Copper-bearing clay minerals of the oxidized zone of the Rakha-Chapri Block, Singhbhum Copper Belt, India

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Abstract. In the oxidized zone of Rakha-Chapri Block of the Singhbhum Copper Belt, alteration of biotite, chlorite and muscovite extends down to ~ 60 m. Below this level, these minerals are not altered, implying a supergene origin for the clay alteration products. The altered host-rock profile consists of an upper, predominantly kaolinitic zone and a lower illite-chlorite rich zone, with the clay minerals showing an overall tendency to decrease with depth. Kaolinite is the dominant clay mineral, the proportion of which varies considerably with depth, and chlorite, illite and halloysite are the other clay minerals of the oxidized zone.

Incipient removal of copper even from the cap rocks, in-situ transformation of sulphides to oxidized compounds, and the unusual mode of occurrence of copper in the oxidized zone are the characteristic features of the Rakha-Chapri Block. Insufficient localized hydrolysis of silicates is considered responsible for relatively low acidity in the oxidized zone as a whole. Copper forms a component of the clay minerals probably as surface adsorbed or/lattice-bound ions.

Keywords. Copper in clays; kaolinite; illite; oxidized zone; biotite alteration; Singhbhum Copper Belt.

1. Introduction

Copper mineralization in the Singhbhum Copper Belt occurs chiefly within pelitic schists, inter-banded psammitic and granitoid rocks as sheeted veins, that reflect a stratabound nature and/or, equally plausible, a dominant control of mineralization by shear surfaces (S_1) that are parallel to bedding (S_0) over large tract. Pyrrhotite, pyrite and chalcopyrite constitute the bulk of primary sulphides, with minor amounts of bornite, pentlandite, molybdenite and a host of other sulphides occur in trace amounts (Dunn 1937; Sarkar et al 1971).

The Rakha-Chapri Block lies in the Central Sector of the Singhbhum Belt (figure 1). The oxidized ore occurs as a blanket of variable thickness directly overlying the primary ores. Surface manifestation of the oxidized zone is a spectacularly developed Fe-rich cap rock that runs for several kilometers and etches out the mineralized horizon. The zone is ~ 100 m wide at Chapri and narrows down towards Rakha and Tamapahar. In the northern hill range only a strip of gossanized rock is observed on the hill top near the NW border of the block. Lateritic material which simulates in appearance the iron capping of the mineralized horizons but differ totally in texture and mineralogy, occurs further north, overlying exposures of basic rocks.

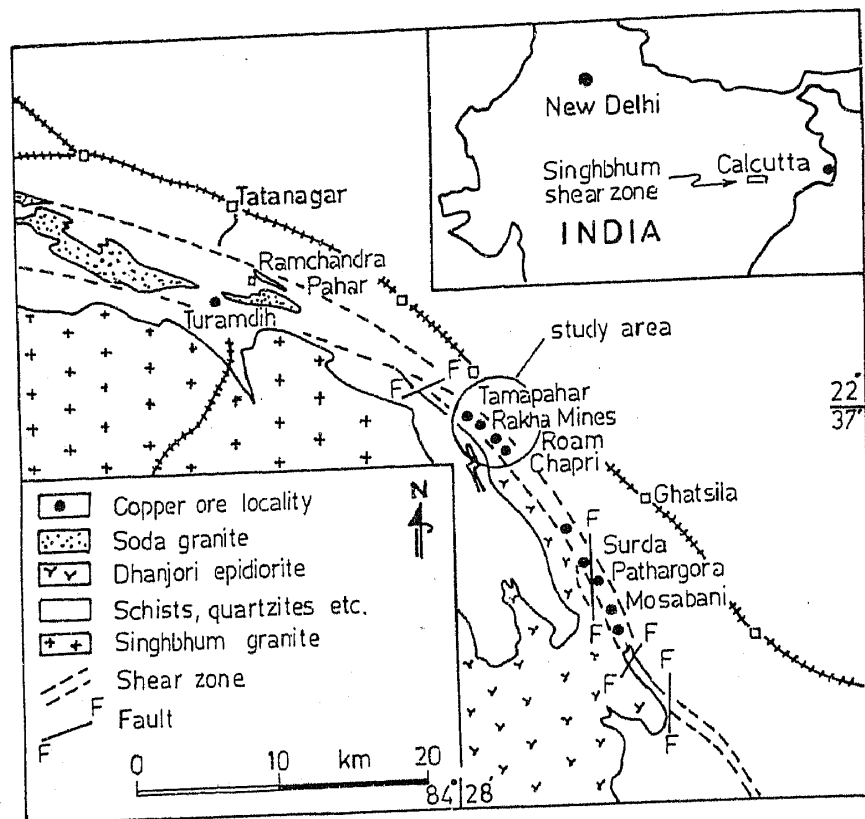The oxidized zone of Rakha-Chapri Block is extensively altered to clayey products.

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Figure 1. Generalized geologic setting of the Singhbhum shear zone showing the important copper ore localities.

The oxidized zone which contain abundant clay minerals does not contain sulphide minerals, was found to contain 0·7% Cu with occasional high values up to 5·5% (Mookherjee and Tenginkai 1977, 1987). Saha (1982) also reported anomalous copper values (1000 ppm) from Tamapahar area which forms a part of the area now under investigation. The purpose of this paper is to describe the mineralogy, distribution and alteration environment of copper bearing clay minerals in the oxidized zone of the Rakha-Chapri Block of Singhbhum Copper Belt.

2. Experimental techniques

For the present study, samples have been collected from the surface and two bore holes SBH 305 and SBH 312. The separation of clay and non-clay fractions of these rocks were analysed following the methods described by Carver (1971). Two types of oriented clay slides namely, untreated and acid and heat-treated clay slides were prepared for the identification of clay minerals by using the X-Ray diffraction techniques employing a powder diffraction unit (Phillips PW 1140). Untreated oriented clay slides were prepared by a method similar to Jackson (1956) and Warshaw and Roy (1961).

Morphologies of clay minerals were examined by transmission electron microscope (model EM6, AEI, UK). Electron microprobe analysis was made to understand the nature of copper and/or aluminium distribution in the altered and unaltered grains of biotite qualitatively by employing microprobe (model Mark 2, USSR).

The clay and non-clay fractions were analysed for copper by either the idiometric method of Vogel (1961) or the colorimetric method of Snell and Snell (1949), depending on whether the total copper content was respectively high or low.

3. Mineralogy of the oxidized zone

The caprock has a brilliant red colour for a couple of meters, and assumes a dull earthy look. Pure jaspar as well as limonitic jasper, occurring in patches, continues at depth. The oxidized compounds and the relative proportions of different clay minerals change downward, suggesting strong zonation of the entire weathered/oxidized profile.

Table 1 depicts the vertical zonation in terms of oxidized compounds of ore minerals and also shows depthwise changes in host-rock mineral assemblages. It may be noted from the table that malachite, which is pervasive at the surface, dies out at a depth where cuprite is dominant. Native copper and tenorite are encountered at 50 m depth. The thin, incipient transition zone contains djurleite, digenite, violerite and marcasite, admixed with some cuprite. Corresponding changes in the host-rock within the

Table 1. Vertical zonation of principal mineralogical associations of the supergene altered profile in ore and host-rock.

| Zone | Ore body mineral assemblage | | Host-rock mineral assemblage |
	Major minerals	Accessory minerals	
'Gossan'	Hematite Goethite Chert Jasper	Malachite	Amorphous/crypto-crystalline silica, hydrobiotite (?) Halloysite and Jarosite
Carbonate	Malachite Chalcanthite Jasper	Brochantite	Ore lenses and kaolinite + illite away from ore lenses
Carbonate-oxide	Malachite Cuprite Jasper	Chalcanthite Delafossite	Silicification of clays decreases with depth
Oxide	Tenorite Cuprite Native-Copper Jasper	Malachite Hematite	Martitization of magnetite decreases with depth
Transition (incipiently developed)	Covellite Digenite Cuprite Marcasite	Djurleite Chalcocite Violarite	Kaolinite decreases with depth
			Illite-chlorite increases with depth
Primary ore	Chalcopyrite Pyrrhotite	Pyrite Bornite Ni-pyrrhotite Pentlandite	Clay mineral abundance decreases with depth

weathered profile are, a dominant kaolinitic zone at the upper level, underlain by a zone of 2:1 clay minerals decreasing silicification downwards. However, no clear-cut matching with specific oxidized zones in ore bodies exists.

4. Alteration of biotite and chlorite

Two distinct types and intensities of biotite alteration are noted. At relatively shallow depth ($\sim$ 22 meters), all biotite adjacent to the former sulphide veins or even disseminations are totally destroyed. The residue of yellowish amorphous or crypto-crystalline silica, which is similar to that found by Mehmal (1937) in his experiment on leaching of biotite with sulphuric acid as alteration halo, surrounds the sulphide grains. Occasionally the amorphous silica retains outlines and even ghost relic cleavage traces of biotite grains. Commonly the two varieties of biotite are interleaved, and on commonly jarosite is associated with the biotites. The other trend of alteration, much more widespread than the former one is to a fine-grained clayey material with interleaved residual patches of unaltered biotite and/or chlorite. Originally, the green biotite in biotite-tourmaline schists, was altered to brown biotite and chlorite along the grain margins. Later the entire grain was altered to a fine-grained clayey material (figure 2), extends down to $\sim$ 60 meters. Below this, both minerals are absolutely fresh, implying a supergene origin for the 'clayey' alteration products.

5. X-ray diffraction studies

Minerals of kaolin group are present as a major constituent in the samples studied. Chlorite, illite and some expandable minerals are also present. The kaolin group of
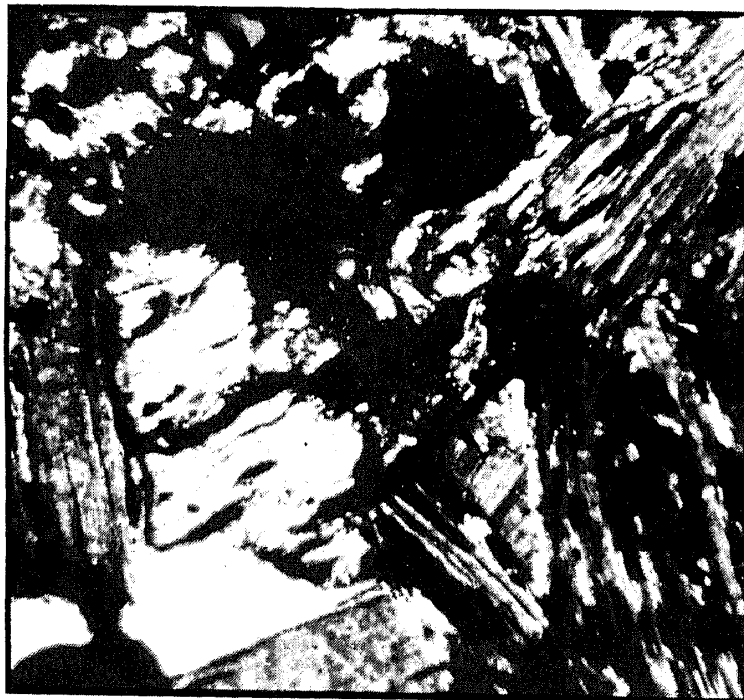

Figure 2. Photomicrograph of biotite exhibiting alteration to chlorite and clays. (100 X).
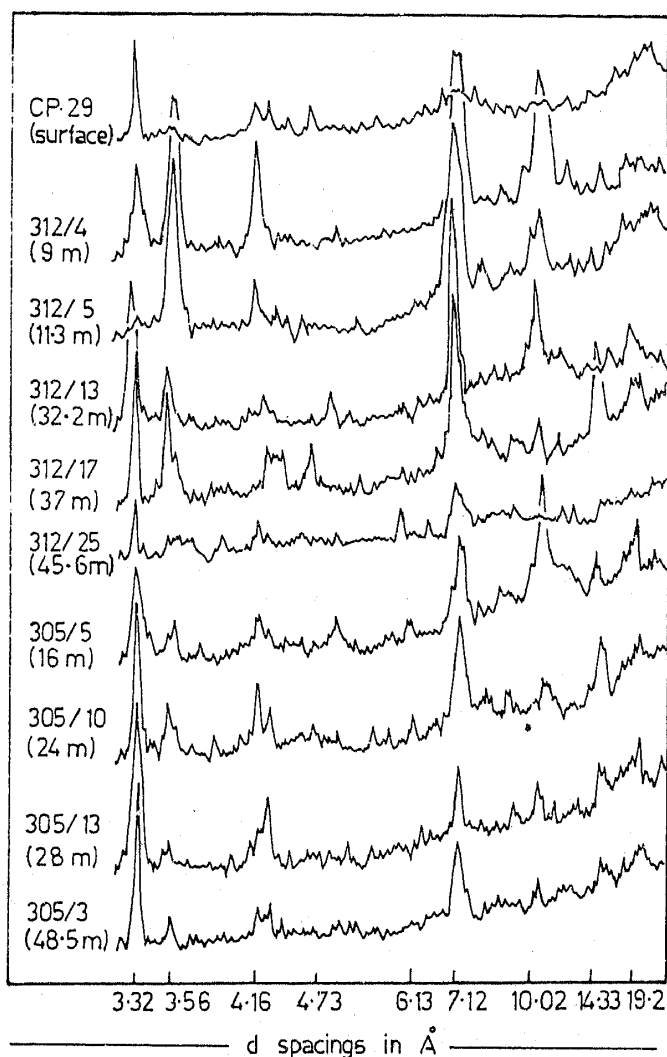
Figure 3. X-ray diffraction patterns of untreated clay fractions belonging to various depths.

minerals are identified on the basis of prominent peaks around 7–7·2 Å, 3·57 Å and 4·18 Å (figure 3). Supergene chlorite is identified on the basis of prominent peaks around 14 Å, 7 Å, 4·12 Å and 3·53 Å. The samples showing the presence of both kaolinite and chlorite are interpreted on the basis of (a) suppression or enhancement of the 7 Å peak after acid or heat treatment (figures 4 and 5), and (b) the appearance of both 3·57 Å and 3·53 Å peaks in untreated oriented clay samples (figures 3, 4 and 5). Illite is identified on the basis of a prominent peak around 10 Å (figures 3, 4 and 5). Hydrated halloysite is identified in a few samples on the basis of two strong peaks at 10·06 Å and 4·44 Å (figure 3). The 10 Å reflection shifts to 7 Å upon heating. Transmission electron microscope study also confirms the presence of halloysite (figure 6).

A small but prominent peak in the 19–20 Å range is observed in all samples. The persistence and unchanged nature of this peak under both acid and heat treatment (550°C for 1 hr, figures 4 and 5). We have been unable to identify this peak. Mcum *et al* (1973) attribute a peak in 18 Å region in the untreated state as montmorillonite-organic matter.
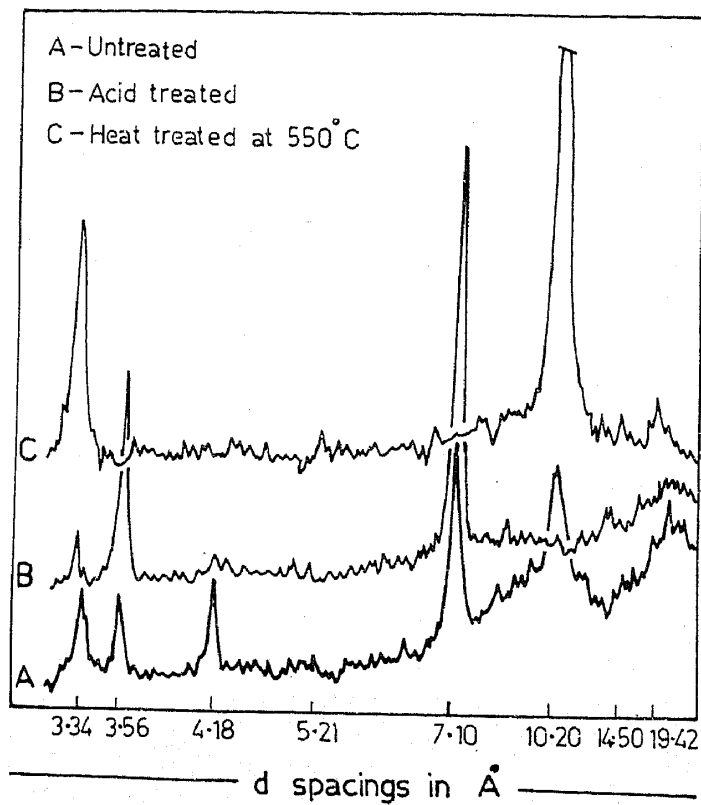
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Figure 4. X-ray diffraction pattern of the clay fractions under various treatments. Sample No. CP/3 (surface)
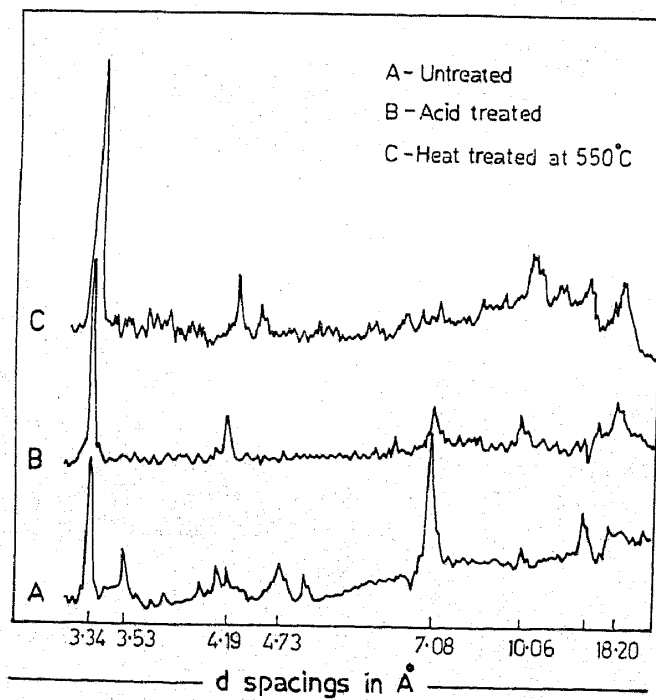

Figure 5. X-ray diffraction patterns of the clay fractions under various treatments. Sample No. 305/4 (14·7 m depth).

Figure 6. Electron photomicrograph showing predominantly tubular halloysite. Also note poorly ordered kaolinite (20,000 X)
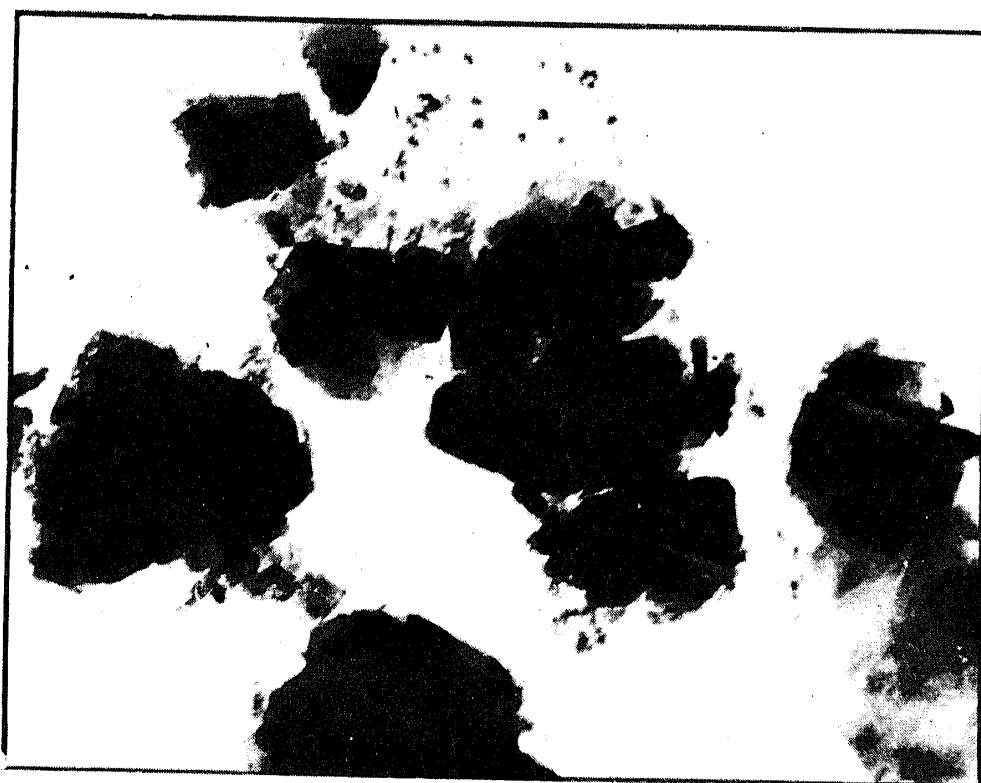

Figure 7. Electron photomicrograph showing well-defined hexagons of kaolinite (25,000 X)

To find out the exact nature of the 7 Å peak whether it was due to (a) entirely to kaolinite, (b) entirely to halloysite or (c) to both kaolinite and halloysite samples were studied under the transmission electron microscope. The study reveals that the 7 Å and 10 Å peaks in the samples are of halloysite and kaolinite (figures 6 and 7).

The halloysite exhibits considerable morphological variability in its commonest form, it consists of fine, tubular particles with large ratio of length/width with poorly ordered kaolinite composed of subsequent, platy particles with no particular well-developed form. These observations are comparable to the forms reported by Nadeau and Tait (1987).

6. Relative proportions of clay minerals

The relative proportions of kaolinite, illite or hydrated halloysite associated with mixed layer expandable material and the supergene chlorite are calculated on the basis of the intensities of peaks at 3·52 Å, 3·57 Å, 4·18 Å, 4·72 Å, 7 Å, 10 Å and 14 Å (of untreated samples) following the methods outlined by Tripplehorn (1970).

Table 2 shows the relative proportions of various clay minerals in surface and sub-surface samples. The kaolin group minerals are invariably present in all the surface samples within the oxidized zone and their amount decreases with depth. Secondary (supergene) chlorite is the mineral which is next to the kaolin group in abundance but its amount varies irregularly. Illite is more or less equally distributed at all depths. It is more commonly present at depth than at surface or near surface. All these clay minerals and secondary chlorite are virtually absent below the zone of oxidation providing their derivation from primary aluminosilicate minerals by weathering.

7. Environmental significance

The oxidized compounds of copper show a zonal distribution of malachite (djurleite $\pm$ chalcocite) from the surface down to top of the primary ore zone. The presence of cuprite, native copper and chalcocite at depth implies decreasing Eh with depth and pH values from mildly strong acidic to strongly alkaline. Cupriferous solutions, in passing through a predominantly alkaline environment, will deposit brochantite or atacamite if the Cu^{2+} concentration is high enough; at very low Cu^{2+} concentrations, on the other hand, malachite (or azurite) and/or tenorite will be precipitated (Barton and Bethke 1960; Kern and Weisbrod 1967; Rickard 1974; Thornber 1985). The occurrence of malachite at the surface and tenorite in deeper parts of the oxidized zone, therefore, points to the effects of solutions containing very low concentrations of Cu^{++} and SO_4^{--}, once again indicating inadequate generation of strong acid at near surface levels and only incipient migration of copper from sites of the dissolution of primary copper minerals.
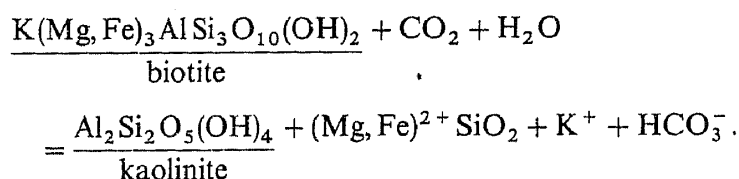
The weathering profile as a whole thus reveals a rather uncommon feature. Secondary copper, instead of being concentrated outwards or downwards, has accumulated with the weathered cover. Samama (1973), while discussing the continental weathering of ore deposits and the geochemical inheritance of heavy metals, demonstrates that the retention of different heavy metals within the weathered cover is due primarily to the major weathering processes operating in an area.

Theoretically, any Al silicate mineral can yield kaolinite by weathering provided K^+, Na^+, Ca^{++}, Mg^{++} and Fe^{++} are leached away, H^+ is added, Al/Si ratio is increased and the concentration of Al^{3+} increases. In an aqueous weathering system, H^+ is internally available; Na^+, K^+, Ca^{++} and Mg^{++} being ions of greater mobility,

Table 2. Relative proportions of clay minerals within the oxidized zone and copper contents of whole rocks and those of corresponding non-clay (<2μ) fractions of surface and drill-core samples.
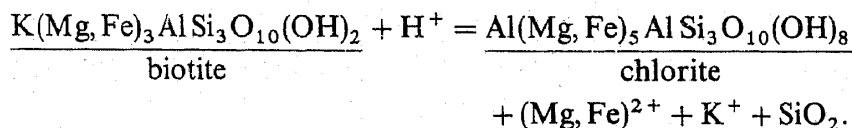
Sample No.	Rock type	Location with depth (m)	Relative proportions of clay minerals in %			Whole rock (Cu%)	Non-clay fraction (Cu%)	Clay (<2μ) fraction
			Kaolinite + Halloysite	Illite with mixed layer	Chlorite			
CP/3	Gossanised ser.qtz.schist	Surface	35	60	5	1·07	0·89	1·15
CP/29	Gossanised qtz.biot.schist	"	90	—	10	0·14	0·13	0·51
CP/39(b)	Gossanised ser.qtz.schist	"	traces	90	traces	0·78	0·88	0·91
CP/41(b)	Gossanised ser.qtz.schist	"	50	—	50	0·08	0·06	0·41
305/4	Weathered biot.qtz.musc. schist with limonite	14·7	10	25	65	0·67	0·36	1·31
305/5	Weathered qtz.biot.schist with limonite	16·0	25	60	15	0·71	0·51	1·19
305/6	Altered qtz.biot.schist	20·0	15	35	50	0·09	0·05	0·60
305/10	Biot.qtz.schist with limonite	24·0	20	50	30	0·20	0·16	0·57
305/13	Biot.qtz.schist	28·0	35	45	20	0·09	0·06	0·57
305/MC/3	Biot.qtz.tourm.schist	48·5	10	45	45	0·18	0·19	0·93
312/4	Altered qtz.biot.schist with limonite	9·0	55	40	5	0·60	0·66	0·51
312/5	Altered biot.qtz.schist	11·3	85	15	—	0·58	0·51	0·21
312/13	Qtz.biot.schist with opaque minerals	32·2	40	60	—	0·33	0·34	0·64
312/17	Biot.qtz.schist	37·0	30	—	55	0·02	0·08	0·26
312/25	Qtz.biot.chlorite schist with abundant malachite	45·6	35	—	65	3·99	3·74	2·08

are easily leached by ground water from permeable rocks with sloping drainage; Fe^{2+} is, in effect, removed from the system chemically by oxidation to Fe^{3+} (Keller 1970; Thornber and Wildman 1984; Hurst and Kunkle 1985; Thornber 1985; Ahn and Peacor 1987; Banfield and Eggleton 1988) and by subsequent precipitation; and K and Na-silicates, formed during hydrolysis are highly soluble, and are leached away, thus raising the Al/Si ratio. The following equation given by Garrels and Mackenzie 1967), further demonstrates that the acidity of ground water need not be particularly high for kaolinite to form. In fact CO_2-bearing water, unaided by any stronger acids (such as H_2SO_4 generated by the decomposition of pyrite), is capable of bringing about the transformation.

$$\underset{\text{biotite}}{\underline{K(Mg,Fe)_3 Al Si_3 O_{10}(OH)_2}} + CO_2 + H_2O$$

$$= \underset{\text{kaolinite}}{\underline{Al_2 Si_2 O_5(OH)_4}} + (Mg,Fe)^{2+} SiO_2 + K^+ + HCO_3^-.$$

It is not surprising, therefore, that kaolinite is abundant in the weathered zone particularly near the surface. The formation of halloysite during weathering, however, requires low pH and a sulphate solution as the solvent (Keller *et al* 1971). Geochemically, the factor responsible for the formation of illite by the weathering of aluminosilicate minerals is the ratio $(K^+)/(H^+)$ in reference to H_4SiO_4. Interstitial solutions have been considered to be important conveyors of K^+. Illite may also form by the reconstitution of other clay minerals such as montmorillonite, through single-stage or multi-stage K-fixation (Keller 1970). The abundance of illite in the surface specimens in places is perhaps to be explained by local differences in the scale of microenvironments where the ratio $(K^+)/(H^+)$ is above a critical value. Illite in deeper zones owes its origin to the fixation of K^+ that was leached out of micaceous rocks during weathering above, and may represent transformation reactions such as Kaolinite $+ KOH = K$-Mica (Velde 1965) or Montmorillonite $+ K = $ Illite (Keller 1970).

Since the structure of the chlorite consists of mica-like sheets with the composition, $(Mg,Fe)_6 (Si, Al)_8 O_{20}(OH)_4$, alternating with sheets having brucite structure and the composition, $(Mg,Al)_6(OH)_{12}$, one way of looking at the chlorite structure is to regard it as similar to that of illite, but with successive layers linked by $(Mg,Al)(OH)^+$ ions instead of K^+. The absence of such chlorite at or near the surface is adequately explained by the leaching out of Mg^+ ions. Direct transformation of biotite to chlorite is also possible and involves total release of K^+ and partial release of $(Mg,Fe)^{2+}$ ions and SiO_2, as in the following reaction:

$$\underset{\text{biotite}}{\underline{K(Mg,Fe)_3 Al Si_3 O_{10}(OH)_2}} + H^+ = \underset{\text{chlorite}}{\underline{Al(Mg,Fe)_5 Al Si_3 O_{10}(OH)_8}}$$

$$+ (Mg,Fe)^{2+} + K^+ + SiO_2.$$

8. Copper in the oxidized zone

In Rakha-Chapri Block, three modes of copper occurrence in the oxidized zone are evident from megascopic and microscopic examination in the following manner;

(i) as in-situ oxidation products occupying the sites of former copper sulfide bands, veins, and disseminations;

(ii) as ultrafine disseminated copper oxide minerals along schistosity planes;

(iii) as thin films or smears of cuprite and malachite along joints, fractures, and grain boundaries of the host-rock.

Several specimens from the oxidized zone which showed no copper minerals under microscope, were found to be rich in copper (Tenginkai 1979). Initially, a few samples of altered quartz-biotite schist occurring at different depths within the oxidized zone and having high amounts of copper were selected for study. These were crushed to −80 to +100 mesh size and subjected to repeated separation by the isodynamic separation. Three major fractions were obtained; (a) altered biotite/chlorite flakes, (b) quartz, coated with iron oxide and cuprite, and (c) residual fraction containing mainly the oxidized copper compounds and tourmaline. Fraction (a) was further purified until 95% purity was obtained. Copper contains of biotite/chlorite fraction were determined by a colorimetric method of copper estimation. The resulting solutions developed a thick dark yellow-brown colour instead of the usual light yellow-brown colour, indicating an unexpected high concentration of copper in this fraction.

It was observed under the microscope that the samples at depth 14·7 m depth containing around 2·38% Cu show much more extensive alteration of biotite than the samples at 62·0 m depth, from primary sulphide zone where the rock as a whole is fresh and does not contain any copper. This indicates that diffused copper of unknown composition has thoroughly mixed up with altered biotite and chlorite. It may be recalled that significant copper is precipitated during the hydration of biotite to form 'cupriferous hydro-biotite' (Henley and Brown 1974; Titley 1988).

9. Copper in altered biotite

In order to confirm the finding of anomalous amount of copper in the altered biotite/chlorite and to establish a relationship of the amounts of copper with the degree of alteration, samples containing good amount of biotite and chlorite flakes were selected. Polished samples were prepared and examined with the electron microprobe analyser. Biotite grains with different degrees of alteration from samples at different depths were scanned across their elongation under electron microprobe analysis (EMPA). Three electron microprobe scangraphs for qualitative analysis (figure 8) revealed progressive increase of copper content from 'fresh' to 'highly altered' biotite grains from three drill-core sample (MC/9, 305/4 and 305/1) collected at 62 m, 14·7 m and 10·5 m depths respectively from the bore hole SBH 305. The fresh biotite grain (from MC/9) is from the primary ore zone, and shows a more or less flat graph indicating the absence of any copper. Traverses across the 'altered' and 'highly altered' biotite grains (from 305/4 and 305/1 respectively) show a number of copper peaks of high intensity that probably coincide with the alteration strips parallel to the cleavage. The 'highly altered' biotite grain, which is from the shallower depth (10·5 m depth), shows a large number of broad peaks with greater intensity, compared to those of 'altered' biotite grain from a deeper level (14·7 m depth) which is less altered.

It can be inferred that there is a strong and direct relationship between the degree
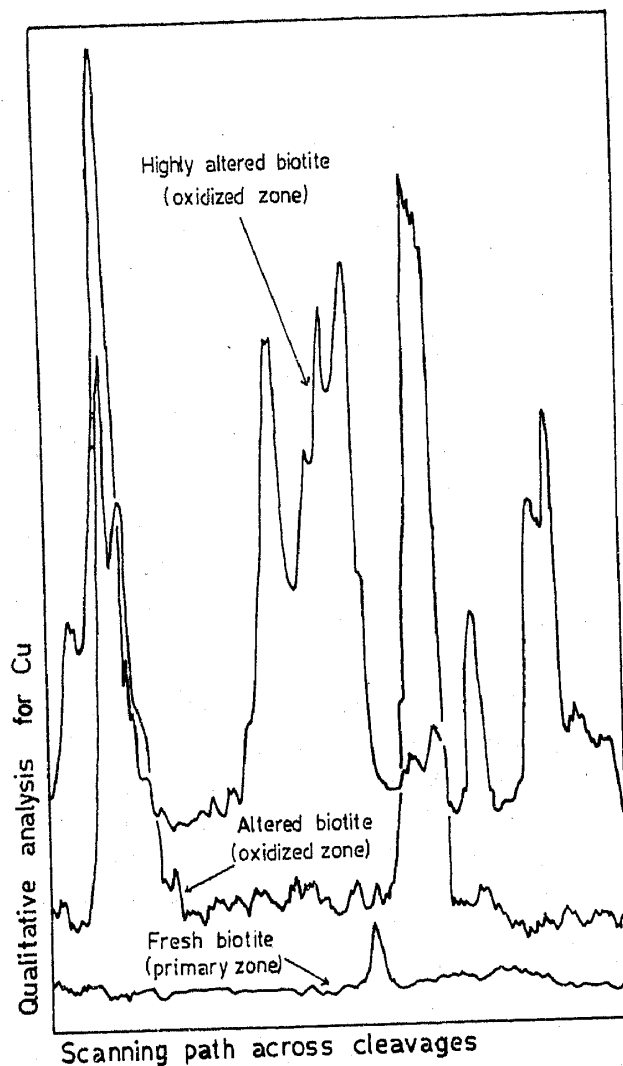
Figure 8. Electron microprobe scan-graphs showing progressive increase of Cu content from fresh to highly altered biotite grains.

of alteration of the biotite grains and the amount of copper in them. The biotite grains, as a rule, alter along the cleavage planes. Incipient alteration starts along the cleavage planes, widens further to give rise to interleaved strips of fresh and altered biotite. The altered strips ultimately coalesce to produce completely altered grain whose outlines are often retained. This is also indicated by two electron probe scanning images of $Cu(CuK_\alpha)$ in partially altered and essentially fresh biotite grains. Figure 9A is an electron scanning image of $Cu(CuK_\alpha)$ of interleaved fresh and altered biotite indicating Cu enrichment in the altered biotite portions. Furthermore, the amount of copper can be directly correlated with an increase in aluminium content in the altered portions of biotite grains. Figure 9B is an AlK_α scanning image of an altered biotite grain and figure 9C is the CuK_α scanning image of the same grain. The Al and Cu scanning graphs across the same grain reveal oscillations of high and low Al and Cu areas (strips) coinciding with 'altered' and 'fresh' patches (figure 10) whereas Al and Cu scanning graphs across the fresh biotite grain do not show oscillations of high Al and high Cu areas (figure 11). Figure 9D is a scanning image of a fresh biotite that shows a virtual absence of copper. Thus it is clear that the sites of higher
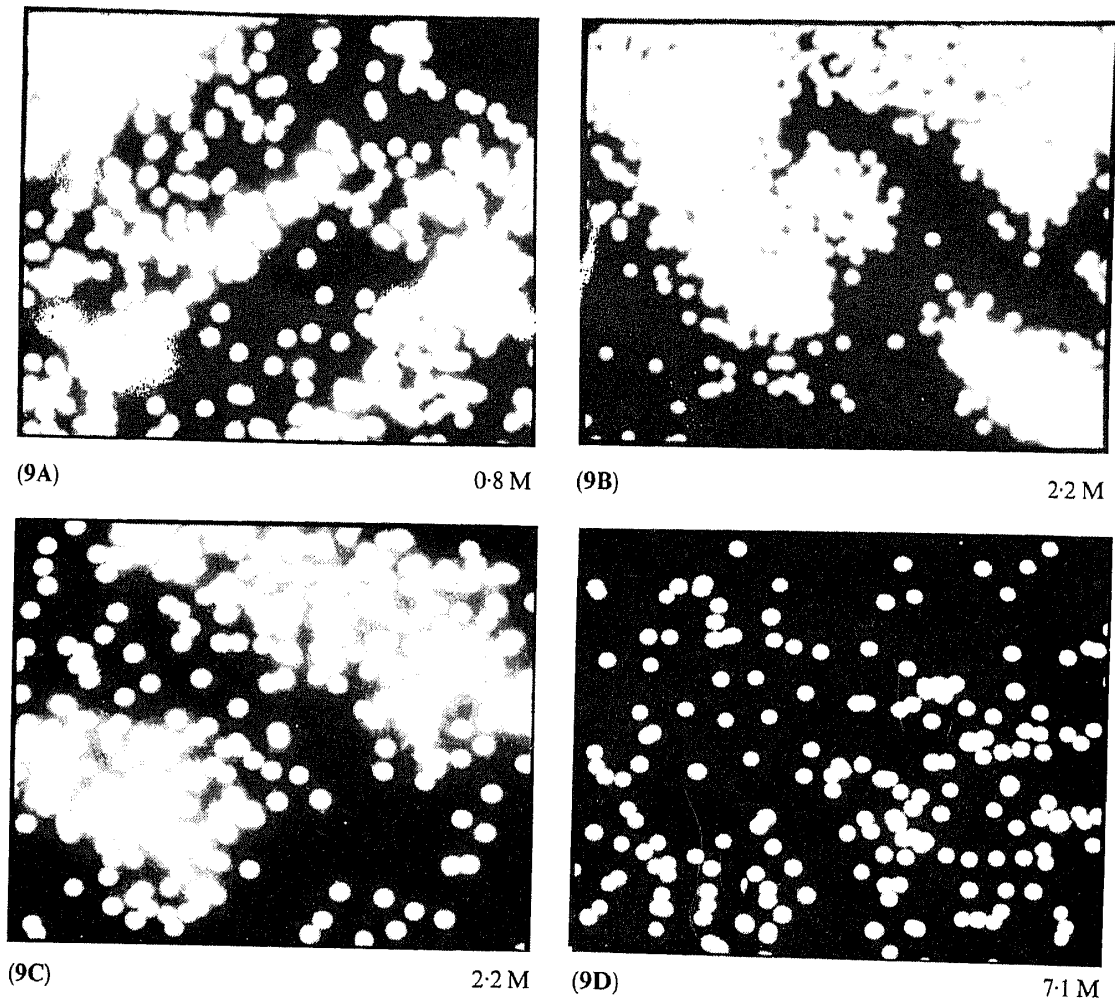
(9A)   0·8 M   **(9B)**   2·2 M

(9C)   2·2 M   **(9D)**   7·1 M

Figure 9. Electron microprobe scanning images. **A.** Cu distribution (CuK$_\alpha$scan) of interleaved fresh and altered biotite. **B.** Al (AlK$_\alpha$scan) of a highly altered biotite grain indicating the presence of a large quantity of clay minerals. **C.** Cu (CuK$_\alpha$ scan) of the same area as **9B** showing high concentration of copper. **D.** Cu (CuK$_\alpha$scan) of fresh biotite indicating virtual absence of copper.

aluminium concentration in altered biotite associated with the formation of clay minerals are also sites of copper enrichment, implying concentration of copper in the clay alteration of micas, which invariably proceeds along the cleavages.

10. Copper in separated clay (< 2μ) fractions

After confirming that a considerable amount of copper is held by the clayey altered portions of biotite and that the concentration of copper increases with greater alteration of biotites, an effort was made to determine the exact mode of occurrence of copper in the clay fraction. The first step in that direction was to determine whether any discrete copper-bearing minerals of ultrafine grain size were associated with the clay fraction.

Accordingly, a set of sixteen rock samples within the oxidized zone was crushed to − 200 mesh size, and separated into clay and non-clay fractions with a view to
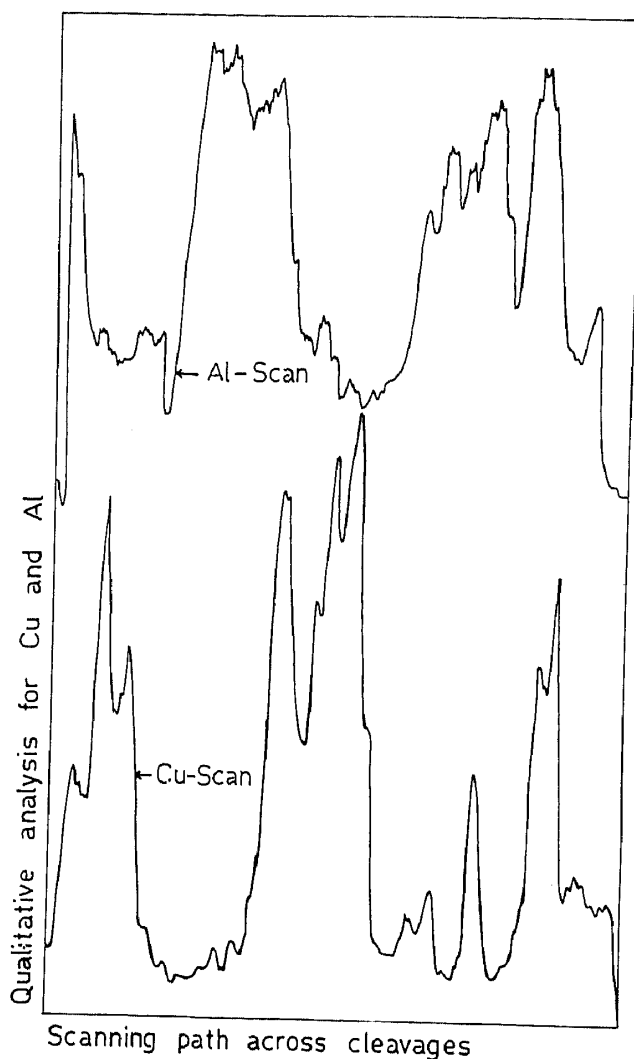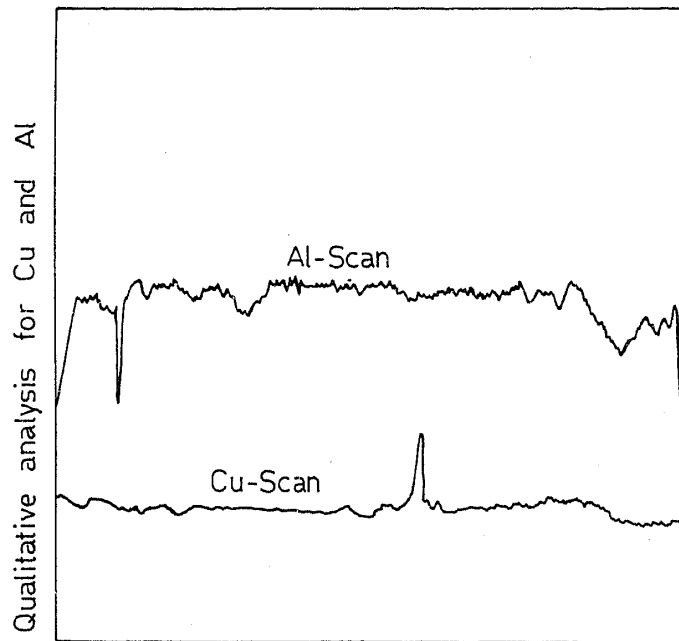
Figure 10. Electron microprobe scan-graphs across an altered biotite grain for Cu and Al (not along the same path) from oxidized zone.

determining distribution of copper and copper-bearing minerals. The clay and non-clay fractions were X-rayed, and then analysed for total extractable copper, by either the idiometric method of Vogel (1961) or the colorimetric method of Snell and Snell (1949), depending on whether the total copper content was respectively high or low. The copper contents of the whole rock samples and their clay and non-clay fractions are presented in table 2. Whole-rock sample No. 312/25 (table 2, 312/25) has a very high copper content, 3·99%. A major portion of this copper is due to the presence of several discrete copper minerals, mainly malachite (note 3·74% copper in the non-clay fraction table 2, 312/25); but a considerable amount of copper is also held by the corresponding clay fraction (2·08% Cu). Considerable amount of copper is also present in the whole-rock parts and non-clay fractions of sample Nos. CP/39 (b) and CP/3. X-ray diffractograms of the non-clay fractions show a number of peaks for the copper minerals, malachite (2·80 Å, 2·50 Å, 1·98 Å), chalcanthite (4·00 Å, 3·74 Å), brochantite (2·50 Å, 1·69 Å), tenorite (2·29 Å, 1·37 Å), Anatase (3·52 Å, 1·67 Å, 1·45 Å), Jarosite (2·99 Å, 1·82 Å) and others. Such peaks are absent in the diffractograms of the corresponding clay fraction, implying a virtual absence of discrete copper minerals

Figure 11. Electron microprobe scan graphs across a fresh biotite grain for Cu and Al from primary sulphide zone.
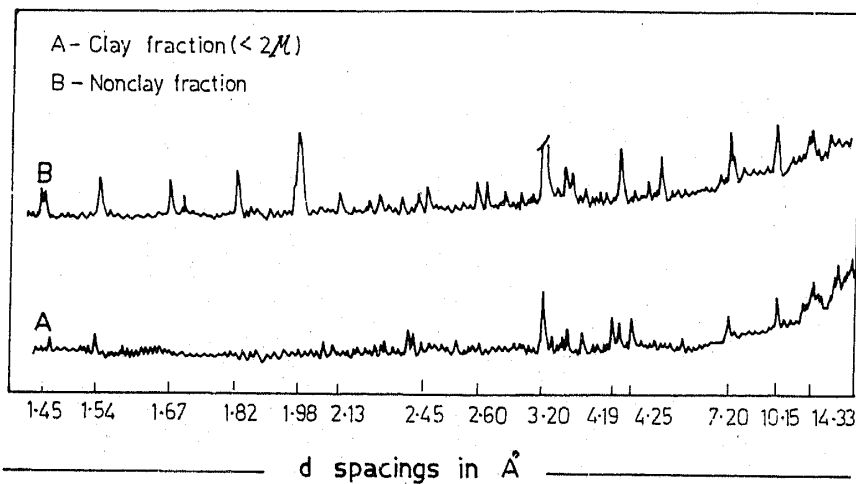

Figure 12. X-ray diffraction patterns of clay and non-clay fractions revealing the absence of copper minerals in the clay fractions.

in the clay fractions, even though their copper contents are significantly high. An example is illustrated in figure 12. Thus it is clear that copper constitutes a component of the clay minerals present. Similar conclusions have been made by different workers elsewhere (Basset 1958; Stephens and Metz 1967; Henley and Brown 1974; Farrah and Pickering 1979; Thornber 1985). Excellent reviews by Bowden *et al* (1980) and Furlong *et al* (1981) give a considerable account on adsorption of cations and anions on to oxide and clay minerals.

11. Conclusions

Conversion of biotite to amorphous silica and the neoformation of jarosite and halloysite indicate generation of strong acid (H_2SO_4). The restricted occurrence of these reaction products to the immediate vicinity of bands and lenses of sulphide, now oxidized, signifies that the generation of such a strong acid was a localized phenomenon. Pervasive kaolinization, illitization and chloritization of the aluminosilicate minerals, on the other hand, imply a dominant role of hydrous metasomatism involving a net increase in the (OH^-/H^+) ratio of the surrounding fluid.

The abundance of kaolinite in the upper part of the oxidized zone is ascribed mainly to the action of mildly acidic CO_2–bearing ground water. The abundance of illite locally near surface zones is explained by local differences (at a scale of microenvironments) in (K^+)/(H^+) ratios in the pervading ground water fluid, while illite in deeper zones owes its origin to the fixation of K^+ leached from micaceous rocks above. The abundance of supergene chlorite in deeper zones, again points to feeble leaching actions at depth or even to the refixation of Mg^{++} from downtrickling groundwater.

A rather unusual mode of occurrence of copper in the oxidized zone is its intimate association with the 'clayey' alteration products of biotite, chlorite, and muscovite. The confinement of such copper within biotite grains only to altered strips within the grains (proved by electron microprobe scanning across altered grains) and the absence of any discrete copper minerals in the clay fraction of the altered rock (proved by X-ray studies) suggest that copper constitutes a component of clay minerals present. Such clay bound copper is locally abundant, and implies availability of cupriferous solutions during the formation of the clay minerals. Thus the retention of practically the entire quantity of original copper within the oxidized zone is mainly due to in-situ oxidation of sulphides, and partly due to fixation to clay minerals during weathering. The conclusion that in the oxidized zone of the Rakha-Chapri Block, copper forms a component of the clay minerals, as surface-adsorbed and/or lattice-bound ions seems justified.

References

Ahn J H and Peacor D R 1987 Kaolinitization of biotite: TEM data and applications for an alteration mechanism; *Am. Mineral.* **72** 353–356

Banfield J F and Eggleton R A 1988 Transmission electron microscope study of biotite weathering; *Clays Clay Miner.* **36** 47–60

Barton P B and Bethke P M 1960 Thermodynamic properties of some synthetic zinc and copper minerals; *Am. J. Sci.* A258 21–34

Besset W A 1958 Copper vermiculite from northern Rhodesia: *Am. Mineral.* 43 1112–1133

Bowden J W, Posner A M and Quirk J P 1980 Adsorption and charging phenomena in variable charge soils, in *Soils with variable charge*. (eds) B K G Theng; N. Z. Soc. Soil Sci., *Spec. Publ.* 147–166

Carver R E 1971 *Procedures in sedimentary petrography*: (New York: Wiley-Interscience) 458 pp

Dunn J A 1937 Mineral deposits of eastern Singbhum and surrounding areas; *Geol. Surv. India Mem.* 69 279

Farrah H and Pickering W F 1979 pH effects in the adsorption of heavy metal ions by clays; *Chem. Geol.* 25 317–326

Furlong D N, Yates D E and Healy T W 1981 Fundamental properties of the oxide/aqueous solution interface in: (eds)s Trassati, *Electrodes of conductive metallic oxides*, Part B. (Amsterdam: Elsevier) pp. 367–432

Garrels R M and Mackenzie F T 1967 Origin of the chemical compositions of some springs and lake. In *Equilibrium concepts in natural water systems*: (ed.) W Stumm *Adv. Chem. Ser.* 67 222–242

Henley K J and Brown R N 1974 Cupriferous hydrobiotite from Ukaparinga, South Australia; *Econ. Geol.* 69 688–692

Hurst V J and Kunkle A C 1985 Dehydroxylation, rehydroxylation and stability of kaolinite; *Clays Clay Miner.* 33 1–14

Jackson M L 1956 *Soil chemical analysis*: Advanced course published by the author; Department of Soil Science, University of Wisconsin, Madison 100–191

Keller W D 1970 Environmental aspects of clay minerals; *J. Sed. Petrol.* 40 788–813

Keller W D, Hanson R F, Haung W H and Cervantes A 1971 Sequential active alteration of rhyolitic volcanic rock to end ellite and a precursor phase of it at a spring in Michoacan, Mexico; *Clays Clay Min.* 19 121–127

Kern R and Weisbrod A 1967 *Thermodynamics for geologists*: (San Francisco: Freeman and Co.) p. 304

Mehmal M 1937 Ab und umbau am biotit; *Chemie der Erde* 2 307–312

Mookherjee A and Tenginkai S G 1977 Study of the oxidized zone in the Rakha-Chapri block of the Singhbhum copper belt, India; *Indian J. Earth Sci. S. Roy Vol.* pp. 143–156

Mookherjee A and Tenginkai S G 1987 Some unusual geochemical features of the oxidized zone of the central sector of the Singhbhum copper belt, India; *Chem. Geol.* 60 51–62

Moum J, Rao C and Ayyar T S R 1973 A natural 17 Å montmorillonite organic complex from Allepey, Kerala State, India; *Clays Clay Min.* 21 89–95

Nadeau P H and Tait J M 1987 Morphology of clay minerals, in: *Handbook of determinative methods in clay mineralogy*; (eds) M J Silson (New York: Chapman and Hall) pp. 209–246

Rickard D T 1974 Low temperature copper geochemistry, geological aspects; *Cent. Soc. Geol. Belgigue, Gisements stratiforms et provinces cupriferes, Liege*, pp. 1–34

Saha H L 1982 Ratio between total copper and gold extractable copper—A case history study from Tamapahar, Singhbhum Copper Belt, Bihar; *Rec. Geol. Surv. India* 111 105–109

Samama J C 1973 Ore deposits and continental weathering; A contribution to the problem of geochemical inheritance of heavy metal contents of basement areas and of sedimentary basins, in *Ores in Sediments* (eds) G C Amstuz and A J Bernard (New York: Springer-Verlag) pp. 247–265

Sarkar S C, Deb M and Choudhury K 1971 Sulphide mineralization along the Singhbhum shear zone, Bihar, India; *Soc. Min. Geol. Jpn. Spec. Iss.* 2 226–234

Snell F D and Snell C T 1949 *Colorimetric methods of analysis*, (New York: D Van Nostrand) Vol. 2 pp. 950

Stephens J D and Metz R A 1967 The occurrence of copper-bearing clay minerals in oxidized portions of the disseminated copper deposits at Ray, Arizona; *Geol. Soc. Am. Abs. Prog. Annual Meeting* (New Orleans) pp. 213

Tenginkai S G 1979 *Economic geology and geochemistry of the oxidized zone of the Singhbhum Copper Belt, Bihar, India*; Unpublished PhD Thesis, I I T Kharagpur 200 p

Thornber M R 1985 Supergene alteration of sulphides VII. Distribution of elements in the gossan-forming process; *Chem. Geol.* 53 279–301

Thornber M R and Wildman J E 1984 Supergene alteration of sulphides IV. The binding of Cu, Ni, Co and Pb with iron-bearing gossan minerals; *Chem. Geol.* 44 279–301

Titley S R 1988 Silicates flushed with copper; *Nature (London)* 334 472–473

Tripplehorn D M 1970 Clay mineral diagenesis in Atoka, Pennsylvanian sandstones, Crawford Country Arkansas; *J. Sed. Petrol.* 40 838–847

Velde B 1965 Experimental determination of muscovite polymorph stabilities: *Am. Mineral.* 50 436–449

Vogel I A 1961 *A text-book of quantitative inorganic analysis* (London: Longman Green) pp. 359

Warshaw C M and Ray R 1961 Classification and a scheme for the identification of layer silicates; *Bull. Geol. Soc. Am.* 72 1455–1492