

Deformation of Pyrite at Varying Metamorphic Grades in Sediment-Hosted Base Metal Sulphide Deposits of Rajasthan, India



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Abstract The ubiquitous iron sulphide, pyrite, occurs in trace amounts in rocks or may form massive pyritic ore bodies with all perceivable gradations in between. Very often it shares the deformational and metamorphic history of its host rocks. Textural characteristics of pyrite, and its behavior in natural ores and in experimental conditions under varying temperature and pressure, have therefore been studied by different workers from time to time. An overview of these studies shows that there is a mismatch between the experimentally achieved deformation mechanisms at different temperature and pressure, and the observed brittle or ductile behaviour of pyrite in naturally deformed sulphide bodies. An attempt is made here to analyze the deformation behaviour of pyrite under different temperature-pressure conditions, by studying pyritic ores in three sediment-hosted Pb–Zn sulphide deposits of Rajasthan (Balaria-Zawar, Rajpura-Dariba and Rampura-Agucha), occurring in broadly similar geological settings, but deformed and metamorphosed at different grades (upper greenschist, middle amphibolite and upper amphibolite to granulite facies respectively). Observations of hand specimens and optical microscopy of pyritic ores from Rajasthan have shown that the mineral behaved in a macroscopically ductile manner—not only in the form of mesoscopic and microscopic folding of layers, but also by distortions, bending and stretching of individual grains. In general, pyrite plasticity increases with temperature as revealed by more definitive evidences of plastic deformation in higher metamorphic grade deposits (e.g. Rajpura-Dariba and Rampura-Agucha) than in lower grade Balaria ores from the Zawar ore district. However, the Balaria ore, characterized by the coexistence of framboidal (sedimentary-diagenetic) and idiomorphic (metamorphic) pyrite, is more intensely folded. Higher grade ores may, on the other hand, induce

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more grain growth and thereby are likely to lose the evidence of plastic deformation through polygonization and grain coarsening. This may be one reason behind the apparent scarcity of plastic deformation textures observed in pyrite from naturally deformed and metamorphosed sulphide ore deposits.

Keywords Pyrite · Diagenesis · Metamorphism · Plastic deformation
Annealing · Rajasthan

Introduction and Rationale of the Study

The iron sulphide, pyrite, is probably the most common metallic mineral in all kinds of rocks and occurs either as a dominant phase in sulphidic ores or is ubiquitous as a minor phase in most ore deposits due to its wide stability range, i.e., from low temperature conditions (25 °C, 1 atm.) to higher temperature-pressure regimes (743 °C, 10 kbar). It is particularly abundant in carbonaceous sediments since its formation is encouraged by biogenic intervention in euxinic environment. The sulphur present in the original protein of organic matter and in the form of sulphate in the sea water is largely reduced to hydrogen sulphide and the remaining sulphur combines with iron to form fine grained hydrotroilite ($\text{FeS}\cdot n\text{H}_2\text{O}$) which is immediately transformed into a more stable phase, pyrite (FeS_2) (Krauskopf 1967). Pyrite occurs in close association with black shale across the globe and in many parts of India. Such pyritic black shales are distributed all across the stratigraphy, from Archean to recent.

The mineral pyrite is commonly known to deform by brittle fracturing. Owing to the greater differential force of crystallization, in comparison to other sulphides, pyrite tends to recrystallize in the form of euhedral crystals exhibiting an idiomorphic texture at elevated temperature and pressure during metamorphism. At higher temperatures, during or after deformation, pyrite may anneal, eventually leading to polygonization with well-developed triple junction points with 120° angles. In the presence of other ore minerals, the interfacial angles may however vary (Stanton 1972). Early deformation experiments have shown that pyrite fails by cataclasis after a small amount of recoverable compression, over a wide range of temperature, confining pressure and strain rate (Graf and Skinner 1970). It has also been proposed that wherever it exhibits flattened and elongated forms, as often found in mica-rich metamorphic rocks, the orientation of mica is considered responsible in guiding the form of pyrite. The common occurrence of euhedral pyrite in metamorphosed rocks led early researchers to believe that the mineral does not deform plastically. Without doubting the common prevalence of cataclasis in pyrite, Mookherjee (1971), however, suggested the possibility of plastic deformation of pyrite under unusual conditions (e.g. extremely slow strain rates). Mechanisms suggested for such deformation included wedge dislocation and subsequent block formation through redistribution of dislocation, while retaining the continuity of the crystal structure. The proposition put forward by Graf and Skinner

(1970), that the orientation of flaky minerals controls the crystal growth of pyrite, was also later contested by Sarkar and Deb (1974). They showed the presence of elongate grains of pyrite in rock samples from Singhbhum Shear Zone in eastern India in which flaky minerals were not sufficient to guide the formation of such habits. Plastic deformation of pyrite under slow strain rates was suggested as a possible explanation. Later, experimental work using dry polycrystalline pyrite under 20–400 °C temperature and 100–300 MPa confining pressure (Atkinson 1975) showed cataclastic textures at all stages, which led to the conclusion that all macroscopic ductility was due to cataclastic flow—a process combining dislocation movement along with abundant microcracking. Atkinson (1975) suggested that plastic deformation of pyrite is possible only at higher temperatures (>400 °C) along with high sulphur vapour pressure. However, these experimental conditions are usually not attainable in nature.

Based on the above and more recent studies on pyrite deformation, reviewed in a later section, it is clear that there is a mismatch between the experimentally achieved deformation mechanisms at different temperature and pressure and the observed ductility of pyrite in naturally deformed sulphide bodies. Although pyrite stretching and folding have been described, undoubted plastic deformation in single pyrite grain has not been demonstrated from naturally deformed sulphides. To address these issues, the present contribution attempts to record and analyze the deformation behavior in pyrite in three major sediment-hosted Pb–Zn sulphide deposits in Rajasthan, enclosed by Aravalli Supergroup of rocks deposited in a complex system of rift basins in Bhilwara and Aravalli belts (Roy and Jhakar 2002), but deformed and metamorphosed under different grades under varying temperature–pressure conditions (Deb and Sarkar 1990). Textural characteristics of metamorphosed pyritic ores from the three deposits ranging from middle to upper greenschist facies (Balaria-Zawar) through middle amphibolite facies (Rajpura-Dariba) to upper amphibolite-granulite facies (Rampura-Agucha) were studied. They represent a broad temperature range of 400 to ~700 °C and about 4–6 kbar pressure (Deb 1990; Deb and Sehgal 1997; Mishra and Bernhardt 2009; Sarkar and Banerji 2004). All the three deposits, according to Pb isotope studies (Deb et al. 1989) have Paleoproterozoic ages between 1800 and 1700 Ma. More recently, the Paleoproterozoic model age of sulphide mineralization at Rajpura-Dariba (1.8 Ga, Deb et al. 1989) has been corroborated by the 1869 ± 22 Ma U–Th–Pb monazite age (Hazarika et al. 2013). This recent study with a different approach also establishes that the Pb isotope composition of the sulphide ores was not significantly altered during later metamorphism.

Our observations, as presented in this contribution, are restricted to the somewhat similar pyritic ores in carbon phyllites and schists in the three deposits mentioned, and are not concerned with the other ore types in these deposits. Out of more than hundred samples of this ore type in the three deposits, about two dozen samples with well preserved deformation features were studied in details (Mukherjee 2013) and from these a few representative ones were chosen to feature in this contribution. Mesoscopic folds were noted in hand specimens from Balaria and Rajpura-Dariba while the samples from Rampura-Agucha were mostly

massive. To bring out the grain boundary relationships of pyrite clearly, polished sections of ore-bearing rocks were etched with conc. HNO_3 acid for 30 s and then observed under reflected light microscope. The geologic setting of the deposits is described in the next section, followed by detailed observations of the textural characteristics of the pyrite-bearing ores from these three deposits.

Geologic Setting of the Pb–Zn Sulphide Deposits

The Aravalli Supergroup of rocks in Rajasthan, India (originally Aravalli ‘System’ of Heron 1953) is spread out in three contiguous basins from south to north: the Lunavada basin, the Aravalli basin with type locality in Udaipur valley and the Bhilwara basin in the north-east (Fig. 1), juxtaposed against the two tectonic blocks of the Banded Gneissic Complex (BGC) basement. Two of these, the Aravalli basin on the western side of the southern block of BGC and the Bhilwara basin on the eastern side of the northern block of BGC, are known to be the biggest repositories of sediment-hosted Pb–Zn sulphide deposits in India. The Aravalli-Jharol rocks are considered to represent a passive continental margin-cum-continental rise setting (Sugden et al. 1990) and the former are hosts to the Zawar Pb–Zn ore district, south of Udaipur. The Bhilwara rocks, on the other hand, are generally considered to have deposited in an intra-continental rift setting (Deb 1993) and host both the Rajpura-Dariba and Rampura-Agucha deposits. The relevant geological attributes of these three deposits is presented briefly in Table 1 below. For more details about these ore deposits, the reader is referred to the comprehensive volume by Deb and Goodfellow (2004).

Though the exact stratigraphic position of the three deposits being considered in this contribution is not crucial to the discussion on deformation of pyrite in them, we would still like to point out that the above-mentioned geologic-cum-stratigraphic setting of these deposits do not conform with the regional geologic ideas of Gupta et al. (1980, 1997), still prevalent among some geologists (mainly from the Geological Survey of India). This is in spite of the fact that some of the most recent GSI publications (e.g., Gouda et al. 2015) concede that the stratigraphic position of linear metasedimentary belts with significant sulphide mineralization, such as, the Rajpura-Dariba belt, within the gneissic rocks of the Mangalwar complex (BGC) remains controversial. Such belts have been considered to represent (i) post-Aravalli but pre-Delhi sequence named Raialo ‘Series’ (Heron 1953); (ii) the youngest unit of the Bhilwara Supergroup (Gupta et al. 1997); (iii) Aravalli-equivalent isolated cover sequence deposited in pull-apart basins (Sinha-Roy et al. 1998); (iv) the lithologic packages of Rajpura-Dariba, Rampura-Agucha, Pur-Banera belts are correlated with the upper carbonate horizon of the Aravalli Supergroup, i.e., Zawar Formation of the Udaipur Group (Roy and Jhakar 2002). Our contention regarding the tectono-stratigraphic setting of these three deposits is compatible with the last two options, suggesting a similar setting for all the three deposits.

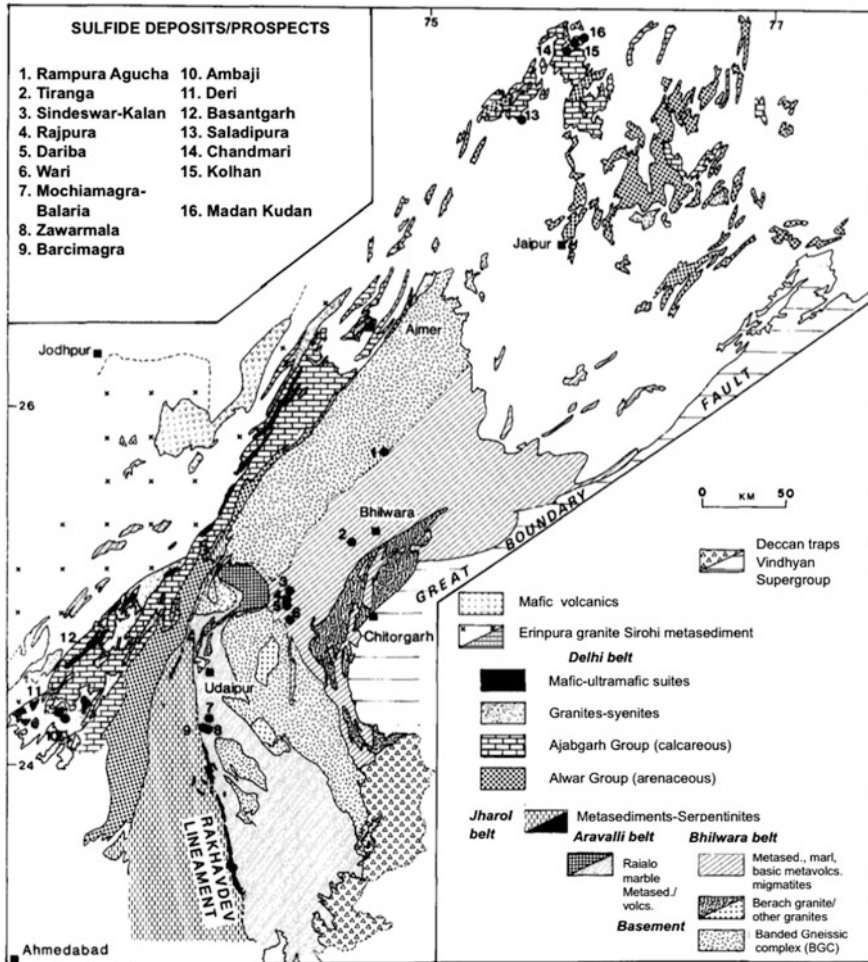


Fig. 1 Generalised geological map of Aravalli-Delhi orogenic belt, Rajasthan (after Deb et al. 1989). Note the position of the sulphide deposits—1 (Rampura-Agucha), 4-5 (Rajpura-Dariba) and 7 (Balaria)

Textural/Microstructural Characteristics of the Pyritic Ores

Zawar (Balaria) Deposit

The host rocks in the Balaria deposit are mainly dolostones with subsidiary carbonaceous phyllite. Quartzites, greywacke and litharenites are also found in the ore zone (Sarkar and Banerjee 2004). Principal ore minerals observed in this deposit in order of decreasing abundance are pyrite, sphalerite, arsenopyrite and pyrrhotite. Pyrite (Py) is present as fine to medium grained idiomorphs (0.08–0.2 mm

Table 1 General characteristics of the three sediment-hosted sulphide deposits of Rajasthan, India (modified after Deb and Sarkar 1990)

Deposit/Tectonic domain	Stratigraphy, structural character	Tectonic setting	Host rocks	Age (Ma)	Grade of metamorphism
Zawar/ Aravalli-Jharol belt	Aravalli Supergroup. Four phases of deformation, of which the first two are most penetrative	Second order rift basin or graben skirting the Sarara inlier	Dolostone, phyllite (carbon) and quartzite	1705	Upper greenschist facies (300–400 °C; 4 kbar)
Rajpura-Dariba/ Bhilwara belt	Aravalli Supergroup. Rocks affected by at least three phases of deformation	Series of half grabens or “pull-apart” basins in an intracontinental rift setting	Recrystallised siliceous dolostone, carbonaceous chert and graphite mica schist	1799	Middle amphibolite facies (555 °C; 5.4 kbar)
Rampura-Agucha/ Bhilwara belt	Aravalli Supergroup. Two main phases of deformation with a weak third phase.	As above, with tectonic inversion of basin-fills resulting in exhumation of high grade rocks	Graphite-sillimanite-mica schist	1804	Upper amphibolite-granulite facies (650 °C; 6 kbar or 780 °C; 6.2 kbar)

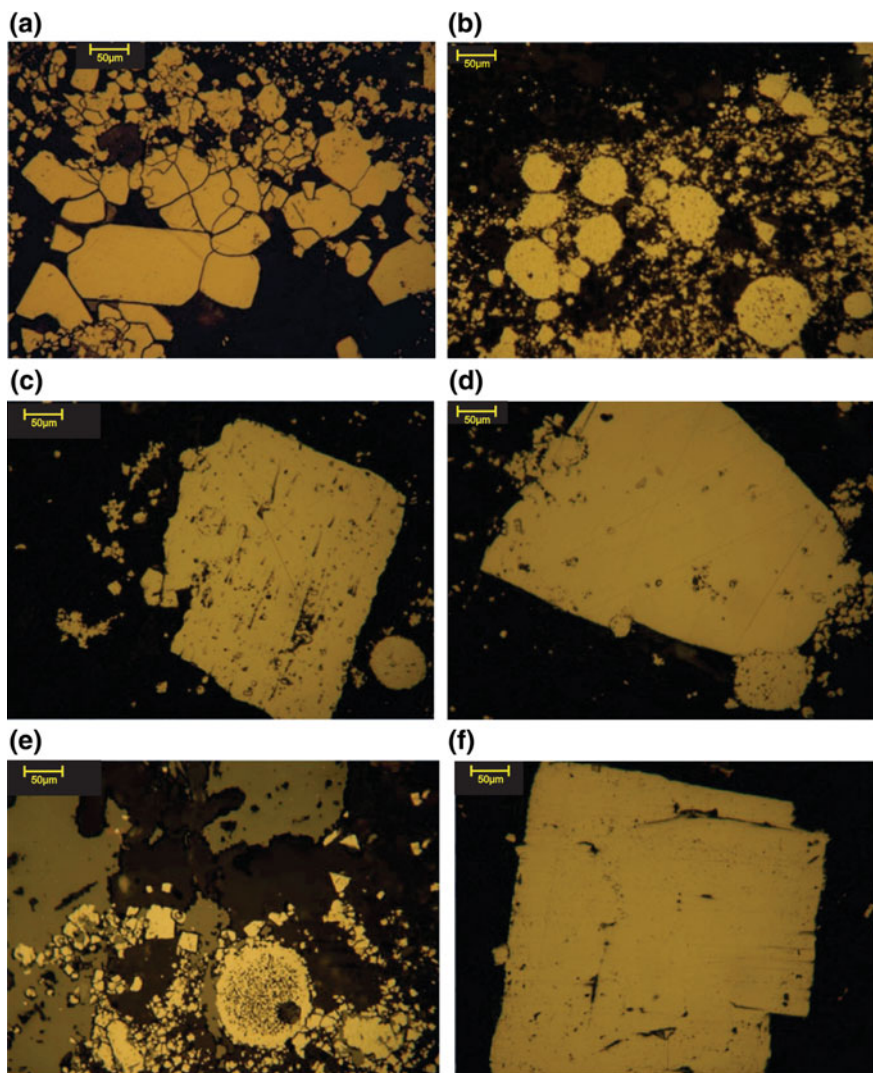


Fig. 2 **a** Fine to medium, idiomorphic grains of pyrite in Balaria ore. Reflected PPL. **b** Medium to fine, spheroidal framboids of pyrite in Balaria ore. Reflected PPL. **c** Co-existence of coarse euhedral pyrite with medium framboidal pyrite in Balaria ore. Reflected PPL. **d** Coarse, idiomorphic pyrite grain encloses or embays fine framboidal pyrite in Balaria ore. Reflected PPL. **e** Co-existence of medium framboidal pyrite with fine euhedral pyrite within Balaria ore. Note the speckled nature of the framboid due to fine carbonaceous inclusions. Reflected PPL. **f** Partial overgrowth of coarse pyrite idiomorph on medium pyrite idiomorph in Balaria ore. Reflected PPL. *Note* All bars in the 6 photomicrographs are 50 μm in length

diameter) (Fig. 2a) and fine framboids (0.01–0.09 mm) (Fig. 2b), while arsenopyrite occurs as medium to coarse grained idiomorphs, sometimes overgrown on fine pyrite euhedra. A conspicuous feature observed here is the coexistence of framboidal pyrite with the coarser (sometimes fine) euhedral form of the mineral (Fig. 2c–e). In some cases, the framboids occur as inclusions within the pyrite euhedra (Fig. 2d). The pyrite framboids are often pitted at the core and contain fine specks of carbonaceous matter (Fig. 2e), pointing to their sedimentary-diagenetic origin. Zoning (brought out more clearly on etching with HNO₃) in pyrite idiomorphs or overgrowth of pyrite euhedra on an earlier formed pyrite idiomorph (Fig. 2f) is a common feature. It is observed that quartz shares irregular and serrated grain boundaries with sphalerite but wherever quartz occurs with cubic, coarse grains of pyrite, the boundaries are regular and straight (Fig. 3a). This feature can be ascribed to differential force of crystallization which is higher in pyrite than in sphalerite, and this causes the grain boundaries in pyrite to be highly regular and straight but irregular and serrated in case of sphalerite. Further, the varying granularity of opaque grains in different layers seems to control the fineness or coarseness of the associated quartz.

Alternate layers of quartzose material comprising fine to coarse grained polygonized quartz and carbonaceous chert (Cc), and sulphide-rich (both fine and coarse) bands that constitute the rock show spectacular folding at hand-specimen scale (Fig. 3b). Folds are commonly disharmonic in nature with the carbonaceous layers showing parallel folds (Class 1B of Ramsay 1967) while the pyritic layers show flame-like protrusions forming Class 3 folds (Ramsay 1967) (Fig. 3b). The folds in cherty layers show high amplitude: wave length ratio indicating that the cherty layers were of higher competence than the adjacent pyritic layers in the prevailing deformational environment. A closer look at the individual pyrite grains near the fold hinges reveals that most of them have a nearly equant subhedral shape and do not show a clear crystal-preferred orientation at this scale (Fig. 3c). Under reflected light microscope, fine grained pyrite shows an oriented growth (i.e. elongated subhedral grains) within the strongly foliated carbonaceous matrix (Fig. 3d). The coarser grained pyrite, in contrast, shows abundant triple point junctions indicating annealing.

Rajpura-Dariba Deposit

The host rock at Rajpura-Dariba is recrystallized siliceous dolostone which shows direct contact with calcareous biotite schist in the footwall and grades to pure quartzite at places. It is also intercalated with black chert-sulphide rhythmities in specific zones and has a hanging wall contact with pyritic graphite schists (Deb 1986).

Ore mineral assemblage in the pyritic ores of Rajpura-Dariba includes pyrite as a dominant phase along with arsenopyrite, sphalerite, and very little galena. Pyrite, with grain sizes ranging from 0.13 to 0.5 mm, occurs in folded layers in which

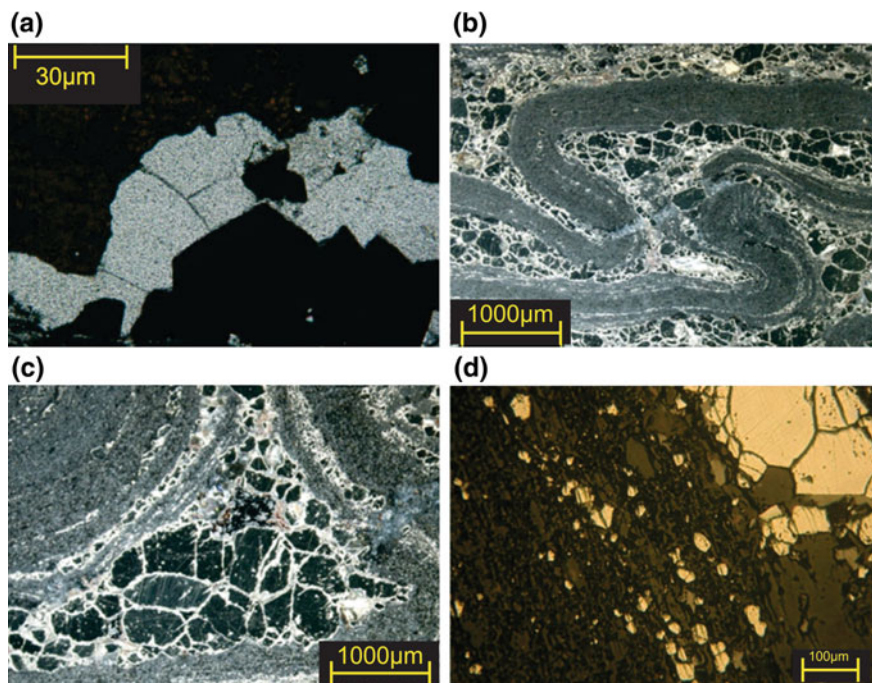


Fig. 3 **a** Grains of quartz in a band share serrated boundary with sphalerite (Sp) on the upper side and straight boundary with idiomorphic pyrite (Py) in the lower. Transmitted PPL. Bar length 30 μm . **b** Hand specimen photograph of Balaria ore under stereo-microscope showing tight folding of carbonaceous chert (Cc) bands interlayered with fine to medium grained pyrite (Py) bands. Bar length 1000 μm . **c** A close-up look at the same hand specimen of Balaria ore reveal that individual pyrite grains near the fold hinges have a nearly equant subhedral shape and do not show a clear crystal preferred orientation. Bar length 1000 μm . **d** Fine grained pyrite (Py) in Balaria ore shows an oriented growth of elongated subhedral grains within the strongly foliated carbonaceous matrix. The coarser grained pyrite, in contrast, shows abundant triple point junctions indicating annealing. Reflected PPL. Bar length 100 μm

individual pyrite grains commonly show well developed triple point junctions (Fig. 4a, b). Arsenopyrite occurs as isolated medium sized grains. Sphalerite is found in triangular intergranular spaces of gangue material, along grain boundaries of pyrite and at its triple point junctions. Quartz, micas and an accessory amount of feldspar comprise the gangue material. Quartz is both fine and medium to coarse grained with size ranging from 0.05 to 0.25 mm while mica is associated as flakes, aligning themselves in a particular direction or wrapping around coarse opaque grains.

Pyrite layers alternating with quartz-mica bearing gangue layers show spectacular folding at hand specimen scale (Fig. 4a). Folds in both pyritic and silicate layers show significant layer thickening at the hinge and thinning in the limbs, indicating macroscopically ductile flow of material towards the hinge during deformation. Commonly pyrite grains show equant shapes forming foam-like texture within the layers. However, at a few places, a weak shape-preferred orientation

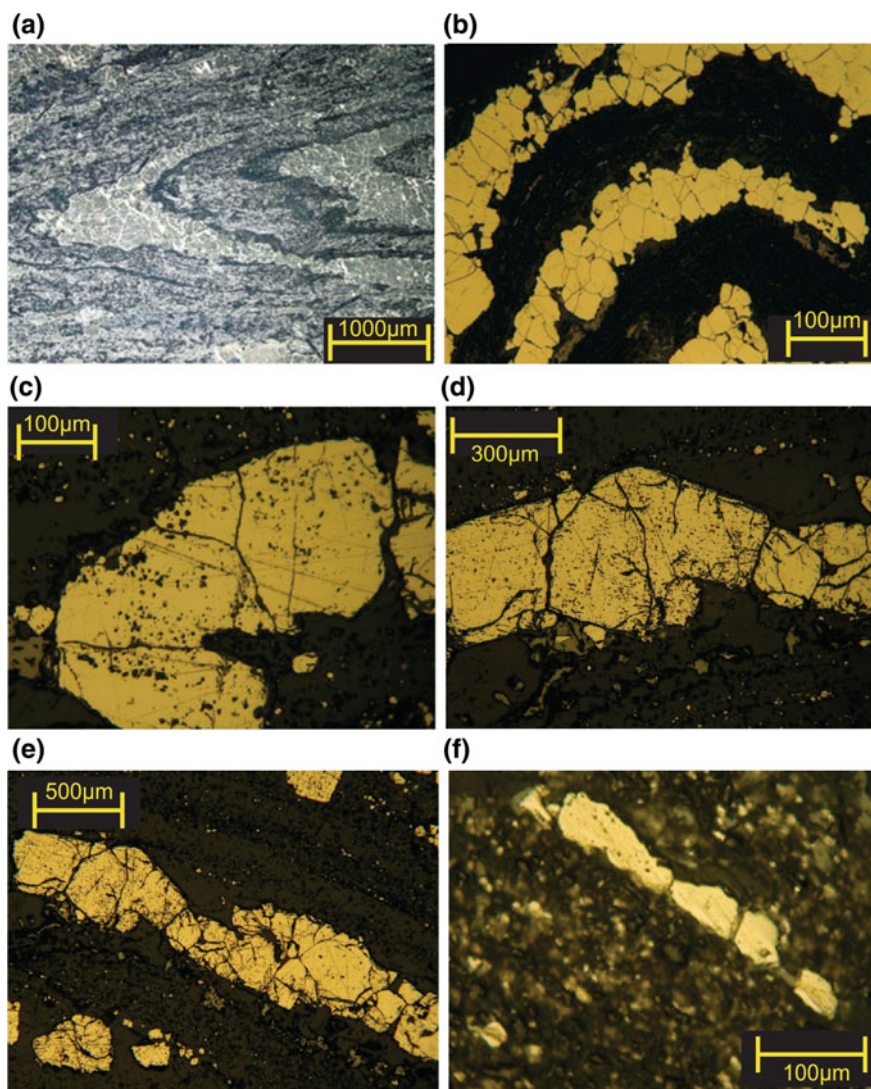


Fig. 4 **a** Tight to isoclinal folds in alternating pyritic (whitish) and silicate (grayish) layers in Rajpura-Dariba ore hand specimen in low power of stereo-microscope. Note thickening at the hinges and attenuation in the limbs. Bar length is 1000 μm . **b** Equant grains of pyrite (Py) producing a foam texture in folded pyrite bands. Note a rough preferred shape-orientation of some grains approximately parallel to the axial plane of the fold. Reflected PPL. Bar length is 100 μm . **c** Hook shaped folded pyrite grain showing radial fractures in Rajpura-Dariba ore. Reflected PPL. Bar length is 1000 μm . **d** Open fold in a pyrite grain showing fracture along the axial plane, in Rajpura-Dariba ore. Reflected PPL. Bar length is 300 μm . **e** Hook shaped fold in the same pyrite grain (originally), in Rajpura-Dariba ore. Reflected PPL. Bar length is 500 μm . **f** Spindle or barrel shaped pyrite grains parallel to the silicate layers with extensional fractures occurring in the neck portions, suggesting plastic deformation. Rajpura-Dariba ore. Reflected PPL. Bar length 50 μm

of elongate pyrite grains parallel to the axial plane of folds is observed (Fig. 4b). Under reflected light microscope, folded individual pyrite grains are observed (Fig. 4c–e). Radial fractures in such grains, and absence of any internal grain boundary indicate that these should be individual grains folded by plastic deformation. Small pyrite grains occurring parallel to the axial planar foliation in the silicate layers adjacent to some of the macroscopic folds show clear evidence of plastic strain as they have developed pinch-and swell structure followed by boudinage (Fig. 4f). Spindle or barrel shaped pyrite grains with extensional fractures (Fig. 4f) occurring in the neck portions indicate pre-fracturing plastic stretching of these grains. To summarize, after the formation of pyrite-rich rock and its subsequent metamorphism up to amphibolite facies, the annealed texture with triple point junction was formed. Later, during the waning stages of the second deformation when kyanite and tremolite grew in a disoriented fashion in the host rocks at temperatures >320 °C (cf. Deb 1990), plastic behaviour was imparted to the ore in the form of folds and flowage.

Rampura-Agucha Deposit

The dominant host rock in Rampura-Agucha is graphite schists associated with garnet-biotite-sillimanite gneiss. The ore minerals present are pyrite, pyrrhotite, sphalerite, arsenopyrite and chalcopyrite where pyrite occurs as coarse euhedral grains. Sphalerite and pyrrhotite occur as anhedral masses where the former also occurs as inclusions in pyrite (Fig. 5a) and the latter occurs within fractures and gaps between grain boundaries of pyrite. Fine specks of chalcopyrite within sphalerite are present as inclusions. Gangue minerals present are quartz, graphite, orthoclase, microcline, mica, sillimanite and very little plagioclase feldspar.

Folded and kinked graphite flakes are present in the ore-host rock indicating strong deformation of the host rock (Fig. 5a). The rock displays a strongly laminated nature due to deformation. Within individual layers, pyrite and pyrrhotite however show equilibrium annealed texture with abundant polygonization (Fig. 5b). Well developed idiomorphic grains of pyrite in the form of triangular, cubic, trapezoid shapes are found to be present within the pyrrhotite mass. The euhedral grains show fractures (Fig. 5c) in them indicative of brittle deformation. There are however, a number of microstructural features in this ore body that indicate plastic deformation of pyrite. Strongly elongated habit of pyrite is observed in grains oriented parallel to the foliation in silicate layers which can be partly due to growth parallel to the mechanically anisotropic matrix foliation (Fig. 5d). However, distorted shapes of pyrite grains and occurrence of pyrite occupying the intergranular spaces between the matrix minerals possibly point to a plastic flow. A few small pyrite grains also show pinching and boudinage by stretching parallel to the foliation (Fig. 5d).

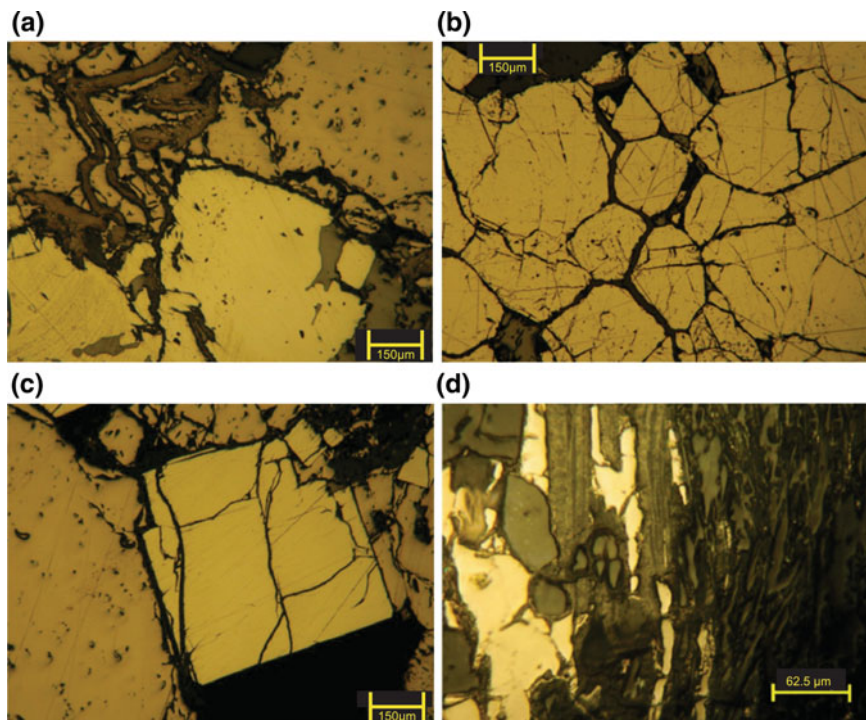


Fig. 5 **a** Idiomorphic coarse grain of pyrite (Py) in pyrrhotite mass containing highly kinked graphite flakes. Sphalerite occurs as inclusions in pyrite. Rampura-Agucha ore. Reflected PPL. Bar length is 150 μm . **b** Annealed mass of medium to coarse grained pyrite showing 120° triple junction point angles in Rampura-Agucha ore. Reflected light PPL. Bar length 150 μm . **c** Fractures in squarish coarse grain of pyrite in pyrrhotite mass in Rampura-Agucha ore suggest brittle deformation. Reflected light PPL. Bar length 150 μm . **d** Stretched pyrite grains or growth of pyrite parallel to the silicate foliation in Rampura-Agucha ore. However, small pyrite grains show pinching and boudinage by stretching parallel to the foliation. Bar length 62.5 μm

Discussion of the Textural Observations

Summarizing the salient aspects of textures seen in the pyritic ores of the three deposits studied, a deformed fabric of ore-host rocks is the most conspicuous feature common to all the deposits. The greenschist facies metamorphosed Balaria (Zawar) ores are the only ones with relict pyrite framboids which retain features of sedimentary-diagenetic growth in a carbonaceous environment. The association of framboids with the coarse idiomorphic pyrite grains and their occurrence as inclusions along the grain boundaries of the latter (Fig. 2b–d) is a significant feature which suggests that the growth of the pyrite euhedra took place at the expense of the framboids during metamorphism. The presence of zoning and overgrowth in coarser pyrite euhedra testify to an interrupted and repetitive growth of pyrite

during metamorphism of the Balaria ores. The pyritic layers of this deposit have been strongly folded with the host rocks indicating macroscopic ductility of the ore during deformation under greenschist facies conditions, but unequivocal evidence of plastic strain was not observed in individual pyrite grains. However, weaker rheological nature of pyrite relative to silicates is evident from the cusped-lobate folding of pyritic layers (Class 3 folds of Ramsay 1967). This does not necessarily indicate plastic behavior of pyrite grains, as individual grains within the aggregate may accommodate strain by grain rotation and grain boundary sliding etc. (a brittle-ductile mechanism) or through cataclastic flow, in which individual pyrite grains did not accommodate much plastic deformation. We may mention in this context that Ray (1977) conducted a detailed analysis of deformed pyrite grains along with the coexisting gangue material (quartz) and suggested that a significant competence contrast exists between quartzite bands and aggregates of pyrite. Pyrite-rich layers showed greater hinge thickening than the quartzite bands, indicating the relatively less competent nature of the pyrite aggregates. Since plastic deformation in an aggregate of quartz grains is common in nature, the same should not be unusual for pyrite grains. However this explanation is best suited for aggregates of pyrite grains and not in the case of single pyrite grains because interstitial fluid/more plastic material may cause the aggregate to impart plastic behaviour (Sarkar et al. 1980). Smaller pyrite grains in the Balaria ore show elongate subhedral nature parallel to the deformational fabric, but coarse grains show equant and euhedral nature with annealed textures. This indicates that pyrite may have undergone only an incipient plastic deformation which has been mostly obliterated during later grain growth.

It is interesting to note that experimental work of Cox et al. (1981) demonstrated that polycrystalline pyrite was able to undergo at least 20% shortening. The samples deformed above 450 °C typically showed grain boundary bulging, grain elongation and deformation bands, indicating significant plastic strain. Above 650 °C dislocation climb became common and led to dynamic recovery, recrystallization and steady state flow. A re-evaluation of Graf and Skinner's (1970) work mentioned earlier, by Graf et al. (1981) also identified plastic deformation of pyrite before brittle fracturing occurred. McClay and Ellis (1983) discounted plastic deformation of pyrite in greenschist facies conditions (<450 °C) and advocated for a solution re-precipitation process and grain boundary sliding, especially for fine grained pyrite, as the major deformation mechanism. They did not observe any unambiguous evidence of dislocation glide or creep in their samples, and concluded that dislocation creep in pyrite possibly occurs at high stress, high temperature and high strain rate (e.g. 10^{-8} to 10^{-4} per second). Diffusion creep (e.g. Cobble creep or Nabarro-Herring Creep), on the other hand, may operate at lower strain rates and at elevated temperatures. At higher metamorphic grade only metablastic growth and annealing was observed which possibly erased much of the evidence of low-grade deformation processes. Kuscu and Erler (2002) found pyrite deformation textures that are in agreement with the observations of McClay and Ellis (1983), and suggested that at lower temperature, deformation of pyrite produces a cataclastic fabric which transforms to annealed textures at higher metamorphic grades. Seven metamorphosed pyrite-rich ore deposits studied by Barrie et al. (2010b), on the

other hand revealed microstructures that indicate plastic deformation of pyrite within a broad temperature range of 320–610 °C. The evidence of such deformation at low temperatures includes lattice disorientation, dislocation creep and dislocation wall development. At higher temperatures, dislocation glide plays a major role. This work brought down the earlier conceived brittle-plastic transition in pyrite by more than 200 °C (e.g. from 500 plus to 320 °C) and indicated that pyrite may be more plastic than was earlier thought. However, it is still not well understood whether pyrite can deform by significant dislocation creep at the natural geological strain rate (10^{-14} per second). Moreover, dislocation glide in these samples appears to operate at a higher temperature than dislocation (climb-assisted) creep, which is rather unusual and goes against the commonly observed deformation behaviour of silicate minerals/metals (Nicolas and Poirier 1976). Cook et al. (1993) found that in stratabound pyritic massive sulphide deposits of Sulitjelma, Norway, the rheological contrast between the massive sulphide ore bodies and their surrounding phyllosilicate-rich alteration envelopes controlled the localization of deformation along the ore bodies and produced macroscopic folding and shearing. In the coarse grained pyrite, there was evidence of textural equilibrium through recrystallization, grain growth and annealing with prograde metamorphism. At a later stage, all these features were overprinted by a pervasive brittle deformation fabric. At a few selected locales of high resolved shear stress (e.g. in the macroscopic shear zones), dislocation flow might have led to the macroscopic ductility. Tiwary et al. (1998) traced the polyphase growth history of pyrite microfabric from the Deri mine, southern Rajasthan, India and related it to the tectono-thermal evolution of the massive sulphide deposit at amphibolites facies superimposed by a later phase of hornblende hornfels facies. The pyrite grains in these ores showed tight to isoclinal folds with stretched limbs and boudinage structure, suggesting both brittle and ductile deformation and post-deformational recrystallization and growth of pyrite.

At a higher metamorphic grade (middle amphibolite facies), the pyritic ore of Rajpura Dariba lost its diagenetic signatures marked by the conspicuous absence of framboidal pyrite. Folding of ore-gangue layers, accompanied by ductile flow, is commonly observed. Again, cataclastic flow could explain such macroscopic ductile behavior in such layered systems. Individual pyrite grains, however, show evidence of plastic strain, axial stretching, pinching and boudinage, and folding which all point to a significant plastic behavior (e.g. Fig 4c–e). Recrystallization of pyrite and attainment of a foam texture at the fold hinges is an artifact of later grain growth favoring Grain Boundary Area Reduction (GBAR: Passchier and Trouw 2005). Even after significant annealing, pyrite grains have occasionally preserved a shape preferred orientation in consonance with the local stress field (Fig. 4b).

At the highest metamorphic grade, encountered in the Rampura-Agucha ore, neither folded layers of pyrite nor folded single grains of pyrite have been noted. However, pyrite has possibly flowed during deformation and occupied intergranular spaces between the matrix minerals. Strong distortion of very small pyrite grains and pinching by axial stretching (Fig. 5d) indicate that pyrite must have deformed plastically at the upper amphibolite-granulite facies of metamorphism. Interestingly, most of the plastically deformed pyrites are fine grained. The coarser pyrite grains

show a high degree of idiomorphism and crystallinity within the pyrrhotite mass. Large pyrite grains are also intensely fractured suggesting intense brittle deformation. In contrast, the associated graphite flakes are either tightly folded or kinked, suggesting that deformation outlasted recrystallization. It may be suggested from the above observations that plastic deformation of pyrite was largely obliterated by grain coarsening (GBAR) processes and by later brittle deformation during the post-peak stages when temperature decreased. The fine grains of pyrite escaped this brittle deformation as they did not constitute the stress supporting network, like the larger grains, and therefore preserve some evidences of plastic deformation. This could also be an example of how rheological differences in minerals could bring about different responses to deformation in the form of different textures. The grain shapes of quartz in the ores are very irregular and are close to amoeboid shape suggesting the dominance of grain boundary migration as a recrystallization mechanism which is a characteristic of higher grade rocks.

We are aware that reflected light microscopic study alone does not reveal all the hidden secrets of pyrite microstructure, and a study like this must be followed up by SEM-based orientation contrast (OC) imaging and electron backscatter diffraction (EBSD) studies (cf. Boyle et al. 1998; Freitag et al. 2004; Barrie et al. 2010a, 2011 amongst others). However, non-availability of these facilities presently was not considered strong enough deterrent for systematically recording for the first time the interesting pyrite microfabrics from genetically similar ores, later imprinted with varying metamorphic grades, from the Indian shield. This lays the foundation for a detailed EBSD work on these pyrite microstructures in future, leading to more refined results.

Conclusions

Earlier works on pyrite deformation have established that pyrite can deform by a combination of cataclastic flow, diffusive mass transfer and local (grain-scale) plasticity over a wide temperature range (e.g. 320–700 °C: Barrie et al. 2010b), which have challenged the experimentally achieved brittle-plastic transition in pyrite (e.g. ca. 650 °C: Cox et al. 1981). However, optical microscopic signature of plastic deformation in pyrite grains has been limited. There is also some uncertainty in the strain rate at which pyrite can behave plastically. In the present contribution we have attempted to establish through hand specimen study and optical microscopy, as a first step, that pyrite has behaved in a plastic manner, not only in the form of mesoscopic and microscopic folding of layers, but also by distortions, bending and stretching of individual grains. In general, pyrite plasticity increases with temperature as revealed by more definitive evidences of plastic deformation in higher metamorphic grade deposits (e.g. Rajpura-Dariba and Rampura-Agucha) than in lower grade Balaria deposit, although Balaria ore is more intensely folded. Higher grade rocks may, on the other hand, induce more grain growth and thereby are likely to lose the evidence of plastic deformation through grain coarsening.

This may be one reason behind the apparent scarcity of plastic deformation textures observed in pyrite from naturally deformed and metamorphosed sulphide ore deposits.

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References

- Atkinson, B. K. (1975). Experimental deformation of polycrystalline pyrite: Effects of temperature, confining pressure, strain rate and porosity. *Economic Geology*, 70, 473–487.
- Barrie, C. D., Boyle, A. P., Cook, N. J., & Prior, D. J. (2010a). Pyrite deformation textures in the massive sulfide ore deposits of the norwegian caledonides. *Tectonophysics*, 483, 269–286.
- Barrie, C. D., Cook, N. J., & Boyle, A. P. (2010b). Textural variation in the pyrite-rich ore deposits of the Røros district, Trondheim region, Norway: Implications for pyrite deformation mechanisms. *Mineralium Deposita*, 45, 51–68.
- Barrie, C. D., Pearce, M. A., & Boyle, A. P. (2011). Reconstructing the pyrite deformation mechanism map. *Ore Geology Reviews*, 39(4), 265–276.
- Boyle, A. P., Prior, D. J., Banham, M. H., & Timms, N. E. (1998). Plastic deformation of metamorphic pyrite: New evidence from electron-backscatter diffraction and foreshatter orientation-contrast imaging. *Mineralium Deposita*, 34, 71–81.
- Cook, N. J., Halls, C., & Boyle, A. P. (1993). Deformation and metamorphism of massive sulphides at Sulitjelma Norway. *Mineralogical Magazine*, 57(1), 67–81.
- Cox, S. F., Etheridge, M. A., & Hobbs, B. E. (1981). The experimental ductile deformation of polycrystalline and single-crystal pyrite. *Economic Geology*, 76(8), 2105–2117.
- Deb, M. (1986). Sulphur and carbon isotope compositions in the stratiform Zn–Pb–Cu sulphide deposits of the Rajpura-Dariba belt, Rajasthan, NW India. *Mineralium Deposita*, 21, 313–321.
- Deb, M. (1990). Regional metamorphism of sediment-hosted, conformable base metal sulphide deposits in the Aravalli-Delhi orogenic belt, NW India. In P. Spry & L. Brindzia (Eds.), *Regional metamorphism of ore deposits* (pp. 117–140). Netherlands: VSP.
- Deb, M. (1993). The Bhilwara belt of Rajasthan—A probable proterozoic 'aulacogen'. In S. M. Casshyap (Ed.), *Rifted basins and aulacogens* (pp. 91–106). Nainital: Gyanodaya Prakashan.
- Deb, M., & Goodfellow, W. D. (Eds.). (2004). *Sediment-hosted lead-zinc sulphide deposits: Attributes and models of some major deposits in India, Australia and Canada*. New Delhi: Narosa Publishing House (367pp).
- Deb, M., & Sarkar, S. C. (1990). Proterozoic tectonic evolution and metallogenesis in the Aravalli-Delhi Orogenic Complex, Northwestern India. *Precambrian Research*, 46, 115–137.
- Deb, M., & Sehgal, U. (1997). Petrology, geothermobarometry and C-O-H-S fluid compositions in the environs of Rampura-Agucha Zn–(Pb) ore deposit, Bhilwara district, Rajasthan. *Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences*, 106(4), 343–356.
- Deb, M., Thorpe, R. I., Cumming, G. L., & Wagner, P. A. (1989). Age, source and stratigraphic implications of lead isotope data for conformable sediment-hosted base metal deposits in the Proterozoic Aravalli-Delhi orogenic belt, NW India. *Precambrian Research*, 43, 1–22.

- Freitag, K., Boyle, A. P., Nelson, E., Hitzman, M., Churchill, J., & Lopez-Pedrosa, M. (2004). The use of electron backscatter diffraction and orientation contrast imaging as tools for sulphide textural studies: Example from the Greens Creek deposit (Alaska). *Mineralium Deposita*, 39, 103–113.
- Gouda, H. C., Fareeduddin, Singh, R. K., Rajaram, H., Kumar, R., Kesavan, R., Golani, P. R., et al. (2015). Aeromagnetic anomaly maps of the Aravalli craton and their interpretations: Some new insights on stratigraphy and metallogeny of region. In *Recent developments in metallogeny and mineral exploration in Rajasthan*. Geological Survey of India, Special Publication, Vol. 101, pp. 1–28.
- Graf, J. L., Jr., & Skinner, B. J. (1970). Strength and deformation of pyrite and pyrrhotite. *Economic Geology*, 65, 206–215.
- Graf, J. L., Skinner, B. J., Bras, J., Fagot, M., Levade, C., & Couderc, J. J. (1981). Transmission electron microscopic observation of plastic deformation in experimentally deformed pyrite. *Economic Geology*, 76, 738–742.
- Gupta, S. N., Arora, Y. K., Mathur, R. K., Iqbaluddin, P. B., Sahai, T. N., & Sharma, S. B. (1980). Lithostratigraphic map of Aravalli region, southern Rajasthan and northeastern Gujarat. Geological Survey of India, Special Publication, Hyderabad.
- Gupta, S. N., Arora, Y. K., Mathur, R. K., Iqbaluddin, B. P., Sahai, T. N., & Sharma, S. B. (1997). The Precambrian geology of the Aravalli region, southern Rajasthan and northeastern Gujarat. *Memoirs of the Geological Survey of India*, 123, 262.
- Hazarika, P., Upadhyay, D., & Mishra, B. (2013). Contrasting geochronological evolution of the Rajpura–Dariba and Rampura–Agucha metamorphosed Zn–Pb deposit, Aravalli–Delhi Belt, India. *Journal of Asian Earth Sciences*, 73, 429–439.
- Heron, A. M. (1953). Geology of Central Rajputana. *Memoirs of the Geological Survey of India*, 79, 389.
- Krauskopf, K. B. (1967). *Introduction to geochemistry*. New York: McGraw Hill (721pp).
- Kuscu, I., & Erler, A. (2002). Pyrite deformation textures in the deposits of the Kure mining district (Kastamonu–Turkey). *Kure Maden Sahasi Yataklarında Pirit Deformasyon Dokulari (Kastamonu–Turkiye)*, 11(3), 205–215.
- Mc Clay, K. R., & Ellis, P. G. (1983). Deformation and recrystallization of pyrite. *Mineralogical Magazine*, 47, 527–538.
- Mishra, B., & Berhardt, H. J. (2009). Metamorphism, graphite crystallinity, and sulfide anatexis of the Rampura–Agucha massive sulfide deposit, northwestern India. *Mineralium Deposita*, 44, 183–204.
- Mookherjee, A. (1971). Deformation of pyrite. *Economic Geology*, 66, 200.
- Mukherjee, I. (2013). *Pyrite-black shale association in varying metamorphic grades in the Precambrian of India: A comparative study of their textural, compositional and deformational characteristics* (M.Sc thesis). University of Delhi, 203pp.
- Passchier, C. W., & Trouw, R. A. J. (2005). *Microtectonics*. Berlin: Springer (366pp).
- Ramsay, J. G. (1967). *Folding and fracturing of rocks*. New York: McGraw Hill (568pp).
- Ray, S. K. (1977). Deformation of pyrite aggregates, Saladipura area, Khetri copper belt, Rajasthan. *Indian Journal of Earth Science*, 4, 169–182.
- Roy, A. B., & Jhakar, S. R. (2002). *Geology of Rajasthan (Northwest India) Precambrian to recent*. Jodhpur: Scientific Publishers (421pp).
- Sarkar, S. C., & Banerji, S. (2004). Carbonate-hosted lead-zinc deposits of Zawar, Rajasthan in the context of world scenario. In M. Deb & W. D. Goodfellow (Eds.), *Sediment-hosted lead-zinc sulphide deposits* (pp. 328–349). New Delhi: Narosa Publishing House.
- Sarkar, S. C., Bhattacharyya, P. K., & Mukherjee, A. D. (1980). Evolution of the sulfide ores of Saladipura, Rajasthan, India. *Economic Geology*, 75, 1152–1167.
- Sarkar, S. C., & Deb, M. (1974). Metamorphism of sulfides of the Singhbhum copper belt, India: The evidence from the ore fabric. *Economic Geology*, 68, 1282–1293.

- Sinha-Roy, S., Malhotra, G., & Mohanty, M. (1998). *Geology of Rajasthan*. Bangalore: Geological Society of India (278pp).
- Stanton, R. L. (1972). *Ore Petrology*. New York: McGraw-Hill (713pp).
- Sugden, T., Deb, M., & Windley, B. F. (1990). Tectonic setting of the mineralization in the Proterozoic Aravalli-Delhi orogenic belt, northwest India. In S.M. Naqvi (Ed.), *Precambrian continental crust and its economic resources* (pp. 367–390). Developments of Precambrian Geology, Amsterdam: Elsevier.
- Tiwary, A., Deb, M., & Cook, N. J. (1998). Use of pyrite microfabric as a key to tectono-thermal evolution of massive sulphide deposits—An example from Deri, southern Rajasthan, India. *Mineralogical Magazine*, 62(2), 197–212.