

Carbon and oxygen isotope geochemistry of Neoproterozoic limestones of the Shahabad Formation, Bhima basin, Karnataka, southern India

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ABSTRACT

Petrography, major (including four trace elements), stable isotopes (carbon and oxygen), and ⁸⁷Sr/⁸⁶Sr geochemistry of limestones of the Shahabad Formation, Bhima basin, Karnataka, southern India are reported. These limestones show a narrow range of $\delta^{13}\text{C}$ (~-1.34–1.96‰) and $\delta^{18}\text{O}$ (~-6.04 to -7.61‰) values. The petrographic study reveals the presence of microsparite and micro- and macrostylolites. The $\delta^{13}\text{C}$ and ⁸⁷Sr/⁸⁶Sr values indicate that these limestones were deposited during the late Neoproterozoic age and the $\delta^{18}\text{O}$ values also are very similar to the average Proterozoic carbonate values. Mn and Sr concentrations and low Mn/Sr ratio (<1) together with the stable and radiogenic isotope data suggest that the studied samples are well-preserved or scarcely altered limestones and probably have retained their primary isotopic signatures.

Key words: geochemistry, stable isotopes, delta oxygen, delta carbon, strontium isotopes, carbonate rocks, diagenesis, Bhima basin, India.

RESUMEN

En este trabajo se reportan resultados de la geoquímica de isótopos estables (carbono y oxígeno) y de elementos mayores (incluyendo cuatro elementos traza) en las calizas de la Formación de Shahabad, cuenca de Bhima, Karnataka, en India meridional. Las calizas de la cuenca de Bhima muestran un estrecho intervalo de los valores de $\delta^{13}\text{C}$ (~-1.34 a 1.96‰) y $\delta^{18}\text{O}$ (~-6.04 a -7.61‰). El estudio petrográfico revela la presencia de dolomía, microesparita y calcita recristalizada con micro y macroestilolitos. Los valores de $\delta^{13}\text{C}$ y ⁸⁷Sr/⁸⁶Sr revelan que estas calizas fueron depositadas durante el Neoproterozoico Tardío y los valores de $\delta^{18}\text{O}$ son muy parecidos a los valores promedio de los carbonatos del Proterozoico. Las concentraciones de Mn y Sr y los valores bajos de Mn/Sr (<1), junto con los datos de isótopos estables y radiogénicos, indican que estas calizas están bien preservadas o escasamente alteradas y probablemente han conservado su firma isotópica primaria.

Palabras clave: geoquímica, isótopos estables, delta oxígeno, delta carbono, isótopos de estroncio, rocas carbonatadas, diagénesis, cuenca de Bhima, India.

INTRODUCTION

Chemical composition of sedimentary rocks is widely used to delineate specific units of carbonate and clastic strata (Primmer *et al.*, 1990). In recent years, much work has been focused on constraining primary $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of Precambrian carbonate sequences to understand the depositional processes, the evolution of the ocean-atmospheric system, and the interactions of biotic and abiotic processes during the Earth's history (Burdett *et al.*, 1990; Veizer *et al.*, 1992a, 1992b; Knoll *et al.*, 1995). The temporal $\delta^{13}\text{C}$ fluctuations of sedimentary carbonates represent secular variations of $\delta^{13}\text{C}$ in ocean water. Strontium isotope stratigraphy is a reliable and precise tool for stratigraphic correlations and age determinations. If these carbonates precipitate in contact with seawater and remain relatively unaltered by post-depositional events during diagenesis, their strontium content should retain a seawater strontium isotope signature (Banner and Kaufman, 1994; Burke *et al.*, 1982; DePaolo and Ingram, 1985). Although extensive isotopic data are available from different parts of the world for Proterozoic

sedimentary rocks, only a few studies have been published on samples from the Bhima basin (Sathyanarayan *et al.*, 1987; Kumar *et al.*, 1997; Kumar *et al.*, 1999; Nagarajan, 2003).

In this study, elemental and stable and radiogenic isotope data of limestones from the Malkhaid quarry (named after Malkhaid village) are presented. The quarry of the Malkhaid village (located near the Mulkod and Mudbol villages; Figure 1) belongs to the Shahabad Formation of the Bhima basin. The Malkhaid quarry section was selected for the present study because it is considered as the best exposed vertical section (~60 m) in the Shahabad Formation. Our main aim was to test if these limestones have retained their original chemical and isotopic compositions without significant post-depositional changes.

GEOLOGICAL SETTING

Sedimentary formations of the Bhima basin are exposed as an array of narrow, E-W stretching, sygmoïdal

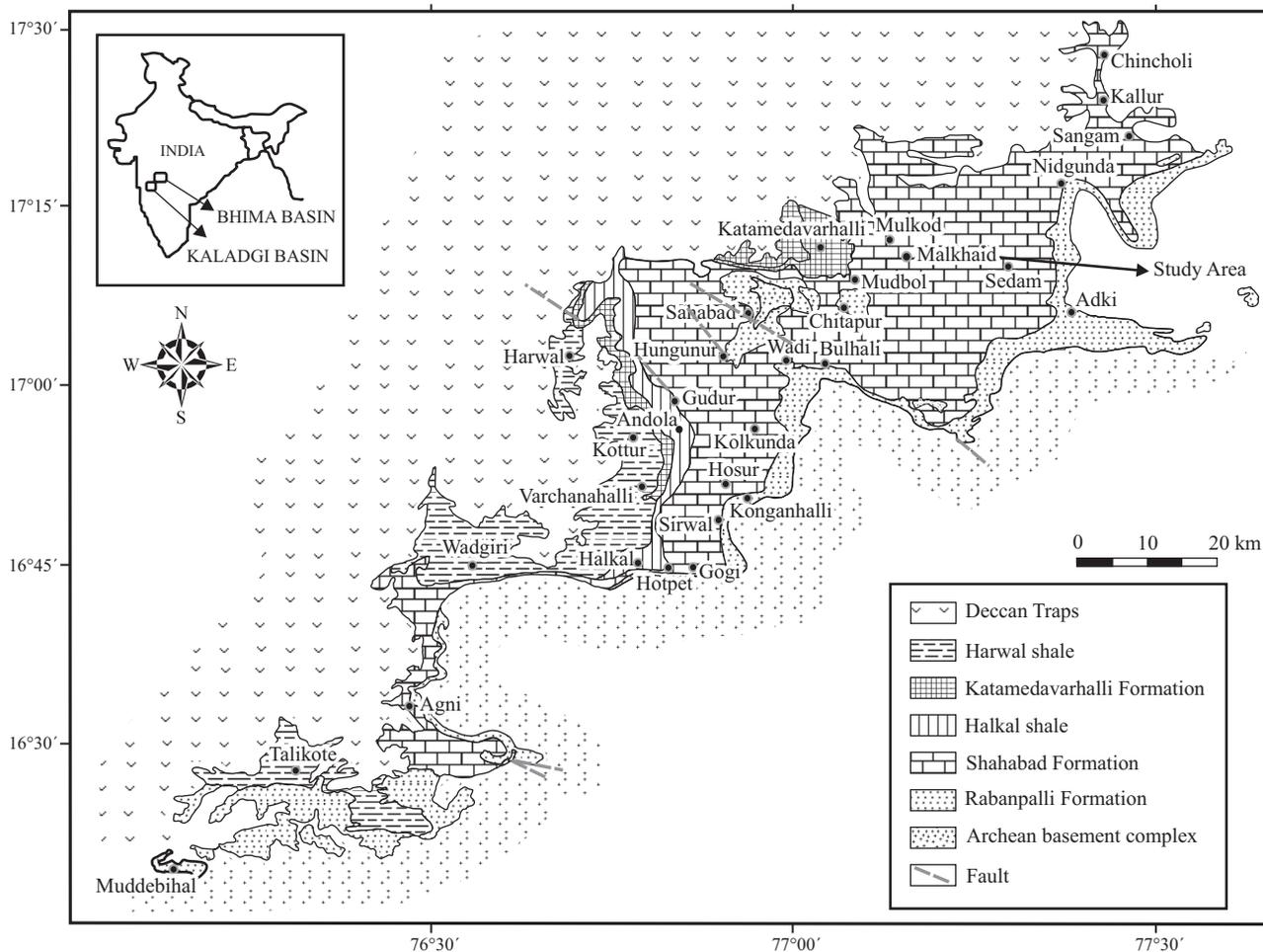


Figure 1. Geological map of the Bhima basin showing the study area. The limestone samples were collected from the Malkhaid quarry section, which belongs to the Shahabad Formation (modified after Rao *et al.*, 1975).

strips arranged in an en echelon pattern, with a thickness of about 300 m, and extended over an area of 5,000 km² (Figure 1). These sedimentary rocks mainly comprise an alternating sequence of clastic and carbonate rocks (Rao *et al.*, 1975; Misra *et al.*, 1987; Kale, 1990; Kale *et al.*, 1990; Nagarajan, 2003). The Mesoproterozoic Kaladgi supergroup and the Neoproterozoic Bhima group overlie the Archean granite-greenstone basement in Karnataka, southern India. The Archean granite-greenstone terrain mainly consists of TTG (tonalite-trondhjemite-granodiorite), popularly known as Peninsular gneisses (Dharwar greenstone belts). The sedimentary rocks of the Mesoproterozoic Kaladgi supergroup and Neoproterozoic Bhima group were deposited on the eroded edges of the Dharwar craton (Kumar and Srinivasan, 2002). The Kaladgi sedimentary basin is exposed E-W for a length of ~160 km, with a width varying from 40 to 65 km, and covers an area of about 8,000 km² to the west of the Bhima basin. The Bhima group is younger than the Kaladgi supergroup, and the Bhima basin rocks have been affected by intense faulting. Major structural faults across the basin define the boundaries of the different sectors (Kale and Peshwa, 1995). As a result of E-W trending faults, the limestones found in the middle part of the basin directly rest on the granitic rocks.

King (1872) coined the term Bhima Series and divided the sedimentary rocks into Muddebihal sandstones and Talikote limestone. Mahadevan (1947) proposed a new threefold classification: 1) Lower Bhima Series, 2) Middle Bhima Series, and 3) Upper Bhima Series. Later, Rao *et al.* (1975) assigned the Group status to the sedimentary rocks of the Bhima basin and divided them into five distinct formations: 1) Rabanpalli Formation, 2) Shahabad Formation, 3) Halkal Shale, 4) Katamedavarhalli Formation, and 5) Harwal Shale. Misra *et al.* (1987) subdivided the Bhima Group into Sedam Subgroup (Rabanpalli Formation and Shahabad Formation) and Andola Subgroup (Halkal Shale, Katamedavarhalli Formation, and Harwal-Gogi Shale). They identified a sedimentation break between the Sedam and Andola subgroups and interpreted it as a paraconformity. Later, Malur and Nagendra (1994) introduced a new name for Shahabad Formation as Kurkunta Formation. Recently, the clastic rocks of the Rabanpalli Formation were studied in detail by Nagarajan *et al.* (2007a, 2007b). The classification proposed by Rao *et al.* (1975) has been adopted for the present study. The five formations seem to represent two major cycles of sedimentation. The Rabanpalli and Shahabad Formations form the first cycle whereas the Halkal, Katamedavarhalli and Harwal Formations form the second cycle of sedimentation. Each cycle of sedimentation commenced with an arenaceous facies.

The limestone member is the dominant lithotype of the Bhima basin and is classified under Shahabad and Katamedavarhalli Formations. The Shahabad Formation is exposed in the central and eastern parts of the Bhima basin (16°15' to 17°35' Lat N; 76°15' to 77°30' Long E; Figure 1). The Shahabad limestones can be classified as (1) flaggy,

pale blue limestone, (2) blocky, light grey limestone, (3) variegated, bluish green or pink/pale blue limestone, (4) massive, dark/bluish grey limestone, and (5) flaggy, dark grey/bluish grey argillaceous limestone (Rao *et al.*, 1975; Malur and Nagendra, 1994). These limestones occupy an area of 2,000 km² in the Bhima basin. According to Kale *et al.* (1990) the vertical thickness of Shahabad Formation is less than 75 m. Representative limestone samples of Malkhaid quarry (60 m depth) were used for this study. The limestone deposits of Malkhaid area (Figure 1) exhibit grey to dark grey and yellowish grey colour. Malkhaid limestones are well exposed near the villages Mulkod and Mudbol. These limestones are classified under the Shahabad Formation, Bhima basin (Figure 1). The well-exposed limestones are quarried by Zuari Cement (private company) for cement manufacturing. The samples were collected from the quarry section, which consists of six 10-m high benches. The vertical profile of the limestone quarry (Figure 2) shows a black cotton soil as surface cover, which is underlain by limestone boulders mixed with yellowish and dark grey limestones. The whole limestone section is micritic in nature and varies in color at different depths. Macrostylolites are identified at certain places with increasing depth.

METHODOLOGY

Twelve limestone samples of the Malkhaid quarry (collected perpendicular to the strike at the different stages; Figure 2) were analyzed for major and some trace elements in the XRF Laboratory, University of Kentucky. The XRF detection limits for Rb-Sr and Mn-Fe pairs were consistent with the systematic behavior suggested by Verma and Santoyo (2005). Carbon and oxygen isotope analyses were carried out at the Stable Isotope Laboratory (LABISE) of the Federal University of Pernambuco, Brazil.

For carbon and oxygen isotopic determinations, CO₂ was extracted from powdered carbonates in a high vacuum line after reaction with orthophosphoric acid at 25°C, and cryogenically cleaned, according to the method described by Craig (1957). CO₂ gas released by this method was analyzed for carbon and oxygen isotopes in a double inlet, triple collector SIRA II mass spectrometer, using the reference gas BSC (Borborema Skarn Calcite), which calibrated against NBS-18, NBS-19, and NBS-20 has a value of -11.28 ± 0.004 ‰_{PDB} for $\delta^{18}\text{O}$ and -8.58 ± 0.02 ‰_{PDB} for $\delta^{13}\text{C}$. The results are expressed in the notation $\delta\text{‰}$ (per mil) in relation to international PDB scale.

Two representative samples were selected for Sr isotope analyses. Limestone samples were leached in 1 N 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 with this method was <200 pg. For mass spectrometry, Sr samples were loaded onto 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 ($1 \times 10^{-11}\text{A}$) $\pm 10\%$ was maintained and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was corrected for mass fractionation using $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$ 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 (1 SD, $n = 17$). To facilitate comparison of Sr isotopic data from different laboratories we have adjusted the $^{87}\text{Sr}/^{86}\text{Sr}$ values of our limestone samples to NIST SRM987 $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710230, following the practice of the Max-Planck Institute, Mainz, Germany (see *e.g.*, the data repository in Verma, 2002).

RESULTS

Petrography

The limestones of Shahabad Formation are micritic (calmicrite) in nature. Stylolites and pressure solution structures are present in the limestones. Some of the pressure solution structures are related to horizontal compressional forces (probably resulting from tectonism). Most of the stylolites have parallel features (Figure 3a-c). The limestones also exhibit crosscutting stylolites and fractures filled by calcite and quartz. Few limestone samples from the top of the section exhibit small grains of saddle dolomite (Figure 3d), which are seen adjacent to stylolites. The limestones also exhibit some mineral grains, which occur along the stylolites (Figure 3e). Limestones of Shahabad Formation show pressure solution and chemical deposition of fibrous void-filling calcite (Figure 3f) on free surfaces of individual crystals and polycrystalline aggregates. Terrigenous particles like quartz and feldspar occur as aggregates and lenses in the inter-laminar areas.

Elemental variations

The results of major (in wt. %), four trace elements (in ppm), strontium isotopes, and carbon and oxygen isotopes (‰) for the Malkhaid quarry section limestones are presented in Table 1. We also report mean values for all elements in these limestone samples without testing if these data represent a normal population and if there are any discordant outliers present. Sample MK11 would probably represent a discordant outlier for SiO_2 and sample MK2 would be for Rb if the method and critical values proposed by Verma and Quiroz-Ruiz (2006a, 2006b) are used for this purpose. Proper handling of discordant outliers would have improved the veracity of mean and standard deviation values, particularly for those parameters that have outlying observations (Verma *et al.*, 2008).

The major and trace element variations with depth are shown in Figure 4. The limestones show high content of CaO (~41.0–46.4 wt.%; except MK11). The distribution of SiO_2 is reverse to that of CaO (~9.18–14.4 wt.%). Other elements like Al_2O_3 (~0.57–1.86 wt.%), K_2O (~0.16–0.41 wt.%), Fe_2O_3 (~0.11–0.93 wt.%), and Na_2O (~0.03–0.04 wt.%) are much lower than the CaO and SiO_2 contents. Na_2O content is uniform throughout the quarry section (Figure 4). The aluminum concentration is a reasonably good measure of detrital flux (Veizer, 1983). Positive correlations of Al_2O_3 with TiO_2 , MgO and Fe_2O_3 (linear correlation coefficient, $r = 0.96, 0.87, \text{ and } 0.81$, respectively; number of samples $n = 12$) are statistically significant at 99% confidence level (for more details on significance levels and the corresponding critical values, see Verma, 2005) and indicate that these elements are associated with detrital phases. Slight differences in the major element concentrations of the sample

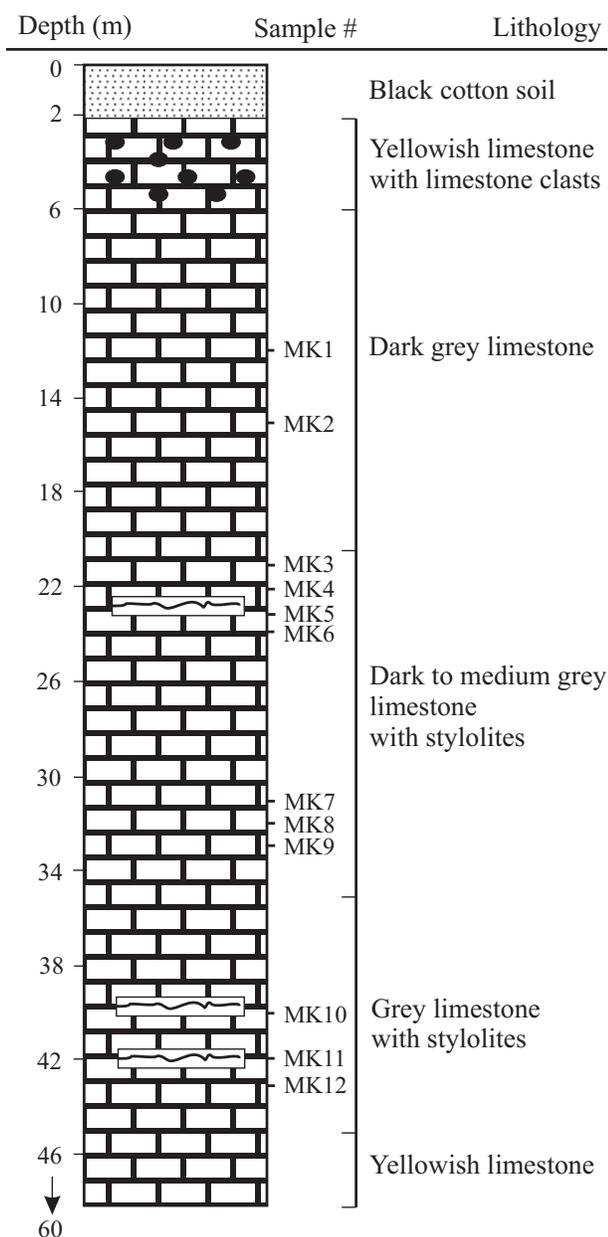


Figure 2. Columnar section of the Malkhaid quarry section from the Shahabad Formation, showing sample locations.

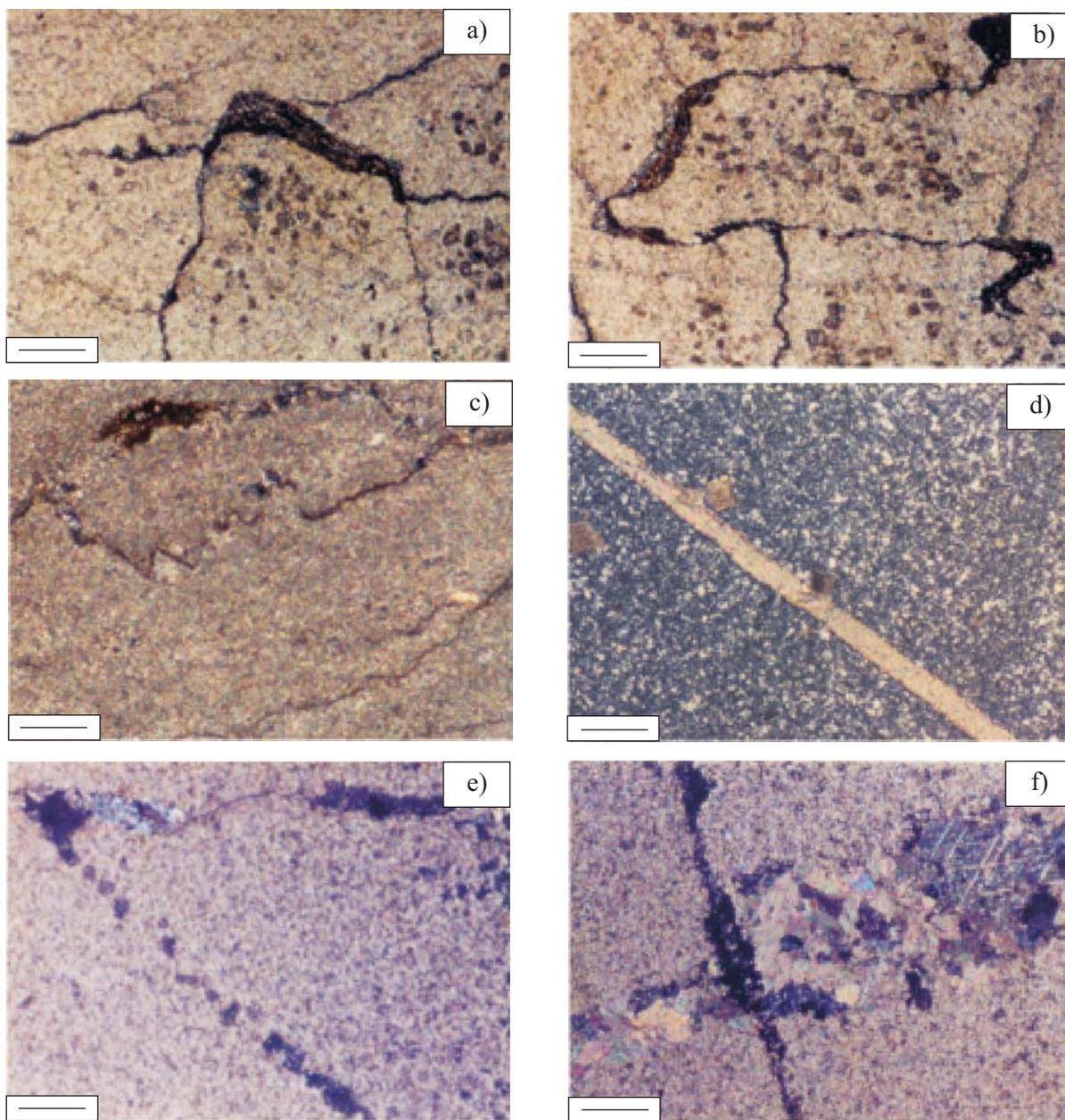


Figure 3. Thin-section microphotographs for limestones of the Malkhaid quarry section from the Shahabad Formation (scale bar = 0.19 mm; parallel Nicols). a-c: different types of stylolites; d: small dolomite grains adjacent to stylolites; e: presence of some mineral grains along the stylolites; f: void filling calcite cement.

MK4 (Table 1) compared to other samples may be due to the presence of clay minerals formed along the stylolitic seams. The limestone samples of this study show very low Mg/Ca ratio (~ 0.005 – 0.030 ; Table 1), even though some minor saddle dolomite grains are present in a few samples (Figure 3d). These low values indicate that the studied samples are not dolomitized, because dolomitization would necessarily cause a marked increase in the Mg/Ca ratio of the limestones (*e.g.*, Kaufman *et al.*, 1992).

Trace element analyses show that the Ba content (~ 127 – $5,700$ ppm) in the samples is much higher than the

Sr (~ 112 – 350 ppm), Mn (~ 77 – 125 ppm), and Rb (~ 1 – 180 ppm) contents. The enrichment of Ba is particularly noted in the samples MK11 (5,700 ppm) and MK9 (2,300 ppm), which show stylolites and veins filled with insoluble residues. The recent shallow marine carbonates have Sr concentrations between 8,000 and 10,000 ppm (Milliman, 1974). The Sr contents of samples in this study (~ 112 – 350 ppm) are also much lower than the average value given for lithosphere carbonates (Sr = 610 ppm; Turekian and Wedepohl, 1961). The abnormal enrichment of Rb in sample MK2 (180 ppm; Table 1) may be due to the influx of clay minerals.

The carbon and oxygen isotope values range from 1.34 to 1.96‰ and -6.04 to -7.61‰, respectively. Two samples (MK1 and MK8) were analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70684 and 0.70696, respectively; Table 1).

DISCUSSION

Identification of primary isotopic signatures

Many criteria have been emphasized to assess the degree of post-depositional alteration in carbonate rocks (Hudson, 1977; Veizer *et al.*, 1992a; Derry *et al.*, 1992; Kaufman and Knoll, 1995). The variations in trace elements have been used as a technique to identify diagenetic alteration (*e.g.*, Brand and Veizer, 1980; Ditchfield *et al.*, 1994; Jones *et al.*, 1994a, 1994b; Price and Sellwood, 1997; Podlaha *et al.*, 1998; Hesselbo *et al.*, 2000; Price *et al.*, 2000; Jenkyns *et al.*, 2002; Grocke *et al.*, 2003). These studies suggest that high concentrations of Fe and Mn are mainly associated with negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. During diagenetic alteration by meteoric fluids, Mn may be incorporated and Sr may be expelled from the carbonate system (Brand and Veizer, 1980; Veizer, 1983). Hence, the diagenetic alteration of low-Mg calcite will decrease the Sr content and increase the Mn content (Veizer, 1983).

However, such a trend is not observed in the limestones of the Shahabad Formation because the linear correlation coefficient (r) between Mn and Sr ($r = -0.16$; $n=12$) is not statistically significant (see Verma, 2005, for statistical significance of r values).

Due to the distinct behavior of Mn and Sr during diagenesis (marine and meteoric) of limestones, Mn/Sr ratio is generally considered as a reliable indicator of the degree of alteration (Jacobsen and Kaufman, 1999). Many studies (Derry *et al.*, 1992; Kaufman *et al.*, 1992, 1993; Kah *et al.*, 1999) reveal that the limestones with $\text{Mn}/\text{Sr} < 2$ generally display unaltered isotopic signature. Furthermore, Jacobsen and Kaufman (1999) proposed a model on the basis of trace elements and stable isotopes, and concluded that the limestones with $\text{Mn}/\text{Sr} < 2$, $\delta^{18}\text{O}$ values from -5 to -10 ‰ and Sr concentrations between 150 and 2,500 ppm show primary isotopic signatures. In the present study, the Mn/Sr ratios (~ 0.26 – 0.86), $\delta^{18}\text{O}$ values (~ -7.61 to -6.04 ‰), and Sr concentrations (~ 112 – 350 ppm), fall well within these ranges and indicate the preservation of primary isotopic signatures.

Many studies have shown that carbon isotopic signatures are well preserved in Proterozoic carbonates (Schidlowski *et al.*, 1975; Knoll *et al.*, 1986), because pore spaces are sealed soon after the deposition, which inhibit subsequent fluid-rock interaction and isotopic resetting

Table 1. Major (wt. %), trace (ppm), stable isotopes (‰) and strontium isotopes for limestone samples of the Malkhaid quarry section, Shahabad Formation, Bhima Basin, Karnataka, southern India.

| Sample # | MK1 | MK2 | MK3 | MK4 | MK5 | MK6 | MK7 | MK8 | MK9 | MK10 | MK11 | MK12 | Mean (n=12)* |
|---------------------------------|---------|--------|--------|--------|--------|--------|--------|---------|--------|--------|--------|--------|---------------|
| Depth m | 12 | 15 | 21 | 22 | 23 | 24 | 31 | 32 | 33 | 40 | 41 | 42 | – |
| SiO ₂ | 11.5 | 11.1 | 12.4 | 10.5 | 14.4 | 10.3 | 9.24 | 10.1 | 10.1 | 11.1 | 47.9 | 9.18 | 14±11 |
| TiO ₂ | 0.04 | 0.04 | 0.05 | 0.08 | 0.03 | 0.03 | 0.02 | 0.03 | 0.05 | 0.08 | 0.02 | 0.05 | 0.04±0.02 |
| Al ₂ O ₃ | 1.06 | 0.91 | 1.08 | 1.86 | 0.81 | 0.76 | 0.69 | 0.77 | 1.29 | 1.74 | 0.57 | 1.47 | 1.08±0.42 |
| Fe ₂ O ₃ | 0.42 | 0.29 | 0.40 | 0.93 | 0.27 | 0.20 | 0.11 | 0.15 | 0.28 | 0.48 | 0.21 | 0.30 | 0.04±0.22 |
| MgO | 0.46 | 0.43 | 0.50 | 0.89 | 0.33 | 0.33 | 0.30 | 0.49 | 0.68 | 1.65 | 0.13 | 1.01 | 0.60±0.41 |
| CaO | 44.1 | 45.2 | 43.3 | 41.2 | 41.1 | 46.1 | 46.4 | 45.3 | 43.7 | 41.0 | 15.6 | 45.0 | 41.5±8.4 |
| Na ₂ O | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.03 | 0.04 | 0.04±0.002 |
| K ₂ O | 0.20 | 0.18 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.30 | 0.40 | 0.20 | 0.30 | 0.22±0.08 |
| Mn | 108 | 85 | 80 | 77 | 88 | 84 | 99 | 77 | 98 | 101 | 96 | 125 | 93±16 |
| Sr | 350 | 329 | 211 | 220 | 170 | 188 | 180 | 210 | 204 | 130 | 112 | 148 | 200±70 |
| Ba | 300 | 300 | 300 | 1500 | 1400 | 1100 | 127 | 249 | 2300 | 257 | 5700 | 557 | 1170±1580 |
| Rb | 3.0 | 180 | 2.0 | 4.0 | 3.0 | 4.0 | 1.0 | 2.0 | 4.0 | 2.0 | 4.0 | 3.0 | 18±50 |
| $\delta^{18}\text{O}$ | -7.61 | -7.61 | -6.87 | -6.74 | -6.69 | -6.42 | -6.15 | -6.13 | -6.51 | -6.04 | -6.16 | -6.16 | -6.6±0.5 |
| $\delta^{13}\text{C}$ | 1.75 | 1.82 | 1.81 | 1.89 | 1.92 | 1.96 | 1.76 | 1.85 | 1.87 | 1.64 | 1.48 | 1.34 | 1.8±0.2 |
| $^{86}\text{Sr}/^{87}\text{Sr}$ | 0.70684 | – | – | – | – | – | – | 0.70696 | – | – | – | – | – |
| Mn/Sr | 0.31 | 0.26 | 0.38 | 0.35 | 0.52 | 0.45 | 0.55 | 0.37 | 0.48 | 0.78 | 0.86 | 0.84 | 0.5±0.2 |
| Sr/Ca | 0.0011 | 0.0010 | 0.0007 | 0.0007 | 0.0006 | 0.0006 | 0.0005 | 0.0006 | 0.0007 | 0.0004 | 0.0010 | 0.0005 | 0.0007±0.0002 |
| Mg/Ca | 0.009 | 0.008 | 0.01 | 0.02 | 0.007 | 0.006 | 0.005 | 0.009 | 0.013 | 0.030 | 0.007 | 0.019 | 0.012±0.007 |
| Fe/Sr | 8.39 | 6.16 | 13.3 | 29.6 | 11.1 | 7.44 | 4.27 | 5.00 | 9.60 | 25.8 | 13.1 | 14.2 | 12±8 |

* Before data presentation in the table, an attempt was made to round the data to the number of significant digits as suggested by Verma (2005).

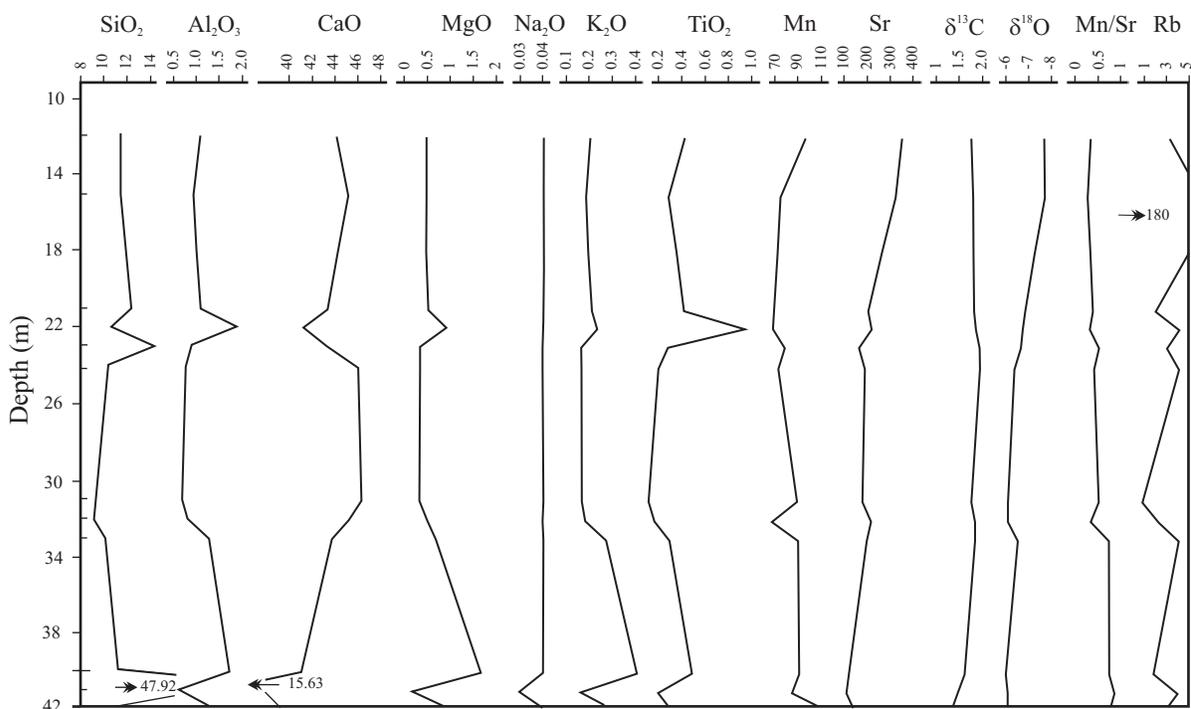


Figure 4. Geochemical variations with depth in limestones of the Malkhaid quarry section from the Shahabad Formation.

(Buick *et al.*, 1995), but meteoric diagenesis can still alter the primary carbon isotope compositions (Veizer, 1983; Kaufman and Knoll, 1995). Similarly, $\delta^{18}\text{O}$ values of carbonate rocks are sensitive diagenetic indicators because the later fluid-rock interactions tend to decrease the primary $\delta^{18}\text{O}$ values imparted by seawater (Veizer, 1983). The diagenetic alteration of the primary $\delta^{13}\text{C}$ signatures can be identified by the covariance relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. A significant positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is an indicator of $\delta^{13}\text{C}$ alteration (Brasier *et al.*, 1996). The lack of a statistically significant positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values ($r=-0.34$, $n=12$; see Verma, 2005 for more details) indicates that diagenetic modification of primary $\delta^{13}\text{C}$ values can be excluded. Thus, geochemical parameters such as Mn, Sr and Mn/Sr ratio, and the relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ strongly support that the limestones of the Shahabad Formation (Bhima basin) retained the primary isotopic signature of Neoproterozoic seawater.

Carbon isotopic composition

$\delta^{13}\text{C}$ excursions studied worldwide imply that the oceanic environment has affected the carbon reservoir in a basin or on a global scale. Variations in the carbon isotopes of limestones and co-occurring organic matter record secular changes in the burial rate of the carbon phases with increasing $\delta^{13}\text{C}$ values (Hayes, 1993). Post-depositional thermal alteration of organic matter often preserves primary carbon

isotopic signatures in carbonate phases (Kah *et al.*, 1999). Therefore, ancient carbonates commonly retain their primary carbon isotopic compositions (Marshall, 1992; Buick *et al.*, 1995; Kaufman and Knoll, 1995; Knoll *et al.*, 1995). During transgression, a greater amount of organic matter is stored in the marginal areas, resulting in the enrichment of ^{13}C , whereas during regressive phases of the sea, the stored organic matter is eroded and oxidized, resulting in ^{12}C enrichment in the deep ocean (Broecker, 1982).

In an isotopic study of the limestones from the Sedam area of the Shahabad Formation (Figure 1), Kumar *et al.* (1999) reported $\delta^{13}\text{C}$ values ranging from 0‰ to 3.7‰. In another study, Kumar *et al.* (1997) obtained a range of $\delta^{13}\text{C}$ values between 0.89‰ and 3.59‰ for the Shahabad Formation and pointed out that the majority of the $\delta^{13}\text{C}$ values cluster around 2‰_{PDB}, except in the basal unit of the Shahabad Formation with a mean value of 3.25‰_{PDB}. In the present study, the limestone samples show a narrower range of $\delta^{13}\text{C}$ values (~1.34–1.96‰) but within the ranges observed by the previous workers. These values are close to the plateau values (2‰; Kaufman and Knoll, 1995) and are similar to the values obtained for limestone sections in Namibia (Grotzinger *et al.*, 1995; Saylor *et al.*, 1998) and Canada (Narbonne *et al.*, 1994). In this context it is also important to point out that after *ca.* 600 Ma the ^{13}C values in carbonates remained high (+2 to +4‰) until the Precambrian-Cambrian boundary (Knoll *et al.*, 1986; Fairchild and Spiro, 1987; Lambert *et al.*, 1987; Kaufman *et al.*, 1991). Afterwards, the ^{13}C values in lower Cambrian carbonates were close to about -1‰. These data therefore

provide age constraints for limestones of the Shahabad Formation.

Oxygen isotopic composition

Oxygen isotope studies of carbonate rocks have provided insight into Precambrian seawater chemistry (Perry and Tan, 1972; Veizer et al., 1992b). Oxygen isotopic compositions of carbonates are much prone to alteration during diagenesis (Hudson, 1977; Veizer, 1983). The results of this study are plotted in a $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ (Figure 5) cross plot diagram (Hudson, 1977), in which the Shahabad limestone samples plot in the fields of late cements and marine limestones. The $\delta^{18}\text{O}$ of a carbonate precipitated

from water depends chiefly on the $\delta^{18}\text{O}$ composition and temperature of the water. Increasing lighter (more negative) $\delta^{18}\text{O}$ value is connected with decreasing salinity and increasing temperatures (Hudson, 1977). The range of moderately depleted $\delta^{18}\text{O}$ values in most limestones is supportive of cementation under mainly burial and/or meteoric conditions rather than by syn-sedimentary marine cements as in many tropical carbonate deposits. The depletion in ^{18}O observed in geologically older carbonates, commonly ascribed to post-depositional isotope exchange with meteoric waters (Clayton and Degens, 1959; Keith and Weber, 1964; Schidlowski et al., 1975), also holds in the case of many Proterozoic carbonate formations. Limestones of the present study show a narrow range of -6.04‰ to -7.61‰ , which is comparable to the 'best preserved' $\delta^{18}\text{O}$ mean value

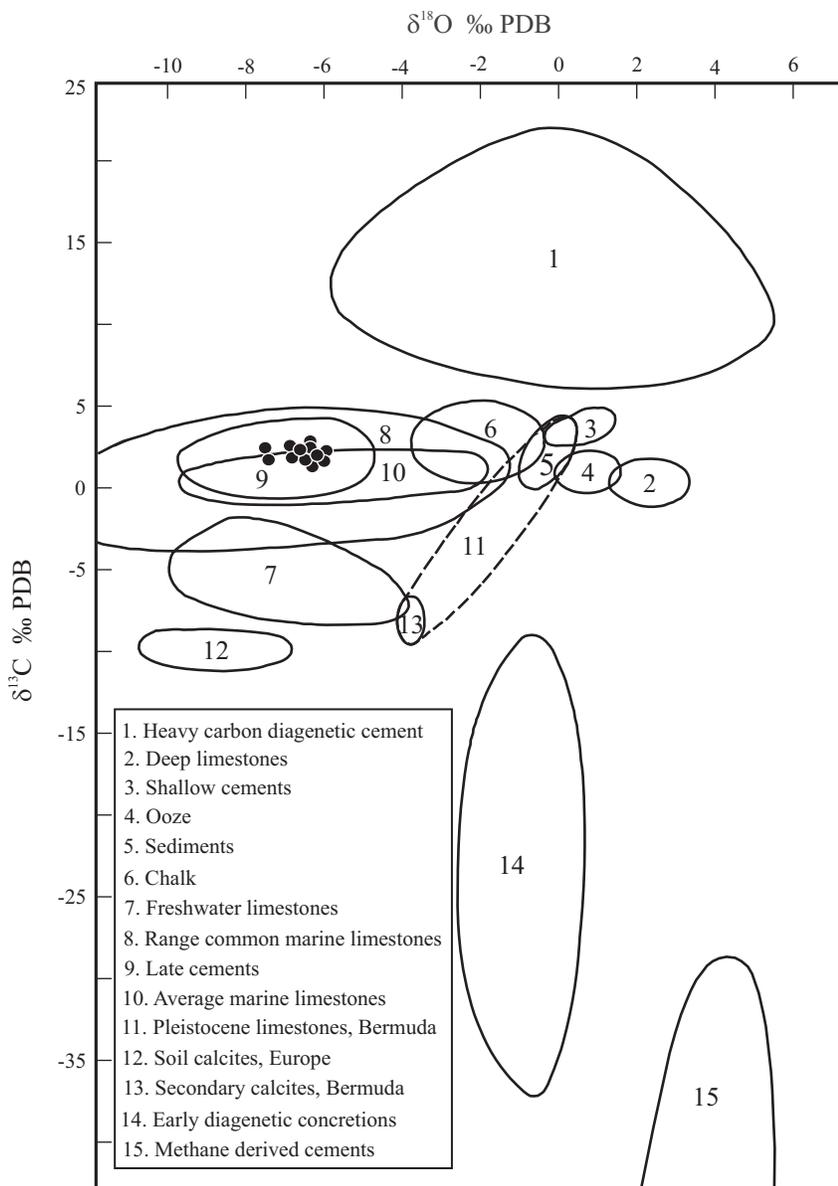


Figure 5. $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ plot for the Shahabad Formation limestones along with the different fields for carbonate rocks proposed by Hudson (1977).

(-7.5 ± 2 ‰) reported for most of the Proterozoic-Early Cambrian limestones (Brasier *et al.*, 1990; Burdett *et al.*, 1990; Kaufman *et al.*, 1991; Veizer *et al.*, 1992a; Hall and Veizer, 1996).

Strontium isotopic composition

The $^{87}\text{Sr}/^{86}\text{Sr}$ composition of seawater has been considered as a powerful tool for making correlations and indirect age assignment, reconstruction of global tectonics, and tracing diagenetic processes (Burke *et al.*, 1982; Veizer, 1989; Banner, 2004; Halverson *et al.*, 2007). $^{87}\text{Sr}/^{86}\text{Sr}$ of the modern ocean (0.7092) generally indicates a combination of hydrothermal alteration of the oceanic crust (~ 0.7035) and input from continental weathering (0.7120; Edmond, 1992). The problems in applying strontium isotope stratigraphy to the Cenozoic record become more important for older time periods (Burke *et al.*, 1982) and are particularly acute for the Precambrian, where the geological record is less complete or incomplete. However, the limited availability of biostratigraphic inferences and meager radiometric dating on the Precambrian rocks require chemostratigraphic methods to correlate and integrate the incomplete stratigraphic records (Knoll and Walter, 1992; Knoll, 2000). Hence, the Sr-isotope stratigraphy is generally applied to the Proterozoic sedimentary rocks. Limestone samples at depths of 12m (MK1) and 32m (MK8) were analysed for $^{87}\text{Sr}/^{86}\text{Sr}$ isotope and yielded values of 0.70684 (MK1) and 0.70696 (MK8). These samples (MK1 and MK8) are very low in Mn/Sr ratio (0.31 and 0.37, respectively) and have positive $\delta^{13}\text{C}$ values (1.75‰_{PDB} and 1.85‰_{PDB}, respectively). Kumar *et al.* (2002) noticed that the Upper Vindhyan carbonates are characterized by positive $\delta^{13}\text{C}$ values at low $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7068 \pm 0.0002), which represent a Neoproterozoic interval of deposition. In general, diagenesis tends to increase $^{87}\text{Sr}/^{86}\text{Sr}$ values. Therefore, a very low $^{87}\text{Sr}/^{86}\text{Sr}$ value from any horizon can be interpreted as a maximum estimate of original seawater composition (Knoll, 2000). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of this study show little variation (0.70684–0.70696). Furthermore, Sr isotopic composition and $\delta^{13}\text{C}$ values of the present study are comparable to that of the upper Vindhyan carbonates, which suggests that the limestones of the Shahabad Formation were deposited during the Neoproterozoic age. Finally, the low $^{87}\text{Sr}/^{86}\text{Sr}$, less positive $\delta^{13}\text{C}$ values, and low Mn/Sr ratio indicate that the studied samples can be considered as well preserved marine limestones that have retained their primary chemical and isotopic signatures.

CONCLUSIONS

A petrographic study showed the presence of microstylolites and siliclastic veins in limestones of the Shahabad Formation. On the basis of chemical and isotopic data, the

studied limestone samples are considered as well-preserved limestones.

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