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**Geochemistry of carbonate formations of the Chhattisgarh Supergroup, central India:
implications for Mesoproterozoic global events**

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Draft

Abstract

The Chhattisgarh Supergroup is one of the major Proterozoic marine sedimentary sequences of India. It consists of largely undeformed and unmetamorphosed siliciclastic, volcanoclastic and carbonate formations deposited in two sub-basins, Hirri and Bharadwar, separated by an Archean greenstone belt. In spite of its apparent importance for Mesoproterozoic oceanic records very few geochemical studies have been carried in the basin. Here, we present results of our high resolution geochemical and C-O-Sr isotopic studies in two carbonate formations of the supergroup - the Charmuria and the Chandi. We observe elevated $\delta^{13}\text{C}$ values increasing from 2.6 to 3.6‰ in these formations, which is consistent with the globally reported late Mesoproterozoic values. Such consistently positive $\delta^{13}\text{C}$ values are attributed to increased organic carbon burial in the basin margins during the deposition of these carbonates. Based on the principles of $\delta^{13}\text{C}$ isotope stratigraphy, we suggest a depositional age between 1.0 and 1.2 Ga for these carbonates which form the upper part of the Supergroup. The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained from the Charmuria and Chandi formations, 0.70723 and 0.70816, respectively, are more radiogenic than the contemporaneous seawater suggesting that the Sr isotopic system of the formations are altered. Based on the similarity in the $\delta^{13}\text{C}$ values, we stratigraphically correlate the carbonate formations of the Raipur Group in both the Hirri and Bharadwar sub-basins. We also present a compilation of available $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ records from all the Proterozoic sedimentary successions of India and compare it with the global datasets. We find that while the

Indian basins possess records of the Bitter Springs and Shuram $\delta^{13}\text{C}$ anomalies, they lack evidence for the other major global events of the Proterozoic.

Keywords

Proterozoic basins, Indian subcontinent, Chhattisgarh, Vindhyan, Marwar, Chemostratigraphy

1. Introduction

The Proterozoic Eon was one of the most eventful periods in the history of the Earth. Two supercontinents, Columbia and Rodinia, formed and disintegrated during this period (Evans 2013). Climate underwent extreme variations in the form of snowball Earth events, and life made tremendous evolutionary leap from prokaryotes to complex multicellular organisms through eukaryotes, culminating in the emergence of Ediacaran biota (Hoffman et al. 1998, Butterfield 2000, Kirschvink et al. 2000, Narbonne 2005, Azmy et al. 2008). Close to the beginning of the eon while the Earth's atmosphere got oxygenated, the deep oceans remained largely anoxic (Och and Shields-Zhou 2012, Lyons et al. 2014). Several lines of evidence suggest episodic oxygenation of the oceans throughout the Proterozoic, before its ventilation at the end of the eon (Sahoo et al. 2012, Gilleaudeau et al. 2016, Planavsky et al. 2018). The above tectonic and biogeochemical changes laid the foundation for the subsequent evolution of life and moulded the planet to its present state.

The Indian subcontinent occupies a significant position in both Columbian and Rodinian reconstructions (Li et al. 2008, Meert and Santosh 2017). It hosts a number of sedimentary basins of Proterozoic antiquity and a majority of these largely undeformed and unmetamorphosed

92 sedimentary sequences are marine and therefore likely to hold clues to tectonic, climatic and
93 biological evolution on Earth during this period. There exists only a handful of studies that
94 attempt to uncover evidence for various Proterozoic global events from the carbonate formations
95 in these basins (e.g., Ray et al. 2003, Mohanty et al. 2015, Ansari et al. 2018, George et al.
96 2018). Most of such data have come from the Vindhyan Basin which hosts the largest
97 Proterozoic sedimentary sequence in India, the Vindhyan Supergroup. The protracted
98 sedimentation in the Vindhyan Basin got initiated around 1.72 Ga and continued up to at least
99 0.80 Ga (Sarangi et al. 2004, Gopalan et al. 2013, George et al. 2018) with a depositional hiatus
100 of ~400 million years during 1.6 Ga and 1.2 Ga (Ray 2006, Tripathy and Singh 2015). Although,
101 the deposition in the Vindhyan Basin resumed at ~1.2 Ga, carbonate formations made
102 reappearance only at the beginning of the Neoproterozoic in the form of Bhander and Lakheri
103 limestones. In order to bridge this gap in the Proterozoic marine record of India and to facilitate
104 global correlations, we carried out geochemical studies in the carbonate formations of the
105 Chhattisgarh Basin located adjacent to the Vindhyan Basin (Fig. 1). Sedimentation in the
106 Chhattisgarh Basin began prior to 1.42 Ga (Das et al. 2011), largely over the ~2.5 Ga granitoids
107 of the Bastar craton, and continued at least up to 1.0 Ga (Patranabis-Deb et al. 2007), forming an
108 ~2.5 km thick repository of siliciclastics and carbonates. With the main objectives of
109 reconstructing the Mesoproterozoic ocean chemistry and understanding the evolution of life at
110 the cratonic margins, we studied the carbonate formations of the Chhattisgarh Supergroup using
111 various geochemical proxies such as major-trace element contents, and C-O-Sr isotopic ratios.
112 Using the data from this study and the available data from the Vindhyan and the Marwar
113 supergroups, we provide a composite curve for the Proterozoic evolution of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in

the Indian basins, assuming that they were all interconnected by one ocean, and correlate it with that of the contemporaneous global seawater, and discuss its implications.

2. Geological setting

The sediments of the Chhattisgarh Supergroup were deposited in two sub-basins, the Hirri in the west and Bharadwar in the east, separated by the Sonakhan Greenstone Belt (SGB), and two proto-basins in the southeast – the Singhora and the Barapahar. The entire basin as a whole covers an area of approximately 33,000 km² (Fig. 1). There is no consensus in the tectonic framework in which the deposition took place. Three tectonic settings – an intracratonic sag, rift, and foreland, were proposed at various points (Patranabis-Deb and Chaudhuri 2007, Chakraborty et al. 2015). Lithostratigraphically, the Chhattisgarh Supergroup is divided into four groups; the Singhora, the Chandarpur, the Raipur and the Kharsiya in temporally ascending order (Das et al. 1992, Saha and Patranabis-Deb 2014; Fig 2). Siliciclastics dominate the Singhora and Chandarpur groups. The carbonate-dominated Raipur Group conformably overlies the Chandarpur Group. The contact between the two groups is gradational with the arenaceous Chandarpur Group grading into thinly bedded limestone-marl rhythmite of the Charmuria Formation (Fig. 3A; Chakraborty et al. 2015). The evenly bedded limestone-marl rhythmite becomes thicker towards the top and grades into bedded pure limestone. The largely micritic Charmuria Limestone contains plenty of disseminated pyrite grains, phosphatized chert, and lacks any current or wave generated sedimentary structures, which suggest its deposition in an isolated shallow water shelf setting, in dysoxic condition (Patranabis-Deb et al. 2016). The Gunderdehi Formation, containing calcareous shales, separates the Charmuria from the overlying

Chandi Formation. Stromatolitic limestone and dolostone make up most of the Chandi Formation along with minor sandstone and shale units (Fig. 3B). These stromatolites are columnar, domal, and stratiform types and display desiccation cracks on individual columns (Chakraborty et al. 2002). The facies variation in the formation includes plane laminated lime mudstone and autoclastic conglomerate made up of stromatolitic clasts. These features coupled with the lack of any current or wave produced structures indicate that the Chandi Formation, for the most part was deposited in a shallow subtidal to intertidal setting, with the plane laminated mudstone likely deposited below the storm wave base (Chakraborty et al. 2002). The Charmuria and Chandi formations in the Hirri sub-basin (Fig. 2) are considered as lateral equivalents of the Sarangarh and Saradih formations, respectively, of the Bharadwar sub-basin, albeit facies variations (Chakraborty et al. 2015). The Tarenga and Hirri formations overlie the Chandi Formation (Fig. 2A). They are mostly composed of shale and dolostone, and form the remaining part of the Raipur Group and the overlying Kharsiya Group in the Hirri sub-basin (Das et al. 1992, Saha and Patranabis-Deb 2014). In the eastern Bharadwar sub-basin, a sandstone unit with basal conglomerate known as the Sarnadih Formation unconformably overlies the Raipur Group and is followed by shale dominated Nandeli Formation (Fig. 2B). They form the Kharsiya Group and overlie the Churtela Formation, the topmost formation of the Raipur Group in the sub-basin, and marks the end of sedimentation in the Chhattisgarh Basin (Mukherjee et al. 2014).

Most of the biostratigraphic studies carried out in the Chhattisgarh Supergroup have ascertained a Meso-Neoproterozoic age for its deposition. Moitra (2003) suggested a late Neoproterozoic age for the topmost Raipur Group based on the stromatolitic assemblages. This inference was supported by the microfossil assemblage of acritarchs and benthic cyanobacteria of different

families recovered from the Saradih Formation of the Raipur Group (Fig. 2; Singh and Babu 2013). There are no radiometric age data available from the carbonate formations of the Raipur Group. However, Pb-Pb ages of magmatic zircons separated from tuff beds located in the underlying Singhora Group and in the shale unit at the top of the Raipur Group provide reasonable time constraints for depositions of the Charmuria and Chandi formations (Fig. 2). A porcellanite formation (lithified tuff) sandwiched between the Rehatikhol and Saraipalli formations of the basal Singhora Group (Fig. 2) was dated by Pb-Pb zircon dating to 1405 ± 9 (2σ) Ma (Bickford et al. 2011b) and by U-Pb EPMA monazite dating to ~ 1500 Ma (Das et al. 2009). There exists a Sm-Nd whole rock isochron age of 1421 ± 23 (2σ) Ma for a diabasic intrusive in the Saraipalli Formation (Fig. 2; Das et al. 2011). These ages provide the maximum limit for the initiation of deposition of the Raipur Group. Magmatic zircons from the Sukhda Tuff deposited above the Churtela Formation in the Bharadwar sub-basin and the correlated Damda tuff of the Tarenga Formation in the Hirri sub-basin at the top of Raipur Group have been dated by Pb-Pb method to 1007 ± 20 (2σ) Ma and 993 ± 8 (2σ) Ma, respectively (Fig. 2; Bickford et al. 2011a; Patranabis-Deb et al. 2007). These establish that both the Charmuria and Chandi formations were deposited between 1.4 and 1.0 Ga.

3. Samples and analytical methods

Limestone samples for the present study were collected from both the Charmuria and Chandi formations of the Raipur Group. Sampling was carried out in vertical sections in limestone quarries located in the Hirri sub-basin, in the western sector of the Chhattisgarh Basin. The Charmuria Limestone was sampled from a quarry (N 21.039, E 80.944) located near Gordha

village, south of Rajnandgaon, whereas the Chandi Limestone was collected from a quarry (N 21.852, E 81.156) located south of Kawardha. Care was taken to avoid sampling weathered horizons and recrystallized surfaces. Fresher interiors of the outcrops were preferred. Thin sections of the samples, studied under plane polarized light, revealed that the limestones were mostly micrite/microsparite with limited carbonate components (Figs. 3C; 3D). Samples for geochemical analyses were micro-drilled.

Stable carbon and oxygen isotope analyses were carried out on a total of 49 carbonate samples and trace element compositions were determined for 29 samples. Samples showing high Sr, low Mn and low Mg contents were analysed for their $^{87}\text{Sr}/^{86}\text{Sr}$. Carbon and Oxygen isotopic ratios were measured in a Thermo MAT 253 isotope ratio mass spectrometer. CO_2 was extracted, using Gas Bench II, from 200-400 μg of sample powder after reacting it with 100% orthophosphoric acid at 72°C. CO_2 injection was done in continuous flow mode and isotopic ratios were measured with respect to a laboratory CO_2 reference. A lab standard (MMB) of known isotopic composition was analyzed after every ten samples to calibrate the reference CO_2 . The mean value of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, based on repeated analyses of the international standard NBS-19, during the analysis period was $2.05 \pm 0.06\text{‰}$ (1SD, $n=5$) and $-2.32 \pm 0.03\text{‰}$ (1SD, $n=5$), respectively. Ca, Mg, Mn and Sr contents of the carbonate samples (6-10 mg) were measured using a Thermo Element X Series 2 Quadrupole-ICPMS. Micro-drilled sample powder was dissolved and further diluted using 2% HNO_3 . Elemental analyses were carried out using COQ-1, a carbonatite standard from USGS, as a calibration standard (George and Ray 2017). COQ-1 was also run as an unknown for accuracy and precision checks. Machine drift was corrected using Ga, In and Bi as internal standards. External reproducibility of the measurements was better than 5% at 2SD

level based on repeated analyses of COQ-1. For Sr isotopic ratio analysis, samples were pre-leached using dilute CH_3COOH and the first leachates were discarded to avoid the contribution of radiogenic Sr from exchangeable sites and secondary carbonate overgrowths. They were leached further using 10% CH_3COOH for sampling. Care was taken to avoid complete dissolution to ensure no contribution of Sr from silicate impurities. Sr was separated by means of column chromatography using Sr-specific resin from Eichrom with H_2O as elutant. The details of this dissolution protocol are given in Ray et al. (2003). $^{87}\text{Sr}/^{86}\text{Sr}$ was measured on an Isoprobe-T TIMS in static multi-collection mode. Isotopic ratios were corrected for mass fractionation using $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of international standard NBS 987 measured in our laboratory over a period of 4 years is 0.710234 ± 0.000008 (2SD, $n=80$).

4. Results and discussion

The stable carbon and oxygen isotopic compositions, major and trace element concentrations, and $^{87}\text{Sr}/^{86}\text{Sr}$ of both the Charmuria and Chandi formations are presented in Table 1. Various elemental and isotopic ratios to estimate the extent of alteration are plotted in Fig. 4 and 5. The variations in the $\delta^{13}\text{C}$ of both the Charmuria and Chandi limestones are plotted against their $\delta^{18}\text{O}$ counterparts in Fig. 4 and with depth in Fig. 6, and their implications are discussed in the subsequent sections.

4.1 Evaluation of sample preservation

A number of petrographic and geochemical criteria were used to ascertain the pristine nature of the geochemical signals from the Raipur Group carbonates. Thin sections of the samples were studied using petrographic microscope to identify grain size, degree of recrystallization and secondary sedimentary structures. Some thin sections were stained using the method of Dickson (1965) to distinguish calcite from dolomite. Only the micritic and microsparry (calcite) components were selected for geochemical analyses. Photomicrographs of two typical sample sections are shown in Fig. 3C and Fig. 3D.

The $\delta^{18}\text{O}$ of the Charmuria Limestone is almost invariant against its $\delta^{13}\text{C}$ ($R^2=0.13$), whereas they show a rough positive correlation in the Chandi Limestone ($R^2=0.41$; Fig. 4), which suggest that the both formations have undergone different degrees of post-diagenetic alteration. Since the $\delta^{18}\text{O}$ of these samples are highly negative ($< -6.5\text{‰}$; highly depleted in ^{18}O with respect to seawater), it is highly unlikely that they have been affected by evaporative fluids during early diagenesis. Therefore, the alteration, if any, would have been by meteoric fluids only. In the following paragraphs we evaluate the effect of such alteration on the primary isotopic signatures of C and Sr in samples using various elemental ratios and $\delta^{18}\text{O}$.

Most of our samples are low-Mg calcites ($\text{Mg}/\text{Ca} < 0.05$) and do not show any trend of diagenetic alteration/dolomitization ($R^2 < 0.1$; Fig. 5A). The Mn/Sr of these samples ranges from 1.2 to 3.4 and does not show any relationship with $\delta^{18}\text{O}$, which suggest no significant meteoric alteration (Brand and Veizer 1981, Veizer 1983, Azmy et al. 2006; Fig. 5B). The low Mn/Sr (< 10), low Mg/Ca (< 0.1) and higher $\delta^{18}\text{O}$ ($> -10\text{‰}$) suggest that the sampled carbonate components have undergone very limited chemical change during diagenesis (Knoll et al. 1995)

and hence, they most likely have preserved their original $\delta^{13}\text{C}$. Therefore, the $\delta^{13}\text{C}$ of Charmuria (2.6 to 3.6 ‰) and Chandi (3.2 to 3.6 ‰) formations can be considered to be representative of the contemporaneous seawater ratios from which they had precipitated.

Primary $^{87}\text{Sr}/^{86}\text{Sr}$ of the carbonates is more susceptible to modification during post-depositional processes than $\delta^{13}\text{C}$, since Sr is a trace element in the carbonates. Post-depositional alteration, depending on the interacting fluid, can make the primary $^{87}\text{Sr}/^{86}\text{Sr}$ either more radiogenic or less radiogenic (Ray et al. 2003, Brand et al. 2010, Paula-Santos et al. 2017). There are indications that the $^{87}\text{Sr}/^{86}\text{Sr}$ of both the Charmuria and Chandi limestones are modified by post-depositional alteration. The Mn/Sr in these limestones is higher than 1.0, the empirical value below which the $^{87}\text{Sr}/^{86}\text{Sr}$ of marine carbonates is generally considered pristine (Derry et al. 1992; Table 1). However, the limits of Mn/Sr for altered calcites may vary from place to place depending on the composition of the diagenetic fluid. Therefore, we further evaluate the degree of alteration of $^{87}\text{Sr}/^{86}\text{Sr}$ we make use of various elemental/isotopic tracers as suggested by Azmy et al. (2001), Azmy et al. (2006), Halverson et al. (2007) and Paula-Santos et al. (2017).

$^{87}\text{Sr}/^{86}\text{Sr}$ of the Charmuria Limestone varies from 0.7072 to 0.7086 and that of the Chandi from 0.7082 to 0.7137. It does not show any relationship with Mn/Sr ($R^2 < 0.3$; Fig. 5C) – a strong proxy for alteration by meteoric water (e.g., Veizer 1983). Interestingly, however, it shows an increasing trend against decreasing Sr content (Fig. 5D), which is consistent with the suggestion that Sr in carbonates becomes more radiogenic due to meteoric diagenesis (Ray et al., 2003; Azmy et al., 2006). We suspect that the alteration of Sr isotopic signals in our samples happened during deep burial diagenesis by Sr rich waters. The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Charmuria and

the Chandi limestone formations, 0.70723 and 0.70816, respectively, are more radiogenic than that reported for Mesoproterozoic carbonates/seawater (Azmy et al. 2001, 2006, Shields and Veizer 2002, Kah et al. 2012, Kuznetsov et al. 2017). Therefore, the Sr isotopic compositions of the Chhattisgarh carbonates cannot be utilized for chemostratigraphy.

4.2 $\delta^{13}\text{C}$ stratigraphy and depositional environment

The Charmuria and the Chandi limestones have $\delta^{13}\text{C}$ in the ranges of 2.6 to 3.6‰, and 3.2 to 3.6‰, respectively (Table 1). In the case of the Charmuria Limestone, there is a unidirectional increase in the $\delta^{13}\text{C}$ from 2.6‰ at the bottom of the formation to 3.4‰ towards the top, whereas the $\delta^{13}\text{C}$ of the overlying Chandi Limestone exhibits an almost constant value of 3.4 ± 0.2 ‰ for much of the formation (Fig. 6). The elevated $\delta^{13}\text{C}$ of the carbonates of the Raipur Group can be attributed to increased flux of organic carbon burial if we interpret the above by the conventional understanding that the organic carbon burial flux is the primary driver of $\delta^{13}\text{C}$ values in the marine carbonates, assuming constant mantle carbon input and biological carbon fractionation (Des Marais 1994, Kump and Arthur 1999). The positive $\delta^{13}\text{C}$ (average = 3.2 ± 0.3 ‰) values of both the Charmuria and Chandi limestones are consistent with the late Mesoproterozoic (1.2 to 1.0 Ga) $\delta^{13}\text{C}$ profiles observed in the lower sections of Grenville Supergroup, USA, Avzyan Formation, Russia, and Bylot Supergroup, Canada (Fig. 6; Whelan et al. 1990, Kah et al. 2001, 2012, Bartley et al. 2007). In comparison, the $\delta^{13}\text{C}$ of the lower part of the Vazante Group, Brazil (Azmy et al. 2001, 2006, 2008, Geboy et al. 2013) are < 3 ‰ with an average of 1.5 ± 0.9 ‰ and therefore, are clearly not correlatable with our data (Fig. 6E). However, it may be consistent with a younger age as suggested by similar $\delta^{13}\text{C}$ variations in the upper sections of the Grenville

Supergroup, Avzyan Formation and Bylot Supergroup (Fig. 6). The $\delta^{13}\text{C}$ values observed in the upper part of the Vazante Group are much lower ($\sim 0\text{‰}$), hence cannot be correlated with the rest (Fig. 6). Since we do not observe any physical or chemical evidence of global glaciations in the Raipur Group, we infer that the Raipur Group got deposited prior to any of the Mesoproterozoic glaciations. The $\delta^{13}\text{C}$ stratigraphy and the available radiometric ages constrain the deposition of Raipur Group to 1.2-1.0 Ga.

4.3 Intrabasinal correlations

The bulk of the Chhattisgarh Supergroup was deposited in two sub-basins; the Hirri in the west and Bhardwar in the east, separated by the Sonakhan Greenstone Belt (Das et al. 1992). Due to its development around two depocentres, lack of sufficient reliable geochronological data and marker horizons, correlation of various formations of the supergroup had remained contentious until recently. The formations in the sub-basins were correlated mostly based on lithostratigraphic principles. In one of the recent developments, felsic tuffs deposited near the top of the Raipur Group in both the sub-basins were dated to be ~ 1000 Ma (Patranabis-Deb et al. 2007, Bickford et al. 2011a). The tuff acted as a marker horizon and facilitated correlation of its host formations; the Tarenga in the Hirri and the Churtela in the Bhardwar sub-basins.

Carbonate sequences in the Raipur Group were traditionally correlated across the sub-basins based on the similarity in their lithological characteristics. Here, we make an attempt to correlate them based on $\delta^{13}\text{C}$ stratigraphy in the absence of sufficient unaltered $^{87}\text{Sr}/^{86}\text{Sr}$ data across the sub-basins. Because of lack of trace element data in the earlier isotopic studies, the pristine

nature of their $\delta^{13}\text{C}$ data was validated using $\delta^{18}\text{O}$. Samples with $\delta^{18}\text{O} > -10\text{‰}$ are considered least altered and their $\delta^{13}\text{C}$ was considered near primary and used for stratigraphic correlation. Comparing the $\delta^{13}\text{C}$ of the limestones, we make the following observations. Barring a few outliers, the $\delta^{13}\text{C}$ of the samples from the Sarangarh Limestone varies between 1.8 and 3.6‰ which falls well within the variations observed in the Charmuria Limestone in the Hirri sub-basin (Fig. 4). The Chandi Limestone in the Hirri sub-basin possesses almost constant $\delta^{13}\text{C}$ variations of $3.4 \pm 0.2\text{‰}$; which overlaps with the field for Saradih which is based on limited data (Fig. 4). Thus, the Sarangarh Limestone in the Bharadwar sub-basin can be considered as stratigraphically equivalent of the Charmuria in the Hirri and the Saradih Limestone with that of the Chandi Limestone.

4.4 Proterozoic $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ record in Indian basins

The $\delta^{13}\text{C}$ of marine carbonates acts as an archive of the biogeochemical evolution in the oceans. In Proterozoic rock records, where biostratigraphic data are meagre, $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ have been used as tools to constrain the relative time of deposition of the carbonates and to correlate global events (Veizer 1989, Halverson et al. 2007, Azmy et al. 2008). We have compiled the available $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ data from three of the largest Proterozoic basins in India, the Vindhyan, the Chhattisgarh, and the Marwar whose sedimentary records together span nearly 1.7 billion years from late Paleoproterozoic to early Cambrian (Fig. 7), and compare it with that of the global datasets (Fig. 8). In order to choose only the primary $\delta^{13}\text{C}$ ratios, we filtered the published data using the criterion of $\delta^{18}\text{O} > -10\text{‰}$ as discussed earlier. Also, wherever trace element data were available, $\text{Mn}/\text{Sr} < 10$ was used as an additional criterion. For $^{87}\text{Sr}/^{86}\text{Sr}$, all the ratios with Mn/Sr

<1 were selected and wherever that criteria could not be fulfilled, the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ was selected. The $\delta^{13}\text{C}$ profiles of individual sections from various sectors of the basins are plotted in Fig. 7 and a composite plot showing the variation in $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ with time is presented in Fig. 8. We used available U-Pb zircon ages from volcanoclastics and Pb-Pb ages from limestone formations to constrain the ages of depositions of the carbonate formations. Since there were no other radiometric ages from the Marwar Supergroup, we used the Rb-Sr isochron age of 703 Ma of a felsic tuff in the lower Marwar and Sr isotope stratigraphy age of 570 Ma for the Bilara Group (George and Ray 2017). Additional radiometric data of Re-Os and Ar-Ar ages were used for the Vindhya (Gregory et al. 2006, Tripathy and Singh 2015).

The $\delta^{13}\text{C}$ record from Indian sedimentary basins largely mimics the global pattern (Fig. 8A). Similar to the Paleoproterozoic and early Mesoproterozoic global values, the $\delta^{13}\text{C}$ from the lower Vindhya, which include the ~1.72 Ga Kajrahat, Salkhan and the ~1.6 Ga Rohtasgarh limestones and their equivalents, fall within 0 ± 2 ‰. The late Mesoproterozoic rise of the $\delta^{13}\text{C}$ in global oceans is captured by the Chhuria and Chandi limestones of the Chhattisgarh Basin which exhibits a steady increase of $\delta^{13}\text{C}$ from 1.4 to 4.3‰, whereas the Lakheri Limestone of the Vindhya possesses the terminal Mesoproterozoic composition. The shift in the $\delta^{13}\text{C}$ to ~5‰ globally in the beginning of the Neoproterozoic is recorded by the 0.9 Ga Bhandar Limestone of the Vindhya, however the reported negative $\delta^{13}\text{C}$ excursion near the top of the formation (Ray et al. 2003) has not yet been correlated with any Neoproterozoic global events. Although the Bhandar Limestone is dated to be 908 ± 72 Ma (Gopalan et al. 2013), in view of the facts that the age data came from the lower part of the formation, the $\delta^{13}\text{C}$ excursion is ~9‰ and the rocks show a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7061, we suspect that this excursion could be correlatable with the

Bitter Springs anomaly of Australia. The positive $\delta^{13}\text{C}$ trend in the Neoproterozoic continues in the lower part of the ~0.8 Ga Balwan Limestone of the Vindhya, before it drops to -5‰ and recovers to the pre-excursion value. This negative excursion of ~12‰ magnitude has been correlated with the globally synchronous Bitter Springs anomaly (George et al. 2018). Between 0.8 and 0.6 Ga there is a glaring gap in the $\delta^{13}\text{C}$ record from the Indian basins. Further $\delta^{13}\text{C}$ records are available from the Ediacaran age Bilara Group of the Marwar Supergroup where the $\delta^{13}\text{C}$ remain at 0‰ at the lower part unlike the elevated global values of 4‰, before descending to a $\delta^{13}\text{C}$ of -5 ± 2 ‰ excursion, that is suspected to represent the Shuram anomaly, and then recovering to its pre-excursion value (Ansari et al. 2018).

The $^{87}\text{Sr}/^{86}\text{Sr}$ of the carbonate formations, however, only partially follows the seawater evolution curve. The Paleoproterozoic carbonate formations of the Vindhya, the Kajrahat and Rohtasgarh limestones, possess lowest $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7046 and 0.7047 which are similar to the contemporaneous seawater ratios (Fig. 8B). Similarly, the $^{87}\text{Sr}/^{86}\text{Sr}$ variations of Balwan Limestone of Vindhya and the Bilara Group of the Marwar (0.7063 and 0.7081 respectively) capture the seawater ratios during the Tonian and Ediacaran periods of Neoproterozoic. All other carbonate sequences from both Vindhya and Chhattisgarh supergroups show $^{87}\text{Sr}/^{86}\text{Sr}$ that is higher than the contemporaneous seawater suggesting alteration of their primary Sr isotopic compositions.

The composite $\delta^{13}\text{C}$ record from the subcontinent as presented in Fig. 8A is preliminary and will evolve with more isotopic data from other Proterozoic basins of India and tighter chronological constraints. There are a number of conspicuous gaps in the record with significant ones in the

early Mesoproterozoic and in the Cryogenian. None of the $\delta^{13}\text{C}$ negative excursions associated with the Neoproterozoic glacial events have been reported yet from the Indian successions. Although there is a negative excursion reported from the top part of the Bhandar Limestone (Ray et al. 2003) and a suspected Shuram anomaly from the Bilara Group (Ansari et al. 2018), better chronology would help ascertain these cases.

5. Conclusions

This work presents high resolution $\delta^{13}\text{C}$ variation in two carbonate formations, the Charmuria and Chandi, of the Mesoproterozoic Chhattisgarh Supergroup. The $\delta^{13}\text{C}$ profile displays a steady increase from 2.6 to 3.6‰, which is consistent with the late Mesoproterozoic values reported globally. The enriched $\delta^{13}\text{C}$ values could be due to increased organic carbon burial at the cratonic margins. Based on $\delta^{13}\text{C}$ isotope stratigraphy and existing radiometric age data, we suggest a depositional age of 1.0-1.2 Ga for the Raipur Group. The similarity in the $\delta^{13}\text{C}$ values suggests that the two lowermost carbonate formations of the Raipur Group in the Hirri sub-basin can be stratigraphically correlated with the two carbonate formations in the Bharadwar sub-basin. The Proterozoic $\delta^{13}\text{C}$ records from Indian sedimentary basins reflect the global trends despite limited data. Globally synchronous $\delta^{13}\text{C}$ negative anomalies such as the Bitter Springs and Shuram have been reported from the Indian basins; however, tighter chronological constraints are required to correlate the observed negative excursion in the Bhandar Limestone with that of the global record.

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412

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417

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419

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Figure Captions

Figure 1:

A generalized geological map of the Chhattisgarh Basin showing various lithological units of the Chhattisgarh Supergroup, modified after Mukherjee et al. 2014; Saha and Patranabis-Deb 2014.

Figure 2:

Simplified litho-stratigraphy of the Chhattisgarh Supergroup in Hirri (east) and Bharadwar (west) sub-basins based on data from Das et al. (1992); Mukherjee et al. (2014); Saha and Patranabis-Deb. (2014). Sources of age data: 1: Bickford et al. (2011a), 2: Patranabis-Deb et al. (2007), 3: Das et al. (2011), 4: Bickford et al. (2011b), 5: Das et al. (2017). The errors on the ages are 2σ .

644

645 **Figure 3:**

646 Field photographs: (A) limestone-marl rhythmites of the Charmuria Formation; (B) stromatolitic
647 limestone of the Chandi Formation. Photomicrographs: (C) microsparitic Charmuria Limestone
648 under plane polarized light; (D) micritic Chandi Limestone under cross polarized light.

649

650 **Figure 4:**

651 $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ plot of the Charmuria and Chandi limestone formations. Also shown are the
652 fields for the Sarangarh and Saradih formations (Chakraborty et al. 2002, Sarkar et al. 2010,
653 Patranabis-Deb et al. 2016) for comparisons.

654

655 **Figure 5:**

656 Elemental and isotopic cross plots: (A) Mg/Ca vs. $\delta^{18}\text{O}$; (B) Mn/Sr vs. $\delta^{18}\text{O}$; (C) $^{87}\text{Sr}/^{86}\text{Sr}$ vs.
657 Mn/Sr; (D) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr of selected samples from the Charmuria and Chandi formations. All
658 the elemental ratios are weight ratios except Mg/Ca, which is plotted as molar ratio. The arrows
659 indicate common trends in diagenetic/ secondary alteration in carbonates.

660

661 **Figure 6:**

662 Chemostratigraphic correlation of the Raipur Group with some late Mesoproterozoic
663 sedimentary successions world-wide. SG: Supergroup, Gp: Group and Fm: Formation. Data
664 Sources: Whelan et al. (1990), Azmy et al. (2001, 2006, 2008), Kah et al. (2001, 2012), Bartley
665 et al. (2007) and this study (Table 1).

666

Figure 7:

Stratigraphic variations of $\delta^{13}\text{C}$ in various Proterozoic sedimentary basins of India. A, B and C present data for the Vindhyan Supergroup from Son Valley (~5.6 km), Chitrakoot (~1 km) and Rajasthan (~3.5 km), respectively. D and E present data for the Chhattisgarh Supergroup from Hirri (~2.5 km) and Bharadwar (~2.5 km), respectively. F presents data for the Marwar Supergroup (~1 km). Data sources of $\delta^{13}\text{C}$: Friedman et al. (1996), Chakraborty et al. (2002), Kumar et al. (2002), Banerjee et al. (2005, 2007), Patranabis-Deb et al. (2016), Ansari et al. (2018), Gilleaudeau et al. (2018), George et al. (2018) and this study (Table 1). The Pb-Pb ages are marked in red, U-Pb zircon ages in green and Sr isotope stratigraphic age in blue. Other radiometric ages are marked in black. The age data are from Rasmussen et al. (2002), Ray et al. (2002, 2003), Gregory et al. (2006), Patranabis-Deb et al. (2007), Bengtson et al. (2009), Bickford et al. (2011a,b), Das et al. (2011), Gopalan et al. (2013), Meert et al. (2013), Tripathy and Singh (2015), George and Ray (2017).

Figure 8:

Temporal variations of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in Proterozoic basins of India plotted onto the global seawater curves; grey band/line in A and dotted line in B, respectively. Data sources: Bartley and Kah (2004); Halverson et al. (2005); Fike et al. (2006); Shields and Veizer (2002); McArthur et al. (2012).

Table 1: Geochemical data of carbonate formations of the Chhattisgarh Supergroup.

Sample ID	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	$\delta^{18}\text{O}_{\text{VPDB}}$ (‰)	Depth (m)	Mn (ppm)	Sr (ppm)	Mg/Ca (mol/mol)	Ca/Sr (ppm/ppm)	Mn/Sr (ppm/ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>Charmuria Formation</i>									
CH15-47	3.4	-7.9	0	626	239	0.015	1309	2.6	0.70742
CH15-48	3.1	-7.8	0.5						
CH15-49	3.3	-7.7	1.1	699	331	0.016	1087	2.1	
CH15-50	3.3	-7.7	1.4	592	244	0.018	1358	2.4	0.70766
CH15-51	3.3	-7.7	2.25						
CH15-52	3.3	-7.6	2.55						
CH15-53	3.6	-7.6	2.75	793	291	0.019	1386	2.7	0.70775
CH15-54	3.4	-7.5	3.05						
CH15-55	3.1	-7.6	3.55	843	251	0.017	1381	3.4	
CH15-56	2.9	-7.7	3.95	643	242	0.025	1115	2.7	0.70861
CH15-57	3.0	-7.7	4.35	665	226	0.015	1224	2.9	
CH15-58	3.0	-7.7	4.75						
CH15-59	3.2	-7.4	5.15	653	337	0.024	891	1.9	0.70734
CH15-60	3.2	-7.6	5.45	696	285	0.016	1035	2.4	0.70725
CH15-61	3.0	-7.7	5.7						
CH15-62	3.1	-7.6	5.95	684	256	0.018	971	2.7	
CH15-63	3.1	-7.8	6.35						
CH15-64	2.9	-7.7	6.85	662	236	0.018	1288	2.8	0.70802
CH15-65	3.1	-7.6	7.25						
CH15-66	3.0	-7.6	7.75	826	410	0.019	793	2.0	0.70723
CH15-67	2.9	-7.7	8.2	713	617	0.022	507	1.2	
CH15-68	2.7	-7.6	8.65						
CH15-69	2.6	-7.8	9.25	843	304	0.021	1027	2.8	0.70782
CH15-70	2.7	-7.7	9.55						
CH15-71	2.6	-7.9	9.95	845	429	0.044	653	2.0	0.70785
CH15-72	2.8	-7.8	10.55						
CH15-73	2.7	-7.8	11.15	909	312	0.021	1016	2.9	
CH15-74	2.7	-7.7	11.45						
CH15-75	2.6	-7.8	11.95	832	308	0.033	821	2.7	0.70814
<i>Chandi Formation</i>									
CH15-21	3.6	-6.5	0	742	229	0.046	1660	3.2	0.71047
CH15-22	3.4	-8.6	0.2	473	168	0.026	1783	2.8	0.70978
CH15-23	3.4	-8.7	0.4						
CH15-24	3.3	-8.8	0.6						
CH15-25	3.4	-8.6	0.8	543	232	0.033	1586	2.3	0.70953
CH15-26	3.2	-8.2	0.85	390	161	0.035	1730	2.4	
CH15-27	3.4	-8.5	1.06						
CH15-28	3.2	-8.8	1.15	466	253	0.036	1492	1.8	0.70962
CH15-29	3.4	-8.8	1.35						
CH15-30	3.4	-7.8	1.6	1416	524	0.262	744	2.7	0.71371
CH15-31	3.3	-8.5	1.66						
CH15-32	3.4	-8.8	1.67						

CH15-33	3.5	-8.5	1.78	646	242	0.028	1611	2.7	0.70816
CH15-34	3.3	-8.7	1.86	554	303	0.041	934	1.8	
CH15-35	3.3	-8.8	2.11						
CH15-36	3.4	-8.8	2.41	546	205	0.030	1496	2.7	0.71065
CH15-37	3.4	-8.6	2.71						
CH15-38	3.3	-8.9	2.91	440	221	0.032	1490	2.0	
CH15-39	3.5	-8.5	3.01	512	208	0.039	1571	2.5	
CH15-40	3.3	-8.9	3.26	787	483	0.157	598	1.6	0.71250

Note: Concentrations were measured using Q-ICPMS. External reproducibility for Ca and other trace elements were <6% at 2 σ level.

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Figure 1: A generalized geological map of the Chhattisgarh Basin showing various lithological units of the Chhattisgarh Supergroup, modified after Mukherjee et al. 2014; Saha and Patranabis-Deb 2014.

185x123mm (300 x 300 DPI)

Figure 2: Simplified litho-stratigraphy of the Chhattisgarh Supergroup in Hirri (east) and Bharadwar (west) sub-basins based on data from Das et al. (1992); Mukherjee et al. (2014); Saha and Patranabis-Deb. (2014). Sources of age data: 1: Bickford et al. (2011a), 2: Patranabis-Deb et al. (2007), 3: Das et al. (2011), 4: Bickford et al. (2011b), 5: Das et al. (2017). The errors on the ages are 2σ .

102x119mm (300 x 300 DPI)

Figure 3: Field photographs: (A) limestone-marl rhythmites of the Charmuria Formation; (B) stromatolitic limestone of the Chandi Formation. Photomicrographs: (C) microsparitic Charmuria Limestone under plane polarized light; (D) micritic Chandi Limestone under cross polarized light.

193x140mm (300 x 300 DPI)

Figure 4: $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ plot of the Charmuria and Chandi limestone formations. Also shown are the fields for the Sarangarh and Saradih formations (Chakraborty et al. 2002, Sarkar et al. 2010, Patranabis-Deb et al. 2016) for comparisons.

157x120mm (300 x 300 DPI)

Figure 5: Elemental and isotopic cross plots: (A) Mg/Ca vs. $\delta^{18}\text{O}$; (B) Mn/Sr vs. $\delta^{18}\text{O}$; (C) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Mn/Sr; (D) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr of selected samples from the Charmuria and Chandi formations. All the elemental ratios are weight ratios except Mg/Ca, which is plotted as molar ratio. The arrows indicate common trends in diagenetic/ secondary alteration in carbonates.

217x156mm (300 x 300 DPI)

Figure 6: Chemostratigraphic correlation of the Raipur Group with some late Mesoproterozoic sedimentary successions world-wide. SG: Supergroup, Gp: Group and Fm: Formation. Data Sources: Whelan et al. (1990), Azmy et al. (2001, 2006, 2008), Kah et al. (2001, 2012), Bartley et al. (2007) and this study (Table 1).

242x113mm (300 x 300 DPI)

Figure 7: Stratigraphic variations of $\delta^{13}\text{C}$ in various Proterozoic sedimentary basins of India. A, B and C present data for the Vindhyan Supergroup from Son Valley (~ 5.6 km), Chitrakoot (~ 1 km) and Rajasthan (~ 3.5 km), respectively. D and E present data for the Chhattisgarh Supergroup from Hirri (~ 2.5 km) and Bharadwar (~ 2.5 km), respectively. F presents data for the Marwar Supergroup (~ 1 km). Data sources of $\delta^{13}\text{C}$: Friedman et al. (1996), Chakraborty et al. (2002), Kumar et al. (2002), Banerjee et al. (2005, 2007), Patranabis-Deb et al. (2016), Ansari et al. (2018), Gilleaudeau et al. (2018), George et al. (2018) and this study (Table 1). The Pb-Pb ages are marked in red, U-Pb zircon ages in green and Sr isotope stratigraphic age in blue. Other radiometric ages are marked in black. The age data are from Rasmussen et al. (2002), Ray et al. (2002, 2003), Gregory et al. (2006), Patranabis-Deb et al. (2007), Bengtson et al. (2009), Bickford et al. (2011a,b), Das et al. (2011), Gopalan et al. (2013), Meert et al. (2013), Tripathy and Singh (2015), George and Ray (2017).

264x193mm (300 x 300 DPI)

Figure 8: Temporal variations of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in Proterozoic basins of India plotted onto the global seawater curves; grey band/line in A and dotted line in B, respectively. Data sources: Bartley and Kah (2004); Halverson et al. (2005); Fike et al. (2006); Shields and Veizer (2002); McArthur et al. (2012).

223x192mm (300 x 300 DPI)