THE HISTORY OF METAL AND SULFIDES IN CHONDRITES. Brigitte Zanda¹,², Yang Yu², Michèle Bourot-Denise¹ and Roger Hewins².¹Muséum d'Histoire Naturelle, 61 rue Buffon, 75005 Paris & Institut d'Astrophysique Spatiale, Orsay – France. ²Dept. of Geological Sciences, Rutgers University, Piscataway NJ 08855-1179 USA.

Introduction. Opaque minerals offer a unique approach to disentangling nebular from asteroidal effects in meteorites. Sulfur will be mobilized in every heating/cooling episode, whether nebular or asteroidal but, unlike any other volatile element, its resulting distribution is easily documented in the reflected light microscope. Fe-Ni sulfurization/desulfurization happened several times in the history of chondrites and several generations of sulfides and metal can potentially be identified: nebular condensates, chondrule melts, post-chondrule formation condensates, parent-body products.

1. First condensation of opaque minerals.
   1. Metal. [1,2] described the condensation of Ni and Fe, but this early metal may not have survived subsequent S and O condensation. P, Cr and Si in metal in carbonaceous chondrites result from chondrule formation [3], not condensation (see below). Remnant condensate metal might be found in fine grained matrix [4].
   2. Sulfides. S condensation by reaction of H₂S with an Fe-Ni alloy was studied experimentally by [5-7] who showed that the Ni-bearing sulfides pentlandite and monosulfide solide solution (mss) would be produced under nebular conditions and suggested that sulfides in Alais [8] may be nebular condensates [5]. The absence of significant Ni in most sulfides in chondrites can be explained by subsequent chondrule formation and thermal metamorphism (see below). Apart from Alais, Ni-bearing sulfide also occurs in primitive matrix [4] and is widespread in the finest grained (least melted) "protoporphyritic" chondrules of Semarkona [9,10]. These chondrules contain little or no metal, showing that when chondrule precursors were assembled metal sulfurization was essentially complete.
   3. Magnetite. The condensation of magnetite is only predicted in restricted conditions [11]. Though systematically present in the finest chondrules of Semarkona, it probably results from parent body alteration [12].

II. Chondrule formation. The sequence of events during chondrule formation can be reconstructed by looking at a sequence of porphyritic chondrules with increasing grain sizes, from the finest grained (least melted and closest to their precursors) to the coarsest ones (efficiently melted) [10]. The opaque assemblages and their textures along this sequence match run products along a temperature gradient in a solar furnace [13].
   1. Melting and breakdown of sulfides. The abundant sulfides in the finest chondrules of Semarkona (up to 14 wt% S) are interstitial to the silicates, as in the coolest region of solar furnace charges [13], in which the silicates have experienced very little melting [10]. With increasing melting, sulfides start breaking down and metal starts appearing, exhibiting typical melt textures with the remaining sulfides [13]. Such textures are found in the "intermediate" region of our solar furnace charges and throughout the grain-size sequence in type II (FeO-rich) chondrules. They are restricted to the "cryptoporphyritic" ones in type Ia (FeO-poor), where bulk S contents rapidly decrease with increasing grain-size [10]. We interpret this as volatile loss, as documented by systematic experiments [10, 13] with sulfide-bearing chondrule analogs.
   2. Regeneration of metal. Fe reduced from chondrule silicates occurs in "dusty" olivine grains [e.g. 14] as experimentally reproduced e.g. by [15]. In ordinary chondrites, however, chondrule metal is not the product of reduction [16] but mostly of desulfurization [13]. Metal is rare in type II sulfide-bearing chondrules. Its abundance gradually increases along the type I grainsize sequence as more and more extensive S loss has taken place: blebs are absent in proto-, appear in crypto- and become abundant in micro-porphyritic type I chondrules (but may be partly altered to carbides and magnetites [12]). As the silicate grain size further increases, Fe-loss from chondrules is observed. The metal grains become coarser, like the silicates, and are distributed closer to the surface of the chondrules. Eventually, no metal is left inside the chondrules, whose surfaces become ornamented with metal grains that occur as a continuous layer or only a few massive grains. It is easy to form similar metal grains by desulfurization in chondrule analogs. Surface grains and crown grains all have a very uniform composition for a given chondrule, and their contents of Cr and Si yield fO₂ matching those based on Fe contents of the chondrule silicates [3]. Metal is thus regenerated by desulfurization during chondrule formation, and its composition is established by equilibration with the silicate melt [3]. Large matrix metal grains (often with fine-grained silicate rims) or "metallic chondrules" [17] were lost by chondrules [3].
   3. S recondensation. S lost from chondrules recondenses on cooling, and metal crowns ornamenting the chondrule surfaces and metallic chondrules are readily available sites. Thus, much metal regenerated by chondrule formation will be sulfurized again during chondrule cooling. Sulfides in opaque encasements around chondrules and in large "opaque chondrules" account for roughly 90% of Semarkona's S, and metal and sulfide are almost always intimately associated [18], as in Allende [19]. These sulfides match the predictions of [5-7] for nebular condensates. In addition to mss, several Ni-bearing sulfides are found: pentlandite in Semarkona, but also heazlewoodite in Allende. They are associated with awaruite [19,20]. There are no Ni and S concentration gradients in the sulfides, however, which have undergone thermal equilibration throughout the rock (see below).
III. Parent body processes.

1. Aqueous alteration. Low temperature aqueous alteration on carbonaceous chondrite parent bodies was pervasive and complex, particularly when thermal metamorphism also occurred [21,22]. This process produced tochilinite, sulfates and ferrhydrite from nebular metal and sulfides [21,22]. However, pyrrhotite may be precipitated as a result of olivine dissolution [23] and tochilinite may breakdown to give sulfide on heating [22]. Limited aqueous alteration on ordinary chondrites resulted in the formation of carbide and magnetite in the opaque assemblages [12] but the dominant secondary process was dry thermal metamorphism.

2. Thermal metamorphism.

   i. Thermal Equilibration. The Ni content of the troilite in the most primitive chondrites is below detection and that of the pentlandite is homogeneous all through a given meteorite. We attribute this to parent-body equilibration, after [24], and determine temperatures of 230°C for Semarkona and 335°C for Allende [20]. A similar equilibration of the sulfide composition is displayed by the gentler reheating experiments of [25].

   ii. Sulfur migration. As shown by [25], the Ni-bearing sulfides eventually decompose into Ni-rich metal (FeNi2) and troilite [25], which produces associations similar to those found in the most primitive chondrites. Sulfur mobilization remained very limited in these meteorites, but it became more extensive as metamorphism progressed from 3.1 to 3.5: the previously sulfide-free metal blebs of type I chondrules contain increasing quantities of troilite [18]. This is in agreement with the experiments of [25] that show that sulfide layers grow on the isolated metal grains of the starting assemblages. Natural opaque assemblages also change: by 3.1 pentlandite and awaruite disappear, and (apart from the relict kamacite) the Ni-bearing phase found in the opaque associations is taenite. A similar change is observed in the short high temperature experiments of [25].

   iii. Sulfur redistribution. By 3.7, a redistribution of the sulfur becomes apparent [18]. The sulfide grains tend to connect, and their original distribution becomes a little blurry. In particular, opaque encasements around adjoining chondrules tend to merge. This effect is observed more clearly in experimental charges in which metal and sulfides were initially separated: thin sulfide trails grow throughout the samples and eventually connect separate metal-sulfide assemblages [25]. The establishment of a connected sulfide network throughout the parent bodies allows extensive cation movement [25], which explains why metal compositions equilibrate from 3.5 to 4 and zoned taenites first appear by 3.8 [18].

   iv. Recrystallization. Between 3.8 and 5, metal and sulfide grains tend to separate, and adjacent metal grains coalesce, eliminating silicate inclusions [18]. This reduces surface free energy. Metal coarsening is reversed at type 6 by chondrule recrystallization, yielding separate interstitial/polygonal metal and sulfide grains evenly dispersed throughout the rock [18].

3. Impact Shock. The results of varying degrees of impact on opaque minerals in ordinary chondrites are summarized in [26].

Conclusions. Chondrites contain two successive generations of sulfides (pre- and post-chondrule formation) and at least one of metal (formed in chondrules). New generations of these minerals form on parent-bodies.

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