

# The geochemical role of primary copper-sulphur mineralization in the crystallization of the Freetown (Sierra Leone) layered gabbro

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**SUMMARY.** The separation of iron-titanium oxide droplets and the formation of olivine, in the Freetown layered gabbro, depleted the magma in iron and enriched the magma in copper. In magma injections in which the sulphur fugacity was sufficiently high, this resulted in the separation of immiscible copper sulphide droplets closely associated with the iron-titanium oxide droplets, and both were subsequently enclosed by olivine. A lower sulphur fugacity in other injections of magma suppressed the separation of the copper, which later appeared as native copper associated with euhedral titanomagnetite, and was enclosed by feldspar. Crystallization of the iron-titanium oxide droplets and subsolidus diffusion has resulted in granular exsolution of ilmenite from the droplets and lamellar exsolution of ilmenite in the euhedral titanomagnetite.

THE layered gabbro of Freetown, Sierra Leone, has been described by Wells (1962) and shown to consist of rhythmically layered units varying from troctolite to anorthosite in composition, with troctolite as the most widely occurring rock type. There is no indication of progressive cryptic variation and the intrusion shows evidence of multiple injection and a prolonged cooling history after injection. Previous studies (Bowles, 1976, 1977) of the iron-titanium oxide phases have illustrated some aspects of this cooling history. A variety of different textural types of these oxide minerals in different silicate environments closed with respect to mobile elements at varying stages during cooling. As a result the same phase possesses contrasting compositions at different locations in a single specimen. Quantitative electron microprobe analysis of these phases and comparison with the geothermometer proposed by Buddington and Lindsley (1964) has indicated the progress of this cooling in the temperature and oxygen fugacity field (Bowles, 1976, 1977).

Native copper and digenite are associated with two particular textural types of these iron-titanium oxides and these are investigated in the present work.

*Occurrence of the copper minerals.* There are two distinct textural situations in which the copper minerals occur and these two situations have not been observed in the same specimen. Within olivine in certain troctolites there are rounded blebs of titaniferous magnetite each of which may contain a single lamella of ilmenite. These blebs are widespread and locally abundant, and a section through a single olivine may reveal as many as twenty-eight blebs (fig. 1*d*) some of which occur in the core of the olivine. Less frequently blebs of digenite are seen moulded on to the exterior of previously formed titanomagnetite blebs as shown in fig. 1*a*. Within labradorite there occurs the second textural relationship and fig. 1*b* shows a typical example of a subhedral titanomagnetite, crossed by a single ilmenite lamella and containing within its boundary a euhedral crystal of native copper. In both cases the titanomagnetite is free from later ceylonite or other lamellae, in contrast to other textural occurrences of titanomagnetite within these rocks.

The composition of the copper minerals represented in fig. 1*a*, 1*b* is given in Table I and was obtained from electron microprobe analysis using the methods described by Bowles (1975) and the quantitative microprobe correction program of Mason *et al.* (1969). The compositions of the coexisting magnetite and ilmenite are given by Bowles (1976) as are the conditions of final equilibration obtained using the geothermometer proposed by Buddington and Lindsley (1964). Investigation, using the microprobe, of the olivine immediately surrounding the opaque grains shows that there is no localized increase in copper content above the low levels characteristic of the rest of the specimen, but the copper content of the associated ilmenite from similar blebs not associated with (1976, Table I) shows the ilmenite associated with the digenite bleb to contain 0.47% CuO whilst the ilmenite from similar blebs not associated with

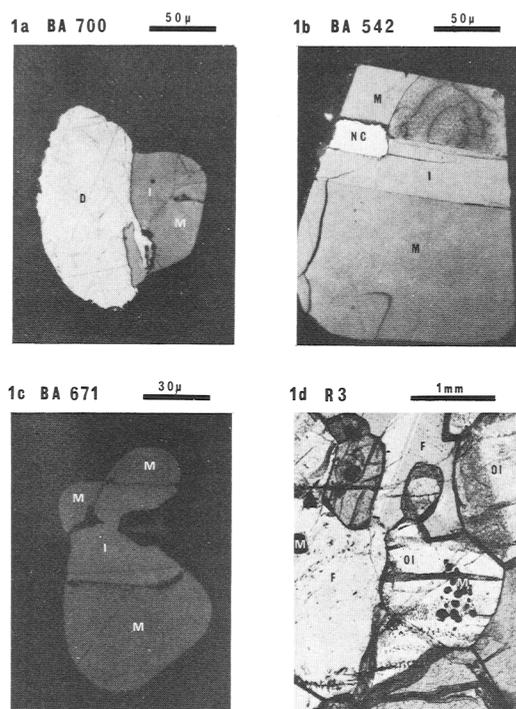


FIG. 1. *a*, coalesced titanomagnetite and immiscible copper sulphide droplets contained within olivine. The titanomagnetite (M) has subsequently exsolved granular ilmenite (I) and the copper-sulphide droplet has formed digenite (D). *b*, subhedral titanomagnetite (M) containing native copper (NC). A lamella of ilmenite (I), exsolved during cooling, has developed along a plane of weakness introduced by the presence of the native copper. *c*, three droplets of titanomagnetite (M), which have coalesced and become trapped in olivine; on crystallization the three droplets became a single crystal which was subsequently crossed by a single exsolved ilmenite lamella (I). *d*, rounded, often coalesced droplets of magnetite (M) are enclosed by olivine (Ol) whilst euhedral magnetite (M) is contained in feldspar (F).

digenite contains only 0.07–0.09% CuO and texturally dissimilar ilmenites within the rock contain no detectable copper (less than 0.01%). A similar, although less-pronounced increase in copper content is recorded for the corresponding magnetites. The oxide phases associated with the native copper do not show such a striking increase in copper

content and only 0.02% CuO is recorded in the magnetite.

The rounded grains contained in the olivine appear closely similar to examples from Skaergaard described by Wager, Vincent, and Smales (1957) who suggest that they are due to the formation of immiscible droplets of sulphide-rich liquid within the silicate magma. There are, however, some important differences. The Freetown droplets contain magnetite and ilmenite with digenite as the only copper sulphide whereas the Skaergaard droplets have assemblages containing bornite and chalcocopyrite or chalcosine in addition to digenite and rare assemblages of bornite, chalcocopyrite, and cubanite. In the Skaergaard droplets, magnetite is frequently present but ilmenite is not recorded. Bartholemé (1957), in an appendix to the work of Wager *et al.* (1957), concluded that the textures and mineralogy observed in the Skaergaard sulphides was due to subsolidus transformation from an original digenite phase to copper-iron sulphides. It appears that the droplets from both localities may have a similar origin as digenite and iron oxide, but the Freetown droplets have remained unaltered whilst those from Skaergaard have recrystallized during cooling. The presence of titanium in the Freetown oxides permitted the re-equilibration of the iron-titanium oxide phases, which may have buffered and thus preserved the original digenite.

There is no record of native copper occurring at Skaergaard, although Wager and Mitchell (1951) published whole rock analyses and separated mineral analyses carried out by Vincent and Mitchell for copper and sulphur, which were ascribed to copper sulphides and to copper in solid solution.

*Origin of the digenite.* The equilibration temperatures of 670 °C obtained on the associated iron-titanium oxides precludes the possibility that any low-temperature (e.g. hydrothermal) process could be responsible for introducing the digenite into the rocks described here. Stumpfl (1966) has shown that copper sulphides have been introduced with platinum and gold during local hydrothermal mineralization where the copper sulphides have clearly altered iron-titanium oxides of a different textural type from those described in the present work.

TABLE I. *Composition of copper-bearing phases*

	Cu	S	Mn	Fe	Ni	Ca	Mg	Al	Cr	V	Ti	Si	Total
Digenite	79.55	20.23	2.07	0.33	0.15	0.06	0.00	0.19	0.09	0.13	0.10	0.18	101.08
Native copper	98.73	—	—	1.29	—	—	—	—	—	—	—	—	100.02

— = not determined.

The rounded nature of the blebs enclosed within olivine suggests that they formed from an immiscible sulphide melt that was separating early in the formation of the olivines. The separation of an immiscible sulphide melt has been investigated by Vogt (1917, 1923) and by many other authors whose work has been summarized by Haughton, Roeder, and Skinner (1974, p. 452). Experimental work by the latter authors has shown again that separation of an immiscible sulphide melt can occur and indicated how temperature, oxygen fugacity, sulphur fugacity, and composition control the separation. This led them to describe the separation of an immiscible sulphide melt: '... when an opaque oxide mineral such as chromite, magnetite, or ilmenite starts to crystallize, the ferrous iron content of the residual liquid will decrease and cause a concomitant reduction in the sulphur-carrying capacity of the magma... the magma composition will be driven toward the sulphide saturation surface. When it reaches the surface, further precipitation of opaque oxides will drive the magma down the sulphide saturation surface, causing the continued precipitation of an immiscible sulphide melt.' These authors, therefore, agree with the observation by Page (1971) that the separation of the sulphide material is triggered by local depletion of  $\text{Fe}^{2+}$  in the magma. Copper sulphide blebs formed in this way may be expected to be closely associated with previously formed titanomagnetite, exactly as observed in this work, and by Page (1971).

*Origin of the titanomagnetite blebs.* The digenite is, however, not the only phase to show a rounded or droplet form. The titanomagnetite shows exactly the same form. The textural evidence thus points to the formation of droplets of titanomagnetite later joined by blebs of copper sulphide melt, which together were enclosed in olivine.

The ilmenite lamellae in the titanomagnetite blebs are due to exsolution from an original titaniferous magnetite as described by Buddington and Lindsley (1964) and illustrated (fig. 1c) by an example from Freetown, which shows three blebs which have coalesced. A single ilmenite lamella crosses all three blebs and clearly the blebs, which were once separate, acted as a single crystallographic unit at the time when exsolution occurred.

Hilty and Crafts (1952), Nagamori and Kameda (1965), Craig and Naldrett (1967), Naldrett (1969), and Haughton *et al.* (1974) have examined the Fe-S-O system and shown that iron-sulphide droplets may be formed. Naldrett (1969) reported that the presence of sulphur markedly lowers the melting-point of magnetite whilst Craig and Naldrett (1967) showed that a small amount of

copper has a lesser effect in the same direction. Similarly Yazawa and Kameda (1954), who investigated the  $\text{Cu}_2\text{S}-\text{FeO}-\text{FeS}$  system, showed that the liquidus of that system dips to  $850^\circ\text{C}$  at the ternary eutectic. Work by MacLean (1969) has shown that at high temperature in the  $\text{FeS}-\text{FeO}-\text{Fe}_3\text{O}_4-\text{SiO}_2$  system the presence of a small quantity of sulphur results in iron sulphide, iron oxide, and silicate liquids. It thus appears possible that at basaltic magma temperatures three separate liquids can occur together and in a natural system corresponding to the Freetown intrusion these were presumably a silicate melt, an iron-titanium oxide melt, and a copper sulphide melt. The occurrence of distinct copper sulphide and iron-oxide melts is supported by the experimental work of Yazawa and Kameda (1954) and by the evidence from natural systems, especially those described by Skinner and Peck (1969) and by Wager, Vincent, and Smales (1957) who report two distinct sulphide melts crystallizing at different temperatures. At  $1100^\circ\text{C}$  the only phases present in the  $\text{Cu}-\text{Fe}-\text{S}$  system are: native copper, digenite, bornite solid solution containing up to 12 wt% Fe, and pyrrhotine containing up to 5 wt% Cu, according to Kullerud, Yund, and Moh (1969), and only iron oxide and digenite are seen in the  $\text{Cu}_2\text{S}-\text{FeO}-\text{FeS}$  system of Yazawa and Kameda (1954).

To obtain the textures observed here it is necessary that the iron-oxide melt appears during crystallization of the olivine and this is clearly possible if the melting-point of titanomagnetite is lowered by the presence of sulphur and copper. The digenite must then be produced by the triggering action described by Haughton *et al.* (1974), as mentioned above, and the whole process completed well before the olivine solidus is reached. The triggering action is probably more complicated than this since the work of MacLean and Shimazaki (1976) on the partitioning of transition metals between sulphide and silicate liquids shows that in a situation where olivine is precipitated under equilibrium conditions, then the partitioning of Ni and Cu is such that the liquids are rapidly depleted in Ni and enriched in Cu. Thus the formation of the olivine enriches the silicate liquid in copper and the separation of the iron-oxide phase triggers the separation of the immiscible copper sulphide melt. Burns and Fyfe (1964) have described the entry of Ni into olivine in preference to other transition metals and, as noted by Wager and Mitchell (1951), this explains the decrease in the Ni content of the Skaergaard magma as differentiation proceeded. Conversely the same process may explain the enrichment of the Skaergaard magma in copper with continued differentiation. The process under present discussion relates to the

localized depletion that occurs within a magma in the vicinity of a growing olivine. Despite the difference in scale the two processes presumably have a common cause.

Wager, Vincent, and Smales (1957) observe that 'sulphur in general separates from igneous rock magmas more commonly as a copper sulphide than as an iron sulphide', and their study of Skaergaard leads them to conclude that copper, if present, readily forms a copper-sulphide melt and an iron-sulphide melt is formed at a later stage of differentiation when there is only a small quantity of copper remaining in the magma, corresponding perhaps to estimates by Skinner and Peck (1969) of globules containing 59% Fe and 5% Cu. The absence of titanium from these natural systems has been noted by the respective authors. Skinner and Peck (1969) provide chemical analyses of their material taken from a Hawaiian lava lake, which show that the magnetites formed from the sulphide melt did not contain detectable titanium whilst the silicate melt in which the globules were found contained 4.0% TiO<sub>2</sub>, and Hawley (1962) believes there to be significant partitioning of titanium between the silicate liquid and the sulphide melt. The Freetown intrusion is distinctive in that the oxide blebs contain a considerable amount of titanium, and it may well be that the titanium has distinctly aided the formation of separate Fe-Ti-O and Cu-S melts.

In the lower units of the Freetown intrusion extensive layers of titanomagnetite occur, which may correspond to a cumulate style accretion (Wells, 1962, p. 107; Umeji, 1975) of titanomagnetite, and it is possible that these formed by precipitation of the immiscible droplets.

*Sulphur and oxygen fugacity.* Thermochemical studies by Holland (1959) permit a discussion of the variation of temperature, oxygen fugacity, and sulphur fugacity, and the effect of those parameters on the stability fields of the phases studied here. Fig. 2 contains data illustrated by Holland but rearranged using techniques he described. The figure shows the stabilities of iron and copper sulphides and oxides for varying oxygen and sulphur fugacities at 727 °C, which approximates to the final equilibration temperatures of the iron-titanium oxides associated with the digenite and native copper.

The field in which digenite is stable in association with magnetite is a small, approximately triangular, area. The limits imposed by the buffer reactions  $\text{FeO} + \text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$  are the same as those used by Buddington and Lindsley (1964) and their work shows that the influence of titanium is contained within those limits. The fact that it is ilmenite and a titaniferous

magnetite in association with digenite does not therefore change fig. 2 at all and the presence of titanium enables the work of Buddington and Lindsley to be used to locate the equilibration conditions more precisely. The oxygen fugacity at 727 °C indicated by the ilmenite and magnetite in association with digenite is  $10^{-16.9}$  bar (Bowles, 1975). The calculations made by Barton (1973) using the data produced by Rau (1967) have indicated the relations between composition, sulphur fugacity, and temperature in a copper-sulphide melt. Using the composition obtained by analysis at room temperature the studies of Barton provide a sulphur fugacity at 727 °C of  $10^{-9.0}$  bar. In general there would be some possibility of error in assuming that the digenite retained the same composition during cooling. In this case, however, the digenite bleb appears to have acted as a closed system and not to have reacted with the enclosing material so that the assumption of constant composition is probably correct. The condition of equilibration at 727 °C between the analysed digenite, magnetite, and ilmenite is therefore fairly certainly located at a  $f_{\text{S}_2}$  of  $10^{-9.0}$  bar and a  $f_{\text{O}_2}$  of  $10^{-16.9}$  bar, indicated on fig. 2 by fine crossed lines within the common stability field of digenite and magnetite.

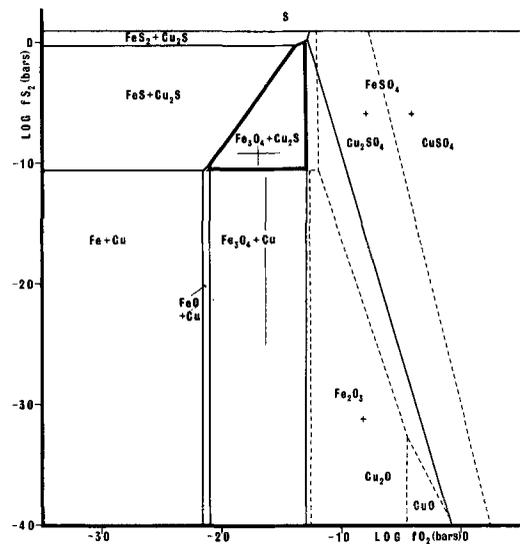


FIG. 2. Stability relations of the Fe-Cu-S-O system in terms of sulphur and oxygen fugacity at 727 °C (after Holland, 1959).

At lower sulphur fugacities, copper becomes the stable phase and the common stability field of native copper and titanomagnetite is an elongated rectangular area immediately beneath the digenite-magnetite triangle. There are no direct criteria

that can be used to judge where to set a likely lower limit to this rectangle, and as discussed by Skinner and Peck (1969) there appear to have been no direct measurements of the sulphur fugacity of a magma at any temperature comparable to the measurements of oxygen fugacity made by Sato and Wright (1966). The upper edge of the rectangle corresponds to a sulphur fugacity of  $10^{-11}$  bar, which is considerably lower than usual estimates of sulphur fugacity (Skinner and Peck, 1966). It is likely, therefore, that the sulphur fugacity corresponding to the formation of the native copper lies within a range at the top of the rectangular area.

The oxygen fugacity relating to the native copper-magnetite-ilmenite association can be estimated more precisely, as before, and this is indicated in fig. 2 by a fine vertical line ( $f_{O_2} = 10^{-16.2}$  bar, Bowles, 1976) but the sulphur fugacity can only be described as contained within the range from  $f_{S_2} = 10^{-11}$  to (say)  $f_{S_2} = 10^{-25}$  bar.

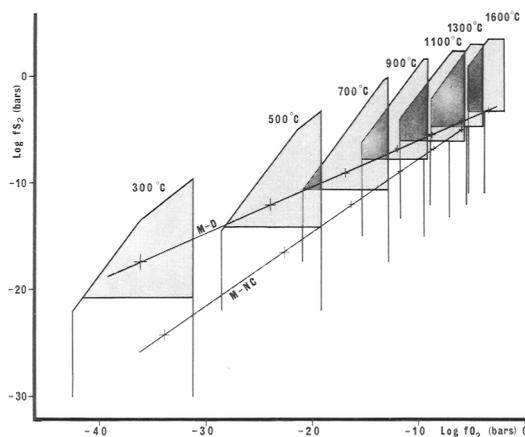


FIG. 3. Stability relations for the magnetite-digenite (M-D) and magnetite-native-copper (M-NC) associations at a range of temperatures. At each temperature the common stability conditions have been estimated as described in the text with an arbitrary choice of sulphur fugacity for the magnetite-native-copper association. Equilibrium cooling lines have been drawn to link these points for each association.

Holland (1959) gives data for lower temperatures, based on direct measurements, and theoretical reasons why the data may be safely extrapolated to higher temperatures. Fig. 3 shows a series of approximately triangular areas, which mark the common stability field of digenite and titaniferous magnetite for a number of widely spaced temperatures. Below each triangle is the rectangular stability field of native copper and titaniferous magnetite with the lower boundary indicated arbitrarily. At low temperatures the two stability

fields become larger and separate whilst they become smaller and converge at higher temperatures indicating the restricted range of conditions that are possible for the formation of droplets of digenite and titanomagnetite.

*Summary of conditions of separation and crystallization.* The textural and geochemical evidence detailed above indicates that titanomagnetite droplets were formed during the crystallization of olivine. The formation of the olivine enriched the melt in copper (MacLean and Shimazaki, 1976) and in iron (as described by Osborn, 1959) sufficiently to enable titanomagnetite to separate as immiscible droplets. Separation of these droplets triggered the separation of a second immiscible melt consisting of copper sulphide in those injections of magma where the sulphur fugacity was high enough to permit this to occur. Representatives of the two types of droplet were both included within the developing olivine whilst other droplets separated from the liquid to form distinct titanomagnetite layers. Occasionally the titanomagnetite droplets coalesced before becoming trapped within olivine and this has generally occurred in the titanomagnetite layers. The initial crystallization of the droplets took place after the crystallization of the olivine.

Labradorite crystallized from the remaining liquid and at these temperatures titanomagnetite forms euhedral crystals, which may be enclosed by the growing labradorite. Native copper can separate at this stage and it is possible that this copper has either remained trapped in the melt in those injections of magma where the sulphur fugacity was too low to permit immiscible droplets to form or that the copper has been concentrated by continued partitioning associated with crystallization occurring after the separation of copper-sulphide droplets. There is no evidence to suggest that the latter process can occur since no specimen yet examined contains both styles of copper mineralization. The mutually exclusive nature of the two styles of copper mineralization suggests strongly that the presence or absence of sulphur, represented here in terms of sulphur fugacity, acts as a switch to determine whether copper-sulphide droplets are formed at a higher temperature or native copper appears at a lower temperature. The influence of volatile components on the crystallization of this intrusion has been noted by Wells (1962) and Bowles (1976) has illustrated a variation in oxygen fugacity for a given temperature between different specimens from the intrusion. The present work adds a change in sulphur fugacity to this phenomenon and both are presumably related to the generation of volcanic exhalative gases within the intrusion during emplacement. Separation of

the titanomagnetite continues after the completion of labradorite crystallization and occupies irregular interstitial locations. Occasionally native copper accompanies these grains.

Over a period subsolidus equilibration of the titanomagnetite occurs permitting the exsolution of discrete grains or lamellae of ilmenite and the final equilibration occurs around 700 °C.

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