Chert association in the mineralized zone of the Proterozoic Dariba–Rajpura–Bethumni belt, Rajasthan: an oxygen isotope study and its implications

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The polymetallic Zn–Pb–Cu–Ag mineralization in the Dariba–Rajpura–Bethumni (DRB) belt, Rajasthan is hosted by metamorphosed Proterozoic calc-silicate-bearing siliceous dolostone, carbonaceous metapelite, tuffaceous schist and carbonaceous chert. The characteristics of the chert-bearing rocks from this belt are described here and based on their nature, field relationships and oxygen isotope composition, comments on their possible mode of origin are made. The present-day origin of chert is mainly biogenic with diatoms and radiolarians playing a dominant role in its formation; but in the Precambrian, the noticeable absence of these organisms did not affect the silica cycle and a chemically precipitated chert-forming mechanism was suggested. It is postulated that sulphide mineralization in the DRB belt resulted from the exhalation of silica-bearing hydrothermal fluids with subsequent precipitation in a semi-restricted basin with euxinic conditions. The chert precipitated out from the same exhalative siliceous mineralizing fluids as evidenced by similar oxygen isotope values in the host rocks and the associated cherty rock units.

Keywords: Chert formation, hydrothermal exhalation, oxygen isotope, sedimentary exhalative deposit.

CHERT, by definition, is a chemically precipitated sedimentary rock composed primarily of microcrystalline and/or chalcedonic quartz with subordinate mega-quartz along with minor impurities. Although appearing similar both chemically and petrographically, the major difference between the Phanerozoic and Precambrian cherts lies in their mode of formation. In the Phanerozoic, silica-secreting organisms played a major role in the silica cycle and consequent chert formation, but in the Precambrian, the noticeable absence of these organisms does not seem to have affected the chert formation. Chert commonly occurs as distinct beds or as lenses, nodules or silicified laminae in carbonate rocks and forms near the surface either during early diagenesis of a chemically precipitated precursor or as a primary precipitate. This communication discusses the characteristics of the various forms of chert from the Dariba–Rajpura–Bethumni (DRB) mineralized belt and based on their nature, field relationships and oxygen isotope constitution, comments on their possible mode of origin and relationship with the mineralization. The DRB belt (Figure 1) is well known not only for the polymetallic Zn–Pb–Cu–Ag mine at Dariba containing a number of rare Sb, Tl, Hg, Ge, V phases, but also for a Palaeoproterozoic mineralization age of ~1800 Ma (ref. 4), making it one of the oldest dated, metamorphosed, sediment-hosted, massive, Zn–Pb sulphide belts around the world.

Cherts within the 17 km long DRB belt occur primarily as mineralized carbonaceous type in the ore zone and as clasts within brecciated iron formation which extends along the footwall of the mineralized zone. In the Sindsar Khurd and Sindsar Kalan prospects (cf. Figure 1), a deformed quartzite unit, which may have been derived from a chert protolith, forms prominent ridges and is underlain by the mineralized host rocks. Besides cherts, the other major rock types in the DRB belt comprise basement gneisses and schists, amphibole–carbonate-bearing pelites, calcareous biotite schist, recrystallized siliceous dolostone, graphite-bearing metapelites and tuffs and garnetiferous quartzite. Among these, the host rocks for mineralization are represented by calc–silicate-
bearing siliceous dolostones, carbonaceous metapelites, tuffaceous schists and carbonaceous cherts.

Carbonaceous chert is an important host rock for mineralization in the Dariba deposit. The rock comprises fine-grained quartz associated with finely disseminated carbonaceous matter imparting a ‘black’ colour to the massive chert alternating with fine bands of coarser-grained quartz and pyrite–sphalerite, visibly devoid of carbonaceous matter. This massive laminated to finely banded chert bears a strong resemblance to ore-chert rhythmites\(^3\) (Figure 2\(a\)). Microscopically, the fine-grained chert comprises individual quartz grains indistinguishable from each other even at high magnifications dominantly masked by carbonaceous matter. Associated ore minerals include sphalerite and pyrite occurring as fine-grained disseminations. Fine bands of coarser-grained recrystallized quartz and pyrite–sphalerite are arranged parallel and alternating with the fine-grained carbonaceous chert and are generally devoid of carbonaceous matter (Figure 2\(b\)). Other accessory minerals in the rock include biotite, carbonate (possibly dolomites) and rare clasts of fine-grained carbonate which are conspicuously different from the preserved carbonate ‘ghost’ inclusions characteristic of carbonate-replacement cherts\(^6\). Deformational textures in the form of folded chert and recrystallized ore minerals are common. A few epigenetic, coarse-grained, quartz–carbonate veins cut across the carbonaceous chert unit.

In Dariba, the carbonaceous chert unit is in close contact with carbonaceous metapelite which contains large (up to 10 cm) kyanite porphyroblasts occurring either as blades or as rosettes\(^5\).

The easternmost extension of the recrystallized siliceous dolostone in Dariba displays a sharp contact with a brecciated iron formation unit (ferruginous breccia)\(^3\) and marks the footwall of the mineralized zone. This brecciated ferruginous unit, with a considerable strike length along the belt, has a narrow width and is most conspicuous in Rajpura, where it occurs in close association with the gossans. The unit extends farther northwards to Bethumni following a N–NNE to S–SSW trend parallel to the bedding plane trend. The monomictic breccia comprises chert clasts of variable shape and size embedded within reddish to dark brown coloured hematitic matrix (Figure 3). The chert clasts are rectangular to sub-rounded along with a few other irregular-shaped fragments. The sizes of the clasts are not uniform and range from a few millimetres to several centimetres. Quartz-rich veinlets commonly crisscross the breccia resulting in a complex network of veins, however, many of the veinlets exhibit striking parallelism. Deformation textures in the form of quartz veins displaying minor folds and faults with detached or rotated/displaced chert are also common. The iron formation has a limited down-dip extension and gradually grades into a red-brown coloured ferruginous chert unit with limonite–hematite-rich coatings.

The ore body in Dariba differs from the other ore bodies in the belt by the presence of a discrete patch of lensoid, diopside-rich carbonate rock with discordant, strata-bound, coarse-grained sulphides\(^5\). This diopside-rich rock commonly associated with quartz also contains rare sulphosalts of Zn–Ag–As–Sb–Tl–Hg–Au and other minor phases in the veins, pods and patches of coarse-grained galena.

The Sindesar Khurd deposit and the Sindesar Kalan prospect are located within a prominent ridge of quartzite, compositionally represented by a meta-chert, with patchy zones of gossans and ferruginous breccia. The quartzite ridge displays prominent F1 folds which have been re-folded coaxially by the second phase of folding (F2). The metachert unit completely conceals the underlying mineralized dolostone and carbonaceous metapelitic units.

Samples of carbonaceous chert and chert clasts within brecciated iron formation from Dariba, and metachert from the Sindesar Khurd were analysed for their oxygen isotopic composition. The oxygen isotopic composition of quartz from the mineralized, diopside-rich rock was also analysed and compared with the isotopic composition of chert from the other parts of the mineralized belt.

The oxygen isotopic data are reported as \(\delta^{18}O\) which represents the deviation in parts per thousand of the \(^{18}O/^{16}O\) ratio of the sample with respect to the international standard – (Vienna) Standard Mean Oceanic Water (VSMOW).

The oxygen isotopic composition of the different samples is presented in Table 1 and plotted graphically in Figure 4. \(\delta^{18}O\) of the carbonaceous cherts varies between 14.7‰ and 16.0‰. The metachert/quartzite from Sindesar Khurd gave an isotopic value of 13.9‰. \(\delta^{18}O\) for the silica clasts within brecciated iron formation varies between 14.1‰ and 17.6‰. \(\delta^{18}O\) values for quartz within mineralized, diopside-bearing rocks associated with the recrystallized siliceous dolostone in Dariba mine are 14.5‰ and 12.1‰.

During the Precambrian, the oceanic silica concentration was much higher (~ 60 ppm; ref. 2), than the present-day dissolved silica concentration (1 ppm or less)\(^5\), facilitating a direct temperature and pH-dependent silica precipitation out of sea water\(^6,8,9\). In the absence of silica-
Figure 3. Field photographs from Dariba showing hematitic matrix-supported ferruginous breccia unit comprising (a) banded to laminated and faulted chert clasts (marker pen as scale highlighted within the circle); (b) linear to disoriented chert clasts and (c) irregularly shaped and sized chert clasts.

Table 1. $\delta^{18}O$ values obtained for the cherts, silica clasts and quartzite from the belt

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Location</th>
<th>Sample description</th>
<th>$\delta^{18}O$‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Dariba</td>
<td>Carbonaceous chert with pyrite and sphalerite</td>
<td>14.9</td>
</tr>
<tr>
<td>C2</td>
<td>Dariba</td>
<td>Carbonaceous chert with pyrite bands</td>
<td>15.8</td>
</tr>
<tr>
<td>C3</td>
<td>Dariba</td>
<td>Carbonaceous chert with banded sphalerite</td>
<td>16.0</td>
</tr>
<tr>
<td>C4</td>
<td>Dariba</td>
<td>Carbonaceous chert with bands of pyrite</td>
<td>15.8</td>
</tr>
<tr>
<td>C5</td>
<td>Dariba</td>
<td>Carbonaceous chert with bands of pyrite</td>
<td>14.7</td>
</tr>
<tr>
<td>Q1</td>
<td>Sindesar Khurd</td>
<td>Metachert</td>
<td>13.9</td>
</tr>
<tr>
<td>Q2</td>
<td>Dariba</td>
<td>Chert clast within brecciated iron formation</td>
<td>16.5</td>
</tr>
<tr>
<td>Q3</td>
<td>Dariba</td>
<td>Chert clast within brecciated iron formation</td>
<td>14.1</td>
</tr>
<tr>
<td>Q4</td>
<td>Dariba</td>
<td>Chert clast within brecciated iron formation</td>
<td>17.6</td>
</tr>
<tr>
<td>F1</td>
<td>Dariba</td>
<td>Silica–iron-rich matrix of brecciated iron formation</td>
<td>14.6</td>
</tr>
<tr>
<td>D1</td>
<td>Dariba</td>
<td>Silica associated with the diopside-bearing recrystallized siliceous dolostone</td>
<td>14.5</td>
</tr>
<tr>
<td>D2</td>
<td>Dariba</td>
<td>Silica associated with the diopside-bearing recrystallized siliceous dolostone</td>
<td>12.1</td>
</tr>
</tbody>
</table>

Figure 4. Distribution of $\delta^{18}O$ from various rock units in the belt.

secrating organisms during this time, a balance was maintained between the rate of inorganic removal/precipitation and silica influx into the oceans. The high oceanic silica concentration has commonly been attributed to increased levels of hydrothermal fluxes. The increased hydrothermal flux during the Proterozoic is also supported by geochemical evidences, including REE data which suggest cherty iron formations to have precipitated from solutions representing a mixture of sea water and hydrothermal input. Maliva et al. had hypothesized that downward diffusion of silica from the Late Proterozoic sea water into sediments might have fuelled the growth of chert nodules nucleated on organic matter or some other attractant.

With the evolution of the diatoms and silica-secreting radiolarian in the Cambrian, the mechanism of chert formation and precipitation underwent a major transformation from abiological silica precipitation in the Archean and Proterozoic, to biologically controlled silica deposition in the Phanerozoic. This mechanism of chert formation has been dominant throughout the Phanerozoic, so much so that in today’s environment these diatoms and radiolarians practically control the silica concentration in the sediments.

The $\delta^{18}O$ values of chert also witnessed a general increase of about 10‰ between the Archean and Phanerozoic, corresponding to an overall decrease in temperature of about 40°C (ref. 11). The documented $\delta^{18}O$ values of all Precambrian cherts are lower than those of...
Phanerozoic cherts with representative Phanerozoic (Eocene) cherts having $\delta^{18}O$ of 35‰, whereas the maximum $\delta^{18}O$ of chert in Palaeoproterozoic iron formation is 24–24.7‰ (ref. 2). These values appear to generally rise throughout the Proterozoic and become similar to Phanerozoic values by 1.2 Ga (ref. 11) (Figure 5).

A detailed $\delta^{18}O$ study of the Palaeoproterozoic Gunflint iron formation (Lake Superior-type) and Kuruman and Hamersley iron formations, giving the maximum $\delta^{18}O$ values in the Proterozoic$^2$, was undertaken by Simonson$^{12}$. The study concluded that the chert was a primary or very early diagenetic precipitate. Amongst the several hypotheses for the direct precipitation of quartz in the granular Lake Superior iron formation, Simonson$^{12}$ suggested that the near-surface chert was formed by the upwelling, silica-rich water which was expelled up-dip along a steep thermal gradient from sediments deeper in the sedimentary basin$^2$.

The chert-bearing brecciated iron formation in the DRB belt closely represents iron formations associated with massive sulphide ores which are considered to be chemical sediments deposited from hydrothermal fluids that vented into submarine basins$^{13,14}$. The chert-breccia with hematite-rich matrix has a limited down–dip extension and gradually grades into ferruginous chert with limonite and hematite-rich coatings. The chert clasts within the brecciated iron formation and the mineralized carbonaceous chert yield almost similar $\delta^{18}O$ values (14.1–17.6‰ for the chert clasts and 14.7–16‰ for the mineralized carbonaceous chert). Furthermore, silica associated with the matrix of the brecciated iron formation also yielded a similar $\delta^{18}O$ value of 14.6‰, suggestive of a similar source for the precipitation of mineralized chert and the brecciated iron formation. There is a close association of these litho-units and mineralization as evidenced by similar oxygen isotope values (12.1–14.5‰) for silica associated with the diopside-bearing recrystallized siliceous dolostone unit, which is strongly mineralized and contains unusual and rare sulpho-salts and other minor phases in veins, pods and patches of coarse-grained gale
na$^{3,5}$. Summarizing, the $\delta^{18}O$ values of the different cherts, chert clasts and quartz (12.1–17.6‰) from the Proterozoic DRB belt are considerably lower than those expected for the Phanerozoic cherts.

The changes in the isotopic signatures of cherts as a result of metamorphism have been a topic of discussion for sometime. It was suggested that the processes of weathering, diagenesis and metamorphism tend to lower the isotopic ratios of chert and as a result old cherts were depleted in $\delta^{18}O$ because they had more time to exchange isotopes with their surroundings than young rocks$^2$. However, it has also been argued that the low permeability of cherts make them less prone to late dissolution/ reprecipitation events compared to carbonates, and low water/rock ratios during metamorphic heating do not result in perturbation of $\delta^{18}O$ in cherts$^{9,11,15}$. Moreover, Jones and Knauth$^{16}$, and Matheney and Knauth$^{17}$ have also demonstrated that silica is highly resistant to isotopic exchange once it is converted to crystalline quartz and thus retains its pristine isotopic character.

Field observations of the carbonaceous schist unit, lying in proximity to carbonaceous chert from the DRB belt, show kyanite porphyroblasts occurring either as blades or exhibiting rosette texture, indicating a stress-free environment for the growth of the mineral. Textural studies of the carbonaceous chert also show coarse-grained ore minerals and recrystallized quartz, which is devoid of any carbonaceous matter, arranged parallel and
alternating with layers containing fine-grained quartz, carbonaceous matter and disseminated ore (Figure 2). The absence of recrystallized ore and quartz grains in the presence of carbonaceous matter is generally ascribed to the phenomenon of inhibition-dependent secondary recrystallization in which the fine specks of carbonaceous matter inhibits the growth and recrystallization of the minerals in its vicinity.

The field and textural observations suggest that although the DRB belt is perceived to have undergone an isofacial amphibolite facies metamorphism, zones within these deformed and metamorphosed rocks (e.g. bands of unrecrystallized carbonaceous cherts) still retain their pristine character and appear not to have been altered and affected by the later metamorphic events which would tend to homogenize the isotope values across the belt. Moreover, it has been reported that recrystallization and metamorphism in chert involves considerably low water/rock ratios, such that δ¹⁸O values remain largely unchanged. In Dariba, the isotopic disequilibrium in sulphides has also been noted with variable δ³⁴S values in three different varieties of sphalerite in successive layers of an ore sample showing an overall isotopic variation (Δ³⁴S = 10‰). This indicates that isotopic equilibration was not achieved even though the ores and host rocks were subjected to amphibolite facies metamorphism. The role of later low-temperature diagenetic fluids altering the isotopic composition of chert is also ruled out as the extreme resistance of the quartz grains fails to alter the isotopic composition of quartz.

The carbon isotope values (δ¹³C) obtained for the carbonaceous cherts from Dariba range from −23.8‰ to −31.1‰ (mean −26.6‰) and conform to a typical biogenic derivation of the carbonaceous matter in the carbonaceous chert. However, it is being proposed in the present study that the Paleoproterozoic chert from the DRB belt has an abiotic origin. This apparent dual mode of formation is best explained by taking into consideration the exhalative nature of the mineralized hydrothermal fluids and their association with chert formation. The silica-rich, mineralized, hydrothermal fluids were introduced in a semi-restricted basin with euxinic conditions facilitating the prolific growth of organic life and consequent development of carbonaceous matter which deposited simultaneously with the precipitating chert resulting in a carbonaceous chert unit. The finely interlaminated nature of the mineralized ore–chert rhythmite is also suggestive of episodic introduction of the silica and ore–silica-rich hydrothermal fluids. This mode of the carbonaceous chert formation best explains the highly depleted δ¹³C carbon compositions representing the biogenic component of the carbonaceous chert, whereas the δ¹⁸O values of the chert correspond well with the hydrothermally evolved chert-bearing units.

It is envisaged that the base metals were leached from the underlying calcareous–argillite prism and gneissic base-mant rocks with mafic flows (amphibolite) and introduced into a rift-related euxinic basin with prolific biogenic activity by exhalation of silica-enriched, mineralized, hydrothermal fluids through dislocation zones. The exhalative nature of hydrothermal fluids is best evidenced by the presence of the brecciated ferruginous unit which extends along the belt. The chert precipitated from the same mineralizing fluids episodically, thus alternating with the ore–silica-rich fluids as evidenced by the nature of the ore–chert rhythmite and similar oxygen isotope values for the cherty breccia clasts and silica associated with the matrix of the chert breccia, the carbonaceous chert and quartz associated with diopside-rich dolostone.

Preliminary optical chronology suggests significant advance in Nubra valley glaciers during the Last Glacial Maximum

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Optical stimulated luminescence chronology obtained on moraines suggests that the Nubra valley was extensively glaciated during the Last Glacial Maximum. We attribute this to the enhanced moisture contribution from the mid-latitude westerlies. Our study negates the suggestion that glaciation in Ladakh and Nubra valley was non-existent due to the weak summer monsoon during the Last Glacial Maximum. Further chronology of the recessional moraines proximal to the present-day Siachen glacier snout suggests insignificant recession in the glacier snout since the last 1 ka.

Keywords: Optical chronology, Last Glacial Maximum, moraines, Nubra Valley, Siachen Glacier.

The elevated mountains environments are significantly affected by global climate change. The Himalayan mountains and Tibetan Plateau which have significant effect on global climate may have played a key role in the beginning of the Quaternary glaciations. The elevated topography facilitated the development of glaciers during the Quaternary and such records can be used to reconstruct the temporal and spatial variations in the intensity of glaciations. Himalayan glaciers are nurtured by two major moisture sources, viz. the mid-latitude westerlies and the Indian Summer Monsoon (ISM). The influence of westerlies-dominated moisture source to the Himalayan glaciers decreases from northwest (Karakoram) at the spread of ISM as one move eastwards.

In the Himalaya, late Quaternary climate variability produced successive glaciations as evidenced by the presence of relict glacial landforms and moraines, which provide an opportunity for reconstructing the regional and global climatic changes provided they are supported by numeric dating. Studies have suggested that the Himalayan glaciers advanced and retreated asynchronously with that of the Northern Hemisphere glaciations, thus emphasizing the role of ISM as a major driving force of glaciations in the Himalaya. It has been suggested that the valley glaciers during the global Last Glacial Maximum (LGM) were less extensive in the Himalaya and virtually absent in Ladakh and Nubra valley.

In the northwestern Himalaya five glacial advances of decreasing magnitude have been identified in the Ladakh Range (Trans-Himalaya) since 430 ka. This is attributed to the reduction in moisture flux (both by ISM and the westerlies) in the glacier accumulation areas due to uplift of the Himalayan ranges to the south and the Karakoram ranges to the west. A recent study in the Nubra valley failed to locate glacial moraines corresponding to LGM, instead the three glacial stages identified by them were dated to 45 ka, 81 ka and 144 ka respectively. This is contrary to the suggestion made that the Siachen glacier probably occupied the entire Nubra valley (up to Nubra–Shyok confluence) during the LGM. Considering that the major source of moisture in Nubra valley is from the mid-latitude westerlies, and the westerlies were known to be enhanced during LGM, it was reasonable to accept that Nubra valley glaciers should have expanded during LGM. In a recent synthesis of the existing chronometric data, it has been suggested that the stratigraphic and chronometric data are too meagre to make any definite inference in favour or against any specific moisture regime for

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