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Investigation of the surface oxidation of bornite by linear potential sweep voltammetry and X-ray photoelectron spectroscopy

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The products of surface oxidation of a natural sample of the copper iron sulphide mineral, bornite, have been determined from analysis of linear potential sweep voltammograms and from X-ray photoelectron spectroscopic examination of the oxidized layer. Anodic oxidation of bornite in alkaline media results initially in the formation of an iron(III) oxide/hydroxide and an iron-free copper sulphide of stoichiometry Cu_5S_4. The latter species is oxidized further at higher potentials to form a copper sulphide of lower copper content and cupric hydroxide. Air oxidation involves the first of these two steps. In acid solution, anodic oxidation yields iron(II) ions rather than an iron oxide in the first stage and copper(II) ions in the second. Sulphate and elemental sulphur are not formed under the experimental conditions investigated.

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1. Introduction

The copper–iron sulphide, bornite (Cu_5FeS_4) occurs as a primary mineral deposit in many copper lodes and as a constituent of the zone of secondary enrichment of chalcopyrite ($CuFeS_2$) ore-bodies. It is a valuable commercial source of copper, following chalcopyrite and chalcocite (Cu_2S) in economic importance.

Bornite is known to oxidize rapidly on exposure to air at room temperature and tarnishes to variegated blues and purples, a property from which it derives the name 'peacock ore'. Losch and Monhemius [1] applied Auger electron spectroscopy to investigate the products of oxidation of synthetic bornite in air at room temperature. They concluded that an iron oxide species was formed in this process, but were not able to identify the other reaction products. However, evidence was obtained that copper is mobile in bornite.

Studies of the reaction of natural [2–5] and synthetic [6, 7] bornite with acidic iron(III) solutions show that all the copper and iron in the mineral can be dissolved according to the equation

$$Cu_5FeS_4 + 12Fe^{3+} \rightarrow 5Cu^{2+} + 13Fe^{2+} + 4S. \quad (1)$$

However, other copper–iron sulphides appear as intermediates during oxidative leaching; 'non-stoichiometric bornite' [6], idaite (Cu_3FeS_4) [7] and chalcopyrite [5, 6] have been identified. Only copper is dissolved during the early stages of leaching [6, 7] and, at temperatures below 40° C, the reaction rate becomes very slow after 1 to 2 atoms of copper have been removed from each bornite molecule. The conversion of one mineral to another with the removal of copper also demonstrates the mobility of copper in the bornite lattice.

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The interfacial electrochemistry of sulphide minerals in aqueous media has been investigated by a number of authors [8–20] using linear potential sweep voltammetry. In a recent study [21], the results of X-ray photoelectron spectroscopic (XPS) examination of pyrite and chalcopyrite surfaces were correlated with those derived from voltammetry. XPS provides information on the chemical environment of atoms in the surface region as well as elemental analysis. Such knowledge is important in identifying the products of surface oxidation of sulphides since, for example, different surface sulphur-containing species, such as elemental sulphur, thiosulphate and sulphate, can be distinguished from each other and from the sulphur atoms present in the metal sulphide itself.

Bornite has been examined by XPS as part of surveys of mineral properties [22, 23], but no detailed studies have been reported in the literature. In the present communication, results are discussed of an investigation of the surface oxidation of bornite using both XPS and linear potential sweep voltammetry.

2. Experimental details

Hand-picked specimens of natural bornite from the Prince Leopold mine in Kipuchi, Zaire were used in this study. Selected pieces were cut from lumps of the mineral (~ 3 cm) and material containing inclusions of other minerals were rejected.

For electrochemical studies, the bornite was encapsulated in an epoxy resin and mounted in a rotating disc assembly as described previously [24, 25]. The exposed surface area was 0.22 cm^2. A fresh surface was produced on the electrodes before each run by wet grinding them on 600 grade silicon carbide paper. This procedure was carried out either in air or under a nitrogen atmosphere in a glove box. In the latter situation, the freshly prepared surface was transferred immediately to the electrochemical cell which was also contained in the glove box.

The glove box and cell were purged with 'high purity' nitrogen which had been passed over heated copper deposited on kieselguhr. The atmosphere in the glove box was monitored with a Honeywell Electrochemical Oxygen Analyzer; experiments were carried out only when the oxygen content was < 50 ppm.

Potentials were measured against a saturated calomel reference electrode (SCE) and converted to the standard hydrogen electrode (SHE) scale, assuming the SCE has a potential of 0.245 vs SHE [26]. All potentials reported are on the SHE scale. The potential was controlled by a potentiostat programmed with a Utah 0151 sweep generator and serviced by a current integrator. The potentiostat and integrator were designed and constructed in these laboratories. Current–potential and charge–potential relationships were recorded simultaneously on a Yew 3086 XY_1Y_2 recorder.

In the voltammograms presented in this paper, positive currents are anodic and negative currents cathodic.

For the XPS investigations, bornite was wet ground, ground under liquid nitrogen, or cleaved in air to exposure a fresh surface. It was examined immediately or, in some cases, after a chemical treatment. The treatment involved exposure for different periods to moist air, or to aqueous solutions of either acetic acid or ammonia. In most experiments, the aqueous solutions were evaporated in a stream of dry nitrogen in order to leave soluble reaction products on the mineral surface.

X-ray photoelectron spectra were recorded on a Vacuum Generators Ltd. ESCA 3 spectrometer, using unmonochromatized Mg$K\alpha$ or Al$K\alpha$ X-rays at an operating pressure of 10^{-7} Pa. The electron analyser pass energy was 20 eV. In a number of experiments, the sample was cooled to $-150°$ C before pump down, and retained at this temperature during XPS analysis, in order to avoid possible loss of volatile materials such as elemental sulphur.

The spectra presented in this communication show electron intensity in arbitrary units as a function of binding energy of the electrons ejected.

The spectrometer energy scale was calibrated using both Mg$K\alpha$ and Al$K\alpha$ radiation assuming that the inflection point of the valence spectrum of pure nickel is at the Fermi level and the $(4f)_{7/2}$ peak for pure gold is at 83.8 eV.

3. Results and discussion

3.1. *X-ray photoelectron spectroscopy*

Survey scans covering a wide range of binding energies demonstrated that, in addition to copper, iron and sulphur, silver was present in the bornite surface. Chemical analysis of the mineral, using atomic absorption spectrophotometry, showed it to contain 0.18 wt % Ag.

X-ray photoelectron spectra were recorded over the regions of iron, copper, silver, sulphur and oxygen binding energies. Cleaved bornite gave much better spectral resolution than the ground surface and all the results presented refer to cleaved specimens unless a ground surface is specified.

Fig. 1 shows spectra covering the region of the iron $(2p)_{3/2}$ binding energy. The formal valence state of the iron in the bornite lattice is high spin iron(III), as it is in chalcopyrite [27]. However, whereas the iron $(2p)_{3/2}$ photoelectron spectrum for a cleaved chalcopyrite surface exposed to the atmosphere for less than one minute had an intensity maximum at 708 eV [21, 28], the corresponding spectrum for bornite shown in Fig. 1, curve B had an intensity maximum at 711 eV, with only a small contribution at 708 eV evident. This indicates that most of the iron present within the outermost few nanometres was bonded to oxygen [21]. Mild sputtering (8.5 μA cm^{-2} min) with 2 kV argon ions resulted in the spectrum in Fig. 1, curve A, which shows an intensity maximum at 708 eV with negligible contribution at 711 eV. Bornite ground under liquid nitrogen to avoid surface oxidation gave the same spectrum. The spectrum is similar to that observed for freshly cleaved chalcopyrite and this is further evidence that there was an iron oxide surface layer prior to sputtering; it has been shown [29] that a dose of 10 μA cm^{-2} min of 2 kV argon ions on a heavily oxidized bornite surface did not result in chemical reduction of iron. The

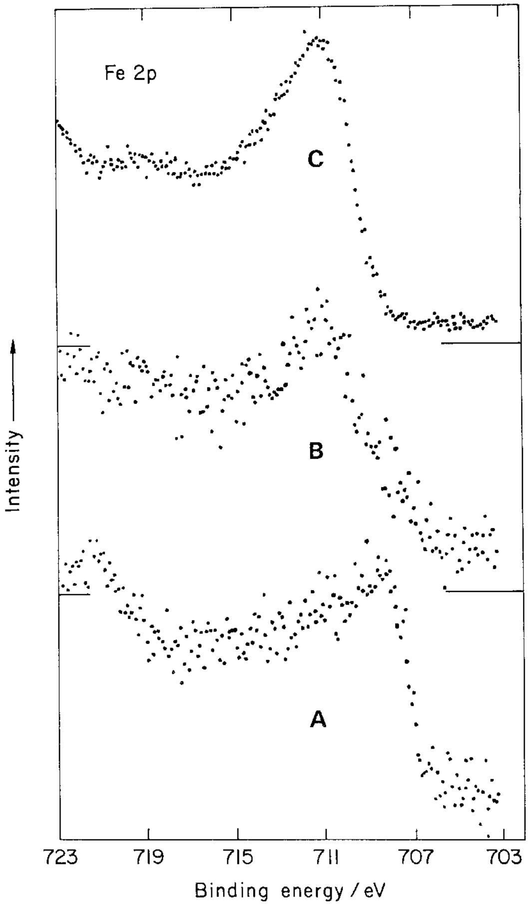

Fig. 1. Iron $(2p)_{3/2}$ spectra for bornite. Curve B, freshly cleaved surface; curve A, freshly cleaved surface after mild sputtering; curve C, exposed for 3 days.

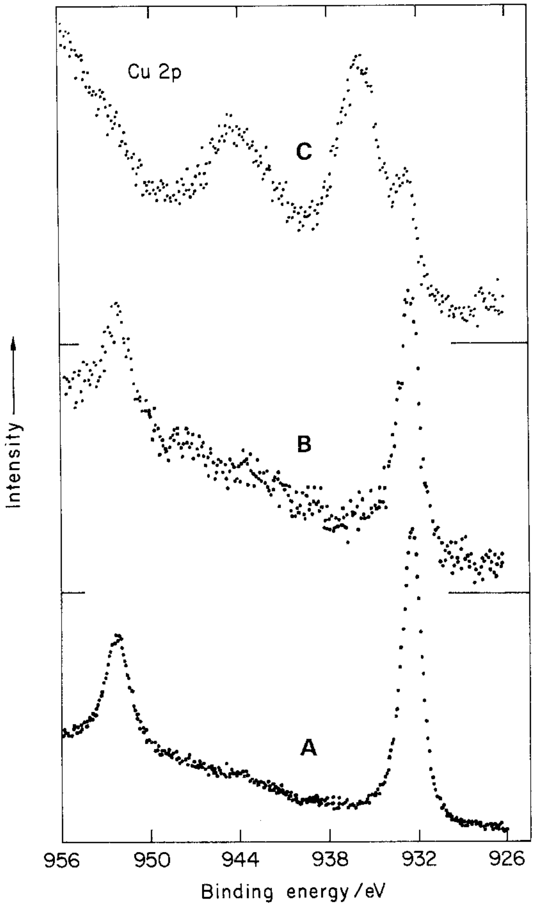

Fig. 2. Copper (2p) spectra for bornite. Curve A, freshly cleaved surface; curve B, surface exposed to moist air for 3 days; curve C, surface treated with ammonia solution followed by evaporation with dry nitrogen.

intensity of the iron (2p) spectrum from a surface exposed to the atmosphere for three days (Fig. 1, curve C) is significantly increased and the 708 eV peak due to iron bonded to sulphur is absent.

Spectra in the copper (2p) binding energy region are presented in Fig. 2. The copper in bornite is in the Cu(I) valence state [27]. The copper (2p) spectrum for freshly cleaved bornite (Fig. 2, curve A) confirms the absence of Cu(II), and there is little change in the spectrum obtained after air oxidation other than a decrease in intensity (Fig. 2, curve B). The presence of Cu_2O would not be revealed by the copper (2p) spectrum, as there is no significant chemical shift between copper oxide and sulphide [23]. However, the $Cu(L_3M_{4,5}M_{4,5})$ Auger peak is sufficiently narrow and intense, and the shift between Cu_2O and copper bonded to sulphur sufficiently large, for differentiation between these species to be made. Determination of the energy of these Auger electrons demonstrated the absence of Cu_2O at all air-exposed surfaces investigated [29]. When bornite was oxidized in the presence of ammonia (Fig. 2, curve C), an additional peak appeared at a 3 eV higher binding energy which is indicative of the presence of a Cu(II) species. The spectrum also shows higher binding energy satellites arising from Cu(II) excited final states. This suggests that copper was dissolved in the ammonia and was re-deposited on the surface during evaporation of the solution. The intensities of other XPS peaks under these conditions were consistent with Cu(II) being on the surface. Furthermore, it can be deduced from the physically adsorbed water O(1s) peak (v.i.) that very little of the 3 eV shift is due to the surface layer being at a different electrical potential from the substrate. Spectra obtained from a surface treated for a shorter period with ammonia solution immediately after cleaving, and washed with water before drying under nitrogen so that a smaller (but still appreciable) amount of Cu(II) remained, provided support for the 3 eV shift being chemical in nature. Copper in bornite has a binding energy close to that of Cu_2O and the shift for CuO with respect to Cu_2O is 1.3 eV [30]. The much greater shift of 3 eV found here indicates that the Cu(II) is likely to be hydrated or complexed.

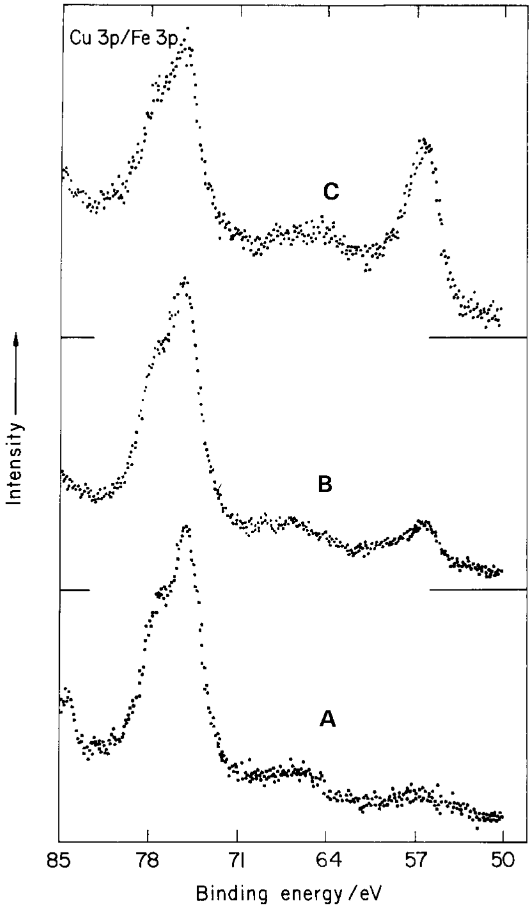

Fig. 3. Copper (3p) and iron (3p) spectra for bornite. Curve A, freshly cleaved surface; curve B, surface exposed to moist air for 17 min; curve C, exposed for 3 days.

Fig. 3 shows spectra covering both the copper (3p) binding energies, near 75 eV, and the iron (3p) binding energies, near 56 eV. As the oxidation of bornite proceeded (Fig. 3, curves A to C), the intensity of the iron (3p) peak increased and the intensity of the copper (3p) peak decreased, so that within the escape depth (about 7 nm) of these electrons, there was a significant concentration of iron relative to copper. After three days exposure to air, the iron to copper ratio was at least five times that for a freshly cleaved bornite surface. The intensity of the iron (3p) peak from a freshly exposed surface was difficult to determine, because the silver (4p) peak from the silver present at the surface is almost coincident with the iron (3p). The silver (4p) intensity can be estimated from the silver (3d) intensity. However, the silver (4p) peak is expected to be quite broad and hence the high binding energy background, and the combined intensity of the Ag(4p)/Fe(3p) peak, will be uncertain.

The relative intensities of the silver and copper spectra indicated that the ratio of silver to copper atoms in an oxidized surface was about 1 : 10. This is much greater than the average ratio for the mineral of 1 : 600 determined by chemical analysis. The possibility of the silver being associated with an impurity mineral present at the cleaved surface is not supported by the consistency of silver content observed from one cleaved surface to another. Furthermore, silver could not be detected by electron microprobe analysis at any point on cleaved surfaces. Thus, it would appear that the silver was present in the bornite lattice and congregated preferentially within the outermost few nanometres during oxidation. The conclusion that silver transport to the surface is associated with oxidation is supported by the observation that the silver content of a surface ground under liquid nitrogen is an order of magnitude less than that of an oxidized surface. It is apparent that the silver in the oxidized surface is present as a sulphide; the energy difference between the silver $(3d)_{5/2}$ and silver $(M_4N_{4,5}N_{4,5})$ Auger electrons is consistent with silver (I) sulphide and inconsistent with silver (I) oxide [29].

Except when the mineral is treated in ammonia solution, the oxygen at the surface was associated only with its iron content. Studies on iron oxides [31, 32] have shown three distinct binding energy regions for oxygen, namely, ~ 530, ~ 531 to 532 and ~ 533 eV, associated with oxide, hydroxide or chemisorbed oxygen species, and physically adsorbed water, respectively.

Spectra in the O(1s) region are presented in Fig. 4. The oxygen spectra can be fitted with peaks at 529.9 ± 0.2, 531.5 ± 0.2 and a third peak within the range 533 to 534 eV. The peak characteristic of oxide for bornite freshly cleaved in air was less intense than the hydroxide/chemisorbed oxygen peak and comparable with the peak attributed to physically adsorbed water (Fig. 4, curve A), whereas after 17 h exposure, the overall intensity had increased and the oxide peak was now the most intense (Fig. 4, curve B).

Fig. 5 shows spectra for freshly cleaved and oxidized surfaces in the sulphur (2p) binding energy region; the $(2p)_{3/2}$ and $(2p)_{1/2}$ components are partially resolved. Each of the spectra presented is indicative of a single sulphur environment. The only variation observed on oxidation (Fig. 5, curves A to C) was a decrease in intensity and an increase in the number of electrons having suffered energy loss due to collisions in the oxidized layer on the surface.

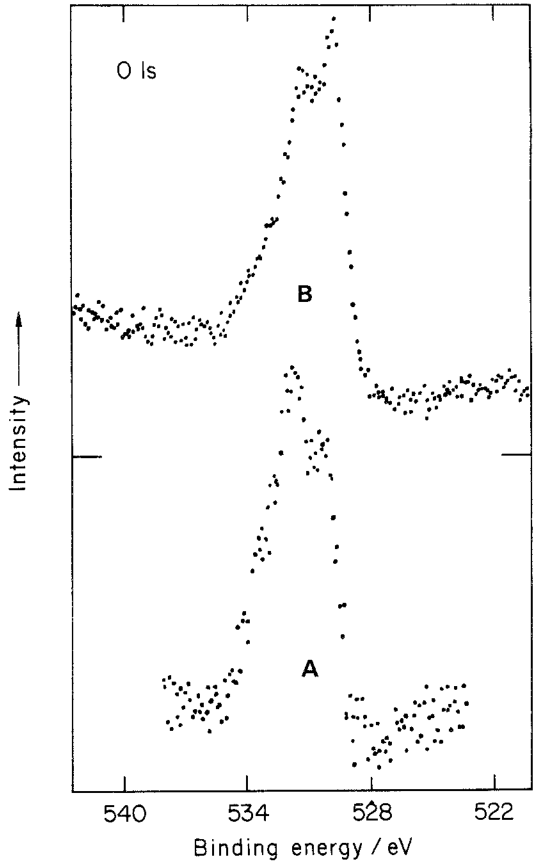

Fig. 4. Oxygen (1s) spectra for bornite. Curve A, freshly cleaved surface; curve B, surface exposed to moist air for 17 h.

No evidence was observed for the formation of elemental sulphur which has a slightly higher binding energy than the sulphur in bornite and would lead to at least a broadening of the sulphur (2p) spectrum as in other sulphides [21]. Also, there was no evidence in any spectra for the presence of sulphate which gives rise to a sulphur (2p) peak near 169 eV [21, 28].

The silver content after oxidation was found to be much less when the surface was prepared by wet grinding in air than by cleaving. Presumably silver becomes depleted in the surface zone during grinding through its concentration in each new sur-

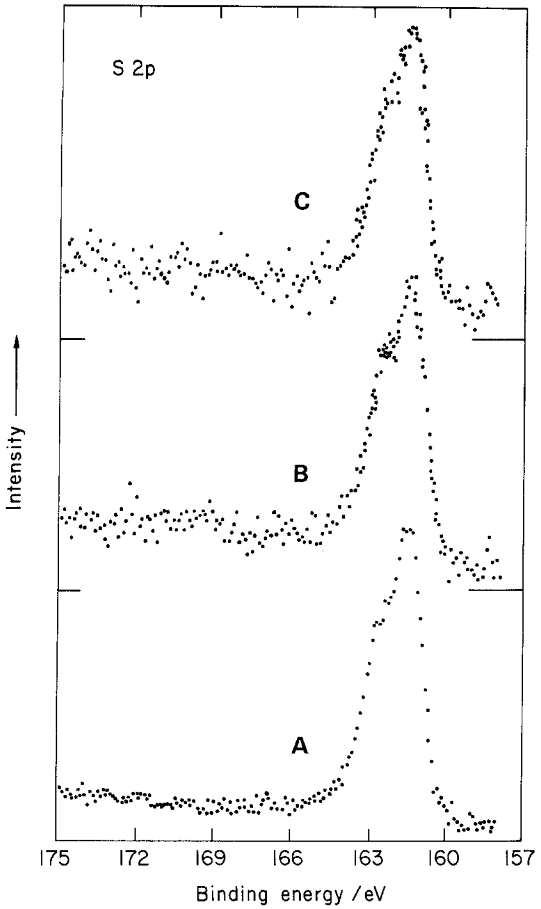

Fig. 5. Sulphur (2p) spectra for bornite. Curve A, freshly cleaved surface; curve B, surface exposed to moist air for 17 h; curve C, exposed for 3 days.

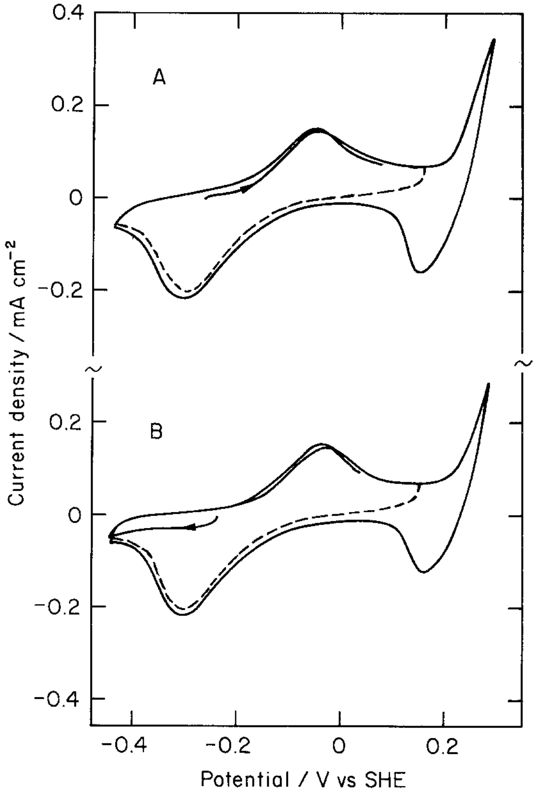

Fig. 6. Voltammograms for a stationary bornite electrode at pH 9.2. Linear potential sweeps at 20 mV s^{-1}. Electrode surface prepared by grinding under a nitrogen atmosphere. Initial scan, Curve A positive-going, and curve B negative-going. Scan reversed at 0.15 V ––––, and at 0.28 V ——.

face which is then removed. The X-ray photoelectron spectra of iron, copper, sulphur and oxygen after oxidation are similar for ground and cleaved surfaces and hence it would appear that the presence of silver does not have a major influence on the oxidation of this mineral.

3.2. *Linear potential sweep voltammetry*

Voltammograms for bornite electrodes in solutions of different pH are presented in Figs. 6 to 11. Fig. 6 refers to investigations in 0.05 mol dm^{-3} sodium tetraborate solution (pH 9.2) with an electrode surface ground under a nitrogen atmosphere in the glove box. The curves display a broad anodic peak with peak potential, E_p, $\simeq -0.05$ V. When the positive-going scan was reversed after this peak (dashed curves, Fig. 6), the products of anodic oxidation were reduced and gave rise to a cathodic peak with $E_p \simeq -0.3$ V. If the positive-going scan was continued above 0.2 V, an increasing anodic current was observed. The oxidation products in this region were reduced on the return scan with $E_p \simeq 0.15$ V.

Taking the positive-going scan to potentials more positive than those traversed in Fig. 6, showed that the increasing current above 0.2 V reached a peak at ~ 0.7 V. Excursions to high potentials resulted in the formation of thick oxidized layers which were difficult to reduce.

Fig. 7 shows voltammograms for bornite at pH 9.2 recorded after the electrode surface had been ground in air. Comparison with the curves in Fig. 6 indicates that the mineral surface had been oxidized before the electrode was inserted into the electrochemical cell. The initial positive-going scan (Fig. 7, curve A) did not

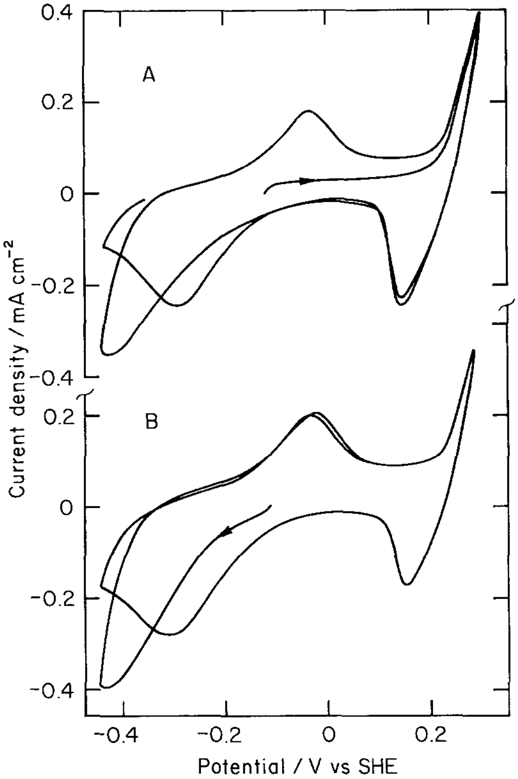

Fig. 7. Voltammograms for a stationary bornite electrode at pH 9.2. Linear potential sweeps at 20 mV s^{-1}. Electrode surface prepared by grinding in air. Initial scan, curve A, positive-going, and curve B, negative-going.

display the anodic peak at − 0.05 V. However, after the products of air-oxidation were reduced on a negative-going scan, either initially (Fig. 7, curve B) or after an excursion to positive potentials (Fig. 7, curve A), the form of the voltammogram was identical to that for an electrode surface prepared under nitrogen.

The curves in Fig. 6 demonstrate that no significant oxidation of the mineral surface had occurred after grinding in the glove box. Thus, the oxygen level in the box was sufficiently low (<50 ppm) for the rate of oxidation to be negligible within the time taken to prepare a new surface and transfer the electrode to the cell.

The curves in Fig. 7 indicate that air-oxidation was restricted to the reaction giving rise to the anodic peak at − 0.05 V in Fig. 6. This hypothesis is substantiated by measurement of the open circuit potential in air-saturated borate solution. A value of 0.20 V was observed which is at the foot of the second anodic wave. Thus, the XPS investigations of air-oxidized bornite provide an identification of the products of the anodic peak.

XPS demonstrated that bornite is oxidized in air to form an iron hydroxy-oxide. No significant change in copper or sulphur environments occurs. After a long exposure to air, the iron detected by XPS was bonded only to oxygen and hence the oxidized layer was sufficiently thick for no signal to be seen from the underlying bornite. Copper and sulphur spectra could still be resolved so the signal was not restricted to an overlying iron oxide. This indicated that iron and copper–iron sulphides were absent from the oxidized layer. These observations suggest that oxidation of bornite yields a copper sulphide and not a ternary sulphide of greater Cu : Fe ratio than the original mineral. We conclude that the anodic reaction is:

$$Cu_5FeS_4 + 3H_2O \rightarrow Cu_5S_4 + Fe(OH)_3 + 3H^+ + 3e \qquad (2)$$

where the iron hydroxy oxide is represented by $Fe(OH)_3$.

The similarity of the sulphur spectra before and after oxidation can be explained by the chemical environment of sulphur in Cu_5S_4 not being significantly different from that in Cu_5FeS_4. This view is supported by XPS studies of a range of minerals [23] which have shown that the binding energy for sulphur (2p) in chalcocite and digenite (Cu_7S_4) is the same as in bornite.

Since copper sulphides can be oxidized, it is reasonable to assume that the increasing anodic current at the high potential region of Figs. 6 and 7 arises from oxidation of the Cu_5S_4 formed by Reaction 2. Oxidation of chalcocite proceeds through a series of copper sulphides of definite stoichiometry, each step proceeding at a characteristic potential [33]. The anodic wave commenced at a potential close to, but slightly negative of, that observed for covellite (CuS) [21]. It is ~ 0.05 V more positive than we find for chalcocite. Thus the potential at which the anodic current occurred is consistent with oxidation of a copper sulphide with a stoichiometry between Cu_2S and CuS, but close to CuS.

$$Cu_5S_4 + 2xH_2O \rightarrow Cu_{5-x}S_4 + xCu(OH)_2 + 2xH^+ + 2xe \qquad (3)$$

The total cathodic charge passed on the reverse scans in Fig. 6 was equal to the total anodic charge passed on the forward scan. Also, the curve for the second positive-going scan was almost identical to that for the initial scan. These observations suggest that the cathodic peaks on the negative-going scans at 0.15 and − 0.3 V arise from the reverse of Reactions 3 and 2, respectively. The conclusion that bornite can be re-formed from its oxidation products is analogous to that reached for chalcopyrite [14].

Sulphate is formed in the oxidation of pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$) [18]. The equality of anodic and cathodic charges on the voltammogram for bornite shows that a negligible quantity of sulphate is formed with this mineral. This conclusion is supported by XPS which did not detect sulphate in bornite oxidized in the atmosphere or in acetic acid or ammoniacal solutions.

Investigations of the influence of pH and of electrode rotation have been shown to be useful in identifying reactions occurring at the surface of sulphide minerals [9, 14, 15, 18]. Many of these reactions are quasi-reversible and the potentials at which features appear on the voltammogram shift with pH in the same manner as the Nernstian potentials. The effect of electrode rotation can be used to distinguish between reactions producing soluble species, which are dispersed, and those producing solid products.

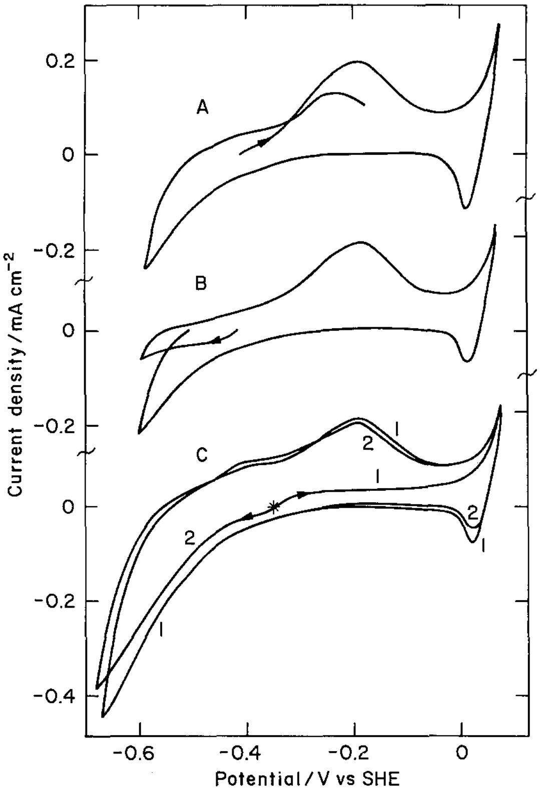

Fig. 8. Voltammograms for a stationary bornite electrode in 0.1 mol dm^{-3} NaOH. Linear potential sweeps at 20 mV s^{-1}. Electrode surface prepared by grinding (A and B) under a nitrogen atmosphere, and C in air. Initial scan, Fig. 8A and 8C, curve 1 positive-going, Fig. 8B and 8C, curve 2 negative-going.

Examination of the voltammograms recorded for borate solution (Figs. 6 and 7) and 0.1 mol dm^{-3} NaOH (Fig. 8) shows that each peak was shifted to more negative potentials by ~ 0.2 V by the increase in pH. This is close to the shift of 59 mV per pH unit expected for both Reactions 2 and 3. Rotation had no influence on the curves in either solution which is as expected for reactions forming solid products.

When ammonia was added to the borate solution, the resulting positive-going scan was identical to those in Figs. 6 and 7. However, the cathodic peak at ≃ 0.15 V was greatly diminished when the electrode was rotated. Ammonia solubilizes copper(II) as ammine complexes and hence a soluble copper(II) species will be formed instead of $Cu(OH)_2$ in the oxidation of Cu_5S_4. This species will be dispersed on rotation and the reverse process will no longer be possible. The XPS investigations identified a soluble copper(II) species after treatment with ammonia which supports this mechanism.

The electrochemical results obtained in 0.5 mol dm^{-3} CH_3COOH, 0.5 mol dm^{-3} CH_3COONa (pH 4.6) further substantiate the interpretation of the voltammetric behaviour in terms of Reactions 2 and 3. The equilibrium diagram for the Fe–H_2O system [34] indicates that Fe^{2+} rather than $Fe(OH)_3$ should be formed at this pH in the potential region of the anodic peak, i.e. the reaction will be

$$Cu_5FeS_4 \rightarrow Cu_5S_4 + Fe^{2+} + 2e. \qquad (4)$$

Similarly, Cu^{2+} ions are the stable species in the Cu–H_2O system at this pH [34]. Oxidation of Cu_5S_4 will then proceed,

$$Cu_5S_4 \rightarrow Cu_{5-x}S_4 + xCu^{2+} + 2xe. \qquad (5)$$

Figs. 9 and 10 are consistent with this mechanism. The voltammograms for a stationary electrode (Fig. 9) are similar to those at the higher pH values because Fe^{2+} and Cu^{2+} remain in the vicinity

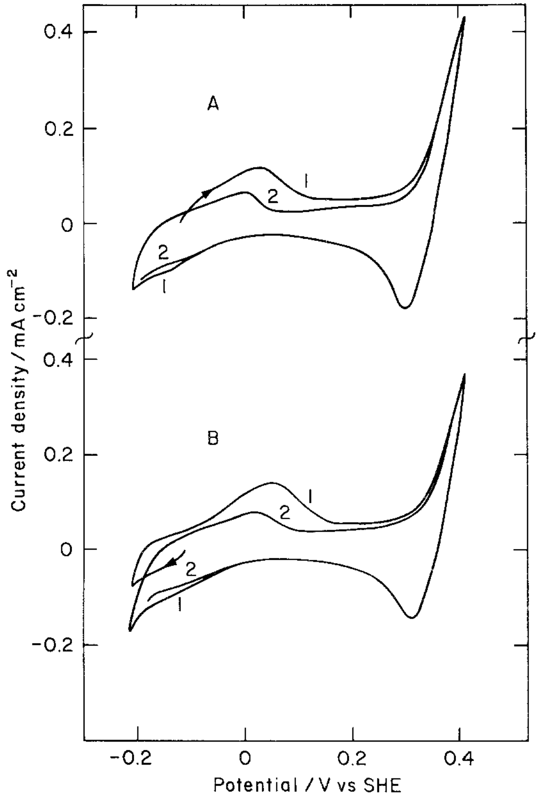

Fig. 9. Voltammograms for a stationary bornite electrode at pH 4.6. Linear potential sweeps at 20 mV s^{-1}. Electrode surface prepared by grinding under a nitrogen atmosphere. Initial scan, curve A, positive-going, and curve B, negative-going.

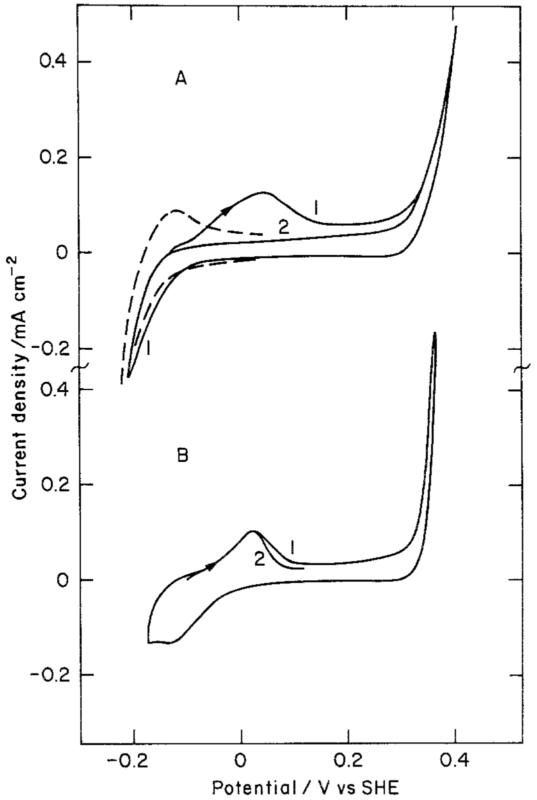

Fig. 10. Voltammograms for a bornite electrode in pH 4.6 solution containing (A) 0 and (B) 5 $\times 10^{-4}$ mol dm^{-3} Fe^{2+}. Linear potential sweeps at 20 mV s^{-1}. Electrode surface prepared by grinding under a nitrogen atmosphere. (A) Curve 1, initial sweep; curve 2, second sweep; solid curves, electrode rotated at 10 Hz; dashed curve, electrode stationary. (B) Electrode rotated at 10 Hz.

of the electrode and hence the reverse of Reactions 4 and 5 are possible on the return scans. However, they disappear on rotation. The peak arising from Reaction 4 was not evident on the second positive-going scan (Fig. 10A, curve 2) because the surface was depleted in iron on the initial scan (Curve 1). A new cathodic process appears at the lower limit of the scan in Fig. 10A. It is not possible to extend the scan to explore this process in detail because bornite is reduced there. However, some information can be obtained by stopping electrode rotation at 0.1 V on the return scan (dashed curve in Fig. 10A). An additional anodic peak now appeared when the scan was again taken in the positive direction. This indicates that a soluble species is formed in the cathodic process which is consistent with the process being the reduction of $Cu_{5-x}S_4$ produced on the preceding positive-going scan,

$$Cu_{5-x}S_4 + 2yH^+ + 2ye \rightarrow Cu_{5-x}S_{4-y} + yH_2S. \tag{6}$$

The subsequent anodic peak with the stationary electrode is the reverse of Reaction 5.

The proposed mechanism is also substantiated by the charge associated with the anodic peak at pH 4.6 ($\sim$ 1.4 mC cm^{-2}) and in alkaline media ($\sim$ 2.0 mC cm^{-2}). The ratio is close to that of 2 : 3 for the number of electrons involved in Reactions 2 and 4.

After the bornite surface was depleted of iron by rotating on a potential sweep at pH 4.6, the electrode was held stationary either at open circuit or at $-$ 0.1 V for periods up to 1 h. The anodic peak did not reappear on subsequent potential sweeps. This indicates that iron does not diffuse from the bulk of the mineral to replace that dissolved from the surface. However, if Fe^{2+} ions were present in solution, bornite could be re-formed by a cathodic reaction between these ions and the copper sulphide oxidation product, by the reverse of Reaction 4. This is demonstrated in Fig. 10B; voltammograms for a rotated electrode in pH 4.6 solution containing 5 x 10^{-4} mol dm^{-3} Fe^{2+} display both the anodic peak at ~ 0.05 V and the cathodic peak at − 0.1 V arising from the forward and reverse of Reaction 4, respectively. This indicates the iron is mobile within the surface layer. The fact that iron is not transported from the bulk into the surface layer is probably due to iron transfer not being thermodynamically favourable. There is no stable copper iron sulphide with a Cu : Fe ratio higher than that of bornite and hence Cu_5FeS_4 cannot react with the overlying layer of Cu_5S_4.

The anodic current above 0.3 V at pH 4.6 continued to flow on consecutive potential sweeps with a rotated electrode. Thus when copper is removed from the surface, it can be replaced from the bulk because there is a stable copper iron sulphide, Cu_3FeS_4, of lower Cu : Fe ratio than bornite.

Since iron can only be dissolved from the surface layer, while copper can be continually extracted, oxidative leaching of bornite results in the preferential dissolution of copper [6, 7], even though iron dissolution, Reaction 4 is thermodynamically more favourable. This situation exists until the leached mineral reaches a composition within which copper transport is no longer favourable.

Voltammograms at pH 4.6 for bornite ground in air are shown in Fig. 11. A cathodic peak with $E_p \simeq 0.15$ V is apparent which is absent from the curves obtained from bornite ground in a nitrogen atmosphere (Fig. 9). This peak appeared only on the first excursion to negative potentials. It arises from reductive dissolution of the iron oxide layer formed by air oxidation during wet grinding which involves a pH high enough for Reaction 2 to occur. The dissolution reaction is,

$$Fe(OH)_3 + 3H^+ + 3e \rightarrow Fe^{2+} + 3H_2O \qquad (E^0 = 1.057\,V). \qquad (7)$$

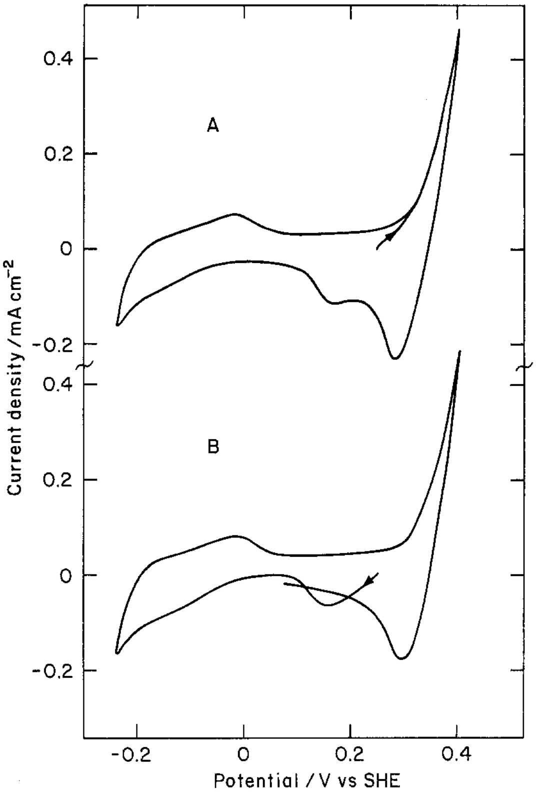

Fig. 11. Voltammograms for a stationary bornite electrode at pH 4.6. Linear potential sweeps at 20 mV s^{-1}. Electrode surface prepared by grinding in air. Initial scan, curve A, positive-going, and curve B, negative-going.

If the air-ground bornite was left at open circuit in the pH 4.6 solution before applying a potential scan, the cathodic peak arising from Reaction 7 no longer appeared. This is probably due to dissolution of the iron oxide by a reaction of the form,

$$Cu_5FeS_4 + 2Fe(OH)_3 + 6H^+ \rightarrow Cu_5S_4 + 3Fe^{2+} + 6H_2O. \qquad (8)$$

Further confirmation of the conclusion that the anodic peak for oxidation of bornite arises from Reaction 2 in alkali or Reaction 4 in acid can be derived from thermodynamic considerations. Since oxidation of bornite and the reduction of the products of oxidation are the forward and reverse of the same process, it is expected that the open circuit potential will be the reversible potential of this process. The latter can be calculated from free energy data. The free energy of formation, ΔG, for bornite at 25° C was estimated by Peters [35] from data presented by Garrels and Christ [36] to be − 355.2 kJ mol^{-1}. Young [37] recommended a ΔG value of − 360.7 kJ mol^{-1}. King *et al.* [38] obtained a ΔG of $-386.4\,\mathrm{kJ\,mol^{-1}}$ by extrapolation of high-temperature data. The copper sulphide product, presented as Cu_5S_4, is within the range of stoichiometry of 'blaubleibender' covellite [28] for which Potter [39] determined a ΔG of $-64.35\,\mathrm{kJ\,mol^{-1}}$. Taking the other ΔG values as tabulated by Garrels and Christ [36], the standard potential of Reaction 3 is 0.40, 0.41 or 0.50 V, if the bornite ΔG is taken as -355.2, -360.7 or $-386.4\,\mathrm{kJ\,mol^{-1}}$, respectively. Therefore, the reversible potential at pH 9.2 lies between -0.14 and -0.04 V. The experimental value of -0.12 V is within this range.

The XPS investigations indicate that silver contained in the natural bornite becomes concentrated in the surface layer after oxidation. It is suggested that the silver is associated with the oxidation product, Cu_5S_4. The driving force for silver transport could be a favourable partition coefficient for silver between Cu_5S_4 and Cu_5FeS_4 or to the presence of lattice vacancies in the Cu_5S_4 generated by the removal of iron from the bornite lattice [40]. Silver is known to be very mobile in sulphides [41] and hence transport to the surface can occur rapidly.

Silver is not expected to be involved in any electrochemical reactions at the potentials of interest in this paper since silver sulphide is stable over this range [42, 43]. However, the presence of silver could affect the characteristics of the reactions involving copper and iron. Free energy data are not available for copper silver sulphides [27] and hence it is not possible to estimate from thermodynamic considerations the extent to which the potentials at which the various processes occur could be altered. However, the agreement between experimental potentials and those calculated from free energy data for silver-free phases indicates that the influence of silver at the level present here is not significant. This conclusion is supported by the observation that the Cu_5S_4 phase begins to be oxidized at a potential close to that expected from investigations of the anodic oxidation of Cu_2S and CuS.

The oxidation of bornite, Reaction 2 occurs at a potential more than 0.1 V below that for the oxidation of chalcopyrite [14] which occurs by,

$$CuFe_2 + 3H_2O \rightarrow CuS + S + Fe(OH)_3 + 3H^+ + 3e. \qquad (9)$$

This fact, together with kinetic considerations, explains why bornite tarnishes much more readily than chalcopyrite.

Thermodynamic considerations identify bornite as an oxidation product of chalcopyrite. The most favourable reaction from the thermodynamic point of view is the process [44],

$$5CuFeS_2 + 2H_2S \rightarrow Cu_5FeS_4 + 4FeS_2 + 4H^+ + 4e. \qquad (10)$$

Reactions involving the nucleation and growth of pyrite are exceedingly slow [45], and this reaction is not observed in the laboratory.

The formation of bornite from chalcopyrite is also favoured if sulphate is a reaction product. The standard potential for the reaction,

$$5CuFeS_2 + 36H_2O \rightarrow Cu_5FeS_4 + 4Fe(OH)_3 + 6SO_4^{2-} + 60H^+ + 48e \qquad (11)$$

is ~ 0.15 V less than that for oxidation of bornite by,

$$2Cu_5FeS_4 + 18H_2O \rightarrow 5Cu_2S + 2Fe(OH)_3 + 3SO_4^{2-} + 30H^+ + 24e. \qquad (12)$$

Reactions involving sulphate formation are generally slow and require considerable overpotentials [41]. Hence, bornite is not observed as a product of anodic oxidation of chalcopyrite or as an intermediate in the leaching of this mineral [36, 41]. On the other hand, when geological time is available for reactions to proceed, as in supergene alterations, bornite is produced in the oxidation of chalcopyrite [36].

The XPS data show that, on extended oxidation, iron becomes concentrated at the surface. This indicates that iron leaves the bornite lattice and forms a layer of iron oxide on the surface. Segregation of iron oxide and copper sulphide results in reduction of the oxidized layer becoming more difficult.

The charge associated with the anodic peak for bornite is approximately equal to that for chalcopyrite [14] for a similar surface treatment. Metal sulphide structures generally involve close packed sulphur layers with the metal atoms ordered or disordered in the various octahedral and tetrahedral sites. It was concluded [14] that the oxidation charge for chalcopyrite corresponded to the removal of iron atoms from ~ 5 sulphur layers.

Since the Fe:S ratio in bornite is only one half that in chalcopyrite, the same charge corresponds to ~ 10 sulphur layers in bornite.

When a bornite electrode was subjected to consecutive potential cycles in borate solution containing ammonia, the anodic peak shifted to more positive potentials on each cycle until a constant E_p value of 0.1 V was reached. In this medium, copper is dispersed on cycling while iron is retained at the surface. The anodic peak for chalcopyrite (Reaction 2) at the same pH is 0.2 V. This suggests that the shift for bornite reflects an increase in the iron content of the copper–iron sulphide at the surface. There is a shift in the anodic peak to lower potentials on cycling chalcopyrite in borate solution, which suggests copper becomes concentrated at the surface of the mineral [14]. It is interesting to note that the final position of the anodic peak is 0.1 V for both bornite and chalcopyrite.

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