

# Geothermometry based on fractionation of Mn and Cd between coexisting sphalerite and galena from some carbonate-hosted sulfide deposits in India

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**Abstract.** Geothermometry based on the fractionation of Mn and Cd between coexisting sphalerite and galena from concordantly banded, strata-bound ores and younger vein ores of Rajpura-Dariba, Zawar, and Bandalamottu has been attempted. Different fractionation trends for the *banded* and *vein* ores in the same deposit at Rajpura-Dariba indicate different thermal regimes of final equilibration for the two varieties of ores. In contrast, a single trend incorporating both types of ores is suggestive of isothermal conditions of final equilibration for the *banded* and *vein* ores at Zawar. Unrealistically high temperatures obtained for the vein ores of Bandalamottu suggest equilibrium in the sphalerite-galena aggregates of this deposit was not attained. Thermometric data from Mn and Cd fractionation are compared with other independent geothermometric determinations obtained from fluid inclusion homogenization studies and based on phase equilibria. It has been found that, in general, the Cd-fractionation temperature ( $T_{Cd}$ ) is a more reliable geothermometer than the Mn-fractionation temperature ( $T_{Mn}$ ). This presumably may be due to the susceptibility of aqueous Mn species to subtle changes in  $f_{O_2}$  in the ore fluid and consequent heterogeneity in Mn concentration in sphalerite, thus affecting the distribution coefficient. The investigation also suggests that  $T_{Cd}$  becomes increasingly more dependable when the ores are metamorphosed and reequilibrated at higher grades of metamorphism.

The fractionation of minor elements between coexisting minerals has been suggested to be generally applicable as a geothermometer (e.g., Friedman 1949; Holland 1956; McIntire 1963), particularly when substitution occurs at regular lattice sites. The experimental findings of Bethke and Barton (1971) on fractionation of Mn and Cd between coexisting sphalerite and galena have been previously used for geothermometry (Hall et al. 1971; Nash 1975; Urabe 1977; Dangic 1985).

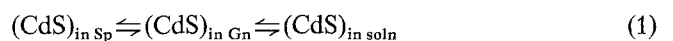
The present work is aimed at testing the applicability of these geothermometers and ascertaining, if possible, the geological situations where they are particularly useful. Accordingly, three Proterozoic sulfide deposits from India were chosen as study areas, i.e., Rajpura-Dariba and Zawar in the Udaipur district of Rajasthan and Bandalamottu in the Guntur district of Andhra Pradesh. These three deposits, besides being conformable carbonate-hosted sulfide depos-

its, share three major attributes: (1) occurrence in an argillaceous-arenaceous-calcareous sequence, (2) presence of spatial metal zoning, and (3) a distinctly "biphase" metalization with an earlier, dominantly banded strata-bound ore facies and a younger, often discordant vein ore facies (Mishra 1985). Such common traits notwithstanding, each of the three deposits registers many distinctive features of its own as recorded in Table 1.

## Minor-element geothermometry

### Theoretical considerations

Contemporaneous crystallization (at equilibrium) of sphalerite and galena from an aqueous solution carrying a small amount of Cd as a minor element is first considered. The distribution reaction can be written as



The equilibrium statement for the above reaction is given by

$$a_{CdS}^{Sp} = a_{CdS}^{Gn} = a_{CdS}^{soln} \quad (2)$$

where Sp and Gn represent sphalerite and galena, respectively, and the activity terms in Eq. (2), say  $a_{CdS}^{Sp}$ , are the absolute activities (cf. Guggenheim 1950) of the components, in this case, CdS in the sphalerite phase. Such absolute activity is related to the chemical potential of the component by the relationship

$$a_{CdS}^{Sp} = \exp(\mu_{CdS}^{Sp}/RT) \quad (3)$$

where  $\mu_{CdS}^{Sp}$  is the chemical potential of the component CdS in sphalerite, R is the universal gas constant, and T is the absolute temperature in Kelvin.

The mole fraction,  $X_1^j$ , of a component (either solid or aqueous) in solution is related to its activity through activity coefficient ( $\gamma_1^j$ ) by the relationship

$$X_{CdS}^{Sp} = a_{CdS}^{Sp} / \gamma_{CdS}^{Sp} \quad (4)$$

Substituting Eq. (4) in Eq. (2) we have

$$X_{CdS}^{Sp} \gamma_{CdS}^{Sp} = X_{CdS}^{Gn} \gamma_{CdS}^{Gn} = X_{CdS}^{soln} \gamma_{CdS}^{soln} \quad (5)$$

The distribution coefficient,  $k_D$ , defined as the ratio of the concentration of minor components in any two phases, may be written as

$$(k_D)_{CdS}^{Sp-Gn} = X_{CdS}^{Sp} / X_{CdS}^{Gn} = \gamma_{CdS}^{Gn} / \gamma_{CdS}^{Sp} \quad (6)$$

Table 1. Comparison of salient features of the deposits at Rajpura-Dariba, Zawar, and Bandalamottu

Deposits and ore types	Tectonostratigraphic setting	Age	Rock types	Metamorphism	Ore minerals	Gangue minerals	Ore texture structure	References
Rajpura-Dariba Banded ore	Third-order basin in epicontinental seas under low-energy euxinic conditions	1700 Ma (Pb age)	Graphite schist, Calc-silicates. No volcanics, intrusives insignificant	Amphibolite facies (550 °C, 5.5 kbar)	Py, Sp, Gn, Cp, Td, Asp, Mt	Gr, Qt, Ky, St, Gt, Mus, Bio, Cht, Dol, Cal, Tm, Act, Di, Sc, Bar, Ft, Ap, Wl	Congruent sulfide layers, evidence of deformation, annealing recrystallization, perfect textural equilibrium	Raja Rao et al. (1971), Poddar (1974), Basu (1981), Deb and Bhattacharya (1980), Deb (1982), Mishra (1985), Mishra and Mookherjee (1986)
Rajpura-Dariba Vein ore	Along irregular fractures after uplift to shallower depth	Postmetamorphic, indicated time gap with the banded ore	Mostly Calc-silicates (Diopside marble). No igneous affiliation indicated	Unmetamorphosed, practically undeformed	Gn, Sp, Cp, Po, Tn, Asp, native As, int. met. comp. (Ag-Au-Hg), various Cu-Pb-Ag-Tl-Sb-As sulfosalts	Dol, Cal, Tm, Qt, Di	Ultrafine-grained, discordant patches, pods, segregation veins, comb. structure, replacement relations and several "frozen" subsystem equilibria	Basu et al. (1980, 1981 a, b, 1983, 1984), Mishra (1985), Mishra and Mookherjee (1986)
Zawar Banded ore	Epicontinental seas under low-energy euxinic conditions	1500 Ma (Pb age)	Siliceous and carbonaceous dolomites, phyllosilicates, and quartzites. No igneous affiliation	Greenschist facies	Py, Gn, Sp, Cp, Po, Asp, Mt	Dol, Cal, Qt, Mus, Bio, Cht, Ser	Sulfide rhythmites, convolute bedding, slump structures, folded sulfide layers. Deformation and recrystallization textures	Mookherjee (1964, 1965), Poddar (1965), Chernyshev et al. (1980), Deb (1982), Mishra (1985)
Zawar Vein ore	Along regular shear planes often subparallel to bedding; also along related dilation structures	No discernible time gap between metamorphism of banded ore and vein ore formation	Quartz-carbonate veins	Unmetamorphosed, syn- to late metamorphic	Py, Gn, Sp, Cp, Po, Asp	Qt, Dol, Cal	Sheeted veins, stringers, coarse grained sulfides at the interstices of silicates and carbonates	Mookherjee (1964, 1965), Mishra (1985)
Bandalamottu Strata-bound ore	Intracratonic basin, no evidence of high reducing conditions	1400–750 Ma (age of the sediments)	Dolomites, phyllosilicates, and quartzites. Granite dome 3 km away from the deposit	Practically unmetamorphosed	Gn, Py, Sp, Cp, Bo, Dg, Cv, Sd	Dol, Cal, Qt	Cross-cutting veins, breccia- and vugfillings corroded margins, reaction rims, gross disequilibrium	Ziauddin and Sharma (1968), Murty et al. (1972), Narayanaswami et al. (1977)
Bandalamottu Vein ore	Along fractures transgressing the strata-bound ore	–	Quartz-carbonate veins	Unmetamorphosed	Gn, Sp, Cp, Py	Qt, Cal	Replacement textures, complete disequilibrium	Mishra (1985)

Act, actinolite; Ap, apatite; Asp, arsenopyrite; Bar, barite; Bio, biotite; Bo, bornite; Cal, calcite; Cht, chlorite; Cp, chalcopyrite; Cv, covellite; Dg, digenite; Di, diopside; Dol, dolomite; Ft, fluorite; Gn, galena; Gr, graphite; Gt, garnet; Ky, kyanite; Mt, magnetite; Mus, muscovite; Po, pyrrhotite; Py, pyrite; Qt, quartz; Sc, scapolite; Sd, siderite; Ser, sericite; Sp, sphalerite; St, staurolite; Td, tetrahedrite; Tm, tremolite; Tn, tennantite; Wl, wollastonite

Since with the possible exception of fluid inclusions, the solution phase is not available for analysis, the distribution of minor components between mineral phases is to be considered.

Assuming that Henry's law holds true – an assumption justified by the findings of Bethke and Barton as discussed below – the distribution coefficient can be taken as constant. Under such composition-independent conditions for the reaction represented in Eq. (1), the free energy expression can be written as

$$\Delta G^0 = \Delta \bar{H} - T\Delta \bar{S} = -RT \ln k_D \quad (7)$$

where  $\Delta \bar{H}$  and  $\Delta \bar{S}$  are, equal to the differences in partial molar enthalpies and entropies of the reactants and the products in the distribution reaction, respectively ( $\bar{H}_{\text{CdS}}^{\text{Sp}} - \bar{H}_{\text{CdS}}^{\text{Gn}}$  and  $\bar{S}_{\text{CdS}}^{\text{Sp}} - \bar{S}_{\text{CdS}}^{\text{Gn}}$  for Eq. (1), considering only the solid phases).  $\Delta G^0$  is the standard Gibbs free energy change of the distribution reaction.

The temperature and pressure dependence on  $k_D$  can be given by

$$\left[ \frac{D \ln k_D}{D(1/T)} \right]_P = -\frac{\Delta \bar{H}}{R}, \quad (8)$$

$$\left[ \frac{D \ln k_D}{D P} \right]_T = -\frac{\Delta \bar{V}}{RT}, \quad (9)$$

where  $\Delta \bar{V}$  is the difference in the partial molar volumes of the reactants and products of the distribution reaction (Eq. 1).

Bethke and Barton (1971) have determined the distribution coefficient ( $k_D$ ) over a wide range of compositions in the MnS–PbS–ZnS (600°–850°C) and CdS–PbS–ZnS (600°–890°C) systems and found that the  $k_D$  values are constant over the compositional range expected in natural samples. The thermometric expressions given by these authors are

$$(\log k_D)_{\text{Mn}}^{\text{Sp-Gn}} = \frac{1,410 - 0.0261 P}{T} - 0.01, \quad (10)$$

$$(\log k_D)_{\text{Cd}}^{\text{Sp-Gn}} = \frac{2,080 - 0.0264 P}{T} - 1.08, \quad (11)$$

where  $(k_D)_{\text{Mn}}^{\text{Sp-Gn}}$  and  $(k_D)_{\text{Cd}}^{\text{Sp-Gn}}$  are the distribution coefficients of Mn and Cd between coexisting sphalerite and galena and are equal to the ratios of the concentrations (weight percent) of the respective minor elements in sphalerite and galena.

#### Sample preparation and analysis

Sphalerite and galena were separated from both banded and vein ore samples of each deposit using magnetic methods (isodynamic separation) and heavy media (bromoform) separation, followed by handpicking under a binocular microscope. In general, the purity was >98%. Since sphalerite is sparse in the primary strata-bound Pb ores of Bandalamottu, only samples from quartz-sulfide vein ores were investigated from this deposit. The samples were chosen considering evidence such as simultaneous or at least overlapping crystallization (without any paragenetic break), occurrence of sphalerite and galena in physical contact, absence of crystal zoning, etc. Such sphalerite-galena pairs meet the criteria of "simple equilibrium" (Barton et al. (1963). Apart

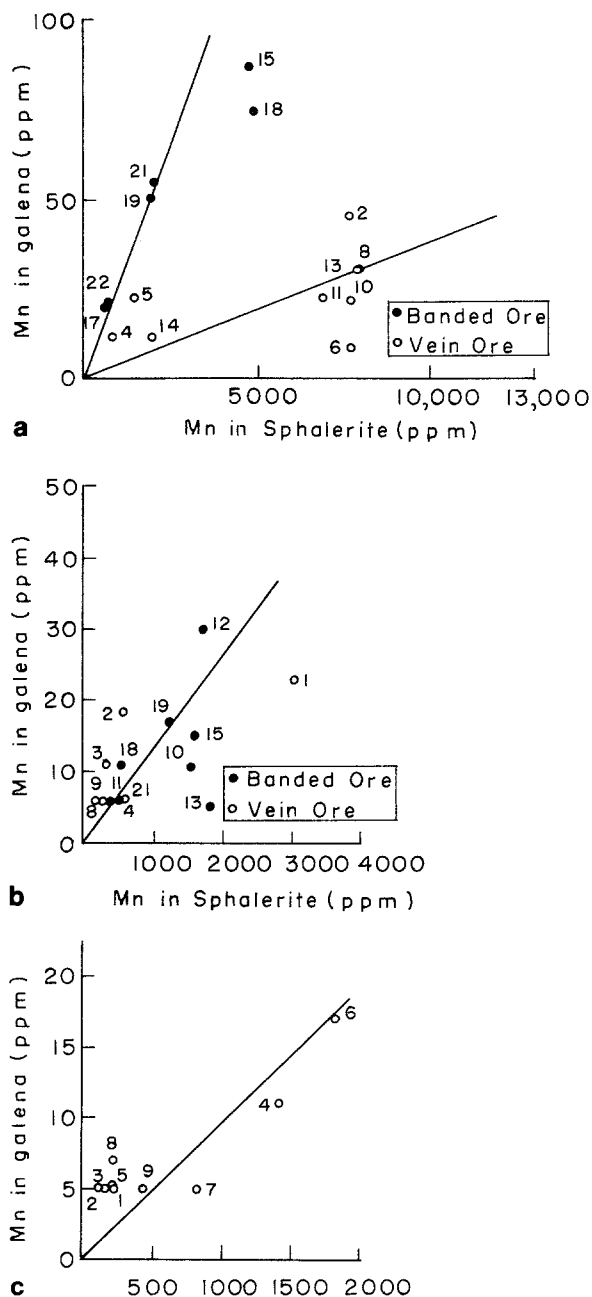


Fig. 1a–c. Fractionation of Mn between coexisting sphalerite and galena in samples from the a Rajpura-Dariba, b Zawar, and c Bandalamottu vein ores

from these criteria, other textural evidence of equilibrium includes mutual straight-edge grain boundaries and appropriate dihedral angles exhibited by the sphalerite-galena aggregates. The grain shape of galena occurring in sphalerite or vice versa has also been considered as evidence of simultaneous crystallization (cf. Stanton 1972, p 249).

Mn and Cd were analyzed by a Verian Tectron atomic absorption spectrophotometer (Model AA 6). Standard solutions were prepared from "specpure"-grade metals or salts (AR grade) as recommended in the instrument manual. Typical sensitivities of Mn and Cd are 0.024 and 0.011  $\mu\text{g/ml}$ , respectively. Triplicate samples were prepared to calculate the precision (reproducibility) of analyses which was calcu-

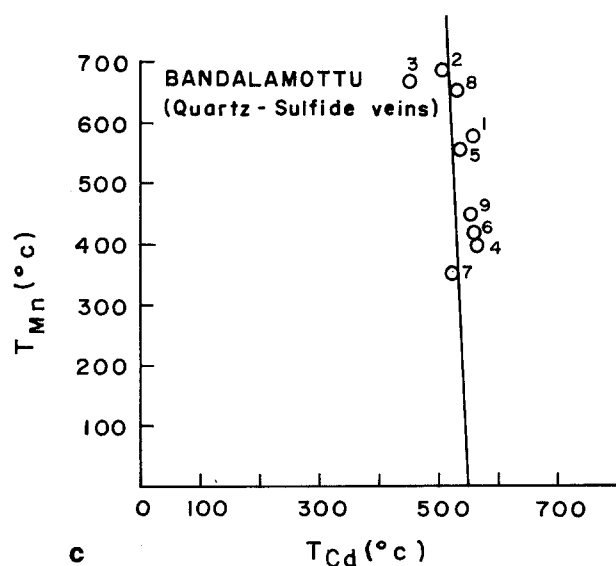
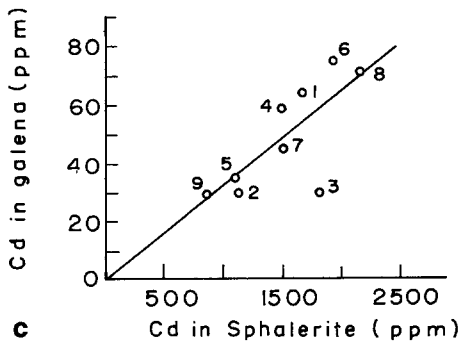
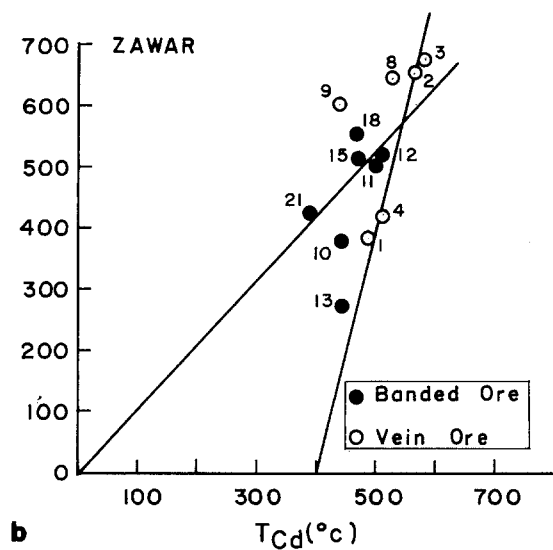
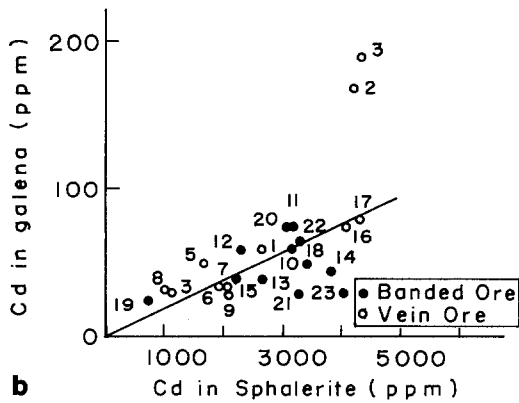
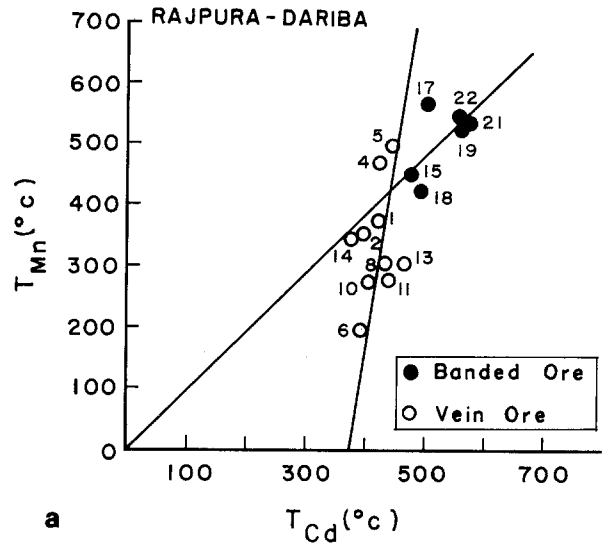
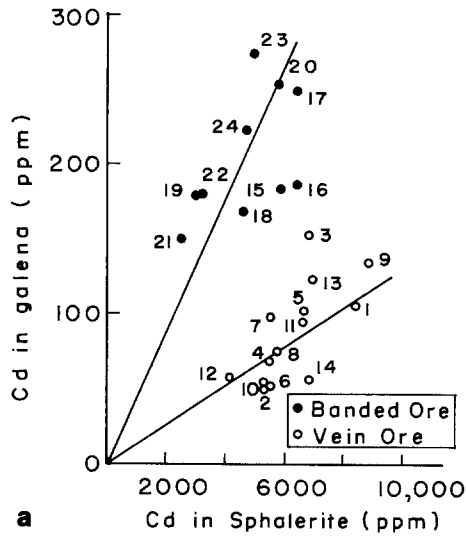


Fig. 2a-c. Fractionation of Cd between coexisting sphalerite and galena in samples from the a Rajpura-Dariba, b Zawar, and c Bandalamottu vein ores

Fig. 3. Correlation of Mn- and Cd-fractionation temperatures ( $T_{Mn}$  and  $T_{Cd}$ ) in samples from the three deposits. Note the narrow dispersal  $T_{Cd}$  relative to  $T_{Mn}$  in all the three cases (a, b, and c as in Figs. 1 and 2)

lated as the coefficient of variation ( $\sigma/\bar{x} \times 100$ ). These values were found to be 1.1% for Mn and 1.8% for Cd.

Contents of Mn and Cd in coexisting sphalerite and galena pairs<sup>1</sup> and fractionation of these two minor elements are shown in Figs. 1 a-c and 2 a-c, respectively. The lines in Figs. 1 and 2 are visual best-fits and are drawn to pass through the origin, assuming that the distributions follow Henry's law. Samples from Rajpura-Dariba show two different trends, i.e., one corresponding to the *banded ore* and the other to the *vein ore* (Figs. 1 a, 2 a), for Mn and Cd.

<sup>1</sup> analytical data are available from the authors on request

**Table 2.** Comparison of results of minor-element geothermometric studies from the three deposits with the published data from other areas

Locality (references)	T <sub>Mn</sub> or T <sub>Cd</sub>	Temp. range (°C)	Mean temp. (°C)	Average (Standard deviation)	No. of samples	Other indepen- dently derived temp. (°C)
Rajpura-Dariba Banded ore (this study)	T <sub>Mn</sub> T <sub>Cd</sub>	419°–571° 465°–564°	505° 523°	58 37	6 10	515°–548° <sup>a</sup> ≈ 550° <sup>b</sup>
Rajpura-Dariba Vein ore (this study)	T <sub>Mn</sub> T <sub>Cd</sub>	198°–497° 381°–489°	343° 430°	90 30	10 14	385°–500° <sup>c</sup>
Zawar Banded ore (this study)	T <sub>Mn</sub> T <sub>Cd</sub>	273°–556° 375°–549°	459° 461°	94 47	8 14	
Zawar Vein ore (this study)	T <sub>Mn</sub> T <sub>Cd</sub>	386°–679° 439°–579°	564° 506°	127 49	6 9	273°–338° <sup>d</sup> Mean = 292 Std. Dev. = 15
Bandalamottu Vein ore (this study)	T <sub>Mn</sub> T <sub>Cd</sub>	356°–686° 452°–562°	529° 531°	128 35	9 9	152°–348° <sup>d</sup> Mean = 277 Std. Dev. = 46
Darwin mine, California (Hall et al. 1971)	T <sub>Mn</sub> T <sub>Cd</sub>	340°–413° 383°–439°	377° 416°	37 26	4 4	
Mayflower mine (Nash 1975)	T <sub>Mn</sub> T <sub>Cd</sub>	335°–522° 395°–447°	426° 409°	105 22	4 5	
Hosokura mine (Urabe 1977)	T <sub>Mn</sub> T <sub>Cd</sub>	289°–565° 224°–377°	443° 344°	139 34	5 9	
Yatani mine (Urabe 1977)	T <sub>Mn</sub> T <sub>Cd</sub>	315°–695° 313°–406°	432° 364°	101 30	12 12	

<sup>a</sup> from tetrahedrite-sphalerite-pyrite equilibrium (Mookherjee and Mishra 1984; Mishra 1985)

<sup>b</sup> from silicate-carbonate equilibria corresponding to metamorphism of the banded ore (Deb and Bhattacharya 1980)

<sup>c</sup> from several sulfosalt-sulfide equilibria (Mookherjee and Mishra 1984; Mishra 1985)

<sup>d</sup> from fluid inclusion homogenization studies in sphalerite (Mishra and Mookherjee 1982; Mishra 1985)

These two fractionation trends for both Mn and Cd confirm two different “thermal regimes of final equilibration” for the (metamorphosed) *banded ores* and the (postmetamorphic) *vein ores* at Rajpura-Dariba. In contrast, samples from Zawar show a single trend (for each of the elements) accommodating samples from both ore types (Figs. 1 b, 2 b). These single trends for both varieties of ores indicate the same isothermal conditions of final equilibration of both the (metamorphosed) *banded ores* and (presumably metamorphic) *vein ores* (Mishra 1985) at Zawar. Samples from the Bandalamottu quartz-sulfide veins also show a single trend for fractionation of each of the two minor elements, although the spread is relatively larger in the case of Mn (Figs. 1 c, 2 c).

As pointed out by Barton et al. (1963) and Bethke and Barton (1971), perhaps the best test for chemical equilibrium between coexisting phases is indicated by element distribution data and their systematic variation. Temperatures were calculated for coexisting sphalerite-galena pairs by Eqs. (10) and (11) and are shown in Table 2, giving temperature range, mean temperature value, and standard deviation for all the ore types. The effect of pressure on  $k_D$  values are small and can be neglected (cf. Bethke and Barton 1971) for all the ore types except the Rajpura-Dariba banded ores, where metamorphic pressure of the order of 5.5 kbar is well documented (Deb and Bhattacharya 1980).

## Discussion

Bethke and Barton (1971) have emphasized the problems to be overcome for successfully applying their experimental

thermometric results to natural ores, i.e., (a) analytical and sampling restrictions and (b) paragenetic constraints (equilibrium problem) imposed by depositional and postdepositional phenomena. Due to strong fractionation in both systems (Mns–PbS–ZnS and CdS–PbS–ZnS) the concentration of Mn and Cd are very low in galena. For this reason, highly sensitive analytical methods have to be employed. Strong fractionation also demands absolute sample purity, because even minute amounts of the enriched phase (sphalerite) may introduce significant errors into the analyses of the impoverished phase (galena). Further, deposition of a mineral pair in mutual equilibrium implies that both the phases were in equilibrium with the ore fluid; activities of different minor components in the ore fluid may fluctuate by several orders of magnitude in response to any change in the physicochemical environment (Barton 1970). Under such fluctuating conditions equilibrium crystallization, if continued, results in zoning in individual crystals or banding in polycrystalline aggregates in simple vein-filling ores. The sluggish nature of solid-state diffusion prevents the crystals from equilibrating internally; the individual zones in a crystal thus represent a succession of compositional equilibria or a set of “local equilibria” in the sense of Thompson (1959). Finally, there is a real possibility that the coexisting sphalerite-galena pairs have undergone postdepositional changes affecting their original minor element contents: sphalerite due to its refractory nature is resistant to such changes, whereas galena is more likely to reequilibrate with the changing physicochemical conditions of the environment.

In spite of these inherent problems that impose severe limitations on the application of minor element geothermo-

metry to natural sphalerite-galena assemblages, the present study was undertaken to (a) test the mutual concordance–discordance of temperature data based on fractionation of Mn ( $T_{Mn}$ ) and Cd ( $T_{Cd}$ ), (b) check their dependability against other independent geothermometric data wherever possible and (c) critically assess their applicability to Precambrian sulfide deposits that have undergone different grades of metamorphism.

The temperature data from the three deposits are given in Table 2. Similar data from elsewhere are also compiled for comparison, including the temperature values calculated from the data of Urabe (1977). Results of geothermometric studies attempted through other independent methods are also included in Table 2. For *Rajpura-Dariba banded ore* (with a pressure correction of 5.5 kbar) the mean values of  $T_{Mn}$  (505°C) and  $T_{Cd}$  (523°C) are close to the temperature estimated for metamorphism of the host rocks ( $\approx 550^\circ\text{C}$ ; Deb and Bhattacharya 1980). Also, the values of  $T_{Mn}$  and  $T_{Cd}$  match well with the temperature determined from tetrahedrite-sphalerite-pyrite equilibria. On the other hand,  $T_{Mn}$  and  $T_{Cd}$  values for *Zawar banded ore* (without a pressure correction) show a relatively wider scatter with mean values of 459°C ( $T_{Mn}$ ) and 461°C ( $T_{Cd}$ ). No independent crosschecking of this geothermometric data, beyond a very generalized assessment of the PT conditions of greenschist-facies metamorphism of the host rock along with the ores ( $T \approx 450^\circ\text{C}$ ), could be made. The *vein ores of Rajpura-Dariba* show a wide variation in  $T_{Mn}$  (198–497°C) with a mean at 343°C, whereas  $T_{Cd}$  for the same ores shows a relatively narrow range of variation (381–489°C) with a mean at 430°C (Table 2). Temperatures estimated from various sulfosalt-sulfide equilibria (Mookherjee and Mishra 1984; Mishra 1985) for these sphalerite-galena assemblages range from 385° to  $< 500^\circ\text{C}$ . The significance of this close match between the  $T_{Cd}$  values of Rajpura-Dariba vein ores and temperatures estimated from phase equilibria will be discussed later. For the *Zawar vein ores* both  $T_{Mn}$  and  $T_{Cd}$  show wide variations; also, the corresponding mean temperatures ( $T_{Mn} = 564^\circ\text{C}$ ,  $T_{Cd} = 506^\circ\text{C}$ ) are unrealistically high when compared with fluid inclusion homogenization temperatures in sphalerite (273–338°C; Mishra and Mookherjee 1982). Similarly, both  $T_{Mn}$  and  $T_{Cd}$  values for *Bandalamottu vein ores* show wide variation with their mean values ( $T_{Mn} = 529^\circ\text{C}$ ,  $T_{Cd} = 531^\circ\text{C}$ ) far above the fluid inclusion homogenization temperatures in sphalerite (152–348°C; Mishra 1985).

Significantly, the temperatures of reequilibration of metamorphosed banded ores from Rajpura-Dariba and Zawar are reliably determined by fractionation of Cd between coexisting sphalerite and galena. Mean  $T_{Cd}$  values are close to the independently derived metamorphic temperatures prevailing under amphibolite-facies conditions of the Rajpura-Dariba orebody (550°C at 5.5 kbar) and to postulated greenschist-facies metamorphism of the Zawar ores. The narrow spread of  $T_{Cd}$  values and close matching of average  $T_{Cd}$  values with independently derived temperatures from silicate and sulfide equilibria (Table 2) are taken to signify a complete and thorough reequilibration under higher metamorphic conditions. However, at Zawar, where metamorphism was of a lower grade and hence reequilibration was less complete, the  $T_{Cd}$  values show a wider spread, and the mean  $T_{Cd}$  value is less definitive.

The mean  $T_{Mn}$  values of the banded ores in both Rajpura-Dariba and Zawar, although compatible with the

mean  $T_{Cd}$  for the same ores, show larger spreads, as reflected by their standard deviation (Table 2). One significant feature in Table 2 is the high standard deviation of  $T_{Mn}$  values in both the types of ores from all three deposits. This is also brought out by plotting  $T_{Mn}$  against  $T_{Cd}$  (Fig. 3) where the spread in  $T_{Mn}$  values is quite large, whereas  $T_{Cd}$  is fairly consistent showing a relatively narrow spread. Data from four other areas, included in Table 2 for comparison, also show similar relationships between  $T_{Mn}$  and  $T_{Cd}$  suggesting the greater reliability of  $T_{Cd}$  in general. Inconsistent values of Mn-fractionation temperatures in the Mayflower mine (Nash 1975) and in some Japanese epithermal deposits (Urabe 1977) have been attributed to heterogeneity in Mn concentration which was first suspected by Bethke and Barton (1971) from large unexpected discrepancies in experimental results. Also, the temperature dependence of  $(k_D)_{Mn}^{Sp-Gn}$  is small.

Heterogeneity in Mn concentration is presumed to be due to changes in the activity of dissolved Mn species in the hydrothermal fluid in response to fluctuations in  $T$ ,  $f_{O_2}$ , pH, etc. Manganese being a transition element with variable oxidation states, the activity of its dissolved species in the ore fluid are particularly sensitive to any subtle change in  $f_{O_2}$ . Such changing activity of dissolved species would have to be reflected in chemical heterogeneity in the host mineral phase in equilibrium with the ore fluid.

The unrealistically high  $T_{Mn}$  and  $T_{Cd}$  values obtained for the vein ores of Zawar and Bandalamottu are far above the temperatures obtained from fluid inclusion homogenization studies (in sphalerite), and merit further discussion. Such discrepancies can be attributed to various factors like initial disequilibrium, postdepositional effects, or sample impurity. Sample impurity can be eliminated as a factor because, had this been the case, its effect would have been more pronounced in the Rajpura-Dariba vein ore samples where intimate intergrowths involving many sulfosalt and sulfide phases (Table 1) make pure mineral separation a very difficult task. As is evident, for the vein ore samples of Rajpura-Dariba there is a close correspondence between the range of  $T_{Cd}$  (381–489°C) and the temperature range derived from several sulfosalt-sulfide equilibria (385–500°C). Therefore the problem of discordance in the temperature data for the vein ores of Zawar and Bandalamottu can be attributed to paragenetic breaks pertaining to the crystallization of sphalerite and galena. However, in the case of Rajpura-Dariba the close match of the two independent sets of temperature data points toward the more definitive nature of the  $T_{Cd}$ ; it also suggests a relatively closely overlapping equilibrium crystallization of sphalerite and galena. On the other hand, for Bandalamottu vein ores with compositional zoning in individual crystals of sphalerite, the assumption of initial equilibrium may be suspect (Mishra 1985).

## Conclusion

The following conclusions seem justified on the basis of this investigation:

1. Separate fractionation trends (for the same elements) for the metamorphosed banded ores and the younger vein ores within the same deposit indicate different thermal regimes of final equilibration, as at Rajpura-Dariba, whereas a single trend for both the varieties of ores suggests metamorphic

remobilization of the vein ores from the banded ores both having equilibrated and reequilibrated under broadly isothermal conditions, as at Zawar.

2. For different ore types in all the deposits listed in Table 2,  $T_{Mn}$  values show greater variation than the corresponding  $T_{Cd}$  values.  $T_{Mn}$  values are also consistently higher than the corresponding  $T_{Cd}$  values, except for the Rajpura-Dariba ore types.

3. Comparison with the results of independent geothermometric determinations suggests that, in general,  $T_{Cd}$  is a more reliable geothermometer than  $T_{Mn}$ . The unreliability of  $T_{Mn}$  may be attributed to the susceptibility of the aqueous species of Mn to change as  $f_{O_2}$  changes in the ore fluid.

4.  $T_{Cd}$  becomes increasingly more dependable as a geothermometer when the ores reequilibrated at higher grades of metamorphism.

5. The unrealistically high temperatures obtained (both  $T_{Mn}$  and  $T_{Cd}$ ) for the vein ores of Bandalamottu suggest initial disequilibrium in sphalerite-galena pairs in these ores.

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