with a non-refractory metal mantle that has condensed around the core (Campbell et al. 2001; Petaev & Wood, this volume).

Petaev et al. (2001, 2003) used the compositional profiles of Cr in zoned CB and CH chondrite metal to constrain the oxygen fugacity during condensation; they reported their results in terms of the dust/gas enrichment that would produce the necessary oxidation (“dust” in those studies included all elements except H and rare gases, in solar proportions). Dust/gas ratios of 10-40 were inferred from metal grains in the CB_b chondrite QUE 94411, but dust/gas ratios of only 1-13 were required to match the Cr distributions in CH and CB_b chondrite metal (Petaev & Wood, this volume). The presence of Si in CH metal (Meibom et al. 1999) and the depletion of Mo in zoned grains in QUE 94411 (Campbell et al. 2001) further indicate that the range of nebular $f(\text{O}_2)$ conditions was variable during formation of the zoned metal grains.

Campbell & Humayun (2004) and Campbell et al. (2005) have studied the trace element compositions of the unzoned metal in CH and CB_b chondrites, respectively. They found that the unzoned metal in both meteorite groups is not simply a homogenized form of the zoned metal, and that in some cases a complementary relationship can be discerned. Campbell & Humayun (2004) and Campbell et al. (2005) concluded that the unzoned metal grains are also condensation products, and that they formed at a range of temperatures that overlapped that in which the zoned metal condensed, extending down to ~ 1100 K (based on higher volatile siderophile element concentrations that are sometimes observed), but at slower cooling rates, permitting chemical homogenization.

The distribution of trace elements in metal in CH and CB_b chondrites thus indicates that this metal is a condensation product, and it is generally consistent with condensation in gases of density and composition similar to that of the solar nebula. However, we cannot

exclude the possibility that the metal condensed in a gas of non-nebular origin, such as an impact plume (Wasson & Kallemeyn 1990; Rubin et al. 2003) that coincidentally had a siderophile element density and composition comparable to those of the solar nebula, and also a H₂ partial pressure similar to that of the solar nebula (Lauretta et al., 2005). An impact plume hypothesis has also been advocated for the formation of metal in CB_a chondrites (Kallemeyn et al. 2001; Campbell et al. 2002; Rubin et al. 2003), but in those meteorites the textures are more suggestive of liquid metal droplets and the trace element compositions are inconsistent with nebular condensation, so an impact setting is more compatible with the observations. The growth rate of metal in CH and CB_b chondrites, on the order of weeks, provides an important constraint for the rate of cooling of the gas during the metal formation process, in the temperature range ~1350 to 1100 K. The different scenarios will be further constrained by emerging data on Ni and Fe isotope mass-dependent fractionation that are becoming available through ion microprobe studies of zoned metal grains in CB chondrites (Alexander & Hewins 2004).

5. CAI Metal

Most of the Ca,Al-rich inclusions (CAIs) in which metal has been studied are from the CV chondrites, particularly Allende. CAIs in Allende experienced significant late-stage alteration, which led to sulfidation and oxidation of their metal phases, and redistribution of all siderophile elements along S-rich veins that cross-cut the inclusions (Blum et al. 1988, 1989; Palme et al. 1994; Campbell et al. 2003). Highly siderophile elements such as the platinum group elements are largely exsolved into tiny PGE-rich nuggets (Blum et al. 1989). CAIs in members of the reduced CV subgroup, such as Efremovka and Vigarano, have experienced much less secondary alteration; much of their metal remains unsulfidized/unoxidized, veining is minimal, and consequently platinum group elements remain dissolved in Fe-Ni metal.

CAIs are enriched in refractory siderophile elements, relative to chondritic abundances, by factors similar to their enrichment of refractory lithophile elements (Sylvester et al. 1990); this is a consequence of the high temperature formation of these inclusions (Grossman 1980). Trace element compositions of metal-rich assemblages in CAIs from CV chondrites have been measured using neutron activation analysis (Palme & Wlotzka 1976; Palme et al. 1994; Sylvester et al. 1990, 1993) and by laser ablation ICP-MS (Campbell et al. 2003). A pattern commonly observed is the uniform enrichment of highly refractory siderophile elements, and lower enrichments of non-refractory siderophiles (e.g., grain #1 in Fig. 8); such a pattern coincides with the expected composition of metal at some point along the condensation sequence. Some CAI metal exhibits trace element abundance patterns that are sloped gradually as a function of the volatility of the elements (grain #2 in Fig. 8). This kind of trace element pattern is not predicted by calculations of metal condensation from gas of solar nebula composition, and the prevailing view is that it represents the accumulation of multiple metal sources, each having formed at a different, high temperature before aggregation in the CAI (Palme et al. 1994; Campbell et al. 2003). It is likely that these metal grains formed by the agglomeration, during melting of the host CAIs, of finely distributed metal particles that formed individually prior to their incorporation into the CAIs.

An equilibrium condensation sequence of metal alloy from a gas of solar composition at 10 Pa is shown in Figure 9 (Palme & Wlotzka 1976; Kelly & Larimer 1977; Campbell et al. 2001). In this calculation it is assumed that, at all temperatures, there is only one metal phase, in which all metallic components of the system are dissolved (cf. Sylvester et al. 1990). Fractionations between highly refractory siderophiles (i.e., Re, Os, W, Ir, Ru, Mo, Pt) occur only at very high temperatures, above the condensation point of Fe-Ni (>1370 K at 10 Pa). Therefore any Fe-Ni alloy that condensed in equilibrium with a gas of solar

composition is expected to have a flat chondrite-normalized abundance pattern of these elements. Below ~1370 K, the factor by which these elements are uniformly enriched rapidly diminishes, reaching chondritic abundances at ~1250 K.

In CAI metal, fractionations between some of these highly refractory siderophiles are frequently observed, indicating very high temperature formation or processing (e.g., grain #2 in Fig. 8). At such high temperatures, the Fe-Ni content is expected to be negligible, and the metal should be essentially a refractory metal alloy. In fact, unaltered CAI metal is normally Fe-Ni rich, and although its refractory siderophile element (RSE) abundances are strongly enriched, they remain at trace element concentrations; i.e. below 1 wt%. This aspect of CAI metal compositions is adequately explained by the model of formation described above on the basis of the sloping trace element pattern. The precursor material of CAIs included many fine metal particles that formed at different temperatures; some were highly refractory but most were principally Fe-Ni metal particles. Upon heating and melting of the CAIs, the metal particles agglomerated together, forming larger metal grains such as those observed in the relatively unaltered CV-reduced group members. These larger metal grains, which typically range from 10 to 200 μm in size, have highly variable trace element compositions despite having formed in the same inclusion. This is a consequence of the stochastic nature by which each individual metal grain incorporated a small number of refractory metal particles, which dominate the trace siderophile element budget of the grain.

An important implication of this scenario is that the CAI precursors included a mix of metal particles recording a wide range of thermal histories. Consider, for example, the elemental abundance pattern measured for CAI metal grain #2, highlighted in Figure 8. The monotonic slope across the highly refractory siderophiles (Re to Pt) strongly implicates volatility as the process by which these fractionations were caused. Comparison with Figure 9 reveals that the observed Os/Ir fractionation is likely to have been produced at a temperature of ~1660 K in the nebula (at 10 Pa total pressure); the extremely high Os and Ir abundances of a metal particle formed at this temperature cause it to dominate the Os-Ir signature of the larger metal grain in which it is eventually incorporated. At the low temperature end, the modest (20x) enrichment of Pt over Ni indicates that most of this grain consists of metal particles that equilibrated with the nebula at temperatures at or below 1375 K. Mass balance calculations show that only a small fraction (less than 0.1%) of ultra-refractory metal can dominate the trace element abundance pattern when it is blended with less refractory Fe-Ni alloy.

The refractory siderophile elements are highly rarified in the canonical solar nebula, and calculated rates of condensation of ultra-refractory metal are extremely low (Blander et al. 1980). Furthermore, at temperatures well above the condensation point of Fe-Ni alloy, where the ultra-refractory metals are predicted to be in equilibrium with the gas, the nebula has extremely low opacity (because of the lack of solid grains), and cooling rates are necessarily high under these conditions (Morfill 1988; Boss 1998; Cassen 2001). Because of this combination of low condensation rates and short timescales, it is unlikely that the ultra-refractory metal precursors that entered CAIs were condensates; rather, they were residues of metal that was highly volatilized during extreme thermal events that occurred before CAI formation.

Depletions in W and Mo, relative to highly siderophile elements of similar refractoriness, are commonly observed in Allende CAI metal (Fegley & Palme 1985; Palme et al. 1994) and occasionally observed also in Efremovka CAI metal (Campbell et al. 2003 and Fig. 8). These depletions have been interpreted as evidence of highly oxidizing conditions in the solar nebula during CAI formation (Fegley & Palme 1985; Palme et al. 1994), in strong contrast to the highly reducing conditions that have been inferred on the basis of the solar composition and CAI silicate compositions (Beckett & Grossman, 1986). It is very possible

that the Mo,W depletions in CAI metal reflect later, low-temperature alteration, but more work is required to concretely resolve this issue.

6. Summary

The diversity of textures and chemistry observed in primitive chondrite metal reflects the diversity of its origins and thermal and chemical histories. Metal evolution is intimately linked to chondrule formation in a number of chondrite classes, including the most common chondrite class, the ordinary chondrites, as well as several carbonaceous chondrite groups, including the CRs, which due to their low metamorphism and the specific nature of their chondrules have yielded several crucial insights into this process. Ambiguities remain regarding the exact nature of the source of metal in the chondrule precursors, which are likely to have been different in CR chondrites than in ordinary chondrites. There are suggestions that desulfurization of sulfides, reduction of oxides, and the incorporation of pre-existing metal could all have played a role. It is more certain, however, that during chondrule formation metal reacted with the silicate and was partially ejected from the molten chondrules. In the case of Renazzo, there is evidence that recondensation of volatilized metal onto the chondrule surfaces was another contributing factor.

Further evidence of gas-solid metal exchange appears in the unusual CH and CB chondrite groups, as well as in CAI metal. Much work has focussed in recent years on the zoned metal grains in CH and CB_b chondrites, because of the strong evidence that these objects formed at least in part by condensation of metal from a gas. The nature of the vapor source remains contentious but the major element and trace element distributions in the zoned metal are consistent with condensation from the solar nebula. Modelling of these grains indicates timescales on the order of weeks, and variations in the oxygen fugacity of the gas; these are important constraints on the dynamics of the gas parcels from which they formed.

There is evidence in a number of chondrite metal sources for the presence of small, refractory metal carriers that dominate the refractory trace element budget of metal by having been incompletely homogenized. This is evident in the wide range of trace element abundances in ordinary chondrite metal, and has been suggested to explain the zoned metal in CH and CB_b chondrites. It can perhaps be inferred from CR chondrules too, but it is best demonstrated in unaltered CAI metal. The extremely high temperature thermal processing that established the trace element abundances of CAI metal left a chemical imprint that was not erased during later incorporation into the CAI precursor, melting, and aggregation into Fe-Ni metal.

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10,379 Words

9 Figures

1 Table

23 Published pages (estimated)

Table 1. Siderophile elements, their abundances in solar abundances relative to Fe (Anders & Grevesse 1989), and their 50% condensation temperatures (after Campbell & Humayun 2004).

	Solar X/Fe (atomic)	Tc (K)
Re	5.74×10^{-8}	1819
Os	7.50×10^{-7}	1815
W	1.48×10^{-7}	1776
Ir	7.34×10^{-7}	1594
Ru	2.07×10^{-6}	1559
Mo	2.83×10^{-6}	1538
Pt	1.49×10^{-6}	1411
Rh	3.82×10^{-7}	1392
Ni	5.48×10^{-2}	1363
Co	2.50×10^{-3}	1359
Pd	1.54×10^{-6}	1349
Fe	1.00	1341
Cr	1.50×10^{-2}	1280
Au	2.08×10^{-7}	1223
As	7.29×10^{-6}	1131
Ga	4.20×10^{-5}	1101
Cu	5.80×10^{-4}	1029
Sb	3.43×10^{-7}	994
Ag	5.40×10^{-7}	988
Ge	1.32×10^{-4}	928

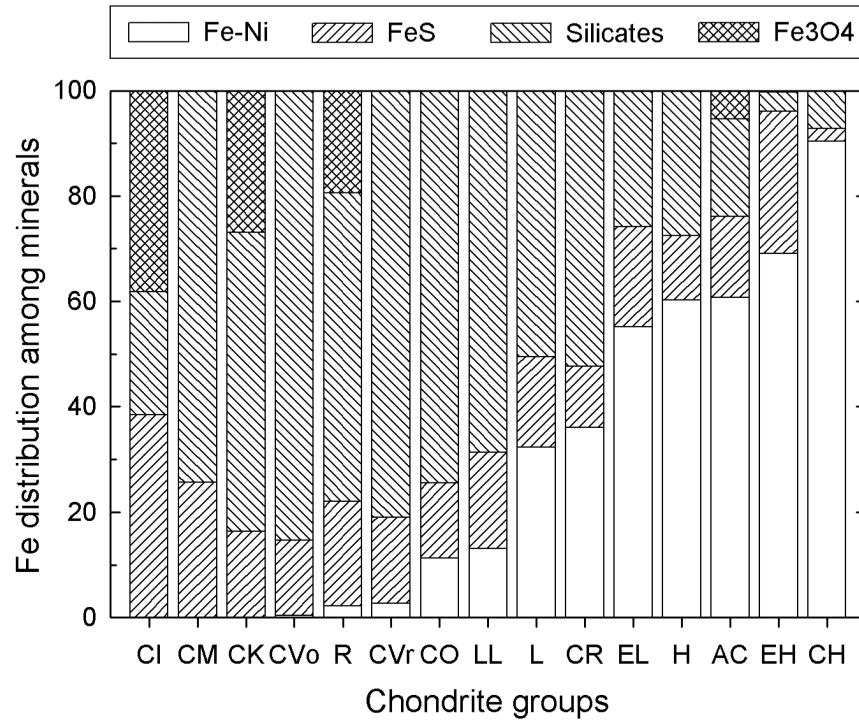


Figure 1. Distribution of Fe among various minerals in the chondrite groups and acapulcoites, arranged from left to right in order of increasing metal content (when no metal is present, the groups are ranked in order of increasing reduction state). Based on averages for the different groups except CI (Orgueil), CVr (Vigarano), CR (Renazzo) and CH (ALH 85085). (data from Koblitz, 2003 database). Magn = magnetite; CVo = CV-oxidized subgroup; CVr = CV-reduced subgroup; AC = acapulcoites.

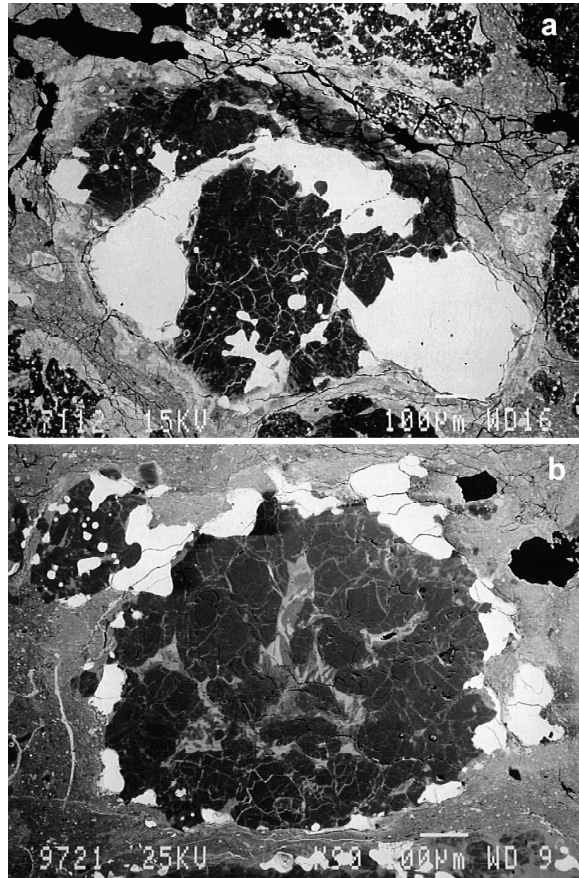


Figure 2. Backscattered electron images of two extensively melted chondrules in Renazzo. In this and all subsequent BSE images, the bright regions are Fe-Ni metal. The silicate melt and crystals have efficiently separated from the metallic melt. (a) Only 3 large metal grains are visible in this surface. One of them appears to have been “fossilized” as it was ready to fall off from its parent chondrule. (b) The main chondrule has no visible interior metal. One large central grain could however be present above or below the visible surface. This chondrule resembles the most melted experimental charges of McCoy et al. 1999.

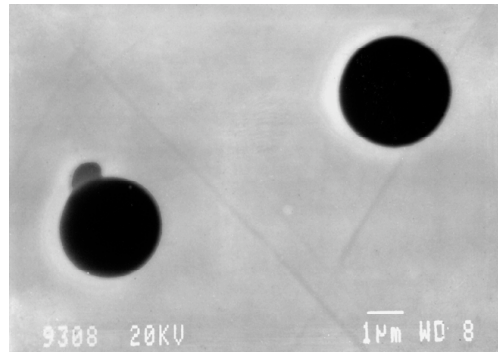


Figure 3. Two silica droplets in a metal grain from Renazzo. These droplets pepper the surface of the metal grains from the most reduced chondrules in Renazzo. They are also found in the large isolated grains in the matrix. Their size is sometimes much larger (tens of microns), in which case only one or two may be visible at the surface of a grain. They are formed from oxidation at high temperature (above 1986 K) during chondrule cooling of Si dissolved into the metallic melt at higher temperatures during chondrule formation.

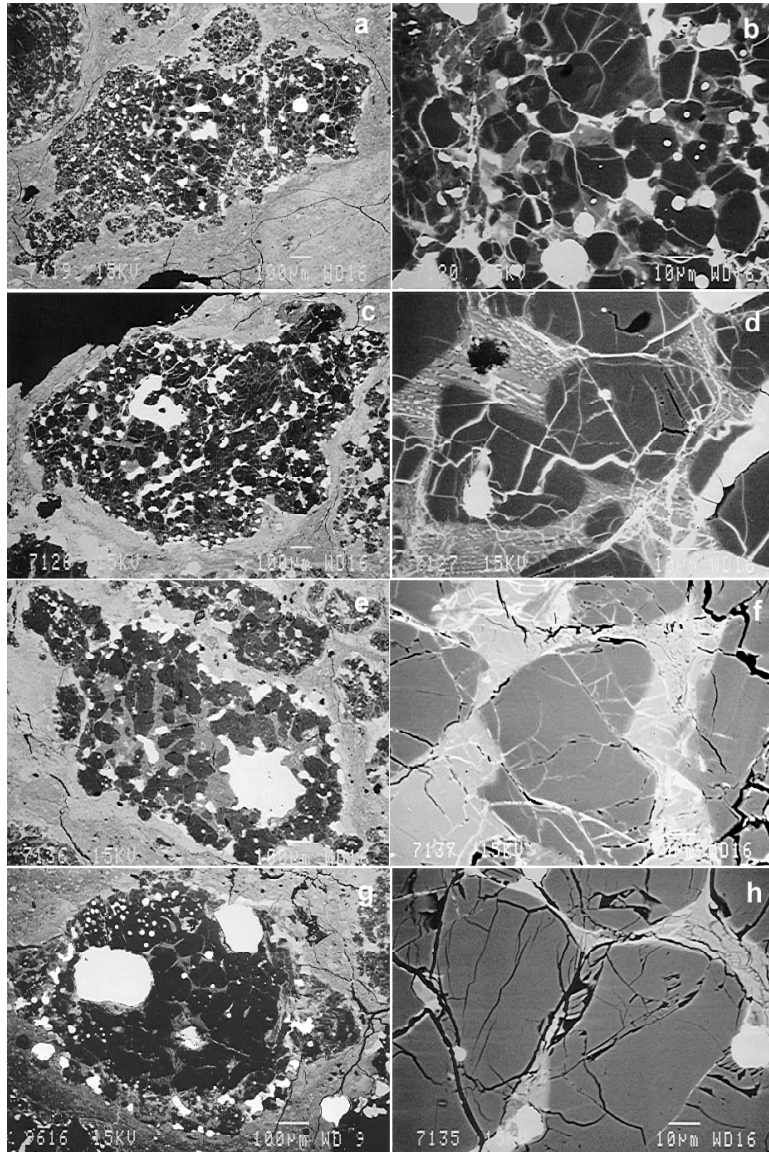


Figure 4. A suite of increasingly melted chondrules from Renazzo (CR2). The outline of the chondrules evolves down the sequence from highly convoluted (a) to close to spherical (g). Details at the right are all at the same scale and show the gradual coarsening of the silicates down the sequence. In the least melted object (a,b) metal is finely dispersed between the silicates, but it gradually coalesces into larger grains as the silicates coarsen and ends up as large grains inside the chondrule or as a rim around its surface (g,h).

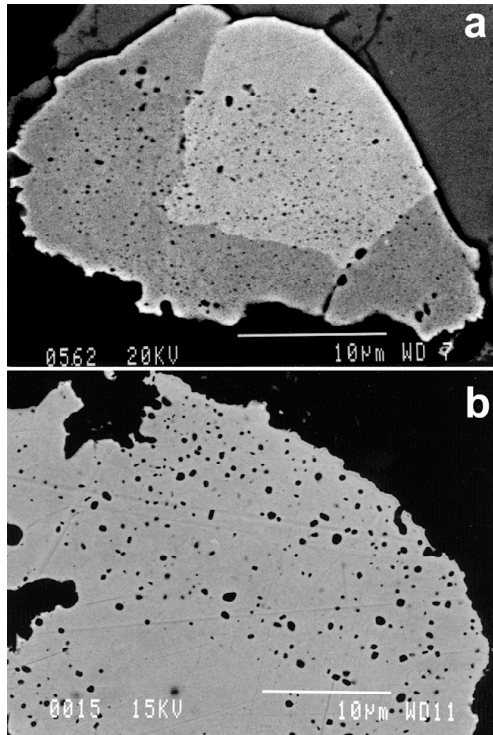


Figure 5. Inclusions exsolved in the solid state (during metamorphism) from chondritic metal by oxidation of a trace element (a) chromites (FeCr_2O_4) in a metal grain from the Kymka LL3.1 (light gray is tetraenaite (FeNi), darker gray is kamacite); (b) Sarcopside ($(\text{Fe})_3(\text{PO}_4)_2$) in a metal grain from the Leoville CV3.

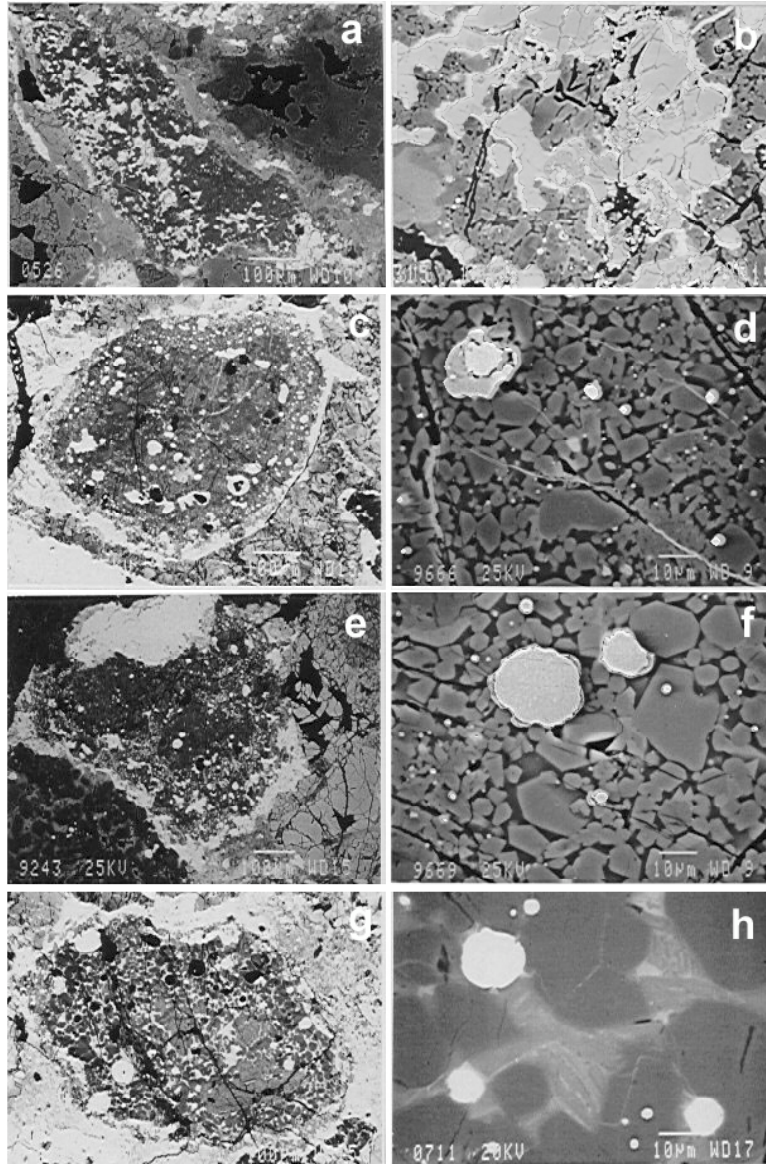


Figure 6. A suite of increasingly melted chondrules from Semarkona (LL3). The details at the right are all at the same scale, and show the progressive coarsening of the silicate crystals. In the least melted object (a,b) relict patches are present, and the opaque phases (primarily sulfides) are irregular in shape. In the intermediate objects (c,d) and (e,f), metal and sulfide are both present (with metal more abundant in (c,d)), and typical melted textures are apparent. In the more melted object (g,h), sulfide is no longer present and spherical metal blebs are present between the silicate crystals. Note that this latter chondrule only corresponds to a microporphyry. Objects more extensively melted than shown here exist in Semarkona and, as for Renazzo (Fig. 4), the metal will gradually separate from the silicates and form rims or large grains at the surface of the chondrules (Zanda et al. 1992).

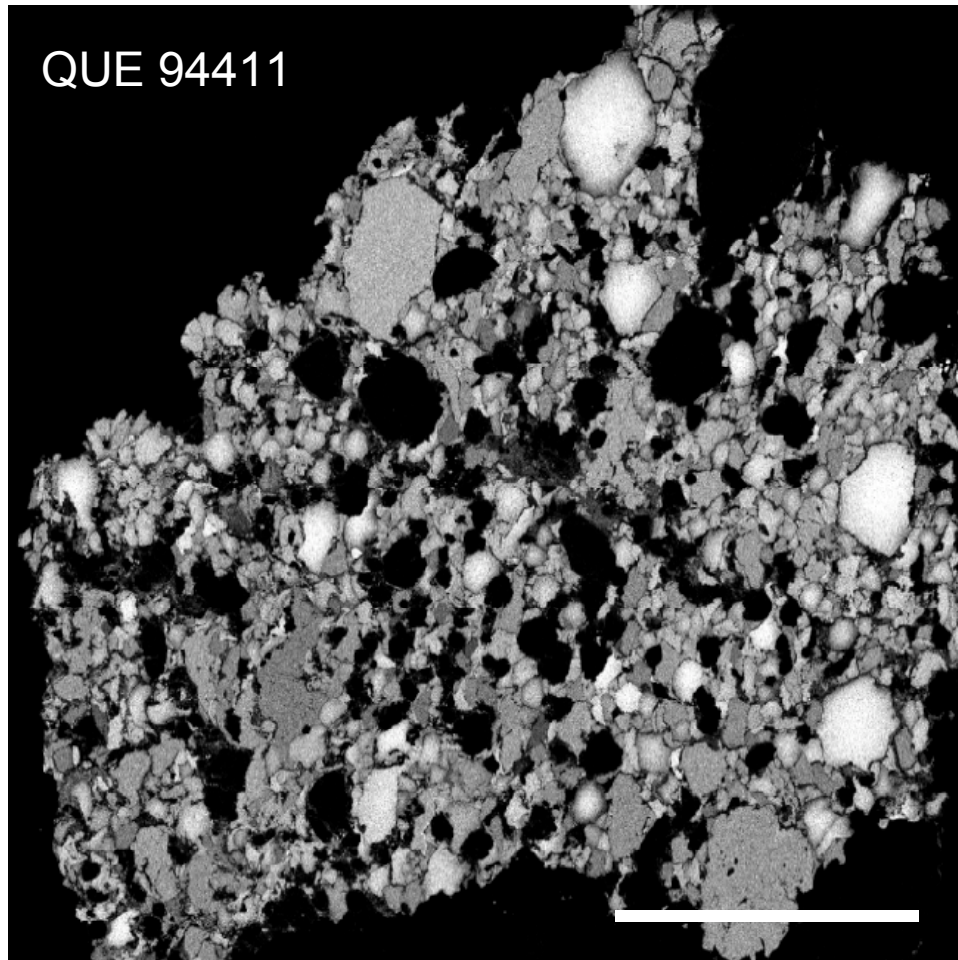


Figure 7. Nickel $K\alpha$ map of QUE 94411. Zoned metal grains have Ni-enriched (bright) cores and darker rims. Unzoned metal grains are uniform gray, but different Ni contents from grain to grain. Black grains are silicate. Scale bar = 1 mm.

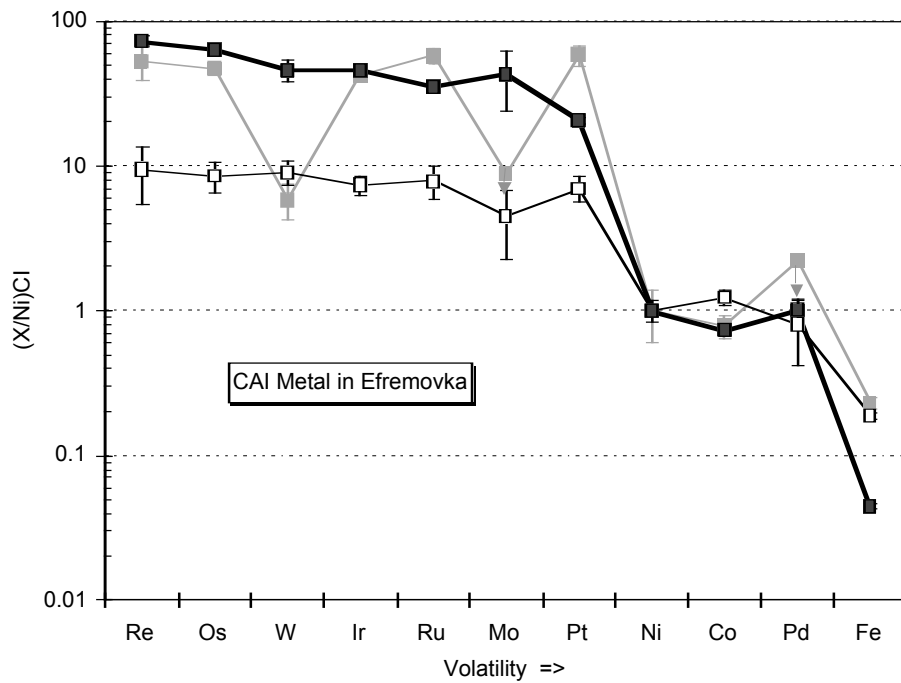


Figure 8. Compositions of three metal grains in CAIs from Efremovka (CV3-reduced). Open squares: grain #1; solid squares: grain #2; gray squares: grain #3. $(X/Ni)_{CI}$ = abundances normalized to Ni and CI chondrite abundances. Data from Campbell et al. (2003).

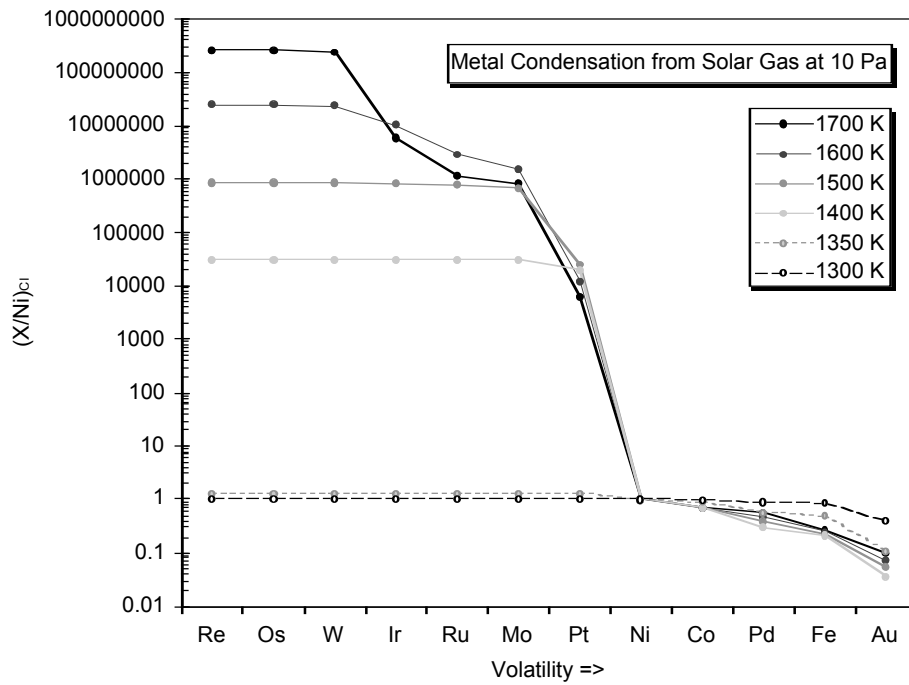


Figure 9. Calculated compositions of a single phase metal alloy condensing under equilibrium conditions from a gas of solar composition at 10 Pa total pressure. $(X/Ni)_{CI}$ = abundances normalized to Ni and to CI chondrite abundances. Calculations from Campbell et al. (2001).