# Reconstructing physico-chemical parameters of hydrothermal mineralization of copper at the Malanjkhand deposit, India, from mineral chemistry of biotite, chlorite and epidote

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Mineral chemistry of biotite, chlorite and epidote associated with the granitoid ore body of the Malanjkhand coppermolybdenum deposit have been studied to constrain temperature, oxidation and sulfidation states as well as fugacity ratios of HF, HCl and H<sub>2</sub>O of the hydrothermal mineralizing fluid. Calculated mineralizing temperatures from biotite, chlorite and epidote are mutually consistent and agree well with earlier estimates derived from fluid inclusion studies. Major element chemistry of biotite indicates low oxidation state (FMQ-NNO) and re-equilibrated nature (~300°C). However, exchange of Cl–F–OH between biotite and the fluid continued to lower temperatures. Subtle differences between the Malanjkhand deposit and known porphyry copper deposits have been evidenced by the fugacity ratios of halogens and water. Chlorite registers equilibrium with fluid down to 200°C and, together with biotite composition, indicates that copper was transported as chloride complex in the fluid. Sulfide deposition occurred during a prompt rise in fugacity of H<sub>2</sub>S at 300°C, possibly resulting from a coupled oxidation of Fe<sup>2+</sup> and reduction of SO4<sup>2-</sup>. Interaction of ore fluid with epidote in the wall-rock favored the deposition of chalcopyrite, enhanced the Ca<sup>2+</sup> activity in the fluid and inhibited a fall in pH and a subsequent acid alteration of K-feldspar in the wall-rock. These physicochemical characteristics of the mineralized fluid suggest that the Malanjkhand deposit represents an ancient granitoid-associated geothermal system rather than a classic porphyry copper ore deposit.

Keywords: hydrothermal, temperature, fugacity, copper, complexing

### INTRODUCTION

Reconstructing the physico-chemical conditions in which ore-forming fluids originate and evolve is a fundamental step in the understanding of how mineralization occurred. Temperature, pressure and fugacities of volatile species can be deduced from appropriate sulfide  $\pm$  oxide equilibrium assemblages. In their absence, silicates coexisting with ore minerals provide alternate tools for characterizing the environment in which mineralization and alteration was produced (Barton *et al.*, 1977; Jacobs and Parry, 1979; Charles *et al.*, 1988). Among them, chlorite, biotite, and epidote are the most frequently used to decipher physicochemical parameters in the fluid of fossil and active hydrothermal systems (Bird and Helgeson, 1980; Munoz, 1984; Walshe, 1986; Charles *et al.*, 1988; Cho *et al.*, 1988).

Elements residing in the hydroxyl site of biotite have greater exchangeability relative to ions in the tetrahedral and octahedral sites (Fortier and Giletti, 1991). Biotite, once equilibrated at higher temperatures, undergoes F-Cl-OH equilibrium exchange with the fluid responsible for formation of the alteration assemblage (Parry et al., 1978; Jacobs and Parry, 1979; Munoz, 1984; Selby and Nesbitt, 2000). Chemical composition of biotite from various ores has been considered for constraining activity ratios of the halogen and hydroxyl species in the fluid. Chlorite is a ubiquitous product of fluid-rock interaction in fossil hydrothermal systems associated with metal ores. Its use helps to constrain the temperature and fugacities of oxygen and sulfur of the hydrothermal regime associated with the mineralization and alteration (Cho et al., 1988; Lonker et al., 1990, 1993; Cathelineau, 1988; Barton et al., 1977). Epidote is one of the most common minerals observed in hydrothermal systems (Shikazono 1984; Cho et al., 1988; Charles et al., 1988; Bird et al., 1988; Caruso et al., 1988; Bird and Spieler, 2004) and exhibits octahedral substitution of Al<sup>3+</sup> for Fe<sup>3+</sup>, which can be used to estimate the temperature, composition and oxygen fugacity of the mineralizing fluid (Bird and Spieler, 2004 and references therein).

Here we present a detail study on the mineral chemis-

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Fig. 1. Ore silicate assemblages from mineralized part of the granitoid at Malanjkhand Cu + Mo deposit: (a) typical assemblage of biotite, magnetite, pyrite and K-feldspar corresponding to the stippled area in Fig. 8; (b) typical massive variety of chlorite with K-feldspar; (c) magnetite in association with fine grained chlorite and quartz with unaltered biotite; (d) pyrite, conspicuously fractured with medium grained chlorite filling the fractures and surrounding pyrite fragments; (e) fine grain chlorite interwoven with chalcopyrite observed commonly in the mineralized granitoid as well as quartzo-feldspathic veins; (f) epidote + chlorite (massive) with chalcopyrite rimmed by fluorite (purple colored) as commonly observed in the mineralized granitoid; (g) typical epidote + chalcopyrite assemblage observed in the mineralized granitoid and (h) K-feldspar (unaltered) with chalcopyrite in the fractures and cleavage spaces, a strikingly recurrent feature in all the ore types at Malanjkhand.

try of biotite, chlorite and epidote from different mineral assemblages such as biotite + K-feldspar  $\pm$  magnetite  $\pm$ pyrite; biotite + K-feldspar + chalcopyrite; chlorite + chalcopyrite and epidote + chalcopyrite from the Malanjkhand copper-molybdenum deposit, the largest open pit copper mine in India (Seetharam, 1976; Jairath and Sharma, 1986; Sikka, 1989; Panigrahi et al., 1991, 1993, 2004; Sarkar et al., 1996; Panigrahi and Mookherjee, 1997, 1998; Bhargava and Pal, 1999, 2000; Stein et al., 2004, 2006). An estimated reserve of 789 million tons of copper ores with a grade of 0.83% Cu (Sikka, 1989) underlines the economic importance of this deposit. Although the Malanjkhand deposit has been studied for nearly thirty years, the physicochemical environment of the hydrothermal fluid and its evolution is yet to be addressed. Since a porphyry-type affinity has been suggested for the Malanjkhand deposit (Sikka, 1989; Sikka and Nehru, 1998, 2002; Stein et al., 2004), we will compare the physicochemical environment of the hydrothermal fluid-estimated from the mineral chemistry of biotite, chlorite and epidote-to the existing generalized scenario of fluids involved in the formation of porphyry copper deposits.

## **GEOLOGICAL SETTING OF MALANJKHAND ORE**

The Malanjkhand copper-molybdenum deposit is hosted by a granitoid complex of early-Proterozoic age that occurs in the northern part of Bhandara Craton, Central India. This granitoid complex is surrounded by older granitic gneiss; metasedimentary rocks of the Saussar Group; volcano-sedimentary sequences of the Dongargarh Group and sedimentary rock units of Chhatisgarh Group (see Stein *et al.*, 2004).

The origin and evolution of the Malanjkhand coppermolybdenum deposit is still under debate (Sikka, 1989; Sarkar *et al.*, 1996, 1997; Panigrahi and Mookherjee, 1997, 1998; Sikka and Nehru, 1998; Stein *et al.*, 2004, 2006; Panigrahi *et al.*, 2006). The age of the major phase of the granitoid complex hosting the copper deposit has been constrained by U–Pb dating on zircons (~2476  $\pm$  8 Ma; Panigrahi *et al.*, 2004). Stein *et al.* (2004, 2006) provided Re–Os models and isochron dates (ranging from 2491 to 2439 Ma) of molybdenite from the mine pit and from the leucogranite. The molybdenite age spectrum overlaps those of zircon and indicates protracted or episodic hydrothermal activity, interpreted by Stein *et al.* (2004) as discrete deformation episodes and molybdenite deposition.

Mineralization at Malanjkhand occurs as an arcshaped, 1.8 km-long and N-S oriented quartz reef, containing chalcopyrite-pyrite mineralization. The granitoid enveloping the mineralized reef is less mineralized with sulfide-rich quartz and quartzo-feldspathic veins and

stringers in the vicinity of the reef. In the mine pit, the granitoid body is conspicuously enriched with pink Kfeldspar, commonly referred to as "pink granitoid", if compared to the gray color of the rest part of the pluton, which are devoid of any ore mineral and low in abundance of K-feldspar. The average width of the quartz reef (70 m) indicates extensive mobilization of silica though a major fracture zone and represents a unique feature in granitoid-hosted copper deposits worldwide. Panigrahi et al. (1991), on the basis of mode of occurrence, categorized the ores into four types: (i) the reef ore, which constitutes the bulk of the Cu mineralization where ore minerals are dominantly associated with quartz and subordinately K-feldspar; (ii) stringer ore; (iii) pegmatoidal ore; and (iv) disseminated ore. These last three categories occur within the enclosing pink granitoid where ore minerals are intimately associated with quartz, K-feldspar, chlorite, biotite, and epidote (Fig. 1). The four types of ores can be ascribed to a common paragenetic sequence (Panigrahi and Mookherjee, 1997). Here we address only the biotite, chlorite and epidote paragenetic sequence in detail; the complete sequence being reported in Table 1. It would be worth reiterating that the quartzsulfide ore assemblages at Malanjkhand are devoid of pyrrhotite and that there is no occurrence of anhydrite anywhere in the deposit.

Chlorite resulted from the alteration of biotite ( $\pm$ hornblende) and deposition in discrete domains from a hydrothermal fluid. Similarly, epidote is the product of hydrothermal alteration of plagioclase and breakdown of hornblende. However, in the ore zone epidote is very much recurrent in medium to fine grained varieties intimately associated with chalcopyrite. Fluorite in the mineralized part of the granitoid is mostly confined to cleavage spaces of biotite or as rims around biotite and formed as a result of the F<sup>-</sup> ion released from biotite. Fluorite rimming chalcopyrite (Fig. 1f) indicates later precipitation.

On the basis of similar mineralogy, fluid composition and a common paragenetic sequence, Panigrahi and Mookherjee (1997) suggested that mineralization at Malanjkhand deposit resulted from a single episode of hydrothermal activity. However, Bhargava and Pal (1999) suggested that the mineralized reef and veins/stringers in the granitoid represent two different stages of quartz deposition. Stein et al. (2004) considered there were several episodes of fracturing and molybdenite deposition. The issue of single versus multiple stages of mineralization is yet to be clarified. Previous fluid inclusion studies have been performed by Jairath and Sharma (1986), Ramanathan et al. (1990) and Panigrahi and Mookherjee (1997). Jairath and Sharma (1986) inferred a CO<sub>2</sub>bearing hydrothermal fluid, with temperatures ranging from 210 to 470°C containing appreciable amount of Na and K. Boiling at 370°C likely caused precipitation of

Minerals	Pre-ore stage (wall rock)	ry ore stage	Secondary ore stage	
		Early ferrous stage	Main chalcopyrite stage	Supergene oxidation and sulfide enrichment
		Oxide stage	Sulfide stage	
Quartz				•
Micro.		(?)		
Plag.				
Biotite				
Chlorite		(?)	<b>— — — —</b> (?)	
Epidote			(?)	
Calcite			—	
Fluorite				
Mt				
Hm				
Py Cr			_	
Ср МЪ			- (2)	
Sn			(.)	
Bn				
Dø			—	
Cc				
Cv				_
Dj				
Ču				
Tn				
Df				
Mal.				_
Nat Cu				

Table 1. Paragenetic sequence of the observed ore-silicate mineral assemblage modified after Panigrahi and Mookherjee (1997)

Micro, Micrcline; Plag, plagioclase; Mt, magnetite; Hm, hematite; Py, pyrite; Cp, chalcopyrite; Mb, molybdenite; Sp, sphalerite; Bn, bornite; Dg, digenite; Cc, chalcocite; Cv, covellite; Dj, djurleite; Cu, cuprite; Tn, tenorite; Df, delafossite; Mal, malachite; Nat Cu, native copper.

the ore, with a later separation between a CO<sub>2</sub>-rich fluid of low salinity and a more saline fluid containing less CO<sub>2</sub> (Jairath and Sharma, 1986). Based on the occurrence of K-feldspar, the absence of pyrrhotite and primary bornite, and considering pyrite-magnetite-chalcopyrite and hematite in the ore assemblages, they predicted  $\log f_{O_2}$  of -30.2 to -34.4,  $\log f_{S_2}$  of *f* -8.8 to 11.6, pH of 4.5-6.5 and pressures from 225 to 440 bars during ore deposition. Using temperature-salinity plots, Panigrahi and Mookherjee (1997) concluded that the mineralization was brought about by a mixture of two fluids: A hightemperature (~375°C) and low-saline (4 to 8 wt.% NaCl equivalent) fluid, containing appreciable amounts of CO<sub>2</sub> and sulfur (from now on referred to as "F1"); and a lowtemperature (180-200°C), moderately saline (20 to 24 wt.% NaCl equivalent) metal-rich fluid (F<sub>2</sub>). They also suggested that F2 was the dominant fluid component and

was derived from the main phase of the Malanjkhand granitoid, the coarse grained granodiorite-tonalite exposed in the mine pit and its surroundings (Panigrahi et al., 1993, 2004). A minor phase of leucogranite, whose temporal relationship with the main phase is unclear as of yet, is exposed in the ore zone vicinity at Malanjkhand. Studying fluid inclusion on the leucogranite occurring in close proximity of the ore zone, Naik (2006) suggested that the F1 fluid component could have been derived from the leucogranite. However, the exact derivation mechanism of fluid from the source has yet to be worked out. Panigrahi and Mookherjee (1997) inferred a two-stage evolution of the ore fluid: First, a mixing of the two fluid components leading to the deposition of ore minerals, and a later separation of the carbonic component (preserved as pure CO<sub>2</sub> inclusions) resulting in the observed increase in salinity of the aqueous component.



Fig. 2. Classification of biotite from the mineralized Malanjkhand granitoid on mica discrimination diagram of Tischendorf et al. (1997) with IMA approved names.

Bhargava and Pal (1999) presented a sketch summarizing their interpretation of hydrothermal alteration at Malanjkhand. They delineated patches of potassic, biotitic and chloritic alterations within the mineralized granite in the plan view of the mine pit. It should be noted that there are no separate potassic and biotite alteration zones in porphyry deposits. Besides, the absence of porphyry-type alteration zones was previously discussed and debated (Sarkar *et al.*, 1996; Panigrahi and Mookherjee, 1997, 1998). Although the present work emphasizes on reconstructing the hydrothermal environment, spatial reference of our samples will be furnished with respect to the potassic, biotite and chloritic alterations of Bhargava and Pal (1999) in order to further examine the proposition of such alteration zones.

# **ANALYTICAL METHODS**

Thin polished sections were prepared for routine optical microscopy and EPMA. Assemblages of chlorite + quartz, chlorite + magnetite, chlorite + pyrite and chlorite + chalcopyrite were selected for electron microprobe analysis. Similarly, biotite-bearing sub-assemblages from biotite  $\pm$  magnetite  $\pm$  pyrite  $\pm$  chalcopyrite assemblages and epidote in close spatial association with ore minerals from the vein ore and disseminated in the host granitoid were also analyzed. Major element compositions of biotite and chlorite were determined with a Cameca SX-50 at the University of Tennessee at Knoxville. Raw data were collected using wavelength dispersive techniques and



Fig. 3. Plots of  $X_{Mg}$  vs. wt.% of SiO<sub>2</sub>, TiO<sub>2</sub>, FeO, MnO, F, and Cl of biotite from different parts of the mine pit. Symbols ( $\triangle$ ), ( $\Box$ ) and ( $\bigcirc$ ) represent potassic zone, chloritic zone and biotite zone of Bhargava and Pal (1999) respectively.

corrected with the Cameca PAP procedure. An accelerating voltage of 15 kV, a beam current of 20 nA, a beam size of 5  $\mu$ m and 20 second counting time were used for all elements. Calibration standards were as follows: wollastonite (Si, Ca), orthoclase (K), albite (Na), spinel (Al, Mg), hematite (Fe), rutile (Ti), rhodonite (Mn), topaz (F), and sodalite (Cl). Epidote analyses have been taken from Panigrahi (1992, unpublished data), analyzed using a JEOL 8600 M EPMA. The reported operating conditions were 15 kV of accelerating voltage with a beam current of 15 nA. Biotite chemical compositions obtained by EPMA (Table 2) were processed using the MICA+ program of Yavuz (2003) which provides standard classification and discrimination plots and calculates temperature, fugacities of oxygen and halogen species using existing formulations.

#### RESULTS

# Mineral chemistry of biotite, chlorite and epidote

Biotite from the mineralized granitoid was analyzed to study the possible chemical variation in spatial reference to the alteration zones of Bhargava and Pal (1999)

Table 2. Electron microprobe analysis of biotites from Malanjkhand deposit. The terms "Potassic", "Chlorite" and "Biotite" refer to samples from these zones identified by Bahrgava and Pal (1999) in the mineralized Malanjkhand granitoid

	-				Date							Chlori	
					Pola	assic zone						Chiori	te zone
	004/2-12	004/2-12	004/2-12	304	304	304	304	304	304	304	304	3116	3116
SiO <sub>2</sub>	36.81	36.68	36.25	34.81	35.19	36.88	36.91	37.29	37.15	36.92	36.42	34.51	36.99
TiO <sub>2</sub>	0.78	1.60	1.43	1.18	1.22	1.41	1.35	1.30	1.41	1.60	1.51	1.03	1.52
$Al_2O_3$	14.41	14.49	14.40	17.76	17.58	15.10	15.06	15.03	15.34	15.17	15.02	15.49	14.86
MgO	12.24	10.97	11.36	13.06	11.95	12.39	12.51	12.77	12.36	11.91	12.39	14.64	12.61
CaO	0.04	0.03	0.05	0.08	0.08	0.01	0.02	0.00	0.01	0.00	0.03	0.02	0.00
MnO	0.18	0.13	0.19	0.23	0.18	0.25	0.27	0.23	0.23	0.27	0.23	0.31	0.26
FeO(t)	19.84	21.03	20.82	18.02	16.91	18.09	19.02	18.57	18.45	18.76	18.62	19.01	18.46
Na <sub>2</sub> O	0.04	0.07	0.08	0.06	0.05	0.05	0.06	0.08	0.06	0.09	0.04	0.05	0.09
$K_2O$	9.80	9.50	9.36	8.59	9.34	9.86	9.92	10.11	9.99	10.06	9.94	6.89	9.85
$H_2O$	3.54	3.45	3.58	3.88	3.80	3.87	3.77	3.83	3.78	3.80	3.76	3.60	3.48
F	0.54	0.70	0.38	0.00	0.09	0.00	0.27	0.18	0.27	0.18	0.20	0.47	0.86
Cl	0.26	0.30	0.30	0.09	0.07	0.10	0.09	0.08	0.08	0.08	0.09	0.02	0.08
Total	98.45	98.94	98.20	97.76	96.44	97.98	99.25	99.48	99.12	98.85	98.24	96.03	99.04

	Chlorite zone											
-	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520
SiO <sub>2</sub>	37.22	36.55	37.34	36.92	36.68	36.74	37.35	37.12	36.86	37.48	37.60	37.48
TiO <sub>2</sub>	1.49	1.28	0.79	1.16	1.14	1.26	1.42	1.32	1.40	1.42	1.48	1.39
$Al_2O_3$	14.78	14.77	14.59	14.60	14.37	14.63	14.83	14.50	14.66	14.84	15.01	15.01
MgO	12.27	11.98	14.16	12.34	11.50	11.97	12.35	12.44	12.50	12.08	12.38	12.22
CaO	0.04	0.07	0.01	0.01	0.02	0.03	0.02	0.01	0.06	0.03	0.03	0.06
MnO	0.16	0.19	0.16	0.20	0.22	0.15	0.20	0.22	0.20	0.22	0.15	0.17
FeO(t)	18.89	19.24	17.92	18.76	19.19	18.92	19.33	19.50	19.70	18.84	19.05	19.76
Na <sub>2</sub> O	0.08	0.13	0.02	0.07	0.07	0.04	0.04	0.04	0.07	0.04	0.05	0.07
K <sub>2</sub> O	9.94	9.78	9.65	9.82	9.98	9.51	9.68	9.74	9.69	10.05	9.84	9.67
$H_2O$	3.57	3.51	3.49	3.46	3.45	3.32	3.82	3.65	3.60	3.62	3.75	3.54
F	0.72	0.73	0.92	0.87	0.78	1.11	0.22	0.52	0.65	0.63	0.42	0.86
Cl	0.02	0.02	0.02	0.00	0.02	0.01	0.02	0.02	0.00	0.00	0.01	0.02
Total	99.16	98.23	99.08	98.21	97.43	97.70	99.27	99.10	99.41	99.23	99.75	100.24

(Table 2). Features in the mine pit and petrography of the mineralized granitoid do not provide any clue on the existence of such zones (Sarkar *et al.*, 1996; Panigrahi and Mookherjee, 1997, 1998). Biotite from the Malanjkhand deposit is classified using the classification scheme of Foster (1960) and Tischendorf *et al.* (1997). In the (Al<sup>VI</sup> + Fe<sup>+3</sup> + Ti)–(Fe<sup>+2</sup> + Mn<sup>+2</sup>)–Mg triangular discrimination diagram of Foster (1960), biotite occupies the Mgbiotite field. Similarly, on the "mgli" (Mg + Li) versus "feal" (Fe<sub>Tot</sub> + Mn + Ti–Al<sup>VI</sup>) discrimination diagram, the samples fall into the "ferroan phlogophite" (Mg Biotite) field (Fig. 2). Biotite from the Malanjkhand deposit shows more Fe-rich nature than biotite from porphyry deposits (Beane, 1974).

Mole fraction of Mg in the octahedral site of biotite  $(X_{Mg})$  is one of the most significant parameters that distinguish least altered and altered biotites (Selby and Nesbitt, 2000). Our analytical data on biotite in samples from mineralized granitoid corresponding to potassic, biotite and chlorite alteration zones of Bhargava and Pal

(1999) are plotted on  $X_{Mg}$  versus SiO<sub>2</sub>, TiO<sub>2</sub>, FeO(total), MnO, F and Cl variation diagrams (Fig. 3). The lack of distinction between biotites from different alteration zones of Bhargava and Pal (1999) is clearly discernible from the plots. There is a negative correlation between FeO and  $X_{Mg}$ , whereas SiO<sub>2</sub>, TiO<sub>2</sub>, MnO, F and Cl do not exhibit any correlation with  $X_{Mg}$  (Figs. 3a–f) in general.

Plots of  $X_{Mg}$  versus F and Cl for biotite from Malanjkhand fail to give any significant correlation as seen in Figs. 3e and f. Thus, the lack of correlation between Mg–Cl indicates that the composition of biotite at the Malanjkhand deposit was modified by a low-temperature hydrothermal fluid, which limited the exchange of ions in the octahedral site compared to those in the hydroxyl site.

Selby and Nesbitt (2000) observed that biotite from alteration zones in porphyry copper deposits display higher molecular ratios of Mg/Fe than typical igneous biotite. This relationship is well observed when the ferromagnesian biotite composition is plotted on the Pro-

	Chlorite zone											
	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520
SiO <sub>2</sub>	37.52	37.36	37.52	37.13	37.28	37.10	37.13	35.76	37.40	36.95	38.49	38.86
TiO <sub>2</sub>	1.38	1.44	1.45	1.38	1.43	1.10	1.41	1.18	1.24	1.34	0.91	0.72
$Al_2O_3$	14.92	14.83	14.96	14.96	14.75	14.43	14.63	14.75	13.95	14.53	13.24	12.83
MgO	12.56	11.34	11.10	11.92	11.63	12.72	11.67	12.83	12.99	12.09	14.83	15.57
CaO	0.02	0.07	0.05	0.02	0.02	0.04	0.01	0.10	0.01	0.00	0.02	0.05
MnO	0.18	0.18	0.17	0.18	0.16	0.20	0.19	0.21	0.22	0.16	0.17	0.15
FeO(t)	19.29	19.64	19.81	19.38	19.28	18.77	19.18	19.78	18.51	18.58	17.29	16.25
Na <sub>2</sub> O	0.07	0.09	0.12	0.06	0.08	0.02	0.09	0.04	0.05	0.10	0.06	0.05
$K_2O$	10.02	9.84	9.83	9.96	10.22	9.91	10.02	8.67	10.06	9.88	9.97	9.83
$H_2O$	3.58	3.69	3.74	3.71	3.59	3.74	3.66	3.68	3.47	3.50	3.51	3.25
F	0.78	0.43	0.35	0.41	0.64	0.31	0.46	0.34	0.88	0.76	0.92	1.47
Cl	0.03	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.01
Total	100.33	98.91	99.12	99.14	99.09	98.34	98.47	97.34	98.78	97.89	99.43	99.03

		(	Chlorite zon	e		Biotite zone						
-	001/520	001/520	001/520	001/520	001/520	211	211	211	211	211	211	
SiO <sub>2</sub>	36.62	36.70	37.08	37.10	36.88	36.93	36.91	36.98	36.39	36.67	36.27	
TiO <sub>2</sub>	1.36	1.21	1.47	1.58	1.42	1.79	1.74	1.81	1.72	1.62	1.65	
$Al_2O_3$	14.57	14.35	14.78	14.66	14.71	15.43	15.49	156.46	15.24	15.21	15.47	
MgO	11.98	13.61	12.61	12.39	12.43	11.31	11.70	12.11	11.40	11.91	11.76	
CaO	0.03	0.03	0.00	0.01	0.01	0.05	0.06	0.03	0.05	0.00	0.04	
MnO	0.12	0.15	0.23	0.18	0.22	0.31	0.28	0.33	0.25	0.27	0.27	
FeO(t)	18.53	17.46	18.76	19.00	19.12	18.84	18.67	18.52	18.46	18.58	18.27	
$Na_2O$	0.07	0.06	0.04	0.07	0.06	0.11	0.10	0.09	0.09	0.05	0.07	
K <sub>2</sub> O	9.91	9.97	9.72	9.87	9.93	10.01	10.04	9.94	9.68	9.94	9.72	
H <sub>2</sub> O	3.50	3.42	3.57	3.47	3.55	3.79	3.69	3.72	3.84	3.67	3.59	
F	0.71	0.94	0.72	0.91	0.72	0.20	0.44	0.41	0.00	0.44	0.55	
Cl	0.02	0.03	0.01	0.02	0.02	0.07	0.07	0.07	0.04	0.04	0.06	
Total	97.42	97.93	98.98	99.24	99.07	98.83	99.18	99.47	97.17	98.39	97.70	

ton-deficient oxyannite-annite-phlogopite ternary diagrams of Beane (1974). Biotite from the Malanjkhand deposit has intermediate chemistry between primary biotite and those from potassic alteration of porphyry deposits. In the chemical classification plot of Nachit *et al.* (1985), biotite from the Malanjkhand deposit occupies the "re-equilibrated" primary biotite field (Fig. 4). This re-equilibrated nature is also reflected in the lack of proper correlation of  $X_{Mg}$  and F/Cl in Figs. 3e and f.

Figures 5a and b show the range of log(  $f_{\rm H_2O}/f_{\rm HF}$ ); log ( $f_{\rm H_2O}/f_{\rm HCl}$ ), and log ( $f_{\rm HF}/f_{\rm HCl}$ ) ratios in the fluid from biotite chemistry for the Malanjkhand deposit. The plots show the fields of biotite mainly from potassic and phyllic alteration zones in a large number of porphyry copper deposits of the world (Selby and Nesbitt, 2000). Biotite analyses from the mineralized granitoid at Malanjkhand clearly plot outside the fields demarcated for porphyry copper deposits. Selby and Nebitt (2000) ascribed the variation in the parameters amongst porphyry deposits to differences in the processes of magmatic crystallization and exsolution of fluid from host granitoids. On that

premise, the figure indicates fundamental differences of crystallization evolution of the Malanjkhand pluton compared to host granitoids in porphyry deposits.

One of the fundamental tenets of the modern porphyry Cu (Mo–Au) model is that ore fluids are relatively oxidized, with O<sub>2</sub> fugacity ranging between the nickel-nickel oxide (Ni–NiO) and the hematite-magnetite (HM) buffer (e.g., Burnham and Ohmoto, 1980). Malanjkhand biotite samples, plotted on the ternary Fe<sup>3+</sup>–Fe<sup>2+</sup>–Mg diagram of Wones and Eugster (1965) as is shown in Fig. 6, indicate that a lower oxidation state occurred during mineralization, with  $f_{O_2}$  from quartz-fayalite-magnetite (QFM) to Ni–NiO buffer.

The temperature of re-equilibration between biotite and the hydrothermal fluid has been calculated using the Mg/Fe ratio (Beane, 1974) and ranges from 236 to 384°C. The temperature distribution is centered at 280–300°C (Fig. 7). The observed range is lower than the temperature range of potassic alteration (350 to 600°C) in most porphyry copper deposits worldwide (Beane, 1974; Seedorf *et al.*, 2005).



Fig. 4. Re-equilibrated nature of biotite from the mineralized Malanjkhand granitoid as revealed from the  $TiO_2$ -FeO<sup>total</sup>-MgO triangular plot (after Nachit et al., 1985).

One of the objectives leading to the analysis of chlorite mineral chemistry was to examine the spatial variability of chlorite composition and retrieved parameters *vis-àvis* the different alteration zones deciphered by Bhargava and Pal (1999). Textures of analyzed chlorites (Table 3) are illustrated in Fig. 1: (i) massive grains, mostly resulting from complete or partial chloritization of biotite (Figs. 1b and f), (ii) medium-size grains associated with magnetite, magnetite + pyrite or pyrite + chalcopyrite aggregates (Fig. 1d) and (iii) extremely fine-grained aggregates associated with magnetite as well as interwoven chalcopyrite (Figs. 1c and e). All these textures result from chlorites belonging to different generations.

The six-component solution model of Walshe (1986) has been adopted in the present study for the estimation of temperature, mole fractions and activities of the six components, fugacity of oxygen and sulfur at any given pressure. Walshe (1986) defined the six components as  $C1 - Mg_6Si_4O_{10}(OH)_8$ ,  $C2 - (Mg_5Al)(Si_3Al)O_{10}(OH)_8$ , C3 -  $(Fe_5Al)(Si_3Al)O_{10}(OH)_8$ , C4 -  $(Fe_5Fe^{3+})(Si_3Fe^{3+})$ .  $O_{10}(OH)_8, C5 - Al_4Si_4O_{10}(OH)_8, C6 - (Fe_4Fe^{3+}Al)(Si_3Al) \cdot$  $O_{11}(OH)_7$ . Temperatures obtained using the model are shown in Fig. 7. The empirical geothermometer of Cathelineau (1988) has also been used and depicetd in the same figure for comparison. Temperatures obtained from the empirical geothermometer are higher than those obtained with the thermodynamic model of Walshe (1986), although there is broad correspondence in the range of 260 to 300°C. Temperatures obtained from biotite using the formulation of Beane (1974) are comparable to



Fig. 5. Comparison of calculated log  $f_{H_2O}/(f_{HF})$ ;  $(f_{H_2O})/(f_{HCl})$ , and  $(f_{HF})/(f_{HCl})$  ratios of biotite from the mineralized Malanjkhand granitoid with those of important porphyry Cu deposits of the world considered by Selby and Nesbitt (2000).

values obtained from the chlorite geothermometers as shown in Fig. 7.

Textural relationship of epidote and chalcopyrite (Figs. 1f and g) indicates that epidote represents a fluid-present phase during hydrothermal precipitation of chalcopyrite.



Fig. 6. Plots of biotites composition from the Malanjkhand deposit on the  $Fe^{3+}-Fe^{2+}-Mg$  diagram of Wones and Eugster (1965). The  $Fe^{2+}$  and  $Fe^{3+}$  allocation is done following the calculation scheme of Dymek (1983).

Thus, equilibrium with the fluid at local scales may be assumed. Mineral chemistry of epidote is taken from Panigrahi (1992, unpublished data) in order to allow comparison with the newly obtained mineral chemistry from biotite and chlorite (this study). Temperature was calculated based on the Al–Fe substitution in the octahedral site of epidote using the solid solution model of Bird and Helgeson (1980). A temperature range of 147 to 333°C with a maximum in the range of 250 to 300°C (Table 4) was obtained and shown in Fig. 7. This temperature range is in close agreement with those obtained from biotite and chlorite thermometry and thus may represent equilibration temperature with the fluid.

# DISCUSSION

# Stability diagrams of ore minerals

The paragenetic sequence presented in Table 1 may now be crosschecked with the established phase diagrams involving the ore and silicate minerals to understand the evolution path of hydrothermal mineralizing fluid. The ore minerals considered are magnetite, pyrite, chalcopyrite, hematite and sphalerite and the silicate minerals are K-feldspar, biotite and chlorite. A number of standard oxidation and sulfidation reactions were considered at isothermal-isobaric conditions to depict the stability fields of ore and silicate minerals. Simple hydrolysis reactions involving the same mineral phases are also considered at isothermal-isobaric conditions in order to plot abridged activity diagrams at discrete intervals of fugacity of H<sub>2</sub>S, following Brimhall (1980). The temperatures chosen for the construction of these diagrams are those obtained from chlorite, biotite, and epidote. They broadly conform to the paleotemperatures furnished by the fluid inclusions (Panigrahi and Mookherjee, 1997).



Fig. 7. Temperature distribution of hydrothermal fluid calculated from biotite, chlorite and epidote compositions. Biotite temperatures are obtained using the formulation of Beane (1974); chlorite temperatures are calculated using the empirical and thermodynamic models of Cathelineau (1988) and Walshe (1986) respectively and labeled as (C) and (W). Epidote temperatures were obtained using the model of Bird and Helgeson (1980), by rearranging their equation-41 in the form of T (K) as a function of logK.

Because the effect of pressure is negligible on the equilibrium constants of the reactions considered, the phase diagrams shown can be taken as a representation of the broad pressure range of 1500 to 500 bars, which represents that of the mineralization (Panigrahi and Mookherjee, 1997). Figure 8 presents the log  $f_{O_2}$  versus log  $f_{S_2}$  diagram at 300, 250 and 200°C and is constructed to cover the range of temperatures obtained from chlorite, showing the phase boundaries and stability fields of ore minerals. Reactions considered for Fig. 8 are listed in Appendix. The reactions involving biotite-magnetite-K-feldspar (oxidation) and biotite-pyrite-K-feldspar (oxidation-sulfidation) were also considered assuming that the fluid was in equilibrium with these assemblages at 300°C. The ranges of log  $f_{O_2}$  obtained from biotite compositions for reaction-6 (Appendix) and those of  $\log f_{O_2}$  -log  $f_{S_2}$  values obtained for reaction-5 (Appendix) were considered. The two reactions involving biotites yield a region of intersection on the magnetite-pyrite boundary at 300°C. From Fig. 8, it may be suggested that the fluid initially deposited magnetite in the presence of biotite and K-feldspar anywhere in the region below the Py-Mt boundary (but above the Cp-Bn-Mt boundary since bornite is absent) and started to deposit pyrite with the increase of  $\log f_{S_2}$ . Textural relations between magnetite (I) and pyrite (I) support this hypothesis. Although

Table 3.	Electron microprobe	analyses of chlor	tes from the minerc	ilized Malanjkhand	granitoid. (terms as	s explained in Table 2)
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	Potassic zone											
-	004/2-12	004/2-12	004/2-12	004/2-12	004/2-12	004/2-12	004/2-12	004/2-12	004/2-12	304	304	
SiO <sub>2</sub>	28.49	25.80	27.33	27.07	28.06	27.76	28.11	28.57	28.42	27.81	28.00	
TiO <sub>2</sub>	0.04	0.03	0.01	0.04	0.02	0.04	0.00	0.01	0.05	0.02	0.04	
$Al_2O_3$	16.30	20.13	17.94	17.68	16.74	17.30	16.97	16.44	16.64	17.14	17.30	
MgO	17.63	15.39	17.19	17.11	17.86	17.80	17.86	18.06	17.34	18.55	17.68	
CaO	0.04	0.02	0.01	0.04	0.05	0.02	0.01	0.02	0.05	0.06	0.04	
MnO	0.30	0.39	0.41	0.35	0.31	0.28	0.36	0.33	0.38	0.40	0.30	
FeO (t)	24.55	26.47	24.73	25.52	24.59	24.30	24.36	24.14	24.50	22.68	22.32	
Na <sub>2</sub> O	0.02	0.02	0.02	0.01	0.00	0.03	0.02	0.01	0.02	0.00	0.01	
K <sub>2</sub> O	0.14	0.01	0.01	0.03	0.11	0.02	0.01	0.03	0.09	0.03	0.03	
$H_2O$	11.36	11.37	11.37	11.31	11.35	11.41	11.35	11.35	11.36	11.39	11.30	
F	0.07	0.00	0.06	0.11	0.14	0.02	0.20	0.21	0.09	0.00	0.00	
Cl	0.00	0.00	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.01	0.01	
Total	98.89	99.63	99.08	99.26	99.23	98.98	99.24	99.18	98.94	98.07	97.02	

P	otassic zo	ne				(	Chlorite zo	ne			
304	304	304	3116	3116	3116	3116	3116	3116	3116	3116	3116
27.56	27.31	27.44	27.69	27.97	28.03	27.35	27.89	27.41	27.30	27.56	28.31
0.03	0.08	0.05	0.06	0.03	0.05	0.00	0.07	0.00	0.03	0.03	0.08
17.796	17.63	17.54	17.62	17.46	17.16	18.01	17.50	17.76	17.89	17.77	17.53
17.73	18.15	17.83	18.41	18.20	18.11	17.99	18.31	18.37	17.55	17.78	17.97
0.08	0.04	0.02	0.08	0.15	0.04	0.03	0.01	0.03	0.02	0.03	0.04
0.34	0.34	0.39	0.41	0.40	0.38	0.41	0.36	0.36	0.39	0.45	0.42
22.65	23.31	23.36	22.53	22.45	22.42	23.68	22.69	23.27	23.38	22.95	22.94
0.01	0.05	0.03	0.02	0.05	0.00	0.02	0.00	0.00	0.02	0.03	0.02
0.18	0.19	0.17	0.15	0.34	0.53	0.07	0.34	0.11	0.10	0.22	0.50
11.37	11.39	11.36	11.37	11.36	11.30	11.44	11.42	11.43	11.31	11.30	11.47
0.00	0.00	0.00	0.13	0.16	0.18	0.00	0.05	0.00	0.07	0.16	0.00
0.02	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00
97.92	98.47	98.19	98.46	98.57	98.21	99.00	98.64	98.73	98.06	98.29	99.01
	P 304 27.56 0.03 17.796 17.73 0.08 0.34 22.65 0.01 0.18 11.37 0.00 0.02 97.92	Potassic zo           304         304           27.56         27.31           0.03         0.08           17.796         17.63           17.73         18.15           0.08         0.04           0.34         0.34           22.65         23.31           0.01         0.05           0.18         0.19           11.37         11.39           0.00         0.00           97.92         98.47	Potassic zone           304         304         304           27.56         27.31         27.44           0.03         0.08         0.05           17.796         17.63         17.54           17.73         18.15         17.83           0.08         0.04         0.02           0.34         0.34         0.39           22.65         23.31         23.36           0.01         0.05         0.03           0.18         0.19         0.17           11.37         11.39         11.36           0.00         0.00         0.01           97.92         98.47         98.19	Potassic zone           304         304         304         3116           27.56         27.31         27.44         27.69           0.03         0.08         0.05         0.06           17.796         17.63         17.54         17.62           17.73         18.15         17.83         18.41           0.08         0.04         0.02         0.08           0.34         0.34         0.39         0.41           22.65         23.31         23.36         22.53           0.01         0.05         0.03         0.02           0.18         0.19         0.17         0.15           11.37         11.39         11.36         11.37           0.00         0.00         0.01         0.00           97.92         98.47         98.19         98.46	Potassic zone         3116         3116         3116           304         304         304         3116         3116           27.56         27.31         27.44         27.69         27.97           0.03         0.08         0.05         0.06         0.03           17.796         17.63         17.54         17.62         17.46           17.73         18.15         17.83         18.41         18.20           0.08         0.04         0.02         0.08         0.15           0.34         0.34         0.39         0.41         0.40           22.65         23.31         23.36         22.53         22.45           0.01         0.05         0.03         0.02         0.05           0.18         0.19         0.17         0.15         0.34           11.37         11.39         11.36         11.37         11.36           0.00         0.00         0.01         0.00         0.00           97.92         98.47         98.19         98.46         98.57	Potassic zone         304         304         304         3116         3116         3116         3116           27.56         27.31         27.44         27.69         27.97         28.03           0.03         0.08         0.05         0.06         0.03         0.05           17.796         17.63         17.54         17.62         17.46         17.16           17.73         18.15         17.83         18.41         18.20         18.11           0.08         0.04         0.02         0.08         0.15         0.04           0.34         0.34         0.39         0.41         0.40         0.38           22.65         23.31         23.36         22.53         22.45         22.42           0.01         0.05         0.03         0.02         0.05         0.00           0.18         0.19         0.17         0.15         0.34         0.53           11.37         11.39         11.36         11.37         11.36         11.30           0.00         0.00         0.01         0.00         0.01         0.16         0.18           0.13         0.16         0.18         0.13         0.16 <t< td=""><td>Potassic zone         3116         311         317         313         313         313         313         313         313         313         313         313         313         31</td><td>Potassic zone         Chlorite zo           304         304         304         3116         314         31316         3131         31316</td><td><math display="block">\begin{array}{c c c c c c c c c c c c c c c c c c c </math></td><td>Potassic zone         Chlorite zone           304         304         304         3116         3130         314         313</td><td>Potassic zone         Chlorite zone           304         304         304         3116         3113         3130         31316</td></t<>	Potassic zone         3116         311         317         313         313         313         313         313         313         313         313         313         313         31	Potassic zone         Chlorite zo           304         304         304         3116         314         31316         3131         31316	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Potassic zone         Chlorite zone           304         304         304         3116         3130         314         313	Potassic zone         Chlorite zone           304         304         304         3116         3113         3130         31316

	Chlorite zone											
-	3116	3116	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520
SiO <sub>2</sub>	27.18	27.97	26.65	26.57	27.14	26.02	27.11	26.30	28.32	28.17	26.59	27.99
TiO <sub>2</sub>	0.03	0.03	0.00	0.03	0.05	0.03	0.01	0.03	0.00	0.01	0.00	0.01
$Al_2O_3$	18.33	17.46	18.24	18.34	18.48	18.12	17.61	19.09	16.77	16.77	20.31	16.20
MgO	17.55	18.20	14.98	14.94	16.36	15.74	16.83	15.37	18.12	17.65	17.06	18.39
CaO	0.06	0.15	0.06	0.05	0.00	0.02	0.04	0.03	0.05	0.01	0.05	0.02
MnO	0.41	0.40	0.29	0.37	0.24	0.30	0.33	0.34	0.29	0.31	0.28	0.35
FeO (t)	22.61	22.45	26.67	26.50	25.95	26.65	26.08	26.12	24.20	24.69	24.22	24.30
Na <sub>2</sub> O	0.11	0.05	0.04	0.04	0.01	0.02	0.04	0.00	0.02	0.03	0.05	0.03
K <sub>2</sub> O	0.12	0.34	0.24	0.18	0.05	0.03	0.03	0.05	0.06	0.01	0.06	0.04
$H_2O$	11.35	11.36	11.14	11.13	11.42	11.14	11.36	11.23	11.47	11.33	11.53	11.32
F	0.00	0.16	0.11	0.11	0.01	0.02	0.00	0.07	0.00	0.17	0.10	0.10
Cl	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.02	0.00	0.19
Total	97.74	98.57	98.43	98.26	99.71	98.10	99.45	98.63	99.31	99.15	100.25	98.75

this region is well within the chalcopyrite stability field, it did not precipitate until the activity ratio of Cu/Fe reached a favorable value for its deposition. This could have happened after that substantial amount of Fe was consumed during magnetite and pyrite deposition. Textural studies indicate that sphalerite was a minor phase during chalcopyrite deposition although there is no definite clue to the exact temperature range of co-precipita-

Tuble 5. (Commueu)	Table	e 3.	(continued)
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	Chlorite zone										
-	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/520	001/544
SiO <sub>2</sub>	27.79	28.34	28.37	27.65	27.81	28.09	27.75	28.00	28.23	28.35	25.93
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.04
$Al_2O_3$	17.41	16.50	17.92	18.05	15.92	16.63	16.44	16.07	16.14	16.26	17.29
MgO	17.83	17.55	17.33	16.90	17.91	16.83	17.34	18.26	18.18	17.84	9.10
CaO	0.03	0.04	0.06	0.04	0.03	0.05	0.01	0.00	0.04	0.02	0.04
MnO	0.34	0.34	0.22	0.30	0.27	0.31	0.33	0.26	0.30	0.31	0.33
FeO (t)	24.39	24.29	23.61	24.64	24.29	24.28	25.34	24.25	24.57	24.57	35.38
Na <sub>2</sub> O	0.02	0.04	0.06	0.00	0.00	0.04	0.01	0.01	0.02	0.01	0.03
K <sub>2</sub> O	0.04	0.06	0.10	0.03	0.08	0.06	0.01	0.00	0.01	0.01	0.02
H <sub>2</sub> O	11.38	11.36	11.47	11.35	11.18	11.19	11.28	11.27	11.32	11.31	10.73
F	0.16	0.03	0.08	0.16	0.10	0.15	0.04	0.10	0.14	0.16	0.13
Cl	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.03
Total	99.38	98.55	99.24	99.13	97.60	97.63	98.55	98.19	98.97	98.84	99.05

	Biotite zone											
-	001/544	001/544	001/544	001/544	001/544	001/544	211	211	211	211	211	211
SiO <sub>2</sub>	26.80	26.80	27.02	27.09	26.98	27.57	27.23	27.20	27.05	27.26	27.60	27.17
TiO <sub>2</sub>	0.09	0.57	0.63	0.93	0.84	0.56	0.04	0.03	0.03	0.07	0.03	0.03
$Al_2O_3$	15.73	15.61	15.90	16.04	15.43	16.68	18.54	18.58	18.32	18.28	18.24	18.21
MgO	10.94	10.60	10.36	9.74	10.13	10.41	18.82	18.73	18.85	18.13	18.70	18.54
CaO	0.06	0.26	0.30	0.46	0.45	0.45	0.03	0.01	0.03	0.04	0.03	0.24
MnO	0.34	0.32	0.30	0.29	0.33	0.40	0.27	0.32	0.34	0.33	0.37	0.32
FeO (t)	33.33	33.27	33.49	32.23	32.81	32.18	22.33	22.43	22.39	21.76	22.06	21.87
Na <sub>2</sub> O	0.00	0.03	0.00	0.02	0.02	0.03	0.00	0.01	0.00	0.00	0.00	0.00
K <sub>2</sub> O	0.03	0.26	0.31	0.72	0.60	0.77	0.03	0.01	0.06	0.05	0.06	0.06
$H_2O$	10.77	10.74	10.83	10.70	10.79	10.97	11.49	11.47	11.41	11.30	11.42	11.31
F	0.08	0.19	0.16	0.29	0.04	0.19	0.02	0.07	0.09	0.11	0.15	0.19
Cl	0.00	0.02	0.02	0.02	0.02	0.04	0.02	0.01	0.01	0.01	0.01	0.00
Total	98.15	98.67	99.30	98.52	98.45	100.26	98.83	98.85	98.57	97.34	98.67	97.92

tion. Panigrahi (1992) analyzed sphalerite coexisting with chalcopyrite from all ore types and obtained a  $X_{\text{FeS}}^{\text{Sp}}$  range of 0.0079 to 0.028. This range, when translated to  $\log f_{S_{2}}$ using the equation of Scott and Barnes (1971) under pyrite-stable conditions, provides ranges in  $\log f_{S_2}$  of -13.56 to -14.66, -10.5 to -11.7 and -8.15 to -9.25 at 200°, 250° and 300°C respectively. If chalcopyrite deposition started at 300°C, then the log  $f_{S_2}$  indicated from sphalerite is higher than the biotite-K-feldsparmagnetite-pyrite stage. Thus, an increase of log  $f_{S_2}$  after magnetite-I and a considerable increase of log  $f_{S_2}$  after pyrite-I in the fluid seems probable. Interestingly, the values of log  $f_{O_2}$  and log  $f_{S_2}$  obtained from chlorites at temperatures of both 300 and 250°C are higher and mostly correspond to sphalerite compositions if the range of sphalerite composition is broadly considered. The temperature and the range of  $\log f_{O_2}$  and  $\log f_{S_2}$  calculated from chlorite are plotted on Fig. 8 with phase boundaries in the Cu-Fe-S-O system at 300, 250 and 200°C in order to have a broad correspondence with the temperature

ranges from chlorites and fluid inclusions. Chlorite very much conforms to the log  $f_{O_2}$  and log  $f_{S_2}$  conditions during chalcopyrite deposition at the inferred temperature range. Two points gives a slightly higher temperature of 320°C, falling out of range from the 300°C stability regions. However, the biotite-magnetite-K-feldspar and the biotite-pyrite-K-feldspar reactions fail to have a common intersection region in the log  $f_{O_2}$  -log  $f_{S_2}$  space at temperatures lower than 300°C (not shown), indicating that biotite was out of equilibrium (with respect to octahedral cations) during the later stages of decreasing temperature. On the other hand, chlorite re-equilibrated under conditions of changing temperature and increasing  $\log f_{S_{2}}$ (Fig. 8). The observed textural features and mineral chemistry of chlorite indicates that there was an initial rise in  $\log f_{S_2}$ , followed by a decrease of temperature since chlorite of higher temperature (~300°C) registers log  $f_{S_2}$ conditions corresponding to the main chalcopyrite deposition, as indicated by sphalerite composition. In the reverse case (a decrease in temperature first followed by

Sample No.	Biotite zone					Chlorite zone							
	32/508	32/508	32/508	32/508		26/520	26/520	26/520	26/520	26/520			
SiO <sub>2</sub>	37.04	36.86	37.16	36.85		37.48	36.71	37.39	37.22	37.22			
$Al_2O_3$	22.28	21.91	20.2	19.65		22.09	21.95	22.2	21.19	21.53			
Fe <sub>2</sub> O <sub>3</sub>	15.97	14.15	17.02	16.69		14.69	13.61	13.89	14.35	13.39			
MnO	0.15	0.05	0.11	0.03		0	0.09	0.01	0.86	0.01			
MgO	0.07	0.67	0.26	0.05		0.13	0.27	0.14	0.17	0.14			
CaO	20.7	21.31	21.01	21.45		21.89	21.61	22.45	20.71	22.05			
Total	96.21	94.95	95.76	94.72		96.28	94.24	96.08	94.5	94.34			
Ps	0.31	0.29	0.35	0.35		0.3	0.28	0.29	0.3	0.28			
Cz	0.68	0.71	0.65	0.65		0.7	0.72	0.71	0.68	0.72			
Sigma	0.805	0.825	0.727	0.729		0.821	0.831	0.83	0.822	0.834			
logK	-1.932	-2.038	-1.601	-1.608		-2.014	-2.068	-2.066	-2.018	-2.085			
$T(^{\circ}C)$	293	272	333	283		277	267	267	276	264			

Table 4. Electron microprobe analysis of epidotes (in association with chalcopyrite) from the mineralized Malanjkhand granitoid. Data have been taken from Panigrahi (1992) and labeled as explained in Table 2

Sample No.	Potassic zone									
-	5/508	5/508	11/568	11/568	11/568	11/568	11/568	11/568	11/568	
SiO <sub>2</sub>	37.44	36.98	36.26	37.07	36.79	37.12	36.28	36.68	36.69	
$Al_2O_3$	22.76	23.07	21.5	21.67	20.58	20.68	21.63	20.19	22.03	
Fe <sub>2</sub> O <sub>3</sub>	12.61	11.98	13.09	13.65	15.03	15.69	14.11	16.36	13.24	
MnO	0	0.01	0.01	0.01	0.02	0	0.01	0.02	0	
MgO	0.27	0.17	0.26	0.14	0.08	0	0.29	0.17	0.22	
CaO	22.06	22.24	21.81	22.03	21.94	22.11	22	22.13	21.93	
Total	95.14	94.45	92.93	94.57	94.44	95.6	94.32	95.55	94.11	
Ps	0.26	0.25	0.28	0.29	0.32	0.33	0.29	0.34	0.28	
Cz	0.74	0.75	0.72	0.71	0.68	0.67	0.71	0.66	0.72	
Sigma	0.845	0.852	0.835	0.831	0.812	0.806	0.824	0.736	0.835	
logK	-2.153	-2.195	-2.091	-2.068	-1.969	-1.938	-2.03	-1.636	-2.093	
$T(^{\circ}\mathrm{C})$	252	244	263	267	285	292	274	147	262	

an increase of fugacity of sulfur) chlorite at 300°C would have registered lower sulfur fugacity than what is observed. To support this hypothesis, isothermal isobaric abridged activity diagrams (log(  $a_{Cu^*} / a_{H^+}$ ) versus  $\log(a_{\text{Fe}^{++}}/a_{\text{H}^{+}}^{2}))$  were constructed at different  $\log f_{\text{H}_2\text{S}}$ (-2.5 to -1.5). The values of log  $f_{\rm H_2S}$  were chosen following Brimhall (1980) and relevant hydrolysis reactions (reactions 10 to 15 in Appendix) were considered. The diagrams in Fig. 9 indicate that in order to move from a magnetite to magnetite + pyrite and then to a dominantly chalcopyrite stage with minor hematite, the log  $f_{H_2S}$  in the fluid must have increased during the decrease of temperature. Thus, Fig. 9 (a) represents the conditions of the early ferrous stage followed by (b) hematite precipitation and then (c) and (d) correspond to the chalcopyrite stage. On the basis of these observations and given the fact that magnetite and pyrite were in equilibrium for only a very short span, the paragenetic sequence has been alternatively labeled as "early oxide stage", "early sulfide stage" and late chalcopyrite stage (Table 1). Figure 9 further indicates that the  $\log(a_{Cu^*}/a_{H^+})$  remained restricted to chalcopyrite precipitation since primary bornite is rare.

## Hydrothermal fluid characteristics

Halogens have a potential role in the transportation of metals. Consequently, much attention has been focused in determining the fugacities of halogens in igneous and hydrothermal ore-forming systems (Gunow *et al.*, 1980; Loferski and Ayuso, 1995; Selby and Nesbitt, 2000; Coulson *et al.*, 2001; Munoz, 1984, 1992; van Middelaar and Keith, 1990). Copper is dominantly transported in solution in the form of chloride complexes (Candela and Holland, 1984; Ruaya, 1988; Xiao *et al.*, 1998). Burnham and Ohomoto (1980) explained that the acid alteration of wall-rock minerals (mostly K-feldspar) accompanying sulfide precipitation is due to the liberation of free HCl during the sulfidation of the metal-chloride complexes. At Malanjkhand, retention of fresh K-feldspar grains occurring with chalcopyrite (Fig. 1h) indicates that there



Fig. 8. Isothermal-isobaric (1 kb) fugacity diagram for the observed ore mineral assemblages. The elliptical area represents beginning of deposition and arrow indicates the inferred increase in the parameters for chalcopyrite deposition at 300 °C only. (A) The phase boundaries at 300, 250 and 200 °C are represented as solid, dashed and dotted lines. Phase names with prime and double prime are for 250 and 200 °C. The hatched area represents magnetite + biotite + pyrite + K-feldspar + fluid at 300 °C. The three differently hatched areas (vertical, oblique and horizontal) are for 300, 250 and 200 °C, respectively.

was no sharp fall in pH of the fluid accompanied by deposition of sulfides. In that case, either Cu was transported dominantly by ligands other that Cl<sup>-</sup> or some other factor inhibited the liberation of free HCl into solution. Therefore, the possibility of chloride complexing of copper is examined using the chemistry of biotite and chlorite in association with chalcopyrite. An attempt is also made to work out the possible change in chemical parameters in the fluid as a consequence of deposition of chalcopyrite.

Biotite is the only silicate in which OH-F-Cl exchanges as a function of temperature have been worked out and used extensively to constrain the fugacity ratios of halogens and water (Munoz, 1984). As previously discussed, we assume that the fluid equilibrated with biotite at 300°C, experiencing a rise in the fugacity of H<sub>2</sub>S. It is also assumed that fluid exchanged OH-F-Cl with biotite at lower temperature. Assuming the fluid to be in equilibrium with the biotite-K-feldspar-chalcopyrite assemblage, the following reaction has been considered at 300°C:

$$2KFe_3(Si_3Al)O_{10}(OH)_2 + 6Cu^+ + 12H_2S + 1.5O_2 = 2KalSi_3O_8 + 6CuFeS_2 + 6H^+ + 11H_2O.$$
 (1)

The equilibrium constant of the reaction at 300°C was calculated using SUPCRT92 program (Johnson *et al.*, 1992) and the results presented in Table 5. A pH of 4.5 to 6.5 suggested by Jairath and Sharma (1986) was considered. The range in Cl<sup>-</sup> ion activity is calculated from the biotite composition taking the homogeneous equilibrium reaction in the fluid in contact with biotite.



Fig. 9. Abridged activity diagrams of  $log(a_{Cu^+}/a_{H^+})$  vs.  $log(a_{Fe^{++}}/a_{H^+}^2)$  for the observed paragenetic sequence of deposition of ore minerals.

Table 5. Range in log( $a_{Cu^+}/a_{H^+}$ ) at different temperature obtained from the reaction involving biotite and chalcopyrite. The log  $K_{CuCl}$  value has been calculated using tables 2 and 4 of Ruaya (1988)

T°C	<i>a</i> <sub>H<sup>+</sup></sub>		a	a <sub>Cl</sub> -		$a_{{ m Cu}^*}$			log	K <sub>CuCl</sub>	
	max	min	max	min		max	min		max	min	
300	10 <sup>-4.7</sup>	10-6.7	$10^{0.94}$	10-4.52		10 <sup>-2.71</sup>	10 <sup>-10.43</sup>		-1.77	-14.95	-5.944

$$OH^{-} + HCl = Cl^{-} + H_2O.$$
 (2)

From the equilibrium constant of the above reaction:

$$\log a_{\mathrm{Cl}_{\mathrm{fluid}}^{-}} = \log K - \log \left( f_{\mathrm{H}_{2}\mathrm{O}} / f_{\mathrm{HCl}} \right)_{\mathrm{fluid}} + \log a_{\mathrm{OH}_{\mathrm{fluid}}^{-}}.$$
 (3)

In order to calculate the range in  $\log a_{Cl^{-}}$ , the last term on the right hand side can be replaced by pH. The second term on the right hand side of Eq. (2) is calculated from biotite composition. The resulting range of  $\log a_{\rm Cl^-}$  and  $\log[(a_{Cu^*})(a_{Cl^-})]$  values are given in Table 5 and compared to the formation constant value of CuCl (CuCl being the most dominant species under the observed  $f_{O_2}$ condition; Ruaya, 1988). The range of activity product encompasses the value of  $K_{CuCl}$  and hence chloride complexing of copper in the fluid is plausible (Ruaya, 1988). The activity products of Cu<sup>+</sup> and Cl<sup>-</sup> drop below the formation constant at higher pH and higher  $\log f_{H_0S}$ corresponding to the conditions at sulfide deposition (Brimhall, 1980). Because chlorite was inferred to have equilibrated with the ore-forming fluid, a reaction involving chalcopyrite and chlorite was also considered to constrain the activity of Cu<sup>+</sup> ion in the fluid:

$$Fe_5^{2+}Fe_2^{3+}Si_3O_{10}(OH)_8 + 7Cu^+ + 14H_2S + 1.25O_2 = 7CuFeS_2 + 3SiO_{2(aq.)} + 7H^+ + 14.5H_2O.$$
(4)

The equilibrium constant of the reaction was computed using SUPCRT92 and thermodynamic data from Walshe (1986). The log[ $(a_{Cu^*})(a_{Cl^-})$ ] ratio was calculated at different values of log  $f_{H_2S}$  for log  $f_{O_2}$  values imposed by the chlorite intra-crystalline oxidation reaction. The range of the activities of Cu<sup>+</sup> ion obtained at the lowest log  $f_{H_2S}$  and pH of 4.5 is 10<sup>-4.1</sup> to 10<sup>-6.2</sup>. The range of the activity product log[ $(a_{Cu^*})(a_{Cl^-})$ ] for the range of chlorite compositions ( $a_{Cl^-}$  values taken from biotite composition, see Table 5) varies from -3.15 to -10.72, which when compared with the  $K_{CuCl}$  value indicates that copper is likely to have been transported as CuCl complex. The calculated values of the activity product of Cu<sup>+</sup> and Cl<sup>-</sup> ions are consistent with chloride complexation in the fluid at low fugacity of H<sub>2</sub>S and low pH.

It becomes necessary to account for the absence of acid alteration of K-feldspar in the ores i.e., the factor that inhibits the fall of pH in the fluid on deposition of sulfides. As pointed out by McKibben and Williams (1989), a higher activity of  $Ca^{2+}$  in the fluid favors the formation of the  $CaCl_2$  that in turn inhibits the fall in pH. The intimate association of epidote with chalcopyrite in the mineralized part of the granitoid assumes significance in this context since epidote can exert some influence on the chemistry of the fluid (Caruso *et al.*, 1988). In the present case, the chalcopyrite-epidote assemblage has been taken into account to examine the influence in terms of  $Ca^{2+}$  activity in the fluid. The reaction considered at the representative temperature of 250°C to examine the possible effect of epidote on the fluid is:

$$3Ca_{2}FeAl_{2}Si_{3}O_{12}(OH) + 3Cu^{+} + H^{+} + 6H_{2}S$$
  
=2Ca\_{2}Al\_{3}Si\_{3}O\_{12}(OH) + 3CuFeS\_{2} + 2Ca^{++} + 3SiO\_{2} + 7H\_{2}O  
(5)

for which

$$\log(a_{Ca^{++}}/a_{H^{+}}^{2})_{\text{fluid}} = \frac{\left(3\log\left(\frac{a_{Cu^{+}}}{a_{H^{+}}}\right)_{\text{fluid}}\right) + \log K + 3\log a_{\text{ep}} + 6\log f_{H_2S} - 2\log a_{\text{clz}}}{2}}{2}$$
(6)

The log( $a_{Ca^{++}}/a_{H^+}^2$ ) values were calculated in the range of log[( $a_{Cu^+}$ )( $a_{H^+}$ )], log  $f_{H_2S}$  for the chalcopyrite deposition (shown in Fig. 9). Then, by using a pH from 0 to 3.5, the activity of the Ca<sup>2+</sup> ion was worked out. The range of  $a_{Cl^-}$  was calculated from biotite compositions at 250°C assuming re-equilibration of biotite with the fluid. The range in the activity product of the Ca<sup>2+</sup> and Cl<sup>-</sup> ions is compared with the association constant for CaCl<sub>2</sub> (Williams-Jones and Seward, 1989). The log( $a_{Ca^{++}}/a_{Cl^-}^2$ ) value ranges from -7.2 to 3.67 at 250 °C. This range is

only valid if higher values of pH (6.0 to 6.5) are considered, which is likely to be the case considering deposition of chalcopyrite. The several orders of magnitude variation in the parameters are a result of the combination of the ranges of activity ratio of Cu<sup>+</sup>/H<sup>+</sup> and fugacity of H<sub>2</sub>S considered in the calculation. It may therefore be surmised that epidote in the wall rock possibly played a role in increasing the Ca<sup>2+</sup> ion activity which in turn made the CuCl complex unstable and favored chalcopyrite precipitation at appropriate  $f_{H_2S}$  condition without significant free HCl being liberated into the solution. The reaction considered above also consumes H<sup>+</sup> and provides a mechanism by which the pH of the fluid would have remained high towards the deposition stage of chalcopyrite and explains the lack of acid alteration of K-feldspar. The dominance of CaCl<sub>2</sub> in the fluid was also indicated from freezing studies of fluid inclusions (Panigrahi, 1992). McKibben and Williams (1989) concluded an overall decrease in chloride ion activity in the solution due to high Ca<sup>2+</sup> content of geothermal brines. The overall decrease in chloride ion activity would have affected the efficacy of transport of metals by solution and triggered deposition. Panigrahi and Mookherjee (1997) earlier inferred that the pH of the fluid was buffered in the process of unmixing of the fluid into aqueous and carbonic components. Chemistry of epidote in association with chalcopyrite indicates that chloride ions liberated on deposition of sulfides were mostly bound as CaCl<sub>2</sub> ion pairs thus inhibiting a fall in pH. Late calcite veins indicate predominance of  $CO_3^{-2}$  ion in the fluid which further indicates that pH remained high in the fluid. The suggested mechanism of consumption of H<sup>+</sup>, high Ca<sup>2+</sup> activity and the absence of a phyllic alteration zone all indicate that the pH of hydrothermal fluid at Malanjkhand never fell to values required for phyllic and argillic alterations (see figure 5 of Seedorf et al., 2005).

The rise in fugacity of  $H_2S$  following magnetite precipitation as inferred from mineral paragenesis, stability conditions of phases and results of calculation on mineral fluid equilibria still needs to be explained. Panigrahi *et al.* (2002) suggested an increase mechanism for the fugacity of  $H_2S$  in the fluid through the following coupled oxidation-reduction reaction:

$$3Fe^{2+} + 1/4SO_4^{2-} + 3H_2O = Fe_3O_4 + 1/4HS^- + 5.75H^+.(7)$$

Such a reaction would require a sink for the H<sup>+</sup> ion, since for every mole of magnetite there would be 5.75 moles of H<sup>+</sup> ions released to the fluid that could cause acid alteration in the wall rock. Haynes *et al.* (1995) suggested an almost identical mechanism for formation of hematite through a coupled oxidation-reduction reaction and increase of H<sub>2</sub>S in the fluid as a result of fluid mixing in the Olympic Dam deposit. In the case of the Olympic Dam

deposit, a mixing of two fluids, one hotter (~250°C) and one cooler (~150°C), was observed. The cooler component was calculated to be  $SO_4^{2-}$  rich and the hotter component was interpreted to be Fe-rich. The hotter fluid was speculated to be magmatic in origin or deep-circulating meteoric water. The cooler fluid was assumed to be meteoric water evolving through interaction with the basalt adjacent to the deposit. The model proposed for the Olympic Dam deposit suggests that the Fe<sup>2+</sup> contained in the hotter fluid reduced the  $SO_4^{2-}$  of the cooler fluid. The Malanjkhand situation seems to have experienced the opposite, but with identical fluid thermal regimes. As speculated by Panigrahi and Mookherjee (1997) the S and CO<sub>2</sub>-bearing fluid that mixed at the fracture zone was the hotter component  $(F_1)$ . The source of the hotter component was also speculated to be of deeper origin. The cooler fluid might derive from the surrounding granitoid through prolonged fluid-rock interaction and enrichment of metals. Early magnetite deposition and attendant rise in fugacity of H<sub>2</sub>S at Malanjkhand is a strong possibility which could explain the chloritization of wall rock ferromagnesian minerals (biotite and hornblende) on the basis of reaction-9.

#### CONCLUSIONS

A comparison between the deposition mode of the Malanjkhand ore and that of porphyry-copper deposits can be made on the basis of information provided in the present work. Biotite from the mineralized part of the granitoid at Malanjkhand is more Fe-rich than potassic alteration zone in porphyry deposits (Beane, 1974; Hezarkhani, 2006). This may be tentatively attributed to a low-oxidation state (low Fe<sup>3+</sup>/Fe<sup>2+</sup>) of crystallization of the host granitoid (Seedorf et al., 2005). Temperature obtained from biotite narrowly overlaps the lowest values observed in classic porphyry-copper deposits (Beane, 1974), indicating that the magmatic fluid signature is missing at Malanjkhand. The lack of correlation of halogen and hydroxyl species with major octahedral ions also indicates re-equilibration at low temperatures (Fig. 7). Deviation from porphyry affinity is also observed for the fugacity ratio of halogen and hydroxyl species as well as lower oxidation state of the fluid (Figs. 5 and 6). Additionally, the absence of anhydrite in the hypogene ore assemblages is a major point of difference from porphyry systems (Audètat et al., 2004; Seedorf et al., 2005). Generalized morphology models of porphyry copper deposits available from older literature (see Misra, 2000; Tosdal and Richards, 2001) depict a central potassic core surrounded by a phyllic zone that coincides with the ore shell. The Malanjkhand deposits deviates from the generalized model by having the centrally located richly mineralized quartz reef surrounded by a thinly mineralized zone in the granitoid without a phyllic zone. The chemical composition of biotite, chlorite and epidote (Tables 2 and 3) do not display any difference amongst the alteration zones deciphered by Bhargava and Pal (1999), which do not strictly conform to porphyry-type alteration zones.

In summary, the Malanjkhand copper deposit represents an older granite-ore system where the ore fluid was at lower temperatures compared to magmatic fluiddominated ores. The situation is more akin to meteoric water-dominated, fracture-controlled epithermal systems in terms of the thermal regime of the fluid, chemistry and mineralogical environment in granitic terranes (Ellis, 1979). Dominance of epidote and K-feldspar in the host rock is in agreement with a higher pH during sulfide deposition stage (Figs. 1g and h).

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#### APPENDIX

Reactions considered for stability diagrams

- 1)  $FeS + 0.5S_2 = FeS_2$
- 2)  $3\text{FeS} + 2\text{O}_2 = \text{Fe}_3\text{O}_4 + 1.5\text{S}_2$
- 3)  $3\text{FeS}_2 = 2\text{O}_2 = \text{Fe}_3\text{O}_4 + 3\text{S}_2$
- 4)  $Fe_3O_4 + 0.5O_2 = 3Fe_2O_3$
- 5)  $Kfe_3Si_3AlO_{10}(OH)_2 + 3S_2 = KalSi_3O_8 + 3FeS_2 + H_2O + 1.5O_2$
- 6) Kfe<sub>3</sub>Si<sub>3</sub>AlO<sub>10</sub>(OH)<sub>2</sub> + 0.5O<sub>2</sub> = KalSi<sub>3</sub>O<sub>8</sub> + H<sub>2</sub>O + Fe<sub>3</sub>O<sub>4</sub>
- 7)  $5CuFeS_2 + S_2 = Cu_5FeS_4 + 4FeS_2$
- 8)  $Cu_5FeS_4 + 2Fe_2O_3 + 3S_2 = 5CuFeS_2 + 3O_2$
- 9)  $Cu_5FeS_4 + 4Fe_3O_4 + 9S_2 = 15CuFeS_2 + 8O_2$
- 10)  $\operatorname{Fe_3O_4} + 4\operatorname{H^+} + 2\operatorname{H_2S} = \operatorname{FeS_2} + 2\operatorname{Fe^{++}} + 4\operatorname{H_2O}$
- 11)  $\operatorname{Fe}_2O_3 + 2\operatorname{Cu}^+ + 4\operatorname{H}_2S = 2\operatorname{CuFeS}_2 + 2\operatorname{H}^+ + 3\operatorname{H}_2O$
- 12)  $\operatorname{Fe_3O_4} + 2\operatorname{Cu^+} + 4\operatorname{H_2S} = 2\operatorname{CuFeS_2} + \operatorname{Fe^{++}} + 4\operatorname{H_2O}$
- 13)  $3Cu_5FeS_4 + 4Fe^{++} + 2H_2S + O_2 = 7CuFeS_2 + 2H_2O + 8Cu^+$
- 14)  $2Cu_5FeS_4 + Fe^{++} + 8H^+ + 4H_2O = Fe_3O_4 + 10Cu^{++} + 8H_2S$ 15)  $Cu_5FeS_4 + GU^+ + 0.5FeS_4 + 5Cu^+ + 0.5Fe^{++} + 2U_2S_4$
- 15)  $Cu_5FeS_4 + 6H^+ = 0.5FeS_2 + 5Cu^+ + 0.5Fe^{++} + 3H_2S$

Equilibrium constants of these reactions were computed at chosen temperature and pressure using the SUPCRT92 package (Johnson et al., 1992) with the SLOP thermodynamic database.