Depositional setup of the faunal coal balls from Bichom Formation of Lower Gondwana Group of Arunachal Himalaya: insights from EPMA and Raman Spectroscopy

Bashab N. Mahanta1 · K. Sekhose2 · Tapos Kr. Goswami3 · V. Vitso2 · Ranjan Kr. Sarmah3 · Amit Kumar4 · Raman Kumar5

Received: 30 September 2020 / Revised: 13 December 2020 / Accepted: 15 December 2020 / Published online: 16 January 2021
© The Author(s), under exclusive licence to Springer Nature Switzerland AG part of Springer Nature 2021

Abstract
An attempt is made to study the composition of the carbonate minerals and silica in the faunal coal balls of Lower Gondwana Group of rocks of Arunachal Himalaya using Electron Probe Micro Analyser (EPMA) and Raman Spectrometer (RS). It is observed that, the carbonates developed in the coal balls contain Fe, Mg and Mn which corresponds to the concentration of dolomite and indicates a relatively high salinity in the sedimentary environment or of the formation water. Raman spectrum of silica indicates the presence of hydroxylated nanometre sized α quartz-chalcedony in the coal balls. We construe the incorporation of electrolyte rich solution in the coal swamps near sea shore took place due to repeated influx of sea water in lagoonal condition facilitating precipitation of chalcedony in a restricted alkaline environment thus created.

Keywords Faunal coal ball · Carbonate · Silica · EPMA · Raman spectroscopy · Gondwana · Arunachal Himalaya

1 Introduction
Coal balls are irregularly dispersed inorganic concretions of variable size and shape found within some coal beds of the world, especially from North America and Europe (Stopes and Watson 1908; Noé 1923; Andrews 1951; Mamay and Yochelson 1962; Nelson 1983; Prakash et al. 1988, Barwood 1995). Coal balls can be classified into three types, (a) normal coal balls, containing only plants; (b) mixed coal balls, containing both plants and marine invertebrate animals such as bryozoas, ostracodes, trilobites, foraminifers, molluscs etc.; and (c) faunal coal balls, containing only these marine invertebrate animals (Mamay and Yochelson 1962). There are reports of concretions from Indian coalfields (Ghosh 1971; Chandra et al. 1971), though faunal coal balls with nuclei of animal fossil are only reported from the Bichom Formation of Lower Gondwana Group of rocks from Garu-Gensi area of West Siang District, Eastern Arunachal Himalaya (Prakash et al. 1988). The coal balls from this area are composed of Ca, Mg and Fe carbonates, Fe-oxides and varying proportions of clay and silt. Most of these are massive and calcareous in nature and have marine fossils, such as Chonetes sp., and Platytichium sp. (brachiopods, bivalve molluscs) (Prakash et al. 1988). It suggests the possibility of marine incursions in the coal forming swamps in this particular area. Prakash et al. (1988) suggested seaward extension of the peat swamps which were periodically inundated by the sea water thereby facilitating the formation of the coal balls with animal remains. Geochemistry of associated coal samples from the area reveals that the coals are of sub-bituminous variety enriched with clay matter and deposited under marine/lagoonal conditions (Mahanta et al. 2017). Sediments in the Indian Gondwana basins are mostly deposited under continental setup, though some marine influences are also recorded (Sastry and Shah 1964; Shah and Sastry 1975; Dickins and Shah 1979; De 1979; Venkatadhala and
Tiwari 1987; Gupta 1999; Dutt and Mukhopadhyay 2001; Mukhopadhyay et al. 2010). In addition, the exclusive outcrop of marine Gondwana in Arunachal Himalaya demands special attention with respect to reconstruction of this supercontinent. An attempt in this work is made to study the faunal coal balls using Electron Probe Micro Analyser (EPMA) to acquire precise, quantitative molecular and elemental analyses at very small spot size. Furthermore, the spatial distribution of quartz grains and their mineralogical composition in the groundmass of carbonate minerals of the faunal coal ball is also studied through EPMA. This is because the quartz grains are small (< silt size) and below the resolution capabilities of a standard Petrological microscope.

Additionally, samples of microcrystalline silica associated with the faunal coal balls have been examined with Raman Spectrometer (RS) to investigate the types of polymorphs of quartz and the characteristics of the component phases.

2 Location and geological setting

The area is located in West Siang District of Arunachal Pradesh, India (Fig. 1). The Gondwana rocks in the area occur as a linear belt trending WSW-ENE and are designated as Bichom Formation of the Lower Gondwana Group. These rocks are overlain by the Miri Group of rocks. The rocks of the Miri Group are thrust over the Gondwana rocks along Miri Thrust. Towards South, the Gondwana rocks are juxtaposed against the rocks of the Siwalik rocks along the Main Boundary Thrust (Fig. 2). The Bichom Formation can be divided into Rilu and Bomte members. The Rilu Member is composed of diamictite, orthoquartzite, khaki shale, coal, carbonaceous shale, siltstone, sandstone, concretions with marine fossils. The Bomte Member is comprised of carbonaceous shale, grey shale, coal, shaly coal, sandstone occasionally with marine fossils (Roy Chowdhury 1978; Mahanta et al. 2017, 2019). A generalised stratigraphic succession after GSI 2010 is given in Table 1.

2.1 Nature and occurrence of the coal balls

The faunal coal balls of Garu-Gensi area generally occur in the coal and carbonaceous shale of Bomte Member of Bichom Formation (Table 1). These concretions can be easily identified on surface by their sub-rounded to oval and occasional elliptical shape (Fig. 3a, b). The coal balls are very hard to break and are arranged along the bedding planes of the coaly shale (Fig. 3a). These coal balls have yielded well preserved marine fossils viz. brachiopods, bivalves,
Depositional setup of the faunal coal balls from Bichom Formation of Lower Gondwana Group of…

Some of the balls contain one fossil as nuclei but in most occasions, fossils are found to be dispersed in irregular manner in the entire coal ball (Fig. 3c, d).

### 3 Methodology

The basic objective of the study of chemical composition of carbonate minerals in faunal coal ball is to understand the principle that these minerals were formed after deposition of the enclosing sediment and, therefore, contain host rock mineralogy to a considerable extent. The interaction of the carbonate minerals and the host solution plays an important role in the development of the early localised carbonate cementation (Pettijohn 1984). The Electron probe offer high resolution images and fine details of spot analysis and hence widely used to study micro textures and minute features which are normally difficult to study under a microscope. In addition, it is a non destructive technique to obtain chemical analysis of solid samples. The quartz present in the faunal coal ball is also targeted in Raman spectrooscope (RS) to delineate the host solution prevalent during the formation of the primary concretion which results in the precipitation of quartz. The analyses are carried out using a five spectrometer (viz. TAP, PET, LPET, LIF and LIF first to five, etc. (Singh 1978a, b, c, d; Prakash et al. 1988).
respectively) CAMECA SX-100 model EPMA machine (accelerating voltage of 15 kV and a current of 20 nA, with a beam diameter of 1 μ with a counting time of 20 s) and Renishaw Invia Reflex Micro-Raman instruments (with Wire 3.1 software) in the Central Petrological Laboratory of Geological Survey of India, CHQ, Kolkata, India.

For the analysis, well preserved and fresh samples of faunal coal balls have been collected from Bomte (27°48′56″, 94°42′01″), Garu (27°48′49″, 94°43′13″) and Rilu (27°50′38″, 94°46′58″) localities in the study area. The split coal balls are initially studied for petrography and it was observed that the quartz grains in the coal balls are small (< silt size) and below the resolution capabilities of a standard Petrological microscope though on rotation of the stage under crossed nicols, at places shows mild undulose extinction of micro quartz grain (Fig. 4). Considering the limitations of the optical microscopy, the sections are subjected to EPMA study and thus the chemical composition of the groundmass of carbonate mineral of the faunal coal ball is ascertained. RS is carried out for the quartz grain units in the coal balls.
4 Results of EPM analysis/mineral chemistry

The EPMA studies revealed that the mineralogical constituents observed in the coal ball are calcite, dolomite, siderite and apatite (Fig. 5a). Along with the carbonate minerals, very fine grained irregular shaped quartz grains are also recorded (Fig. 5b). The quartz grains occur as irregular organic relic infillings, embedded in dolomitic groundmass (Fig. 5a, b). Fine grains of pyrite occur in considerable amount along with carbonate minerals and quartz. The chemical composition of carbonate minerals in the faunal coal ball is given in Tables 2 and 3 and presented in Fig. 6.

The content percent of CaCO$_3$, MgCO$_3$, FeCO$_3$, MnCO$_3$ are calculated using the formulae, {content percent of the carbonate element = content percent of the oxide element × (molecule weight of the carbonate element/ molecule weight of the oxide element)} (Li-hua 1991) and then the ratios of Ca/Fe, Ca/Mg are calculated (Table 2). When CaCO$_3$ and MgCO$_3$ are found as main components and the ratio Ca/Mg < 3.6, the mineral is named as dolomite; if the main ingredients were CaCO$_3$, MgCO$_3$, and FeCO$_3$ > 10%, it is ankerite and when the ingredient is CaCO$_3$, and content of other ingredients is less than 1%, then the mineral is named as calcite; and if the main ingredient is CaCO$_3$, content of FeCO$_3$ > 1%, and Ca/Fe > 3.5, then it is named as ferroan calcite (Li-hua 1991; Chengdong et al. 2011).

The quartz grains in EPMA, occur as irregular grains and organic relic infillings embedded in dolomitic groundmass (Fig. 5b). The irregularity of the quartz grains is attributed to the precipitation of the minerals in situ in the presence of grained irregular shaped quartz showing colloform texture (QTZ and grey areas) in faunal coal ball. CAL calcite, DOL dolomite, PY pyrite, QTZ quartz.

![Fig. 5 a](image1.png) Backscattered electron (BSE) image showing the composition of faunal coal ball composed of CaCO$_3$, MgCO$_3$, organic relic, quartz and pyrite, b BSE image showing dolomite with very fine grained irregular shaped quartz showing colloform texture (QTZ and grey areas) in faunal coal ball. CAL calcite, DOL dolomite, PY pyrite, QTZ quartz.

Table 2 Analysed EPM chemical composition of faunal coal balls

| Pts | Na$_2$O | SiO$_2$ | MgO | P$_2$O$_5$ | K$_2$O | CaO | TiO$_2$ | Cr$_2$O$_3$ | MnO | FeO | NiO | Al$_2$O$_3$ | Remarks |
|-----|---------|--------|-----|-----------|-------|-----|--------|-----------|-----|-----|-----|---------|---------|
| 1   | 0.05    | 0.73   | 9.9 | 0.32      | 0.03  | 29.98| 0.04   | 0.07      | 0.91 | 12.35| 0.01| 0.13    | Carbonate |
| 2   | 0.01    | 7.56   | 0.24| 0.66      | 1.16  | 50.01| 0      | 0.55      | 0.4  | 2.15 | 0   | 0.45    | Carbonate |
| 3   | 0.02    | 6.5    | 9.04| 0.33      | 0.08  | 26.96| 0      | 0.05      | 0.6  | 13.25| 0.06| 0.18    | Carbonate |
| 4   | 0.17    | 4.72   | 0.46| 34.84     | 0.1   | 49.27| 0.23   | 0.03      | 0.07 | 0.44 | 0   | 0.23    | Apatite  |
| 5   | 0.04    | 1.25   | 8.42| 0.12      | 0.07  | 7.93 | 0      | 0         | 1.49 | 38.41| 0   | 0.72    | Siderite |
| 6   | 0.03    | 98.44  | 0   | 0.06      | 0.07  | 0.05 | 0      | 0.11      | 0.08 | 0.08 | 0   | 0.24    | Silica   |
| 7   | 0.73    | 44.53  | 0.34| 0         | 8.88  | 0.05 | 0.29   | 0         | 0.08 | 1.49 | 0.02| 35.99   | Clay     |

Table 3 Mineral contents calculated according to the data analyzed by EPMA in carbonate minerals of faunal coal balls and minerals' naming (%)

| Pt | CaCO$_3$ | MgCO$_3$ | MnCO$_3$ | FeCO$_3$ | Ca/Fe | Ca/Mg | Naming   |
|----|----------|----------|----------|----------|-------|-------|----------|
| 1  | 39.20    | 10.80    | 1.17     | 16.37    | 2.394 | 3.62  | Dolomite |
| 2  | 55.45    | 0.226    | 0.44     | 2.452    | 35.77 | 387.7 | Calcite  |
| 3  | 33.1     | 9.427    | 0.73     | 16.82    | 1.96  | 3.511 | Dolomite |

Fig. 5 a Backscattered electron (BSE) image showing the composition of faunal coal ball composed of CaCO$_3$, MgCO$_3$, organic relic, quartz and pyrite, b BSE image showing dolomite with very fine grained irregular shaped quartz showing colloform texture (QTZ and grey areas) in faunal coal ball. CAL calcite, DOL dolomite, PY pyrite, QTZ quartz.
carbonate rich solution. Generalised chemical composition of quartz in faunal coal ball analysed by EPMA is 98.44% SiO₂ with negligible amount of other oxides (Table 2).

4.1 Results of Raman spectroscopy of the faunal coal balls

Due to the microscopic size and heterogeneity of the mineral constituents of the faunal coal ball, Raman spectrum gives very low range of count approximately of 200–800 cm⁻¹. A very poor intensity of the counts is recorded in the study. The Raman spectrum of quartz, measured from selected areas of the thin sections are 465 cm⁻¹, 466 cm⁻¹ and 467 cm⁻¹ which is the relative peak in Raman spectroscopic study for hydroxylated nanometre α quartz–chalcedony.

The Raman frequencies of Si–O stretching modes and O–Si–O bending modes can be compared with the number of tetrahedra forming rings within framework structures of silicate (Sharma et al. 1981; Kingma and Hemley 1994). The position of the 465, 466 and 467 Raman shift cm⁻¹ mode in the hydroxylated nanometre α quartz–chalcedony spectrum is constant with this model, as the structure of α quartz–chalcedony consists of four-membered rings of corner-sharing SiO₂ tetrahedra (Kingma and Hemley 1994). The Raman spectrum of pure quartz or α quartz-chalcedony, measured from selected areas of the thin sections of the faunal coal balls samples, are shown in Fig. 7. Micro-Raman measurements in the range of 50–1250 cm⁻¹ reveal sharp bands with frequencies and relative intensities throughout the entire sample. The most intense peaks are centred at between 400 and 500 cm⁻¹ and less intense peak at 600–650 cm⁻¹. The variance in the Raman shift cm⁻¹ from 465 to 468 is due to motions of Si and O atoms within the framework structures of tetrahedrally coordinated phases (Etchepare et al. 1974; McMillan and Hess 1990; Kingma and Hemley 1994).

5 Discussion

The presence of marine animal remains in the coal balls indicates proximity of coal swamp to the sea waters (Mamay and Yochelson 1962). The occurrence of faunal coal balls with marine fossils such as brachiopods, bivalves, gastropods, etc. undoubtedly indicates a marine influence for the coal bearing strata in this particular Gondwana basin of Arunachal Himalaya (Singh 1978a, b, c, d; Prakash et al. 1988). Biswas (1999) also indicated presence of a narrow sea arm connected to the Tethys Sea at the north of the area as shown in Fig. 8. Nevertheless, these faunal coal balls are subjected to Electron probe as well as Raman spectroscopy for obtaining insights to assist in understanding of the paleogeography.

The EPMA study of the faunal coal balls shows that, the carbonate developed had a certain content of Fe, Mg and Mn which corresponds to the concentration of dolomite. The chemical composition and ratios derived thereof (Ca/Fe: 1.96–2.394; Ca/Mg: 3.511–3.62), indicate incorporation of Mg and Fe rich solution in the sedimentary environment of deposition.

Chalcedony is regarded as a secondary, metastable, transitional phase and apparently forms in a rather restricted environment, characterised by low to intermediate conditions of temperature and pressure which is alkaline (White and Corwin 1959). The notion that the formation of chalcedony is preceded by a viscous silica gel, was proposed by some workers (Liesegang 1915; Oehler 1976; Kastner 1980). However, there are reports of a gelatinous origin for chalcedony (Shaub 1955; Landmesser 1988; Moxon 1991; Heaney 1993). On the basis of the analysis of quartz, using RS, the presence of hydroxylated nanometre chalcedony, a variety of α quartz, in the faunal coal ball indicates a high alkaline condition of the source solution (Lovering 1972). Precipitation of silica requires either of the following conditions, i.e. (1) a suitable source of silica; (2) fluids capable of dissolving and transporting the silica to the site of deposition; (3) conditions at that site causing silica to displace the host rock with faster or same rate of dissolution of the host, compared to the rate of precipitation of silica. The solubility of amorphous silica at low temperatures and pressures is pH dependent and is more in strongly alkaline solutions than in weakly acid to neutral solutions (Lovering 1972). The presence of sodium chloride and alkaline carbonate accelerates the solution of colloidal silica in alkaline solutions (Gruner 1922; Boydell 1924, 1927; Iler 1955). Van Lier et al. (1960) established that dilute NaCl greatly
accelerates the equilibration of silica in solution, resulting in its precipitation. Change of pH causes neutralisation of the solution and contributes towards the precipitation of dispersed colloidal silica. Iler (1955) was of the view that gelation or precipitation of colloidal silica takes place most readily in the pH range of 5–6. It is reported that the addition of soluble salts causes gelation or flocculation of supersaturated silica solutions; and if the sodium salts are present in high concentration, that causes silica to precipitate (Iler 1955; Lunevich 2019).

6 Conclusions

From the Electron probe analysis of the faunal coal balls it is inferred that, incorporation of Mg and Fe rich solution in the sedimentary environment was due to mixing of sea water and terrestrial acidic water which is indicative of a shoreline environment favourable to coal deposition. This proximity has contributed towards periodic influx of saline water to the coal swamps. Subsequently, pH neutralization

Fig. 7  a Raman range 300–600 cm−1 showing the Raman shift cm−1 peak 465 cm−1 indicating occurrence of α quartz-chalcedony. b Raman peaks in the range 200–800 cm−1 delineate the Raman shift cm−1 peak of 466 cm−1—α quartz-chalcedony also indicating Raman spectra of tetrahedrally coordinated silica polymorphs. c α quartz-chalcedony 468 cm−1 Raman peaks in the range 400–550 cm−1. The labelled peaks correspond to the symmetric Si–O–Si stretching-bending modes
of this solution has occurred due to the intermixing of terrestrial acidic water carried by fluvial processes and saline sea water. The restricted alkaline condition was created when the sea regressed forming the lagoon with sufficient amount of carbonaceous matter to form peat. The large interstices present within the peat were filled with mud lumps containing marine animals carried by the sea water during its periodic influx. The high salinity condition hence created in the swamps, therefore, created favourable condition for precipitation of colloform chalcedony in the carbonate cements of the coal balls containing invertebrate marine fossils in them.

Though presently it is a part of the eastern Himalayas, the Gondwana basin of Arunachal Pradesh deserves greater attention due to its occurrence far south of the Tethyan Himalaya. This is suggestive of a separate narrow incursion of the sea from the east. Elemental and spectral information generated from the study of coal balls from this basin enhances this possibility.

![Map showing Indian rift basins during early Permian](image)

**Fig. 8** Map showing Indian rift basins during early Permian. 1. Narmada-Son rift zone, 2. Pranhita–Godavari rift, 3. Son-Mahanadi rift, 4. Purnia-Galsi rift, 5. Kuchma rift, 6. East Himalayan rift (present day Gondwanas of the study area), 7. Indo-Australian rift and 8. Greater India-Cimmeria rift. Solid arrow indicates entry of Tethys sea into the rift basins, red rectangle indicates the study area. **AF** Africa, **ANT** Antarctica, **AR** Arabia, **AUS** Australia, **IND** India, **MAD** Madagascar (after Biswas 1999)

**Acknowledgements** With deep sense of grief, the authors would like to acknowledge the assistance and support rendered by Late B. R. Syngai, Suptdg. Geologist, Geological Survey of India during the fieldwork who lost the battle with Covid-19 on 18th July, 2020. Authors are highly indebted also to the Additional Director General & HOD, NER, Geological Survey of India, Shillong for permitting them to publish the work.

**Author contributions** BNM field data collection, writing original draft, methodology, software. KS data collection, methodology. TKG conceptualisation, writing. VV field data collection. RKS conceptualisation, writing. AK field data collection. RK field data collection.

**Funding** None.

**References**

Andrews, H. N., Jr. (1951). American coal-ball floras. *Botanical Review, 17*(6), 431–469. https://doi.org/10.1007/BF02879039.
Singh, T. (1978b). A new species of spiriferoid genus *Subansiria*, Subansiri district, Arunachal Pradesh. In V. J. Gupta (Ed.), *Contributions to himalayan geology* (pp. 162–164). Delhi: Hindustan Publishing Corporation (India).

Singh, T. (1978c). Brachiopods from Permian Formation of Siang District, Arunachal Pradesh. In V. J. Gupta (Ed.), *Contributions to himalayan geology* (pp. 171–188). Delhi: Hindustan Publishing Corporation (India).

Singh, T. (1978d). Lower Permian cephalopods from Eastern Himalaya, India. *Himalayan Geology*, 8(1), 178–193.

Stopes, M. C., & Watson, D. M. S. (1908). On the present distribution and origin of the calcareous concretions in coal seams, known as “coal balls.” *Philosophical transactions of the Royal Society of London*, 200, 167–218.

Van Lier, J. A., De Bruyn, P. L., & Overbeek, J. T. G. (1960). The solubility of quartz. *Journal of Physical Chemistry*, 64(11), 1675–1682.

Venkatachala, B. S., & Tiwari, R. S. (1987). Lower Gondwana marine incursions: Periods and pathways. *Palaeobotanist*, 36, 24–29.

White, J. F., & Corwin, J. F. (1959). Synthetic chalcedony. *Geological Society of America Bulletin*, 70(12), 1696–1697.