CARBON, OXYGEN, AND STRONTIUM ISOTOPE GEOCHEMISTRY OF THE PROTEROZOIC CARBONATE ROCKS, BHIMA BASIN, SOUTH INDIA: IMPLICATION FOR DIAGENESIS

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Abstract: A carbonate dominated shallow marine Proterozoic Bhima basin consists of carbonates and clastic rocks, and is widely distributed in the northern part of the Karnataka state, south India. Limestones of the Shahabad Formation have been selected for this study and secular variations in C, O, and Sr isotope compositions are reported. $\delta^{13}C$ values are varying from +3.50 to -1.38‰$_{PDB}$. Similarly, the $\delta^{18}O$ values recorded a range between -5.76 and -12.93‰$_{PDB}$ $^{87}Sr/^{86}Sr$ ratio for these limestones is varying between 0.70699 and 0.7117. Higher burial rate of organic matter could have been responsible for the positive $\delta^{13}C$ values, which is common in the Proterozoic carbonate rocks. The $\delta^{18}O$ values in most of the samples are similar to the average value of the Proterozoic carbonate rocks. Albeit some of the samples are modified in their original isotopic signature, which shows high negative $\delta^{18}O$ values < -10‰$_{PDB,}$ Mn/Sr ratios > 1.5 and a negative trend between $\delta^{18}O$ and $^{87}Sr/^{86}Sr$, suggesting that the $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ isotopic signatures of Bhima carbonates have been altered by diagenesis. The post depositional diagenetic alteration is also supported by the petrographic characters of these carbonates.

Keywords: Stable isotopes, limestones, diagenesis, Bhima Basin, southern India

1. INTRODUCTION

Stable isotopes in sedimentary carbonates are used extensively to elucidate the depositional and diagenetic processes. The C and O isotopic compositions of ancient limestones may change during epigenesis, or may continue to reflect the sedimentary environment in which they were formed (Magaritz, 1991). In recent years, much work has been focused on constraining primary $\delta^{13}C$ and $\delta^{18}O$ compositions of carbonate sequences in understanding the evolution of the ocean-atmosphere system, interactions of biotic and abiotic processes during the earth's history (Knoll et al., 1995; Mishra et al., 2010; Préat et al., 2010; Sial et al., 2000; Tewari et al., 2010; Veizer et al., 1992a;

1992b), paleo oceanographic changes (Madhavaraju et al., 2004; Shen, 2002), Precambrian-Cambrian boundary (Melezhik et al., 2001; Tewari & Sial, 2007) and diagenesis (Armstrong-Altrin et al., 2009; 2011; Nagarajan et al., 2008; Nagendra et al., 2011). The preponderance of extremely negative $\delta^{18}O$ values has fostered a heated debate concerning the relative influences of diagenetic overprints, ocean temperature, and ocean chemistry on the oxygen isotope compositions of the Precambrian marine sediments (Holmden & Muehlenbachs, 1993). Oxygen isotope data derived from the Precambrian carbonates are commonly neglected under the assumption that primary signatures have been obliterated during the burial and prolonged exposure to isotopically light diagenetic fluids. The $\delta^{18}O$

values of various depositional and diagenetic carbonate components were used to constrain the diagenetic environments and the extent of diagenetic modifications (Armstrong-Altrin et al., 2009, 2011; Macouin et al., 2012). The most extensively used tracer of the physical environment is the oxygen isotopic ratio of marine carbonate, which is controlled mainly by the temperature of mineral formation and the isotopic ratio of marine waters. The depletion in ^{18}O observed in geologically older carbonates, commonly ascribed to post-depositional isotope exchange with meteoric waters (Schidlowski et al., 1975). The depleted ^{18}O values in many Precambrian limestones would be a reflection of the secular evolution of seawater δ^{18}O (Hudson & Anderson, 1989) and also due to the diagenetic shift of ~ 2‰ (Ray et al., 2003).

Measurements of strontium isotopic compositions of marine carbonates have made significant impact in reflecting seawater composition at the time of deposition (Banner & Kaufman, 1994). Comparison of ^{87}Sr/^{86}Sr data with a global Neoproterozoic carbon isotopic curve has proven to be successful in confidently correlating interbasinal successions (Knoll & Walter, 1992; Narbonne et al., 1994), in evaluating intrabasinal depositional and diagenetic trends (Pelechary et al., 1996), and in determining the relative timing of environmental (Hoffman et al., 1998; Kaufman et al., 1997), and evolutionary events (Brasier et al., 1996; Narbonne et al., 1994). Neoproterozoic carbonates have been studied worldwide for variations in oxygen and carbon isotope ratios with special reference to inorganic and organic carbon reservoirs (Brasier et al., 1996; Hoffman et al., 1998; Nagarajan et al., 2008; Tewari & Sial, 2007; Chakrabarti et al., 2011, 2013).

In this study, carbon, oxygen, and strontium isotope compositions of limestones from the Shahabad Formation are presented. The objective of this study is to understand the diagenetic effects on the primary isotopic signature of the shallow marine limestones of the Shahabad Formation, Bhima basin.

2. GEOLOGICAL SETTING

Bhima basin, South India is a NE-SW trending Neoproterozoic, epicratonic, extensional basin (Fig. 1), which formed due to gravity faulting. Sedimentary rocks of the Bhima Basin are exposed as an array of narrow, E-W stretching, sygmoidal strips arranged in an enechelon pattern. Neoproterozoic Bhima Group overlies the Archaean granite-greenstone basement in Karnataka, Southern India. Bhima exposures are sandwiched between Early Precambrian granite - greenstone terrain of the East Dharwar Craton in the south and the Late Cretaceous - Paleocene Deccan Trap volcanic Province in the north. The Bhima basin sediments extend further towards north, which concealed under Deccan Traps.

Janardhana Rao et al., (1975) assigned the Group status to the Neoproterozoic sedimentary rocks of Bhima Basin. They classified the Bhima Group into five distinct formations, which includes (from base to up), i) Rabanpalli Formation, ii) Shahabad Formation, iii) Halkal shale, iv) Katamadevarhalli Formation, and v) Harwal shale. Misra et al., (1987) subdivided the Bhima Group into Sedam Subgroup (Rabanpalli Formation and Shahabad Formation) and Andola Subgroup (Halkal Shale, Katamadevarhalli Formation and Harwal-Gogi Shale). They identified the sedimentation break between Sedam and Andola Subgroup and interpreted as paraconformity. The classification proposed by Janardhana Rao et al., (1975) has been followed in this study.

The sedimentary rocks of Bhima Basin mainly comprise an alternating sequence of clastic and carbonate rocks (Janardhana Rao et al., 1975; Kale et al., 1990; Misra et al., 1987) and covering an area of 5,200 km^2. The Rabanpalli Formation has been considered as the oldest sedimentary formation of the Bhima Basin, which deposited over the Archean basement. Harwal shale is the youngest formation of the Bhima Group, which is overlained by Deccan Trap with intratrappean sediments. The Rabanpalli Formation is placed under the lower series of the Bhima Basin and quartz arenites, arkoses, siltstones and shales are the dominant members of this Formation (Nagarajan et al., 2007a, b). The limestone member is the dominant litho-unit of the Bhima basin and is classified under Shahabad and Katamadevarahalli Formations (Nagarajan et al., 2011).

The Shahabad Formation is exposed in the central and eastern parts of the Bhima Basin (lat. 16°15′ to 17°35′ N long. 76°15′ to 77°30′ E). Shahabad Formation was described by different names by different authors such as Talikote limestone by Newbold (1842), Upper Bhima Series by Foote (1876), Middle Bhimas by Mahadevan (1947) and subsequently Janardhana Rao et al. (1975) named this formation as Shahabad limestone Formation. The limestones of Bhima Basin are non-stromatolitic and non-dolomitic nature. These limestones cover an area of 2,000 km^2 in the Bhima Basin with the vertical thickness of < 75m including exposures of the Katamadevarhalli limestone (Kale et al., 1990). These limestones are micritic type,

petrographically cryptocrystalline in texture (Nagendra & Nagarajan, 2003) with number of macro and micro stylolites, which are filled with secondary minerals (Nagarajan et al., 2008). The limestones are classified into five different varieties, representing microfacies in the carbonate platform of the Bhima basin. The five varieties are (i) flaggy impure limestone; (ii) blocky micritic limestone; (iii) variegated limestone; (iv) blue-grey massive limestone; and (v) argillaceous micritic limestone. Flaggy impure limestones are creamy brown to dusty bluish grey colour. The petrographic classification of Bhima limestones is characterized by their colour and texture (Nagarajan et al., 2011). The black to dark grey, grayish black to purple, fine-grained, massive flaggy, siliceous, and argillaceous limestones are exposed with randomly distributed pyrite grains. The thinly bedded limestones are argillaceous in nature. For this study, representative samples were collected from the exposures at the Chincholi, Malkapur, Kurkunta, Gundgurti, Shahabad, Sedam, Malkhaid, Mubol, Gudur, idki, Chitapur, Ravur, Wadi, Itgi, Sirwal, and Gogi regions of the Shahabad Formation (Fig. 1).

3. SAMPLING AND METHODS

C and O-isotope analyses for thirty nine limestone samples were carried out at the stable isotope laboratory (LABISE) of the Department of Geology, Federal University of Pernambuco (UFPE), Brazil. CO_2 gas was extracted from powdered carbonates in a high-vacuum line after reaction with 100% orthophosphoric acid at 25°C for one day. The CO_2 released, after cryogenic cleaning, was analyzed in a double inlet, triple collector SIRA II mass spectrometer and the results are reported in δ notation (‰, PDB scale). The uncertainties of the isotope measurements were 0.1‰ for C and 0.2 ‰ for O, based on multiple analyses of an internal laboratory standard (BSC).

Fourteen samples were selected randomly for Sr isotope and were analyzed at the Scottish Universities Environmental Research Centre (SUERC). Limestone samples were leached in 1N ammonium acetate prior to acid digestion. Sr was separated in 2.5 M HCl using Bio-Rad AG50W X8 200-400 mesh cation exchange resin. Total procedure blank for Sr samples prepared using this method was < 5 pg.
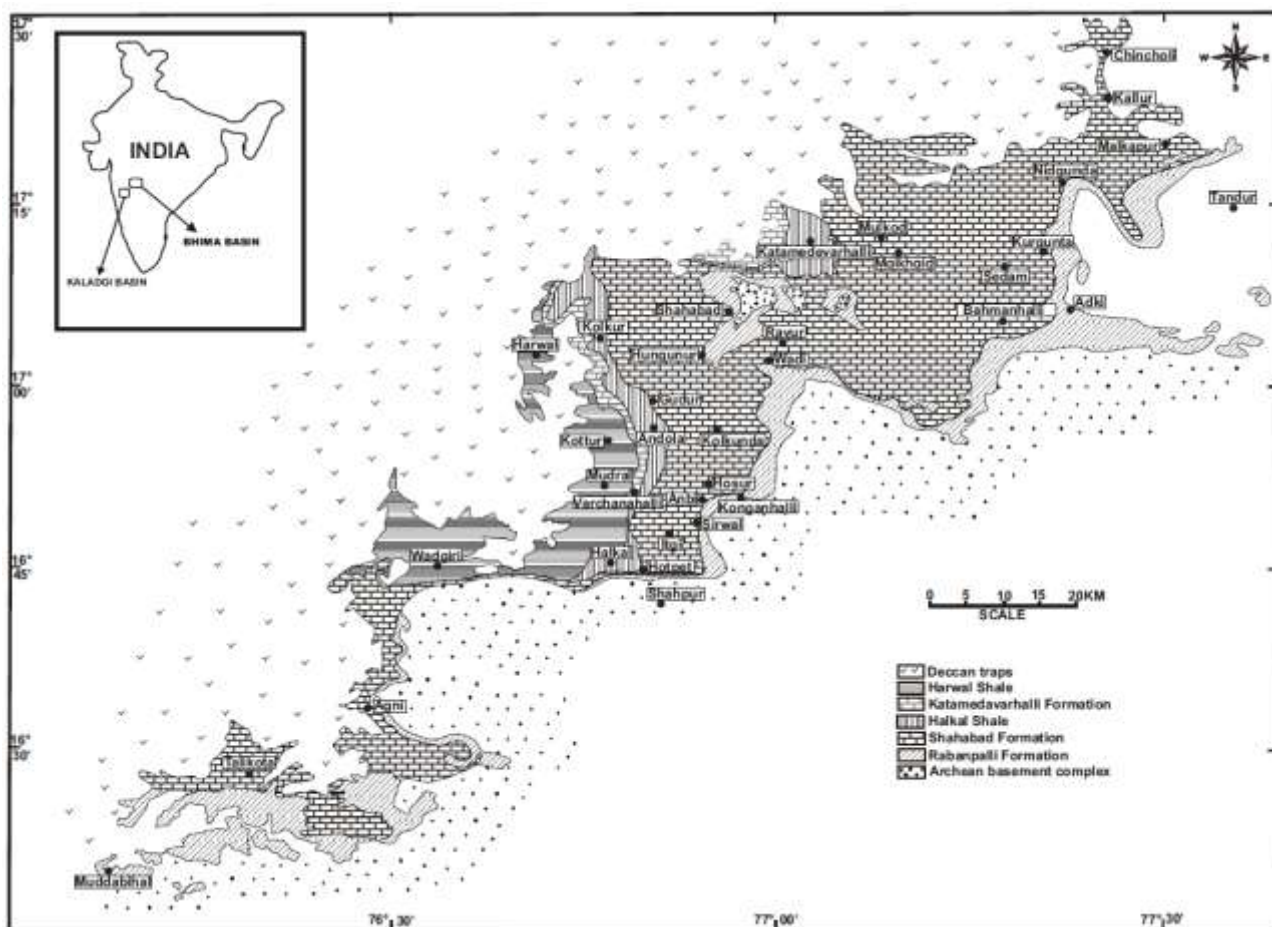

Figure 1. Geological map of Bhima Basin (after Janardhana Rao et al., 1975).

For mass spectrometry, Sr samples were loaded on to single Ta filaments with 1 N phosphoric acid. Sr samples were analyzed on a VG Sector 54-30 multiple collector mass spectrometer. A ^{87}Sr intensity of 1V (1 x 10^{-11}A) ± 10% was maintained and the ^{87}Sr/^{86}Sr ratio was corrected for mass fractionation using ^{87}Sr/^{86}Sr = 0.1194 and an exponential law. The VG Sector 54-30 mass spectrometer was operated in the peak-jumping mode with data collected as 15 blocks of 10 ratios. For this instrument, NIST SRM987 gave a value of 0.710260 ± 11 (2 SD, n = 17) during the period of measurements of the limestone samples analysed in the present study.

36 Samples were analyzed for selected trace elements by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES-Jobin-Yvon Jy138 Ultrace). The samples were prepared by dissolution in HNO$_3$ + HF. The analytical precision for analysed trace elements is better than 5%. Trace elements such as Mn and Sr are discussed in this study.

4. AGE OF THE BHIMA GROUP

Bhima sequence was correlated with Kurnool Group of late Proterozoic age. Previous studies have predicted the age for these sediments based on paleontological and palynological evidences such as *Chuaria Tawuia* (Halkal Formation) (Das Sarma et al., 1992), carbonaceous macrofossils and organic-walled microfossils (Maithy & Babu, 1996), and ichnofossil (Kale & Peshwa, 1995). Terminal Neoproterozic to Cambrian age has been assigned for Bhima Group based on the presence of acritarchs and algal forms (Malur & Nagendra, 1994). Recently, Moitra et al., (2000) discussed about *Chuaria circularis (alga)* assemblages in Halkal (Gangurthi) shale, Bhima Group, and estimated the age as ~ 675 Ma (late Cryogenian) (Moitra et al., 2000). There was no directly determined age for sediments of Bhima basin by geochronological methods until 2008. Recently, Dongre et al., (2008) suggested the age as older than 1100 Ma for Bhima and Kurnool basins, based on the presence of limestone xenolith within the Siddanpalli Kimberlite (1090 Ma age). This observation was also supported by Pandey et al., (2008) on the basis of TIMS U-Pb date of 1266 ± 76 Ma for coffinite mineral collected from the Gogi hydrothermal uranium deposit in the brecciated Shahabad limestone.

5. RESULTS

5.1 Petrography

The Shahabad limestones are micritic in nature and show variation in colour (Nagarajan et al., 2011). The rocks are compact and fine-grained with conchoidal fracture. The recrystallized microspar, rounded sparry calcite fillings, macro and microstylolite structures (quartz and calcite minerals present in the pressure solution cavities) (post depositional) are common (Fig. 2 a-g). These limestones are micritic (calmicrite), resulting from neomorphic re-crystallization of carbonate muds during diagenesis and/or lithification. Most of the samples show a well re-crystallized matrix, perhaps microsparite matrix (Fig. 2 a-c & e). This could be a sign of burial diagenesis. Some of the stylolites seem to have been present even before re-crystallization as they are partially trimmed by the matrix. Micritization by re-crystallization is common in shallow water carbonate grains in tropical regions. Cryptocrystalline textures observed in grey limestone indicate the later stages of re-crystallization process, corresponding to the formation of micrite cement (Reid & Macintyre, 1998). Silica veins, calcite veins (Sirwal area), and sparry calcite cement are observed in these limestones (Fig. 2 a-c). Some calcite cement is twinned suggesting structural deformation in this limestone. The passive infilling of pores and fractures can often be seen optically under the microscope. Late porosity has affected some samples along the old stylolites.

Microstylolites are developed as parallel, inclined and vertical to the bedding plane (Fig. 2 d-f). These are classified based on the geometrical aspects and their attitude with respect to bedding is as simple wavy and suture types. The suture junctions vary with their amplitude and length by differential pressure solution (Malur & Nagendra, 1988), which indicates burial diagenesis. Staining study of these limestones shows that ferrous iron in the carbonate rocks is capable of ionic substitution in calcite lattice and hence rich in ferroan-calcite. The ankerite is intermediate in composition between dolomite and ferroan-dolomite. The dolomite in the Bhima limestones shows patchy appearance. Dolomite and ferroan dolomite are present as cements in Shahabad limestone, and tend to be formed during late diagenesis in the sequence of cementation. Dolomite is generally considered as essentially a diagenetic mineral. However, there is growing evidence that precipitation of dolomite in the Precambrian was either coeval with calcite or

dolomitization, an early diagenetic phenomenon caused by waters isotopically comparable to that of seawater (e.g. Veizer et al., 1992a, b). However, dolomite mineral is not common and rarely present, and sometimes associated with the stylolites (Fig. 2g). Micritic limestones are transformed into neomorphosed microsparite. Pyrites are also common in these limestones particularly samples from Sirwal area. Pyrites are brownish in color in some places due to the presence of iron hydroxide along grain boundaries in slightly altered samples (Fig. 2h).

5.2. Geochemistry

The Shahabad limestones show negative to positive $\delta^{13}C$ values, which vary from -1.38 to 3.80‰ PDB. The variations in carbon isotope values are mainly based on locations rather than its type. The lowest $\delta^{13}C$ value -1.38‰ is recorded in the pyrite bearing limestone. The limestone samples from the marginal area of the Shahabad Formation display $\delta^{13}C$ values from 2.23 to 3.8‰ PDB, whereas samples from the central part vary from -1.38 to +1.91‰ PDB. The $\delta^{18}O$ values in micritic limestones of the Shahabad Formation range from -12.93 to -5.76‰ PDB. The average $\delta^{18}O$ values in Malkhaid (central part of the basin) and its surrounding areas are compatible with the Proterozoic limestones. However, few samples exhibit high negative $\delta^{18}O$ values (-7.04 to -12.93 ‰ PDB). The $^{87}Sr/^{86}Sr$ values in Shahabad limestones range from 0.706995 to 0.711645 and the highest value is recorded in Sirwal-Itki area (lower part of the Shahabad Formation); meanwhile the lowest is recorded in the Malkhaid-Chitapur area (Middle part of the formation).

6. DISCUSSIONS

6.1. Evaluation of post-depositional alteration

Cryptocrystalline textures observed in some limestone samples indicate the later stage of re-crystallization process and the development of micritic cement. Pressure-dissolution during burial is probably the major source for the cryptocrystalline calcite spar cement in micrites, demonstrated by common stylolite seams following the direction of bedding and along low-angle intersecting joints set (Nicol, 1992). Shahabad limestones exhibit re-crystallized calcite and dolomite minerals, which are showing evidence for diagenesis.

Diagenetic alteration causes significant depletion of Sr and enrichment of Mn in the diagenetic carbonate phase (Veizer, 1983) hence the Mn/Sr ratio can be used to evaluate the degree of carbonate preservation. Fluids generated during the path of diagenesis and metamorphism commonly introduce Mn and radiogenic Sr, and decrease the Sr content in carbonate rocks (Kaufman & Knoll, 1995). Hence, the Mn/Sr ratio have been widely used as a criterion for understanding diagenetic alterations, with a maximum variation in the Mn/Sr ratio of 1-3 being accepted as an indicator of unaltered isotopic ratios (Jacobsen & Kaufman, 1999). Jacobsen & Kaufman (1999) modelled the trace element behaviours and presented the isotopic evolution trends of $^{87}Sr/^{86}Sr$ and $\delta^{13}C$, with varying amounts of Mn/Sr and $\delta^{18}O$, for open and closed systems diagenesis of carbonate, which shows that except for $\delta^{13}C$ versus Mn/Sr, highly non-linear trends were observed among other variables, due to diagenesis. The primary isotopic signatures are retained by those carbonates, which are characterized by Mn/Sr < 3, $\delta^{18}O = \sim$ -5 to -10‰, Rb/Sr < 5×10^{-3} and Sr = $\sim$ 150 - 500 ppm. Moreover, Fölling & Frimmel (2002), have considered limestones as "unaltered" when Mn/Sr = 1.5 and $\delta^{18}O > -10‰$. Therefore, $\delta^{18}O$ values between −10 and −14‰ are interpreted as slightly altered, and samples with $\delta^{18}O < -14‰$ are highly altered diagenetically. Most of the samples preserve a wide range of Mn/Sr ratios; particularly 50% of the studied samples show the Mn/Sr ratio > 1.5 suggesting diagenetic alteration. The Mn/Sr ratio permits a comparatively precise determination of the degree of alteration of C-isotopic values. A nonlinear Mn/Sr versus $\delta^{13}C_{PDB}$ (Fig. 3a) relationship indicates that $\delta^{13}C$ values are not affected by post-depositional alterations, which would have otherwise resulted in the depletion of $\delta^{13}C$ and a corresponding increase in the Mn/Sr ratio (Kaufman & Knoll, 1995).

Oxygen isotope values of Shahabad limestones exhibit wide variations and range from -12.9 to -5.86‰_PDB. The $\delta^{18}O$ values for 70 % of the samples studied are in the range from -5 to -9.92‰, except 12 samples, which are showing more negative values (< -10‰_PDB) than an empirical limit of altered Proterozoic carbonates. The $\delta^{18}O$ values from -10 to -5‰ are comparable to the 'best-preserved' value ($\delta^{18}O$ = -7.5 ± 2‰) reported for most of the Proterozoic-early Cambrian carbonate rocks of the world (Hall & Veizer, 1996). Meteoric diagenesis tends to decrease $\delta^{18}O$ value in samples with $\delta^{18}O < -8‰$ and diagenetic fluid are not high enough to alter carbon isotopic values.

If a rock shows $\delta^{18}O$ values above this limit (−10‰), its C-isotope signal is considered a record of the primary marine value (e.g. Jacobsen & Kaufman, 1999).
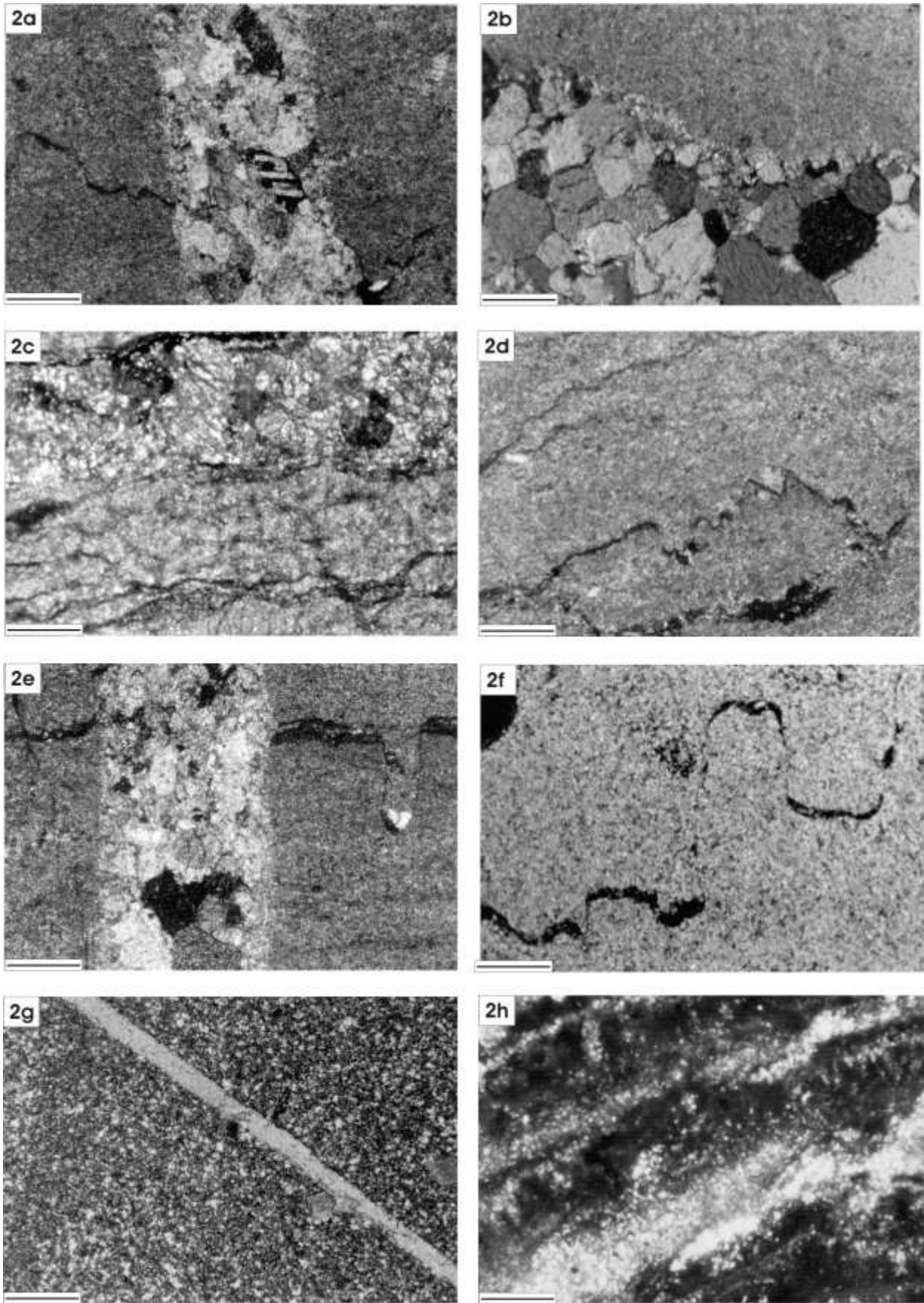
Figure 2 a-h. Microphotographs of limestones of the Shahabad Formation: different types of stylolites (a, d-f); small dolomite grains adjacent to stylolite (g), show a well re-crystallized matrix, perhaps microsparite matrix along the stylolites (a-c & e); void filling calcite cement (g); leached pyrite grains shows the ring (h). (Scale bar – 0.19mm).

Table 1 Carbon, oxygen and strontium isotopic data, with Mn and Sr values for the Shahabad limestones.

Sample No.	Mn	Sr	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$	$^{87}Sr/^{86}Sr$	Mn/Sr
E167	232	127	2.35	-10.52	-	1.83
E/158	190	120	2.29	-10.18	-	1.58
E 60	369	238	1.86	-8.53	-	1.55
E-18	188	122	1.65	-7.21	-	1.54
E081	108	237	1.65	-6.95	0.707198	0.46
BMCP 1	218	130	2.41	-9.65	0.710346	1.68
E/79	218	116	3.15	-9.92	-	1.88
E- 86	287	201	3.29	-6.58	-	1.43
CP/01	239	130	3.35	-7.44	-	1.84
E028	232	102	3.19	-11.09	-	2.27
E143	186	168	2.23	-7.57	-	1.11
E/171	290	120	2.41	-12.93	-	2.42
S001	263	195	3.47	-7.04	0.708405	1.35
MK1	108	350	1.75	-7.61	0.706995	0.31
E144	203	160	2.98	-11.49	-	1.27
E-17	219	119	3.22	-10.1	0.709971	1.84
BMS-40	307	153	3.22	-11.21	-	2.00
C/91	205	158	3.07	-10.54	-	1.30
C/87	232	120	3.5	-8.61	0.710519	1.93
BMSR F	261	201	3.16	-11.81	-	1.30
BMSR E	256	212	3.04	-11.4	-	1.21
BMSR G	-	-	-0.22	-7.31	0.708881	-
C/53	270	196	3.09	-10.18	-	1.38
ITKI-1	257	213	-1.35	-7.14	0.709606	1.20
ITKI-2	91	154	-1.38	-7.12	0.709612	0.59
BMH 1	-	-	0.88	-9.19	0.711645	-
BMID-1	146	138.50	1.65	-5.76	-	1.05
BMID-2	155	187.00	1.66	-5.82	-	0.83
BMID 3	158	196.00	1.91	-5.91	-	0.81
BMID 4	-	-	0.71	-6.59	0.708671	-
E/85	255	114.00	-1.18	-6.85	0.707916	2.24
E/152	196	92.00	1.81	-8.41	-	2.13
S064	280	148.00	3.16	-8.57	-	1.89
S060	271	122.00	3.03	-9.37	-	2.22
BMG 1	143	93.00	1.21	-8.35	0.709473	1.54
C/10	134	267.00	1.42	-6.96	-	0.50
E/75	213	108.00	3.16	-9.77	-	1.97
ISPY-1	267	198.80	-1.31	-7.22	0.710246	1.34
C-91	292	157.50	3.07	-10.54	-	1.85

In cases, if the diagenetic fluid is great enough to alter carbon isotopic composition, then the cross plot of $\delta^{13}C$ versus $\delta^{18}O$ will reveal a straight line of positive slope. The distribution pattern observed in the $\delta^{13}C$ - $\delta^{18}O$ plot (Fig. 3b), for the Shahabad limestones indicates that the amount of fluids

involved were sufficient to re-equilibrate the O-isotopic composition of carbonates, but not enough to have a significant effect on $\delta^{13}C$. When carbonate sediments enter to meteoric zone by uplift or eustatic sea-level fall, both carbon and oxygen isotopes may decrease by the reason of interaction with meteoric water, which exhibits lighter $\delta^{13}C$ and $\delta^{18}O$ values. Shahabad limestones do not show any correlation (Fig. 3b), which indicates that, the carbon isotopes are not altered as much as oxygen isotopes during diagenesis thus show primary characters of $\delta^{13}C$ value. The Shahabad limestones, which are affected by diagenesis are interpreted by the high negative $\delta^{18}O$ values (<-10.0 ‰PDB). The more depleted $\delta^{18}O$ values may be related to the associated temperature-dependent fractionations accompanied by increased burial pressures and calcite re-crystallization, and is indicative of diagenesis in meteoric or mixed marine-meteoric pore waters.

The $\delta^{18}O$ - Mn plot shows the diagenetic trend for Shahabad limestone, in which some samples show a non-linear trend (Fig. 3c). The $\delta^{13}C$ vs $^{87}Sr/^{86}Sr$ plot does not show any perfect trend (Fig. 3d). However, the $\delta^{18}O$ - $^{87}Sr/^{86}Sr$ plot (Fig. 3e) shows alteration trend, indicating that Sr isotope concentrations are influenced by diagénesis. Low concentration of Sr accompanied with more negative $\delta^{18}O$ values in the Shahabad limestones suggest that the alteration occurred under 'open' diagenetic condition (Fig. 3f). Diagenesis has affected $\delta^{18}O$ considerably, mainly through the precipitation of ^{18}O-depleted calcite spar cement that led to a substantial fluctuation of the whole-rock oxygen isotope composition within the Shahabad limestone. The inverse correlation in Figure 3g indicates that the enrichment of Sr isotope ratio in these limestones is due to the diagenetic effect, since the Sr isotopic compositions in marine carbonates are often susceptible to alteration. This alteration processes may include early diagenetic transformations and late diagenetic fluid reactions. Particularly, alteration through the interaction between clay minerals and groundwater would increase $^{87}Sr/^{86}Sr$ isotope ratios, whereas fluid interaction would decrease $^{87}Sr/^{86}Sr$ isotope ratios. Generally, $^{87}Sr/^{86}Sr$ isotope ratios increase due to post-depositional alteration (Brand & Veizer, 1980, 1981). This is confirmed again by a positive correlation (r = 0.51, number of samples = 11; critical t value for 95% confidence level is 0.553; Verma, 2005), between Mn/Sr and $^{87}Sr/^{86}Sr$ isotope ratio (Fig. 3h).

6.2. Variation in carbon isotopes

The temporal fluctuations in $\delta^{13}C$ of marine carbonate constituents represent secular variations of $\delta^{13}C$ in ocean water. The Shahabad limestones show a strong fluctuation in $\delta^{13}C$ values from +3.5 to -1.4‰ (Table 1). Previous studies of limestone from the Shahabad Formation also show heterogeneous isotopic values (i.e. ~ 0.89 to 3.59‰PDB, Gopendrakumar et al., 1997; ~ 0 to 3.7‰PDB, Kumar et al., 1999a; and 2.5 ± 1.4 PDB, Kumar et al., 1999b; Table 2). However, in the present study $\delta^{13}C$ value ranges from −1.4 to + 3.5‰PDB and mostly falls between 1 and 2‰PDB. Thus, the $\delta^{13}C$ values of the Shahabad limestones are considered to be very close to the Proterozoic $\delta^{13}C$ values of Schidlowski et al., (1975).

Variations in the C-isotope of limestone and co-occurring organic matter record secular changes in the burial rate of the carbon phases; an increase in $\delta^{13}C_{PDB}$ value reflects higher burial rates of organic carbon (Hayes, 1993). Average $\delta^{13}C_{TDC}$ (total dissolved carbonate) in modern oceans is around 0‰PDB; in shallow marine carbonate sediments, it ranges from 0 to +4‰PDB (Hudson, 1977). The positive $\delta^{13}C$ values recorded in the Shahabad limestones indicate a shallow marine origin. Much of the Proterozoic carbonates are characterized by ^{13}C enrichment suggesting large proportional burial of organic carbon. The possibility for a similar global enrichment occurred in the Proterozoic can be examined by the compilation of all previous reports of carbon-isotopic compositions of global Proterozoic sedimentary carbonates. These variations in the Proterozoic carbon isotope record seem to be of global significance and have been linked to changes in the burial rates of organic carbon as a result of major environmental changes triggered by tectonics, and glaciations (Knoll & Walter, 1992). Thus, a ^{13}C-minimum in these limestones would indicate a significant reduction in organic burial, which could be a result of reduced overall productivity, and/or an enhanced supply of isotopically light, organically derived carbon into the carbon cycle through regression and erosion.

6.3. Variation in Sr isotopes

The Sr-isotope ratios of Shahabad limestones range between 0.706995 and 0.711649 (Table 1). These values are significantly higher than the maximum $^{87}Sr/^{86}Sr$ ratio (0.709) of the modern and ancient seawaters (Shields, 2007; Veizer et al., 1999) including Proterozoic carbonates elsewhere in the world (Gómez Peral et al., 2007; Halverson et al., 2007). However, the $^{87}Sr/^{86}Sr$ ratio are relatively close to an average of chemical weathering of the continental crust and its sedimentary cover ($^{87}Sr/^{86}Sr$ = 0.712; Palmer & Edmond, 1989) and to the

Ediacaran carbonates (0.70797 to 0.71285) of the Doushantuo Formation from the Yangtze Gorge in South China (Ohno et al., 2008).
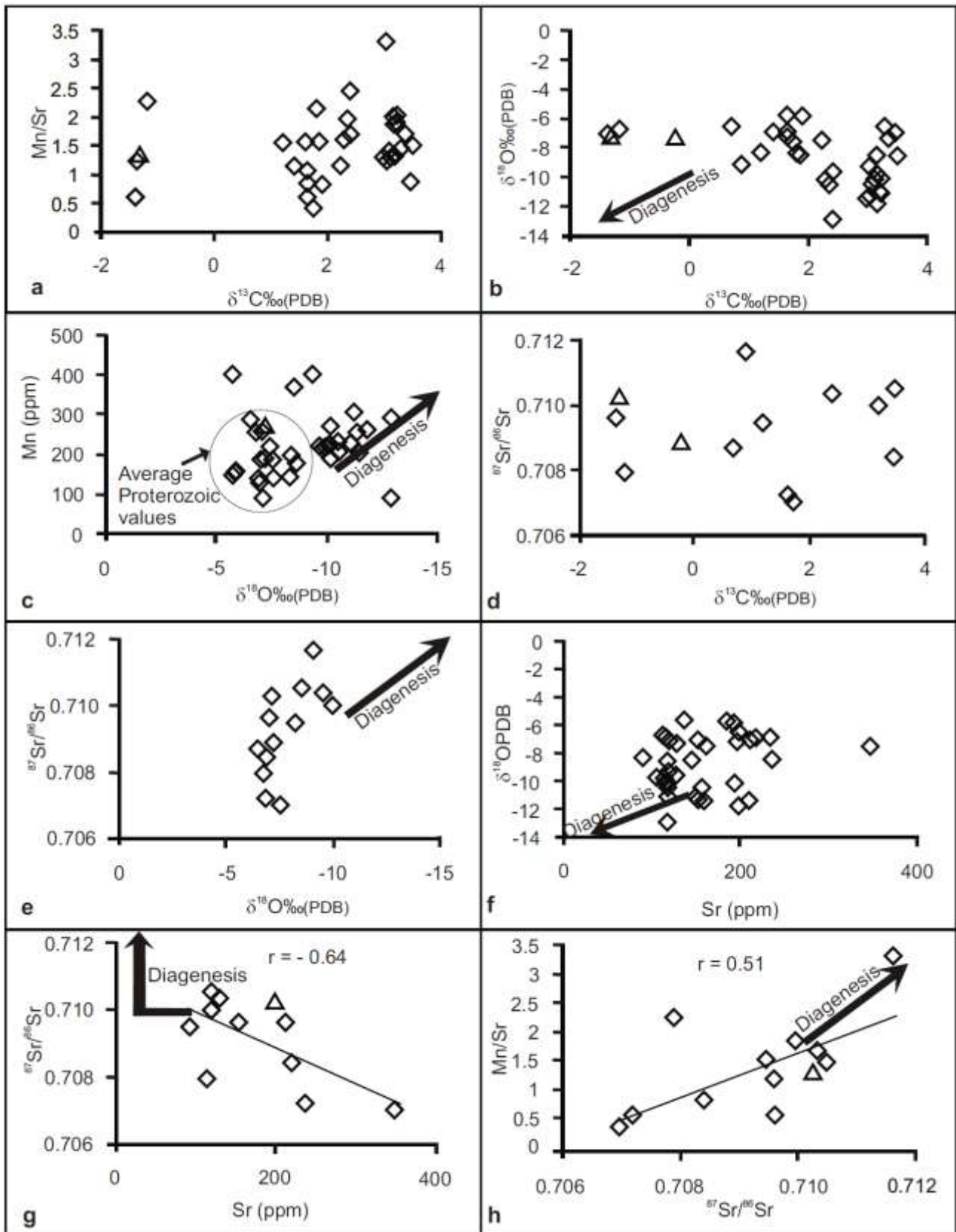

Figure 3. Bivariate plots for the Shahabad limestones (open diamond – micritic limestones, open triangle – micritic limestone with pyrite grains).

Table 2 Comparison of carbon, oxygen, and strontium isotopic data of this study to the published data from the Bhima Basin area.

Reference	$\delta^{13}C$ ‰ PDB	$\delta^{18}O$‰ PDB	$^{87}Sr/^{86}Sr$	Location in Bhima Basin
1	2.8 and 3.8	--	--	Shahabad Formation
2	0.89 to 3.59 (Mean 3.25)	-5.37 to -9.18 PDB	--	[*] Mudbol, Mulkod Villages, Shahabad Formation [**] Kedihalli Village, Katemedavarhalli Formation
3	0 to 3.7[a] 1.8 to 3.3[b]	+23.2 to + 24.2‰ (SMOW) +21 to + 22.3‰ (SMOW)	--	[a] Sedam, Shahabad Formation [b] Katemedavarhalli Formation
4	2.5 ± 1.4[a] 2.6 ± 0.6[b]	--	0.7079 ± 3 0.7087 ± 6	[a]Shahabad Formation [b] Katemedavarhalli Formation
5	1.34 to 1.96	- 6.04 to – 7.61 PDB	0.70687 - 0.70699	Shahabad Formation
6	-1.38 to 3.80	-7.04 to -12.93 PDB	0.70699 to 0.71164	Shahabad Formation

1= Sathyanarayan et al. (1987), (number of samples, n = 2); 2 = Gopendra Kumar et al. (1997), (n = 39)[*], (n =10)[**]; 3 = Kumar et al., (1999a); 4 = Kumar et al., (1999b); 5 = Nagarajan et al., (2008), (n =12); 6 = Present study, (n = 39).

The strontium isotopic composition of seawater is affected by the terrestrial inputs from the continental crust or mantle. The riverine input supplies radiogenic strontium from continental weathering to the ocean with a present-day value at 0.712 ± 0.001 (Banner & Kaufman, 1994). In contrast, a less radiogenic $^{87}Sr/^{86}Sr$ value of 0.704 ± 0.002 characterizes the mantle strontium input into the sea. The $^{87}Sr/^{86}Sr$ values of unaltered marine carbonate minerals will indicate directly the seawater $^{87}Sr/^{86}Sr$ ratios (Banner & Kaufman, 1994). However, $^{87}Sr/^{86}Sr$ ratios in carbonates are more susceptible to diagenetic alteration than C-isotope values, with diagenesis tending to increase the $^{87}Sr/^{86}Sr$ ratios (Knoll, 2000).

Higher $^{87}Sr/^{86}Sr$ ratio in Shahabad limestones can be explained in two ways (1) they are diagenetically altered with radiogenic Sr after their precipitation, or (2) the precipitation fluid had high $^{87}Sr/^{86}Sr$ ratios. If impure limestones contain high Rb/Sr detrital phases (feldspar and phyllosilicate), the phyllosilicate could deliver radiogenic strontium during diagenetic recrystallization and hence cause the secondary carbonates to have high $^{87}Sr/^{86}Sr$ ratios (Alene et al., 2006). However, majority of the Shahabad limestones has moderate strontium concentrations. In addition, a significant negative correlation (r = - 0.64) exists between the strontium concentrations and the $^{87}Sr/^{86}Sr$ ratios for the limestones (Fig. 3g). Therefore, it seems that the Shahabad limestones were associated with radiogenic Sr addition by diagenesis.

7. CONCLUSIONS

This study infers that the Shahabad limestones were deposited in a shallow-marine platform during the Proterozoic age. Positive carbon isotope values are resulted from the burial of organic carbon and likely related to global climatic condition in the Proterozoic age. These chemical events have been invoked as a major factor in organic evolution (as well as extinction), and they can be expected to have had an effect on the C-isotopic composition of seawater. Most of the samples retained the original $\delta^{18}O$ values equivalent to the Proterozoic carbonates and the higher negative $\delta^{18}O$ values of Shahabad limestones suggest that these limestones are affected by meteoric diagenesis. High negative $\delta^{18}O$ values, Mn/Sr ratios, and high $^{86}Sr/^{87}Sr$ ratios in most of the limestone samples also indicate that the isotopic ($\delta^{18}O$ and $^{87}Sr/^{86}Sr$) signatures of these limestones are altered during diagenesis.

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