The conductivity of chalcocite, the richest copper sulphide

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Introduction
Exploration for copper has long been a focus for humankind. Developments in modern technologies have generated even more demand for this most useful metal. The cuprous sulphide, chalcocite (Cu₂S) with a 79.8% Cu content is the richest and most valuable sulphide of copper (compare chalcopyrite, CuFeS₂, 34.5% Cu), but its conductivity has been little investigated. This article aims to contribute to the limited database with some inductive electromagnetic (EM) measurements.

Chalcocite can occur as a primary crystalline sulphide e.g., in the hydrothermal veins of granite in Cornwall, but most of it forms as fine-grained dark blankets under the water table in the supergene enrichment zone above primary chalcopyrite ore, in metasediments. This zone of enrichment is fed by copper sulphate solutions descending through the weathered zones.

The old CSA Mine, Cobar NSW, had a nine metre supergene zone. The Mt Isa Inlier, northwest Queensland, hosts several deposits of supergene chalcocite. Much chalcocite occurs as disseminations in low grade porphyry coppers. Further information on occurrences, genesis, and mines in Australia and overseas can be found in Blanchard (1968), Lindgren (1933), Read (1998), Jones (2016, 2018), and will not be repeated here. An instructive summary of chalcocite and its structure may be found at https://www.mindat.org/min-962.html. Figure 1 shows two examples of collector grade chalcocite.

Ore genesis
Consider a primary chalcopyrite body, usually associated with pyrite, which undergoes weathering and develops an enrichment cap. In the weathered zone, oxidation generates iron sulphate (which, when hydrated, is green vitriol) and very mobile copper sulphate. The copper sulphate descends in solution to interact with chalcopyrite and pyrite, possible reactions are:

\[
\begin{align*}
\text{CuFeS}_2 + \text{CuSO}_4 \rightarrow 2\text{CuS} + \text{FeSO}_4 \quad \text{(covellite + vitriol)}
\end{align*}
\]

then

\[
\begin{align*}
5\text{CuS} + 3\text{CuSO}_4 + 4\text{H}_2\text{O} \rightarrow 4\text{Cu}_3\text{S} + 4\text{H}_2\text{SO}_4 \quad \text{(chalcopyrite + acid)}
\end{align*}
\]

and

\[
\begin{align*}
5\text{FeS}_2 + 14\text{CuSO}_4 + 12\text{H}_2\text{O} = 7\text{Cu}_2\text{S} + 5\text{FeSO}_4 + 12\text{H}_2\text{SO}_4
\end{align*}
\]

Thus, a very desirable secondary ore of copper is produced in secondary, messy, acidic reactions resulting in a highly altered, porous environment. The chalcocite, Cu₂S, is dark, sometimes sooty, soft (Moh’s hardness \(\leq 3\)), imperfectly sectile, dense (5.5 – 5.6 g/cc, t/m³). It is a p-type semiconductor (Shuey, 1975), crystallising in the monoclinic system, but readily pseudomorphs e.g. after pyrite. Usually, it is found as tabular crystals, mainly fine to very fine grained; rarely coarse.

Measurements
Mass property (Emerson, 1990) and EM conductivity (Yang and Emerson, 1997) measurements were carried out at mesoscale on 21 samples from the USA, D R Congo, and Australia. The samples, categorised in Groups I to VII, ranged from high conductivity, collector grade, crystal aggregates through fine grained massive ores varying in chalcocite, chalcopyrite, pyrite and graphite content, to a low conductivity carbonaceous siltstone host rock containing minor amounts of chalcocite and pyrite. Samples were examined under the microscope to estimate mineralogy. In Table 1, for Groups I to V, the samples have been listed in decreasing order of chalcocite content, so for Group V #11 has the most chalcocite and #14 has the least. Group VI is dominantly pyritic with only minor chalcocite, some of these samples show signs of decomposition and disaggregation. The various mineral assemblages were galvanically micro-probed to investigate, qualitatively, relative conductivities. This established that conductivity diminished in the order: graphite – chalcopyrite – chalcocite – pyrite. The samples and results are given in Table 1 along with relevant information and measurement techniques discussed in other previous articles (e.g. Preview 203, 52-64, on pyrite).

Results
The results given in Table 1 are plotted against density in Figure 2. A feature of the results is the extraordinary values...
### Table 1. Mass property measurements on chalcocite samples.

| Category | No. | Plot Symbol | EM Cond. Sim | DBD (dry) | WBD (sat.) | GDA (grain) | $P_a$ porosity % |
|----------|-----|-------------|--------------|-----------|------------|-------------|----------------|
| medium grain size (mm) crystalline | I | high grade Cu | 1 | massive | 1831 | 5.15 | 5.22 | 5.56 (true) | 7.4 |
| | | high grade Cu | 2 | massive | 1285 | 4.98 | 4.99 | 5.04 | 1.2 |
| | II | high grade Cu | 3 | massive | 1100 | 4.99 | 5.00 | 5.04 | 1.0 |
| | | med. grade Cu | 4 | vein | 191 | 3.57 | 3.58 | 3.61 | 1.1 |
| | | low grade Cu | 5 | stringer | 3 | 2.71 | 2.72 | 2.75 | 1.3 |
| micro to very finely crystalline (μm) massive | III | cc > cpy > gr | 6 | | 4330 | 3.68 | 3.97 | 5.20 | 29.2 |
| | | 7 | | | 2660 | 3.91 | 4.15 | 5.09 | 23.1 |
| | | 8 | | | 2010 | 4.40 | 4.53 | 5.02 | 12.3 |
| | IV | cc > py > gr | 9 | | 806 | 3.69 | 3.93 | 4.92 | 25.0 |
| | | 10 (sooty) | | | 188 | 2.14 | 2.61 | 4.02 | 46.8 |
| | V | cc > py | 11 | | 420 | 3.89 | 4.11 | 5.00 | 22.1 |
| | | 12 | | | 129 | 3.91 | 4.02 | 4.38 | 10.8 |
| | | 13 | | | 34 | 2.41 | 2.81 | 4.02 | 40.1 |
| | | 14 | | | 19 | 2.96 | 3.18 | 3.79 | 21.9 |
| | VI | py >> cc | 15 | | 25 | 3.40 | 3.65 | 4.53 | 24.8 |
| | | 16 | | | 18 | 3.83 | 3.95 | 4.36 | 12.1 |
| | | 17 | | | 14 | 4.17 | 4.23 | 4.44 | 6.0 |
| | | 18 | | | 6 | 3.76 | 3.95 | 4.65 | 19.1 |
| | | 19 | | | 5 | 3.97 | 4.11 | 4.63 | 14.3 |
| | | 20 | | | 4 | 3.25 | 3.53 | 4.54 | 24.5 |
| | VII | host carbon. sitrine + minor py | 21 | | < 1 | 2.28 | 2.40 | 2.60 | 12.5 |

Reference values from literature:

1. Cond. Sim: s/m
2. Assumed density: g/cc
3. (Harvey, 1928) H1: 12500 galvanic microarray measurement 5.65 n/a
   H2: 20000 5.65
4. (Telkes, 1950) T1: 370 galvanic measurement 5.65 n/a
   T2: 1667 5.65

Comparison cond. values from some massive deposits (in author’s experience):

- graphite: 10000 2.2
- chalcopyrite: 5000 4.2
- pyrrhotite: 100000 4.6
- pyrite: 200 5.0

Notes:
1. Densities: DBD dry bulk density (105°C dried), WBD fresh water saturated (vacuum technique), $P_a$ apparent (water accessible) porosity, GDA apparent composite grain density of minerals in sample (porosity removed), RTP measurements (22°C). $[\text{GDA} = \text{DBD}/(1-P_a)]$
2. Magnetic Susceptibility: not cited because all quite low (< 10 x 10^-5 cps)
3. EM conductivity: measured on wetted samples; for techniques see previous Preview articles (e.g. Pyrite, Preview 203 Dec 2019 p61, 62 Table 3 Fig 10). Values rounded.
4. Reference values: from Harvey and Telkes who measured galvanic resistivities on presumably single crystals; the resistivities have been inverted to conductivities in the Table; the density ascribed to their materials has been assumed to be about 5.65 g/cc the midpoint of the range of densities, 5.5 - 5.8 g/cc, reported for chalcocite
5. Mineralogy: cc - chalcocite (Cu$_2$S), cpy - chalcopyrite (CuFeS$_2$), py - pyrite (FeS$_2$), graphite (G); chalcocite (cc) has 79.8% Cu content making the most valuable copper sulphide ore; in the listed category cc content increases from #2 to #1, #5 to #3, #8 to #6, #10 to #9, and #14 to #11.
6. Samples #1, 2 are from the Hambeau Mine, Wisconsin, USA where cc occurs in quartz serice schists; #3-5 are from the Katanga Copper Belt, DR Congo, where cc is hosted by carbonate-velined felsic sediments, #6-21 are from the Mount Isa Inlier in NW Queensland where cc is associated with carbonaceous pyritic siltstones. All samples are from Proterozoic metasedimentary sequences.
7. Harvey’s samples from Harvard Uni. mineragraphy collection; Telkes’ T1 Sonora Mexico, T2 Butte Montana (presumably these were all single crystal measurements).
for porosity (up to 47%) recorded for the fine grained massive granular samples #6 – 21 embracing categories II to VII. This is consistent with the mode of genesis. The porosity for #1 (7%) is due to fracturing and intergranular voids. The chief interest in this work is how well the solid materials conduct and, especially, how good a conductor is chalcocite. To this end, conductivity was plotted against inferred solid grain density (porosity removed). Conductivity plotted against porosity, or wet, or dry density was not particularly informative. Although, clearly, porosity development cannot help conductivity it seems that, except for the pyritic dominant Group VI and the host VII, the solid framework of the mineral assemblage is well networked by the conducting elements i.e., sulphides of copper, and graphite. The results here are for mineral aggregates i.e., ores, not single crystals. However, single (presumed) crystal data from the sparse literature are included for reference: Harvey’s (1928), measured by galvanic microprobe arrays (fractions of mm Wenner electrode spacings); and Telkes’ (1950), by a technique that is not clear in her paper. Also included in Figure 2, for comparison, are typical values, encountered by the writer, for deposits of commonly encountered sulphides (pyrite, chalcopyrite, pyrrhotite) and graphite.

Discussion

In Figure 2, generally, conductivity increases to moderate levels as density increases to chalcocite’s nominal value of 5.65 g/cc. This trend in conductivity at lower densities is not due to chalcocite alone as there are contributions from chalcopyrite and minor graphite (Group III) graphite and pyrite (Group IV), pyrite (Group V). Also, metasedimentary host rock content diminishes as sulphide content increases. Chalcopyrite and graphite appear to boost fine grained, massive chalcocite ore conductivity, pyrite seems to lower it. This is a plausible result given the conductivity and nature of both graphite and chalcopyrite: very good conductors with a threading / connecting habit; compared to pyrite which, in aggregate, is often a moderate, not very well-connected conductor (Emerson, 2019). Samples #3 – 5 in Group II diminish in conductivity as density decreases owing to increasing amounts of metasedimentary host rock. The pyrites in Group VI are poor conductors. They are altered, most of them are disaggregating (“sugar” pyrite), and chalcocite content is low.

A pure chalcocite aggregate (#1, Group I) has a conductivity similar to Telkes’ T2 i.e. ~1800 S/m. To which samples #3 – 5, 9 – 14 trend as density increases. This value of 1800 S/m appears to be indicative, but by no means definitive, of very high copper grade chalcocite ore. Until further data becomes available it seems reasonable to regard chalcocite as a good conductor, probably with good connectivity (noted by Shuey, 1975), ranking below chalcopyrite and above pyrite in conductivity.

Concluding remarks

Chalcocite manifests a good, but not excellent, mesoscale conductivity at least for the samples in this limited test. More needs to be done not only on chalcocite, but on the chalcocite family, which includes the little studied, copper deficient variants: digenite Cu₃S₅ (78.1% Cu), djurleite Cu₃S₁₆ (79.4% Cu),...
and perhaps anilite Cu$_7$S$_4$ (77.6% Cu). Digenite may have a conductivity two orders of magnitude greater than chalcocite, and djurleite one order of magnitude greater (Shuey, 1975). These two minerals dominate the economic mineralogy of the Esperanza copper deposit in the Mt Isa Inlier (Richardson and Moy, 1998). Chalcocite is black cuprous sulphide, a closely associated mineral is the indigo-blue cupric sulphide, CuS, covellite (66.4% Cu), which acts as a p-type metal with a conductivity exceeding 1 000 000 S/m. Covellite usually does not occur in abundance, but as inclusions in, or coatings on, other copper sulphides. It does not match its associated sulphides in copper content, but it surely could affect their electrical properties. Although known to occur sometimes as primary sulphides, e.g., in hydrothermal veins, all these minerals are mainly encountered in the supergene zone and, to better to target an important metal resource, they warrant further petrophysical studies. Any such investigations should be tied tightly to chemistry and mineralogy, as work carried out on synthetic copper sulphides (e.g. Okamoto and Kawai, 1973) has shown that conductivity is highly sensitive to variations in stoichiometry.

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