Textures and compositions of cobalt pentlandite and cobaltian mackinawite from the Madan-Kudan copper deposit, Khetri Copper Belt, Rajasthan, India

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The Khetri Copper Belt (KCB), a part of the Proterozoic Delhi–Aravalli fold belt in western India, hosts several Cu deposits, which are known to contain considerable Au, Ag, Co and Ni. Although many Co-bearing phases have been reported from the KCB and adjacent areas, detailed textural and geochemical data are either unavailable or scant except for mackinawite. In this study, we describe the textures and compositions (determined by EPMA) of two very rare Co-rich phases, namely cobaltian mackinawite (containing up to 12.68 wt.% Co, 1.90 wt.% Ni and 2.52 wt.% Cu) and cobalt-pentlandite (containing up to 49.30 wt.% Co and 10.19 wt.% Ni), identified based on composition, from the Madan-Kudan deposit. To the best of our knowledge, neither cobalt-pentlandite nor such highly Co-rich mackinawite have previously been reported from this area. The common sulphide minerals viz. chalcopyrite, pyrrhotite and rare pyrite occur in chalcopyrite-pyrrhotite $\pm$ pyrite-magnetite-chlorite-blue amphibole (Cl-rich hastingsite-pargasite-sadanagaite) $\pm$ marialitic scapolite $\pm$ allanite $\pm$ uraninite veins in amphibole-bearing feldspathic quartzite and garnetiferous chlorite schist. Cobaltian mackinawite is invariably associated with chalcopyrite and occurs as exsolution and inclusion within chalcopyrite or outside, but at the contact of chalcopyrite. On the other hand, cobalt-pentlandite is invariably associated with pyrrhotite and shows similar textural relation with pyrrhotite as that of mackinawite with chalcopyrite. Mineralogically diverse undeformed sulphide veins comprising Cl-rich amphibole and locally Cl-rich marialitic scapolite suggests epigenetic hydrothermal mineralization involving Cl-rich saline fluid in the Madan-Kudan deposit. Transport of metals, derived from a mafic source rock with high intrinsic Ni:Co ratio, by Cl-rich fluid can suitably explain the high Co:Ni ratio of the studied ore minerals. Presence of such highly Co-rich phases and other circumstantial evidences, enumerated in this work, are consistent with variants of Fe oxide (–Cu–Au) (IOCG) style mineralization, at least for some stages of mineralization in the Madan-Kudan deposit.

Keywords. Cobalt pentlandite; cobaltian mackinawite; Madan-Kudan; Khetri; Rajasthan; hydrothermal; copper deposit; India.

1. Introduction

The Proterozoic Delhi–Aravalli fold belt in western India hosts several base metal sulphide deposits

(Sarkar and Gupta 2012 and references therein). Unlike Pb–Zn mineralization in many other deposits in the fold belt, the Khetri Copper Belt (KCB), situated in the northwestern part, is known

primarily for its copper mineralization. Besides Cu, the ore deposits in this belt are known to contain elevated concentrations of Au, U, REE, Fe, Ag, and Co (Knight *et al.* 2002; Sarkar and Gupta 2012). Previous workers have reported chalcopyrite, pyrrhotite, and pyrite as the main sulphide minerals along with minor cubanite, marcasite, molybdenite, sphalerite, pentlandite and mackinawite (Deb and Mukherjee 1969; Sarkar and Dasgupta 1980a, b; Mukherjee and Sen 1991; Sarkar and Gupta 2012) from the KCB. In addition to Ni–Co-bearing mackinawite and cobaltite, two very rare Co-rich phases namely danaite (Co-rich variety of arsenopyrite; Mallet 1881) and jaipurite (CoS; Middleton 1846; Nicol 1849) have also been reported from this region. However, there has been no further report of these minerals since their first reports (*op cit*). On the other hand, textural studies have been done on Co–Ni-bearing mackinawite from the Madan-Kudan, Kolihan and Chandmari deposits (Rao and Rao 1968; Deb and Mukherjee 1969; Mukherjee and Sen 1991). While quantitative chemical composition of Co–Ni-bearing mackinawite is available from the Kolihan–Chandmari deposits, such data from the Madan-Kudan deposit is limited and semi-quantitative (Deb and Mukherjee 1969). In this contribution, we describe the textures and compositions of two very rare Co-rich phases, namely Co-pentlandite and cobaltian mackinawite from the Madan-Kudan copper deposit and discuss their possible implications in mineralization.

2. Geological background

The KCB is the northern extension of the Proterozoic Aravalli–Delhi Fold Belt. The Mesoproterozoic Banded Gneissic Complex (BGC: ~3.3–3.0 Ga; Heron 1953; Gopalan *et al.* 1990; Roy and Kröner 1996; Wiedenbeck *et al.* 1996) with enclaves of isofacially metamorphosed mafic igneous and sedimentary rocks (Roy 1988; Roy and Jakhar 2002) and several Neoproterozoic (~2.8 to ~2.5 Ga; Choudhary *et al.* 1984; Tobisch *et al.* 1994; Wiedenbeck *et al.* 1996) granitoid intrusions form the basement for the younger Proterozoic volcano-sedimentary sequences of this fold belt (figure 1). The part of the Aravalli–Delhi fold belt that comprises Delhi Supergroup rocks is divided into two sub-belts namely the North Delhi Fold Belt (NDFB) and the South Delhi Fold Belt (SDFB; Sinha-Roy 1984). The KCB (figure 1b) is on the northwestern part of the NDFB and comprises

metamorphosed arenaceous, argillaceous, and calcareous sedimentary rocks associated with mafic volcanic rocks belonging to Alwar and Ajabgarh Group (Heron 1953; Das Gupta 1968; Sarkar and Dasgupta 1980a, b; Roy and Jakhar 2002) of the Delhi Supergroup.

The KCB (figure 1b) extends for about 80 km from Singhana (Jhunjhunu district) in the NE to Sangarve (Sikar district) in the SW. The copper belt is divided, physically and geographically, into the North Khetri Copper Belt (NKCB) and the South Khetri Copper Belt (SKCB) by the Kanti Fault (figure 1b; Gupta *et al.* 1998). The Madan-Kudan deposit is located in the NKCB. The basement of the meta-sedimentary units in the NKCB is represented by the ~1.82 Ga calc alkaline granitic rocks and 1.70 Ga albitized A-type granites (e.g., Gothara Granite, figure 2a; Kaur *et al.* 2007, 2009, 2011). The different rock types, exposed in and around the deposits of the NKCB, include mica schist/phyllite, quartzite, garnetiferous chlorite schist, banded amphibole-bearing quartzite and feldspathic quartzite (Sarkar and Gupta 2012). The rocks of NKCB are multiply deformed and poly-metamorphosed (e.g., Das Gupta 1968; Naha *et al.* 1988; Gupta *et al.* 1998). Two phases of regional metamorphism, namely M₁ and M₂ (Lal and Shukla 1975; Lal and Ackermann 1981; Gupta *et al.* 1998) are inferred to have taken place at 550±50°C and 550–650°C, respectively with pressure ranging from 300 to 500 MPa (e.g., Lal and Shukla 1975; Sarkar and Dasgupta 1980a, b; Lal and Ackermann 1981; Gupta *et al.* 1998). The last major metamorphic event has been dated at 950–910 Ma through chemical dating of monazite (Kaur *et al.* 2006; Pant *et al.* 2008). Previous workers have reported widespread post-metamorphic hydrothermal alterations (Roy Chowdhury and Das Gupta 1965; Kaur *et al.* 2012; Knight *et al.* 2002). Roy Chowdhury and Das Gupta (1965) reported Fe–Mg metasomatism, chloritization, biotitization, sericitization and silicification. Knight *et al.* (2002) demonstrated that the NKCB rocks have been overprinted by regionally pervasive calc-silicate and sodic alteration. More recent studies also demonstrate multiple stages of regional sodic alteration (Kaur *et al.* 2012, 2014).

3. Methodology

The samples, collected from the Madan-Kudan underground Cu mine are first studied in hand

Figure 1. Location of Khetri Copper Belt (KCB) in regional geological set-up of Aravalli–Delhi Fold Belt. Map-A shows the position of KCB in Aravalli–Delhi fold belt (redrawn from Roy 1988 and Roy and Jakhar 2002) and Map-B (redrawn from Kaur *et al.* 2009) shows the location of North and South Khetri Copper belt. The study area is a part of NKCB.

specimen and with optical microscope. The ore minerals were analyzed by Electron Probe Micro Analyzer (EPMA), at the Department of Geology and Geophysics, IIT Kharagpur. EPMA analysis was conducted on a CAMECA SX-100 machine equipped with four wavelength-dispersive

spectrometers (WDS). In the minerals, described here, elements other than Fe, S, Co, Ni, and Cu are all below detection limit. Therefore details of the analytical conditions for other elements are not given here. For all analyses, a 20 kV accelerating potential and 15 nA current is used.

Figure 2. (a) Location of Madan-Kudan and other copper deposits in NKC (redrawn from Geological Survey of India 1997). The map also shows the major rock types in and around the study area. (b) The cross section of Madan-Kudan deposit (redrawn from [Sarkar and Gupta 2012](#)) showing the lithounits and ore bodies. Note that ore bodies are not restricted to a single litho-unit.

Iron and sulphur were analyzed for 10s and Co, Ni, Cu for 20s. The background measurement time for Fe and S were 5s and for Co, Ni and Cu were 10s. The following standards were used for the analysis, pyrite (FeK α , SK α), and pure metals of Co (CoK α), Ni (NiK α), and Cu (CuK α).

4. Results

4.1 Host rocks and mode of occurrences of sulphides

Sulphide mineralization in the Madan-Kudan copper mine is hosted by quartzite/amphibole-bearing

Figure 3. Rock types from Madan-Kudan deposit. Note that all the rock types have been dissected by mineralogically different vein, e.g., (a) green amphibole vein, (b) chlorite vein, (c, d and f) sulphide-magnetite-chlorite-blue amphibole vein and (e) massive sulphide vein. Note the presence of colourless amphibole-bearing quartzite/quartzite fragments in the veins.

massive or banded quartzite (figures 1a, 3a and b) and garnetiferous chlorite schist (figure 3e). The quartzite in the study area is commonly feldspathic in nature comprising predominantly of quartz and albite. Amphibole-bearing quartzite consists of quartz, albite and amphibole along with minor chlorite and biotite. Optically colourless amphibole, namely cummingtonite-grunerite, is present as randomly oriented grains (figure 3b) in the quartz-albitic matrix in amphibole-bearing massive quartzite. On the other hand, the banded variety consists of alternate green-coloured magnesioferri-hornblende-rich and quartz-rich bands (figure 3a). Green amphiboles are randomly oriented

in amphibole rich bands. Colourless amphiboles are replaced by chlorite and blue-coloured amphibole, the latter compositionally belonging to hastingsite-pargasite-sadanagaite (figure 4a). In places, the colourless amphibole relicts have been found in chlorite-bearing veins. Similar replacement relation among colourless amphibole and blue amphibole is observed in the Kolihan and Chandmari deposit in the KCB (Baidya *et al.* 2017). Baidya *et al.* (2017) have also found that green amphibole (magnesioferri-hornblende), similar to Madan-Kudan deposit has been replaced by blue amphiboles (hastingsite-pargasite-sadanagaite). The garnetiferous chlorite schist is composed predominantly of quartz,

Figure 4. Microscopic images showing the relation between colourless amphibole and blue amphibole-chlorite and sulphide (a, b) and textures of Co-pentlandite and cobaltian mackinawite. Cobalt-pentlandite is present as inclusions of different shape in pyrrhotite (c, d and e), along the contact zone of pyrrhotite and other minerals (f) and as exsolved tabular/elongated oriented lamella in pyrrhotite (g). Cobaltian mackinawite is present as inclusion in chalcopyrite (h), as thin elongated vein (i and m), at contact zone between chalcopyrite and other minerals (j and k). Amp, Chp, Mag and Po in the microphotographs stands for amphibole, chalcopyrite, magnetite and pyrrhotite, respectively.

feldspar, garnet, amphibole, chlorite and biotite with accessory zircon, ilmenite and magnetite. Garnet occurs either in garnet±amphibole bands (figure 3e) or as disseminated porphyroblasts. The schistosity, defined by oriented chlorite and minor amount of biotite, locally warps around garnet porphyroblasts. In addition, chlorite and biotite, probably of new generation, replaces garnet along fractures and grain boundaries.

In amphibole-bearing quartzite and garnetiferous chlorite schist, sulphides occur mainly in the form of veins and stringers and locally as small pockets and patches (figure 3a–d). The veins commonly cut-across the metamorphic fabric of the rock and above-mentioned green amphibole band/layer/pocket. The blue amphibole is ubiquitously associated with sulphide veins/pockets (figure 4a and b), either as distinct grains or as replacement product of existing colourless and probably green amphiboles (*cf.* Baidya *et al.* 2017). The host rock is highly fractured and brecciated and in some cases the host rock fragments occur in the sulphide veins (figure 3c,f). The sulphide veins are mineralogically diverse (Sen 2015; Baidya *et al.* 2017). The Co-rich phases, described in this study are observed in chalcopyrite-pyrrhotite ± pyrite-magnetite-chlorite-blue amphibole (Cl-rich hastingsite-pargasite-sadanagaite) ± marialitic scapolite ± allanite ± uraninite veins (Sen 2015; Baidya *et al.* 2017). This mineralogical assemblage of the veins is consistently present in the study area, which implies that the formation of the individual sulphide minerals in the veins is not widely separated in time and space. Chalcopyrite and pyrrhotite, the two ubiquitous sulphide minerals in the veins have mutual straight boundary contact. Additionally, inclusions of chalcopyrite occur in pyrrhotite and vice versa. At places, partly corroded grains of pyrrhotite are embedded in chalcopyrite. All these textures collectively indicate a virtually single hydrothermal event of mineralization in which the ore mineral precipitation was largely synchronous. However, in some places chalcopyrite crystallization outlasted that of pyrrhotite and corroded existing pyrrhotite by a somewhat evolved/modified fluid of same parentage.

4.2 Textures of Co-rich sulphide phases

The highly Co-rich mineral (up to ~50 wt.% Co; see section on geochemistry), that we assign as cobalt pentlandite based on its composition (see

sections 5 and 6.1), is characterized by pinkish/creamy yellow colour in reflected plane polarized light and higher reflectance relative to both chalcopyrite and pyrrhotite. Polishing hardness is somewhat higher than chalcopyrite, but distinctly lower than pyrrhotite. Its scratching hardness is higher than that of chalcopyrite, but lower than that of pyrrhotite (see grain boundaries in figures 4f). The mineral is also anisotropic, unlike most common pentlandite *sensu stricto*. This mineral is invariably intimately associated with pyrrhotite. It is present as isolated euhedral to subhedral inclusions within pyrrhotite (figure 4c–e) as oriented flames within pyrrhotite (figure 4g) at the contact (but commonly inside pyrrhotite) of pyrrhotite with other minerals, viz., -chlorite, magnetite and chalcopyrite (figure 4f). The inclusions are of different shapes and sizes. Shape varies from elongated/tabular to almost equidimensional (compare figure 4c–e). The oriented flames are euhedral in shape and smaller in size relative to other grains with different mode of occurrences (figure 4g). This phase is fractured in places and seemed to have been replaced by another unidentified phase (figure 4e).

Mackinawite is pleochroic and anisotropic. In plane polarized reflected light the grains change its colour from grayish pink to pinkish gray. It has higher hardness relative to chalcopyrite and similar to that of pyrrhotite. Mackinawite is exclusively associated with chalcopyrite and present in different forms. It is present as thin lamella and streaks, long elongated (figure 4m) or small anhedral inclusions in chalcopyrite (figure 4h), and along microcracks in chalcopyrite (figure 4i). It also occurs outside, but at the contact of chalcopyrite with other minerals, viz., chlorite (figure 4j), quartz, magnetite (figure 4k) and pyrrhotite (figure 4l). At some places, it occurs onto some silicate veins or inclusions (chlorite and magnetite) in chalcopyrite as if the silicate phase acted as a growth surface for mackinawite (figure 4j and k). Irregular mackinawite, invading into chalcopyrite and pyrite from their contact, contains cobalt-pentlandite inclusions (figure 4l).

5. Compositions of Co-rich phases

The compositions of the highly Co-rich phase and mackinawite, obtained from EPMA, are given in tables 1 and 2, respectively. Both the minerals

Table 1. Chemical composition and calculated formula of Co-pentlandite.

Sample no.	Chemical composition					Formula based on 17 atoms				
	S	Fe	Co	Ni	Total	S	Fe	Co	Ni	$\sum$ metal
S4-G-old_1	32.53	8.98	48.93	9.41	100.67	7.961	1.262	6.516	1.258	9.04
S4-G-old_2	31.82	8.71	49.30	9.06	99.54	7.885	1.239	6.647	1.227	9.11
S4-G-old_3	32.07	8.86	49.09	9.41	100.14	7.893	1.252	6.574	1.265	9.09
S4-G-old_4	32.62	9.39	48.17	9.38	99.88	7.997	1.322	6.425	1.256	9.00
S4-G-old_5	32.81	11.60	45.38	9.65	99.92	8.033	1.631	6.045	1.291	8.97
S4-G-old_6	32.24	9.15	48.94	9.34	100.12	7.916	1.290	6.538	1.253	9.08
S4-G-old_7	32.19	8.46	48.83	9.07	99.21	7.980	1.204	6.587	1.228	9.02
S4-G-old_8	32.49	8.40	47.48	9.96	98.66	8.052	1.195	6.403	1.349	8.95
S4-G-old_9	32.51	8.89	49.24	8.95	100.25	7.969	1.251	6.568	1.199	9.02
S4-G-old_10	32.04	9.60	48.03	9.44	99.76	7.912	1.361	6.453	1.274	9.09
S4-G-old_11	32.39	9.63	47.85	9.30	99.80	7.968	1.360	6.405	1.250	9.02
S4-G-New_1	32.45	9.00	48.10	9.34	99.32	8.004	1.275	6.455	1.259	8.99
S4-G-New_2	32.18	8.63	47.56	9.34	98.08	8.031	1.237	6.458	1.274	8.97
S4-G-New_4	32.92	7.75	48.73	9.09	99.00	8.123	1.098	6.543	1.225	8.87
S4-G-New_6	32.67	9.56	47.16	10.01	100.11	8.016	1.347	6.296	1.342	8.99
S4-G-New_7	32.64	9.21	47.36	10.19	100.17	8.011	1.298	6.325	1.366	8.99
S4-G-New_8	32.71	9.29	47.45	9.81	100.00	8.031	1.310	6.339	1.316	8.97
S4-G-New_9	32.20	8.47	49.18	8.55	98.95	7.992	1.207	6.642	1.159	9.01
S4-G-New_10	32.46	8.59	48.87	9.47	99.81	7.979	1.212	6.536	1.272	9.02

Table 2. Chemical composition and calculated formula of cobaltian mackinawite.

Sample no.	Chemical composition						Formula based on S=1					
	S	Fe	Co	Ni	Cu	Total	S	Fe	Co	Ni	Cu	$\sum$ metal
S4-G_1	35.57	51.73	8.63	1.90	0.23	98.37	1.000	0.835	0.132	0.029	0.003	0.999
S4-G_2	35.21	49.15	12.49	0.91	0.58	98.34	1.000	0.802	0.193	0.014	0.008	1.017
S4-G_3	35.78	51.64	10.60	1.11	0.11	99.30	1.000	0.829	0.161	0.017	0.001	1.008
S4-G_4	34.79	46.93	8.52	1.36	6.63	98.24	1.000	0.775	0.133	0.021	0.096	1.025
S4-G_5	35.63	50.44	10.96	1.04	0.80	99.30	1.000	0.813	0.167	0.016	0.011	1.008
S4-G_6	35.38	49.93	10.89	1.07	1.11	99.17	1.000	0.810	0.167	0.017	0.016	1.010
S4-G-N_1	35.60	48.64	9.78	1.33	2.02	98.01	1.000	0.785	0.149	0.020	0.029	0.983
S4-G-N_2	35.88	49.04	10.35	1.03	2.52	99.40	1.000	0.785	0.157	0.016	0.035	0.993
S4-G-N_3	34.96	50.21	11.39	1.22	0.38	98.81	1.000	0.825	0.177	0.019	0.005	1.026
S4-G-N_4	35.87	49.14	12.68	0.77	0.21	99.72	1.000	0.787	0.192	0.012	0.003	0.994
S4-G-N_5	35.67	47.58	9.37	1.63	2.43	97.24	1.000	0.766	0.143	0.025	0.034	0.968
S4-G-N_6	33.80	41.76	5.56	1.07	12.64	95.24	1.000	0.709	0.090	0.017	0.189	1.005
S4-G-N_7	35.24	49.96	11.15	0.96	0.36	98.09	1.000	0.814	0.172	0.015	0.005	1.006
S4-G-N_8	35.76	49.73	11.20	1.00	0.43	98.94	1.000	0.799	0.170	0.015	0.006	0.990
S4-G-N_9	35.08	50.55	11.50	0.95	0.43	99.23	1.000	0.827	0.178	0.015	0.006	1.027
S4-G-N_10	35.44	49.91	11.42	0.94	0.56	98.82	1.000	0.809	0.175	0.014	0.008	1.006

yield an analytical total of ~ 100 wt.%. We have not observed any difference in the compositions of different textural types of the minerals. Cobalt pentlandite contains Fe in the range of 7.75 to 9.63 wt.%, Co in the range of 45.38–49.30 wt.% and Ni in the range of 8.55–10.19 wt.%. Copper, Zn and As are below detection limits. The mineral is sulphur deficient compared to total metal. The formula calculation is done based on 17 atoms (*cf.* Boradev *et al.* 2007) and the calculated

general formula is $(\text{Co, Ni, Fe})_{9.11-8.86}\text{S}_{7.88-8.05}$. The metal:sulphur ratios in calculated mineral formula are mostly $\sim 9:8$ with $<2\%$ deviation in each site ($\text{Me}_{9\pm 0.18}\text{S}_{8\pm 0.16}$) implying a stoichiometric composition with respect to Me_9S_8 , typical of pentlandite group minerals. Binary plots have been generated from the atoms per formula unit (apfu) of different metals. Cobalt shows negative correlation with Fe and Ni (figure 5a and b). Cobalt also shows strong negative correlation with Fe+Ni.

Figure 5. Binary plots showing the substitutions schemes in Co-pentlandite and cobaltian mackinawite. Note that, in Co-pentlandite, Co has negative correlation with Fe and Ni (a and b) and in cobaltian mackinawite, Co has good negative correlation with Ni (g) and moderately good correlation with Cu (h). In cobaltian mackinawite, Fe has bad correlation with Co and Ni and Cu (d, e and f).

Similarly Fe also shows strong negative correlation with Co+Ni. Pyrrhotite that hosts or is associated with this mineral at places contains high Co and Ni (4300–4800 ppm Co and 1100–1500 ppm Ni).

Mackinawite contains high concentrations of Co, Ni and Cu. Iron content varies from 41.76 to 51.73 wt.%, whereas Co and Ni contents vary from 5.56 to 12.68 wt.%, and 0.77 to 1.90 wt.%, respectively. Copper is detected in all grains and Cu content ranges mostly between 0.21 and 2.52 wt.% in large grains. Very high Cu content, up to 12.68 wt.%, measured in fine-grained inclusions in chalcopyrite may be due to contamination from the surrounding chalcopyrite. Formula calculation is done based on 1 anion. Calculated metal:sulphur ratio is $\sim 1:1$ in most cases. Neither Co nor Ni (apfu) shows any discernible correlation with Fe, whereas Cu shows a very weak negative correlation with these elements (see figure 5d–f). Cobalt and Ni content of host chalcopyrite is below detection limit.

6. Discussion

6.1 Khetri Co-rich phases in the context of global occurrences

Pentlandite, nominally $(\text{Fe}, \text{Ni})_9\text{S}_8$, can accommodate variable amounts of Co and Ni in its structure. Harris and Nickel (1972) classified pentlandites based on the Co contents in the structure. Pentlandite proper can have Co as high as 10 wt.%. Cobalt content for cobaltian pentlandite is ~ 12 –14 wt.%, whereas cobalt pentlandite contains more than 20 wt.% Co. Amongst the above Co-bearing pentlandite group minerals, cobalt pentlandite is a very rare Co-bearing sulphide mineral, which was first reported from Finland (Kuovo *et al.* 1959). Structurally, Co-pentlandite (end member composition is Co_9S_8) is similar to pentlandite, $(\text{Fe}, \text{Ni})_9\text{S}_8$, and there is complete solid solubility between them (Geller 1962). The metal:S ratio of the highly Co-rich phase identified in this study is $\sim 9:8$ resulting in a formula of $\sim (\text{Co}, \text{Ni}, \text{Fe})_9\text{S}_8$, which suggests that the mineral belongs to the pentlandite group. Based on the classification scheme of Harris and Nickel (1972), and reported compositions of Co-pentlandite from different parts of the world, we identify this mineral as Co-pentlandite. The Co-pentlandite that we report here is somewhat anisotropic. It may be noted that anisotropic, exsolved pentlandite in

pyrrhotite has been reported from Sudbury ore and from experimental studies (Francisi *et al.* 1976). Anomalous anisotropism in cubic pyrite is also not uncommon in literature (e.g., Stanton 1959; Gibbons 1967; Bayliss 1977; Murowchick 1992). We propose that our sample contains such an anomalously anisotropic Co-pentlandite. This is the first reported occurrence of Co-pentlandite from the Khetri region and perhaps from India. To the best of our knowledge, anisotropic Co-pentlandite has hitherto not been reported. It needs to be mentioned here that among the highly Co-rich phases, previously reported from this area, the one that is closest in composition to that of this Co-pentlandite is a Co-sulphide containing 64.64 wt.% Co and 35.36 wt.% S (by chemical analysis), first reported by Middleton (1846). He assigned this mineral to be a sulphuret/sub-sulphuret of cobalt occurring in association with iron pyrites (actually magnetic pyrrhotite based on composition given by Middleton 1846). Although Middleton (1846) proposed the mineral to be Co_2S , the mineral formula should actually be CoS based on chemical composition. Subsequently, this mineral was named as Syepoorite by Nicol (1849). Ross (1872) reported sulph-antimonial arsenide of cobalt from the Khetri ores, which he named as Jey-poorite. The mineral that Ross (1872) described is reported (*op cit*) to contain, in oxide percentage, 82 wt.% Co, 7 wt.% Sb, 6 wt.% As, and 5 wt.% S. Neither Middleton's result has been corroborated by later studies nor the mineral CoS , known as Syepoorite/Jeypoorite/Jaipurite in literature, has further been reported from the Khetri region. To the best of our knowledge, no detailed information is available on the physical, optical and chemical properties of Jaipurite from Khetri or other regions. It is possible that such a mineral exists in Khetri ore. However, we also do not entirely rule out the possibility that the Jaipurite reported from this region may actually be the anomalously pleochroic Co-pentlandite reported in our study.

Mackinawite, nominally $\text{Fe}_{(1+x)}\text{S}$ (where x is between 0 and 0.25), can incorporate Cu, Co and Ni (Deb and Mukherjee 1969; Vaughan 1969; Clark 1970; Sarkar 1971; Mukherjee 1976; Mukherjee and Sen 1991; Kwon *et al.* 2015) in its structure. Previously reported Co-bearing mackinawite from Khetri region is more enriched in Ni, compared to Co and the total contents of Co+Ni range between ~ 5 and 11 wt.% (Deb and Mukherjee 1969; Mukherjee and Sen 1991). In contrast, mackinawite described in this study, is more enriched

in Co compared to Ni (table 1) and is closer to cobaltian mackinawite (≥ 15 wt.% Co) in composition. Cobaltian mackinawite is rare in nature and described from a very few deposits from other parts of the world (Clark 1970; Tatsumi *et al.* 1975; Mariko 1988). The Co:Ni ratios (4–16) of the mackinawite, we report here, are quite high relative to other reported Co–Ni-bearing mackinawite.

6.2 Sulphide mineralization vis-à-vis

Co-pentlandite and cobaltian mackinawite

In the Madan-Kudan deposit (this study) and nearby Chandmari and Kolihan mine (Baidya *et al.* 2017) sulphide mineralization is essentially associated with mineralogically diverse sulphide veins in amphibole-bearing quartzite and garnetiferous chlorite schist. Striking differences in the mineralogy of host rocks and that of the veins imply epigenetic hydrothermal sulphide mineralization through ingress of extraneous fluid. These hydrothermal sulphide veins containing Co-pentlandite and Co-rich mackinawite also contain Cl-rich hastingsite-pargasite-sadanagaite and at places Cl-rich marialitic scapolite (Sen 2015; Baidya *et al.* 2017). Chlorine-bearing phases strongly indicate that the sulphide mineralization is genetically related to Cl-rich hydrothermal fluid, which may be linked to magmatic or sedimentary basinal brine (Baidya *et al.* 2017). Some previous works also have proposed hydrothermal origin of the sulphide ores from a Cl-rich hydrothermal fluid in Khetri region (Roy Chowdhury and Das Gupta 1965; Das Gupta 1974; Sahu *et al.* 1977; Jaireth 1984, 1986; Knight *et al.* 2002). Randomly oriented grains and un-deformed nature of the veins indicate that the vein-hosted mineralization described in this study was post-deformation and likely post-metamorphic.

The veins containing Co-pentlandite and cobaltian mackinawite also contain magnetite and pyrrhotite as common minerals, while pyrite is either insignificant or absent. Absence of pyrite in the mackinawite-chalcopyrite-pyrrhotite association has previously been observed from Chandmari mine (Mukherjee and Sen 1991). Co-existence of magnetite with pyrrhotite and rarity or absence of pyrite suggests that the fluid from which the veins formed and the ore minerals crystallized, was of low sulphur fugacity. In the light of this discussion, we propose that this event of Cu-mineralization at Madan-Kudan area took place from a Cl-rich low fS_2 fluid.

It may be noted that Co-pentlandite and Co-rich mackinawite exclusively occur in association with pyrrhotite and chalcopyrite, respectively. The oriented flames of Co-pentlandite in pyrrhotite and oriented lamella of cobaltian mackinawite in chalcopyrite might have formed through solid state exsolution during cooling of the host mineral. Exsolved flames of pentlandite in pyrrhotite are common in nature (Ramdohr 1980). Such textures are produced by homogeneous nucleation at several sites by rapid cooling (Craig *et al.* 1981), whereas the granular Co-pentlandite occurring near fractures and grain boundaries are produced by diffusion and heterogeneous nucleation during slow cooling from high temperature (*op cit*). The oriented lamella of mackinawite in chalcopyrite might also have formed in a similar way as the flames of Co-pentlandite in pyrrhotite. Similar explanation has been given for argento-pentlandite and mackinawite inclusions in chalcopyrite in some previous studies (e.g., Merkle and Gruenewaldt 1986; Kerestedjian and Bonev 2001). Merkle and Gruenewaldt (1986) proposed a higher temperature ($\sim 300^\circ\text{C}$) for inclusion type mackinawite relative to mackinawite of other modes generated at $225 \pm 1^\circ\text{C}$ or lower temperature as described by Deb and Mukherjee (1969). Some of the small isolated inclusions of Co-pentlandite and cobaltian mackinawite may be the cross sections of large elongated grains or of exsolved flames and lamella. However, we cannot entirely rule out the possibility of direct crystallization of these Co-rich phases from the hydrothermal fluid, particularly those without any apparent exsolution texture. Whatever be the origin of these Co-rich phases, it is evident that the hydrothermal fluid from which pyrrhotite, chalcopyrite and other minerals crystallized in the veins was extraneous (outside the depositional locale) and brought in Co and Ni along with Cu and Fe. During crystallization, Co and Ni were incorporated in pyrrhotite and chalcopyrite and during post-crystallization cooling Co-rich phases exsolved in their respective hosts. The distribution, size and shape of the exsolved phases varied depending on temperature and rate of cooling. It is possible that chalcopyrite, which outlasted and partly replaced pyrrhotite might have obtained some Co and Ni from existing pyrrhotite for the formation of some mackinawite at a later stage. Some existing Co-pentlandite also likely replaced by cobaltian mackinawite at this stage.

6.3 Element substitution in Co-pentlandite and cobaltian mackinawite

From the binary plots, it can be inferred that Co→Fe and Co→Ni substitution is dominant in Co-pentlandite. Also strong negative correlations between Co and Fe+Ni and Fe and Co+Ni imply that these elements substituted each other. Similar substitutions were observed earlier as well, especially in pentlandite from continental sources (Riley 1977), and is different from substitution scheme proposed by Borodaev *et al.* (2007) for mid-oceanic ridge hydrothermal system. In case of Khetri, the major substitution is Co→(Ni+Fe).

In case of mackinawite, thermodynamic study indicates that trace element bearing mackinawite is more stable relative to the pure phase (Kwon *et al.* 2015). Cobaltian mackinawite from the Madan-Kudan deposit is trace element-rich, in which Ni+Co content is much higher than that of Cu (which is predicted by thermodynamic calculations of Kwon *et al.* 2015). The trace elements can take three places in the structure of mackinawite: (1) in place of Fe atom by substitution, (2) tetrahedral interstitial site and (3) square-pyramidal site. No significant correlation between Fe and Co or Fe and Ni likely indicate that some or all of the Co and Ni are present in the interstitial spaces. Strong correlation between Co and Ni indicate substitution of Co by Ni and vice versa, presumably at the same site. Similarly, weak negative correlation between Cu and Co and no discernible correlation of Cu with Fe likely indicates incorporation of Cu in the interstitial site too.

6.4 Source of metal and Co enrichment relative to Ni

The host rocks, viz., amphibole-bearing albitic quartzite and garnetiferous chlorite schist are unlikely to contain high intrinsic concentrations of Cu, Fe, Co and Ni. Therefore, the presence of sulphide veins comprising chalcopyrite, pyrrhotite, magnetite, Co-pentlandite, and cobaltian mackinawite in these host rocks indicate that Cu, Fe, Co and Ni were derived from extraneous source (see previous section). Mafic rocks contain higher concentrations of all these elements compared to common felsic igneous and metasedimentary rocks (Taylor *et al.* 1969), the latter constitutes a major part of the rock sequence in and around the deposits. Therefore, the possible source of these ore

metals for this vein-hosted sulphide mineralization might be mafic rocks that are spatially associated (Sarkar and Dasgupta 1980a, b; Kaur and Meht 2005; Kaur *et al.* 2013) with these deposits. However, the ore minerals are significantly more-enriched in Co compared to Ni, as is evident from the compositions of the minerals. Mafic rocks generally contain higher amount of Ni relative to Co (~120 ppm Ni *vs.* ~50 ppm Co; Taylor *et al.* 1969). Therefore, consistently high Co:Ni in the sulphide minerals need an explanation. Liu *et al.* (2012) demonstrated that Co is much more soluble than Ni in a Cl-rich hydrothermal solution. Therefore, transport of metals from a mafic source by Cl-rich solution, as inferred from mineralogy of sulphide veins and mineral chemistry (presence of Cl-rich amphibole ± Cl-rich marialitic scapolite) suitably explains relative enrichment of Co compared to Ni in Co-pentlandite and cobaltian mackinawite. These metals were likely transported from the source to the depositional site as chloride complexes (*cf.* Baidya *et al.* 2017). De-stabilization of Cl-complexes resulted in the crystallization of sulphide and Cl-rich amphibole and at places Cl-rich marialitic scapolite.

6.5 Co-rich phases and probable deposit type

Several models have been proposed regarding the origin of the Cu-deposit of the Khetri copper belt. The proposed models include: (a) syn-sedimentary-diagenetic, prior to deformation and metamorphism, (b) peak- to post-peak-metamorphic hydrothermal, and (c) dual mode involving both the above (Roy Chowdhury and Das Gupta 1965; Das Gupta 1974; Sarkar and Dasgupta 1980a, b; Knight *et al.* 2002). In a latest study by Knight *et al.* (2002) it has been proposed that the mineralization in the Khetri deposit is hydrothermal and belongs to the Fe-oxide (Cu–Au) (IOCG)-type of deposits.

Our study reveals that at least a part of the mineralization in the Madan-Kudan deposit is post-metamorphic and post-deformation hydrothermal in origin (*cf.* Baidya *et al.* 2017). In addition to Cu, the ores are enriched in Co and Ni, particularly in Co, as is indicated by the presence of Co-pentlandite and cobaltian mackinawite. In an independent study, Sen (2015) described the occurrence of Co–Ni (mostly Co)-rich pyrite from the ores of Madan-Kudan deposit. Magnetite in association with these Co-rich phases are also enriched in Co relative to other type of magnetite present

in this area (Chen *et al.* 2015). Cobalt-enriched ores of the deposits have also been reported by Knight *et al.* (2002). Iron oxide Cu–Au deposits are generally characterized by high Co±Ni abundance in general and in some of the deposits these elements occur in economic grade and quantity (Barton 2014). Cobalt-enrichment in IOCG deposits is mainly manifested in the high Co–Ni concentration of pyrite and pyrrhotite (Mazdab 2001; Pal *et al.* 2009; Barton 2014), and in some deposits Co and Ni can form discrete sulphide, arsenide and arseno-sulphides (Slack 2012) similar to that of the Madan-Kudan deposit. The common mineralogical assemblage in which chalcopyrite (the abundant Cu-mineral) occurs is represented by magnetite + pyrrhotite + chalcopyrite + Co-pentlandite + Co-rich mackinawite. Such a mineralogical assemblage is indicative of a relatively low fS_2 condition in which sulphides precipitated. It may be noted that IOCG deposits are invariably associated with a high salinity fluid, a similar situation as has been inferred for the sulphide veins in this study. Therefore Cu–Co–Ni mineralization via a Cl-rich fluid in a presumably low sulfidation environment collectively indicates that the deposit at Madan-Kudan has metal association and mineralogical and fluid characters akin to IOCG-style mineralization. However, more detailed study integrating types and patterns of hydrothermal alterations *vis-à-vis* mineralization, compositions of hydrothermal fluids, and thermo-tectonic evolution of the study area is warranted.

7. Conclusions

In the Madan-Kudan copper deposit, Khetri Cu-belt, Rajasthan, epigenetic, hydrothermal copper mineralization is associated with sulphide veins comprising chalcopyrite-pyrrhotite ± pyrite-magnetite-chlorite-blue amphibole (Cl-rich hastingsite-pargasite-sadanagaite) ± marialitic scapolite ± allanite ± uraninite. These veins occur in amphibole-bearing feldspathic/albitic quartzite and garnetiferous chlorite schist. Cobalt pentlandite and cobaltian mackinawite are the two important Co sinks, among which, to the best of our knowledge, cobalt pentlandite is being reported for the first time from the Khetri Cu-belt (perhaps from India as well). Although the immediate source of Co and Ni for Co-pentlandite and cobaltian mackinawite might have been pyrrhotite and chalcopyrite, the ore metals, viz., Cu, Fe, Co and Ni were brought in by the fluid ultimately from

an external source, most likely the mafic rocks present in and around the study area. High saline Cl-rich nature of the fluid is inferred from the presence of Cl-rich amphibole and Cl-rich marialitic scapolite. Transport of Co and Ni (other metals as well), sourced from a mafic rock with high intrinsic Ni/Co content, by such a high saline fluid suitably explains the dominance of Co over Ni in the ores. Metal association (Fe, Cu, Co, Ni, LREE, U) as evident from the ore mineralogy of the veins, common presence of magnetite and rarity/absence of pyrite, inferred low fS_2 condition during mineral precipitation and high salinity of fluid collectively indicate that the post-metamorphic, post-deformation mineralization has many character akin to IOCG-type deposits of the world.

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