

## Formation of metallic-Cu-bearing mineral assemblages in type-3 ordinary and CO chondrites

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### ABSTRACT

Studies of the new growth and re-distribution of Cu-rich phases in chondrites of different petrologic subtypes can potentially provide insights into post-accretionary parent-body processes. We present a systematic study of the distribution of Cu-rich phases and metallic Cu in Ornans-like carbonaceous chondrites (CO3) that underwent little aqueous alteration or shock (most with shock stages of S1) but exhibit a range of thermal metamorphism (subtype 3.0–3.7). A comparison to ordinary chondrites (OCs), which have undergone a larger range of shock levels, allows us to constrain the relative roles of radiogenic and shock heating in the origin of Cu distribution in chondrites. We found that the Cu content of Ni-rich metal and calculated bulk Cu content of CO3 chondrites (based on mass-balance calculations) show an increase from CO3.0 to CO3.2 chondrites. We speculate that some unidentified phases in the matrix account for a significant portion (nearly ~100 ppm) of the Cu budget in bulk samples of CO3.0 chondrites, while Ni-rich metal is the main Cu-carrier for CO3.2–3.7 chondrites. Within CO3.2–3.7 chondrites, Cu and Ni contents of Ni-rich metal are positively correlated, showing a systematic decrease from lower to higher subtype (~0.41 wt% Cu and ~45.0 wt% Ni in CO3.2 Kainsaz; ~0.28 wt% Cu and ~38.8 wt% Ni in CO3.7 Isna). Metallic Cu grains were found in every sample of CO3.2–3.7 chondrites, but not in any CO3.0–3.1 chondrites. Metallic Cu is: (1) present at metallic-Fe-Ni-pyrrhotite interfaces; (2) associated with fine irregular pyrrhotite grains in Ni-rich-metal-pyrrhotite nodules; (3) associated with fizzed pyrrhotite (fine-grained mixtures of irregularly shaped metal grains surrounded by pyrrhotite); (4) present at the edges of metallic Fe-Ni grains; and (5) present as isolated grains. In some metallic-Cu-bearing mineral assemblages, pyrrhotite has higher Cu concentrations than adjacent Ni-rich metal and shows a drop in Cu concentration at the interface between metallic Cu and Cu-rich pyrrhotite. This implies that the precipitation of metallic Cu grains could be related to the local Cu enrichment of pyrrhotite. We consider that radiogenic heating is mainly responsible for the formation of opaque phases in CO chondrites based on the relatively slow metallographic cooling rate (~0.1–5 °C/Ma), the increasing uniformity of Ni contents in Ni-rich metal with increasing CO subtype ( $44.3 \pm 17.3$  wt% in CO3.00 to  $38.8 \pm 3.4$  wt% in CO3.7 chondrite), and the relatively narrow range of pyrrhotite metal/sulfur ratios (~0.976–0.999). Metal/sulfur ratios of pyrrhotite grains in most CO3.2–3.7 chondrites (mean = ~0.986–0.997; except Lancé) are slightly higher than those in CO3.0–3.1 chondrites (mean = ~0.981–0.987; except Y-81020), possibly indicative of a release and re-mobilization of sulfur during progressive heating as previously reported for type-3 chondrites. In this regard, we suggest most metallic Cu grains in CO3 chondrites may have precipitated from Cu-rich pyrrhotite due to sulfidation of Fe-Ni metal during parent-body thermal metamorphism. Locally, a few metallic Cu grains associated with fizzed pyrrhotite could have formed during transient shock-heating. Both thermal and shock metamorphism could be responsible for the formation of metallic Cu.

Although the systematic decrease in the Ni contents of Ni-rich metal from subtype-3.2 to subtype-3.8 also occurs in OCs, the average Cu contents of Ni-rich metal grains are indistinguishable among type-3 OCs of different subtypes. The paucity of metallic Cu in weakly shocked type-3 OCs could be related to: (1) the relatively low-bulk Cu contents of OCs, and/or (2) the relatively rapid metallographic cooling rates at <500–600 °C (~1–10 °C/Ma for LL chondrites), possibly resulting from early disturbance of OC parent bodies. The intergrowth of metallic Cu and irregular pyrrhotite more commonly occurs in shocked type-4 to type-6 OCs than in CO3 chondrites. This could be due to S in type-4 to type-6 OCs being more mobilized due to shock heating than in unshocked CO3 chondrites. We predict that some other groups of carbonaceous chondrites (e.g., CI and CM) are less likely to produce metallic Cu due to the: (1) relatively low amount of metallic Fe-Ni; (2) relatively low parent-body temperatures of ~100–300 °C; (3) high mobility of Cu in solution for aqueously altered samples; and (4) the short heating duration for metamorphosed samples.

**Keywords:** Metallic Cu, CO3 chondrites, type-3 ordinary chondrites, thermal metamorphism, Cu-bearing minerals

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