Copper in various phases of several olivine-hypersthene and olivine-bronzite chondrites

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Summary. Determinations of Cu in separate phases of three olivine-hypersthene and one olivine-bronzite chondrites show that it is very strongly concentrated in the taenite; appreciable amounts are present in the olivine, less in the pyroxene plus plagioclase; it is probable that the copper found in the 'unattracted, attacked' fraction is present as metallic copper, and that very little is present in the sulphides.

COPPER was first recorded as a constituent of a stony meteorite (Juvinas) by Laugier (1822), and of ten irons by Stromeyer (1833), but the quantity and some other details throw doubt on these reports. L. J. Smith (1870) found copper in all irons he examined,[1] but in stones, although copper is shown in many early analyses, that amount is suspiciously high, and the first indubitable record appears to be Quirke's observation (1919) of flecks of metallic copper in Richardton.

Recent determinations of total copper in stones (Smales, Mapper, and Wood, 1957; Smales, Mapper, Morgan, Webster, and Wood, 1958; Greenland and Lovering, 1965; Greenland and Goles, 1965; Schmitt, Smith, and Goles, 1965) show an average of about 110 ppm in common chondrites, with a range of 50 to 205 ppm; there was no significant difference between bronzite and hypersthene chondrites.

The only previous quantitative observations on the distribution of the copper between the phases appear to be those of I. and W. Noddack (1930), who found 1·5 ppm Cu in the silicates from 42 stones and 4200 ppm in troilite from 5 irons, and of Schmitt, Smith, and Goles (1965) who found the chondrules of Allegan, Bjurböle, Ochansk, and Soko-Banja contain from $\frac{1}{3}$ to $\frac{2}{3}$ as much copper as the whole stone. Greenland and Lovering assumed the metal to be copper-free. Qualitatively, Quirke (1919), Nininger (1941), and Ramdohr (1963) have shown that

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[1] Quantitative data on copper in some sixty irons, listed by Cohen (1894, 1903) but omitted from the data on minor elements collected in the Catalogue of Meteorites (Hey, 1966), are for the most part in good agreement with recent determinations.

copper in chondrites may occur as grains of native metal from 10μ or less to 2 mm in diameter, and as chalcopyrite, chalcophyrrhotine, or valleriite; the metallic grains are commonly found in taenite-rich plessite according to Ramdohr.

TABLE I. Distribution of copper between the phases of four ordinary chondrites (H, olivine-hypersthene chondrite; B, olivine-bronzite chondrite). K, attracted attacked (metal, mainly kamacite); T, attracted unattacked (taenite); M, total metal; Sul., unattracted attacked (sulphides plus metallic copper); O, olivine; P, pyroxene; Sil., unattracted unattacked (total oxidized phases)

	K	T	M	Sul.	O	P*	Sil.	Bulk
Copper, parts per million in the several phases								
H 1	47	2610	565	< 1	17·8	22·3	17·1	61·4
H 2	65	2470	508	103	25·4	12·7	17·3	64·0
H 3	23	2360	517	114	37·1	13·3	24·8	76·6
B 4	22	1610	418	13	41·5	6·0	22·4	90·2
Contributions of the several phases to the total copper (% of total)								
1	5·1	71·0	76·1	—	13·0	10·9	23·9	
2	7·0	59·4	66·4	10·8	16·6	6·2	22·8	
3	2·3	61·5	63·8	9·1	22·1	4·9	27·0	
4	3·2	76·8	80·0	0·7	17·3	2·0	19·3	

1. Barwell (B.M. 1966, 59).
2. Ohuma (B.M. 1966, 53).
3. Wold Cottage (B.M. 1073).
4. Oakley (B.M. 84814).

* Calculated from the copper content of the acid-insoluble oxidized phase on the assumption that this consists of pyroxene and feldspar in the normative ratio found for the meteorite (Moss *et al.*, 1967, p. 115), and that the feldspar is copper-free.

Copper has now been determined in the several fractions of the three olivine-hypersthene chondrites and one olivine-bronzite chondrite previously examined (Moss, Hey, Elliott, and Easton, 1967, to which reference should be made for the general technique), with the results shown in table I.

After chlorination of the magnetic fraction, the unattacked metal (taenite) was dissolved and its copper content determined with 2:2-diquinolyl as in our earlier study (Moss, Hey, and Bothwell, 1961). A part of the unattacked part of the non-magnetic fraction, consisting only of oxidized phases (silicates, phosphates, and oxides), was treated with hydrochloric acid (sp. gr. 1·06) to remove olivine (Fletcher, 1894), and copper estimated in the residue, the copper content of the olivine being obtained by difference. A direct test showed that small grains of metallic copper are efficiently attacked by chlorine. The bulk copper contents found are all well within the range found by Greenland and

Lovering (1965), but the detailed results showed a very marked concentration of the copper in the taenite, which contributes 64 to 80 % of the total copper in the meteorite. This was confirmed by an electron-probe study by Dr. S. J. B. Reed, who found a high copper content (averaging 2000 ppm) for the taenite of Barwell, with no indication that this might be due to minute inclusions of metallic copper. The chlorine-attacked metal probably includes little taenite, to judge from its nickel content (Moss *et al.*, 1967) and from the correlation of its nickel and copper contents, and it is clear that the distribution ratio of copper between taenite and kamacite in the four meteorites studied is at least 40:1 to 100:1 and may well be higher.

In the silicates, which contribute 20 to 36 % of the total copper, the olivine tends to be richer in copper than the pyroxene, the distribution ratio ranging from Ol:Py 0·8 in Barwell to 2·8 in Wold Cottage and 6·9 in the bronzite chondrite Oakley (assuming that the feldspar is copper-free). The contribution of the silicates to the total copper is less than the contribution of the chondrules found by Schmitt, Smith, and Goles (1965), and suggests that their chondrules contained some taenite; additional data is, however, desirable, and we hope to examine the four falls studied by Schmitt *et al.*

The chlorine-attacked non-magnetic fraction, consisting of sulphides and any metallic copper, is surprisingly low in copper in all four meteorites studied, and it is clear that copper is not a chalcophilic element in ordinary chondrites. We have not yet been able to establish whether the copper in this fraction in Wold Cottage and in Ohuma is present as metal or as a sulphide. We hope to extend this study to chondrites known to contain metallic copper or copper sulphides.

That copper is concentrated in the taenite of iron meteorites was established by Nichiporuk (1958), who used acid to dissolve the kamacite and found distribution ratios of the same order as ours. It is also in agreement with the study of the Fe–Cu–Ni equilibrium diagram by Bradley, Cox, and Goldschmidt (1941), who find copper to be much more soluble in taenite than in kamacite.[1]

Finally, we would note that the large difference between the total copper contents of different samples of certain meteorites noted by Greenland and Goles (1965) could stem from irregular distribution of nickel- and copper-rich taenite, but is more probably an indication that

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[1] Bradley *et al.* give no quantitative data for the solubility of copper in kamacite; Köster (1930) found the solubility of copper in iron below about 600° C to be 0·4 % or less.

these meteorites contain metallic copper or copper sulphides as relatively large ($\geqslant$ 0·1 mm) grains. A simple calculation will show that 100 ppm of copper corresponds to approximately 10^4 grains of 10μ diameter per gram, and an average of 35 per cm^2 of a section; but if the grains average 0·1 mm diameter, ten such grains per gram will amount to 100 ppm, and there will only be one per 3 cm^2 of the section.

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Note added in proof: Dr. S. J. B. Reed has kindly brought to our attention some recent data on the solubility of Cu in Fe (G. R. Speich, J. A. Gula, and R. M. Fisher, in The Electron Microprobe, ed. McKinley *et al.*, New York (Wiley), 1966, pp. 525–542); extrapolation of the formulae quoted would give the solubility of Cu in α–Fe as 330 p.p.m. at 500°C, 45 p.p.m. at 400°, and 3 p.p.m. at 300°, and in γ–Fe 2430 p.p.m. at 500°, 780 p.p.m. at 400°, and 170 p.p.m. at 300°C. These figures indicate the relative order of magnitude, but are likely to be considerably affected by the presence of Ni, especially in the taenite.