

# Stable isotope and rare earth element geochemistry of the Baluti carbonates (Upper Triassic), Northern Iraq

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**ABSTRACT:** Stable isotope ratios of  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  and rare earth elements geochemistry of the Upper Triassic carbonates from the Baluti Formation in Kurdistan Region of Northern Iraq were studied in two areas, Sararu and Sarki. The aim of the study is to quantify the possible diagenetic processes that postdated deposition and the paleoenvironment of the Baluti Formation. The replacement products of the skeletal grains by selective dissolution and neomorphism probably by meteoric water preserved the original marine isotopic signatures possibly due to the closed system. The petrographic study revealed the existence of foraminifers, echinoderms, gastropods, crinoids, nodosaria and ostracods as major framework constituents. The carbonates have micritic matrix with microsparite and sparry calcite filling the pores and voids. The range and average values for twelve carbonate rocks of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in Sararu section were  $-5.3\text{‰}$  to  $-3.16\text{‰}$  ( $-4.12\text{‰}$ ) and  $-2.94\text{‰}$  to  $-0.96\text{‰}$  ( $-1.75\text{‰}$ ), respectively; while the corresponding values for the Sarki section were  $-3.69\text{‰}$  to  $-0.39\text{‰}$  ( $-2.08\text{‰}$ ) and  $-5.34\text{‰}$  to  $-2.70\text{‰}$  ( $-4.02\text{‰}$ ), respectively. The bivariate plot of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  suggests that most of these carbonates are warm-water skeletons and have meteoric cement. The average  $\Sigma\text{REE}$  content and Eu-anomaly of the carbonates of Sararu sections were 44.26 ppm and 1.03, respectively, corresponding to 22.30 ppm and 0.93 for the Sarki section. The normalized patterns for the carbonate rocks exhibit: (1) non-seawater-like REE patterns, (2) positive Gd anomalies (average = 1.112 for Sararu and 1.114 for Sarki), (3) super chondritic Y/Ho ratio is 31.48 for Sararu and 31.73 for Sarki which are less than the value of seawater. The presence of sparry calcite cement, negative  $^{13}\text{C}$  and  $^{18}\text{O}$  isotope values, the positive Eu anomaly in the REE patterns (particularly for Sararu), eliminated Ce anomaly ( $\text{Ce}/\text{Ce}^*$ : 0.916–1.167, average = 0.994 and 0.950–1.010, average = 0.964, respectively), and Er/Nd values propose that these carbonates have undergone meteoric diagenesis. The REE patterns suggest that the terrigenous materials of the Baluti were derived from felsic to intermediate rocks.

**Key words:** Baluti Formation, stable isotopes, paleoenvironment, diagenesis, geochemistry

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## 1. INTRODUCTION

The study of  $^{13}\text{C}$  and  $^{18}\text{O}$  stable isotopes in the carbonate rocks is a good tool to infer the palaeoclimatic changes along the geological time (Latorre et al., 1997; Srivastava, 2001; Scott, 2002), the precipitation conditions and the subsequent diagenesis (Wright, 1990; Madhavaraju et al., 2004; Armstrong-Altrin et al., 2011). It can be employed for determination of the origin and temperature of seawater and diagenetic fluids, when it is supported by petrographic study (Allan and Matthews, 1982; Budd and Land, 1990; Rahimpour and Bone, 2001). The oxygen isotope content in the carbonates is influenced by the water composition and

the precipitation temperature (Ali, 1995; Coniglio et al., 2000), and the source of carbonates (Gao et al., 1996; Kumar et al., 2002; Poulson and John, 2003). The  $^{13}\text{C}$  isotope in the carbonate rocks is identified by the  $\delta^{13}\text{C}$  values of bicarbonate/carbonate ions fluctuated in the water through the time, which is influenced by the organic burial changes (Shields, 1999). The  $\delta^{13}\text{C}$  values remain unaffected during most successive crustal processes (Jacobsen and Kaufman, 1999). The negative  $\delta^{18}\text{O}$  values are related to temperature increasing and/or introduction of meteoric water during diagenesis, while the carbon variations are related to the existence of organic matter or  $\text{CO}_2$  from the various organic reactions (Armstrong-Altrin et al., 2009; Armstrong-Altrin et al., 2011) and may reflect the sources of carbon such as bacterial sulphate reduction, dissolution of carbonate minerals, and thermochemical sulphate reduction (Morad and Eshete, 1990; Yoshioka et al., 2003; Ader et al., 2009; Jiang et al., 2015). Fresh water has negative  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values, lower than in marine water carbonates (Madhavaraju et al., 2004; Santos et al.,

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2004; Nagarajan et al., 2008).

The diagenesis of carbonates comprises all the processes that take place after deposition, but before the temperature and pressure conditions reach to the realm of metamorphism (Moore, 2001). When carbonate sediments pass through shallow to intermediate burial diagenesis, meteoric diagenesis is very important for the diagenetic alterations (Land, 1986). <sup>13</sup>C and <sup>18</sup>O isotopes are commonly used to determine the diagenetic processes and paleoenvironment (Veizer and Demovic, 1973; Fairchild et al., 1990; Armstrong-Altrin et al., 2009, 2011).

The REE contents in carbonate rocks are efficient to distinguish the marine and non-marine sources (Zhao et al., 2009). REEs can be also used to identify the depositional environment (German and Elderfield, 1990; Murray et al., 1991), proximity of the source area (Murray et al., 1991), paleoredox conditions (Elderfield and Pagett, 1986; Kato et al., 2002), lithology and diagenesis (German and Elderfield, 1990; Nath et al., 1992; Armstrong-Altrin et al., 2003, 2011; Nothdurft et al., 2004; Madhavaraju et al., 2010; Jiang et al., 2015). The main objective of this study is to investigate the diagenetic processes and paleoenvironment of the Baluti carbonates

through the microfacies analysis, stable isotopes (carbon and oxygen), and rare earth elements.

## 2. GEOLOGICAL SETTING

There are few studies related to the Triassic formations in the Northern Thrust Zone (NTZ) due to the limited exposures and penetrated exploration wells. Baluti Formation belongs to the U. Triassic lithostratigraphic unit; it was firstly studied near Baluti Village (type locality) by Wetzel in 1950 and improved by Morton (Bellen et al., 1959). The formation comprises of grey green and grey shale dominated with intercalation of thin bedded dolomitic, silicified, and oolitic limestone and recrystallization breccias (Bellen et al., 1959; Buday, 1980; Jassim and Goff, 2006). The thickness of the carbonate rocks is ranged between few centimeters and more than 1.5 meters. The studied samples were collected from two outcrop sections: The first locality was at Sararu Village which is located at about 26 km northwest of Amedi Town, at latitude 37°14'21"N and longitude 43°16'56"E in the NTZ (Fig. 1). The second locality is about 15 km southeast of Amedi

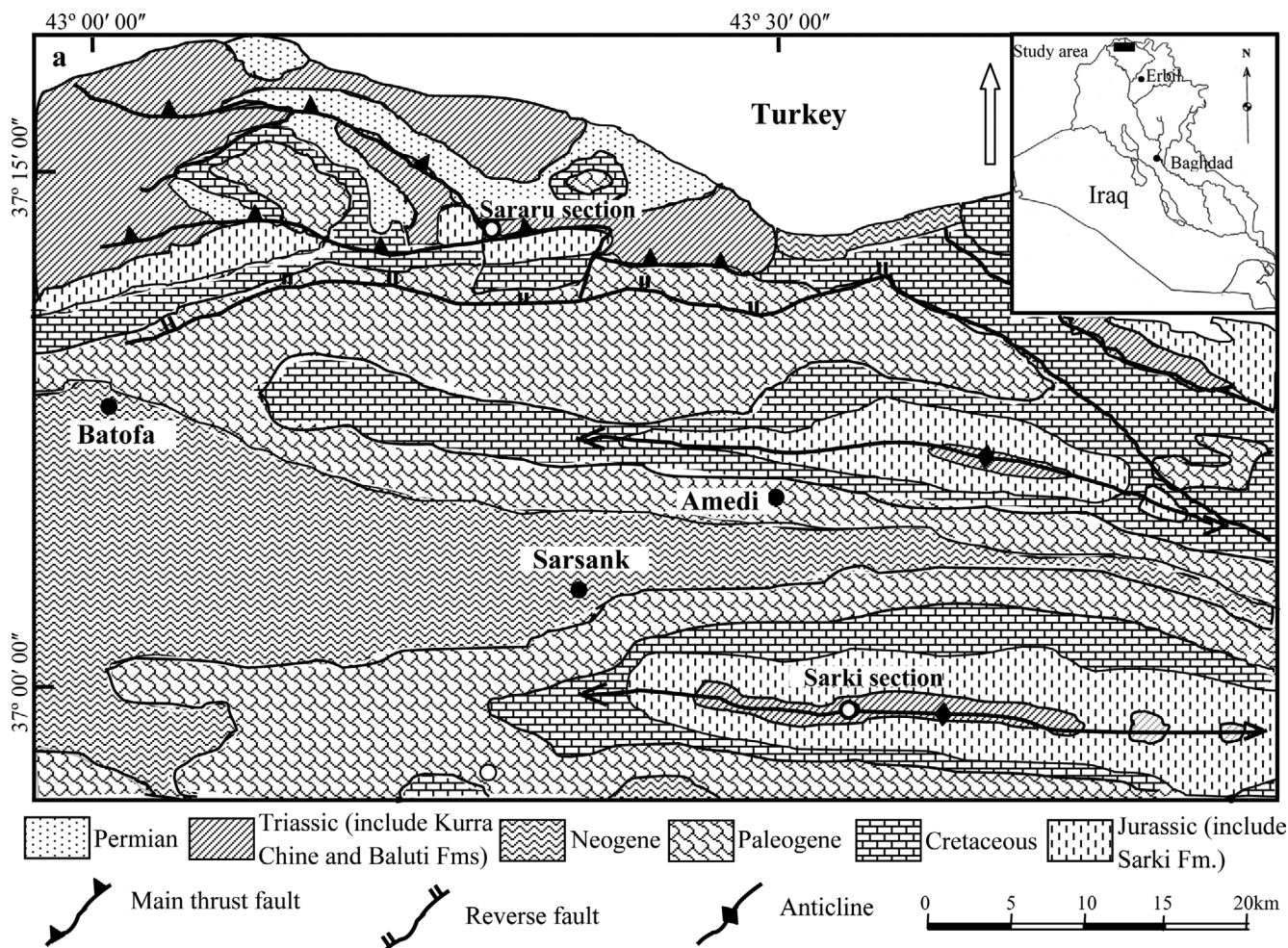


Fig. 1. Geological and location map of the studied sections (Sissakian, 2000).

Town, in the core of Gara anticline near Sarki Village which is situated at latitude 36°59'34"N and longitude 43°32'23"E in High Folded Zone (Fig. 1).

The formation is underlain by Norian Kurra Chine Formation, which comprises of dark brown and black limestone, thin and thick-bedded, with interrupted beds of thick bedded fetid dolomite with, papery shale and slump structures. The Baluti Formation is conformably overlaid by the Liassic Sarki Formation, which consists of about 300 m of carbonates. The Baluti Formation attains a thickness of 66 m and consists of grey shale with thin bedded carbonates at Sararu section, and 43 m of grey to greyish black shale with thin layer of carbonates at Sarki section (Fig. 2).

Hanna (2007) proposed the Carnian age for the upper part of the Baluti, based on the palynozones; and suggested the shore zone depositional environment with influence of fresh water for the lower portion of upper part of the formation. He stated the influence of marine condition on the deposition of the upper portion of the formation.

According to Sharland et al. (2001), the Baluti Formation is within the Tectonostratigraphic Megasequence AP6, from Mid-Permian to Early Jurassic (255–182 Ma). The AP6 megasequence was situated on the north and east flank of the passive margin of the Arabian Plate. The Neo-Tethys Ocean formed during Late Permian when narrow blocks of continental crust drifted away

Sample	Lithology	Lithologic description
		Carbonate rocks of Sarki Fm.
		Grey calcareous shale
BS6 ●		Dark grey marl with thin layer of hard limestone
		Grey calcareous shale with thin layer of argillaceous limestone
BS5 ●		Grey calcareous shale with thin layers of hard limestone
		Grey calcareous shale with thin layer of hard limestone
BS4 ●		Calcareous shale interbedded hard limestone
		Grey calcareous shale with thin layers of hard and fractured limestone
BS3 ●		Grey calcareous shale with thin layer of hard limestone
		Dark grey shale and limestone
BS2 ●		Grey cal. shale with limestone
		Grey limestone
		Cal. shale with hard limestone
BS1 ●		Dark limestone with calc. shale
		Limestone with calc. shale
		Carbonate rocks of Kurra Chine Fm.

Sararu section (a) Scale 1:800

Sample	Lithology	Lithologic description
		Carbonate rocks of Sarki Fm.
B6 ●		Dark grey shale with limestone
		Greyish black shale interbedded with thin beds of limestone
B5 ●		Dark grey limestone
		Greyish black shale
		Greyish black shale interbedded with thin beds of limestone
		Yellowish grey calcareous shale
B4 ●		Brecciated limestone
		Greyish black shale interbedded with thin layers of limestone
B3 ●		Greyish black shale
		Greyish black shale
B2 ●		Bedded limestone with yellowish black shale
		Yellowish green shale
B1 ●		Greenish shale with limestone
		Yellowish grey calcareous shale
		Carbonate rocks of Kurra Chine Fm.

Sarki section (b) Scale 1: 500



Fig. 2. Columnar sections of Baluti Formation. (a) Sararu; (b) Sarki sections.

from the NE margin of Gondwana.

The rifting resumed during Middle or Late Triassic under passive margin conditions, generating a restricted intra-shelf basin in Mesopotamia separated from the open ocean by alkali basaltic narrow rift and an outer ridge of continental crust on which an open marine carbonate platform developed. This rifting was succeeded by slow subsidence in Norian–Liassic resulting in the formation of a passive margin along the northern and eastern margins of the Arabian Plate. As a consequence, the Mesopotamian basin formed during 250–228 Ma (Jassim and Goff, 2006).

During Early and Middle Triassic, the Rutba Uplift was a narrow ridge where its western shoreline was situated in NE Jordan, and the eastern one was along the eastern border of Rutba–Jezira Zone. The igneous-metamorphic complex of Arabian Shield (AS) was exposed above sea level during this time, and it was located to the southwest of the basin of deposition. The AS as part of Arabian Plate, consists of accreted juvenile volcanic arcs, metagabbros, gneisses, metavolcano-sedimentary sequences, granites and gabbro-diorite complexes (Stern, 1994). During 580–540 Ma, the Arabian Shield crust was stabilized and experienced continental uplift and erosion (Moghazi, 2003; Avigad et al., 2005).

### 3. METHODOLOGY

Twelve carbonate bulk samples were collected from two exposed outcrops: Sararu section (6 samples) in NTZ and Sarki section (6 samples) in High Folded Zone (Figs. 1 and 2). A detailed petrographic study covering more than 24 thin sections were carried out, and treated with Alizarin Red-S stain to prove the presence or absence of dolomite and calcite.

The  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  isotopic ratios were determined at

the Stable Isotope Laboratory of the Cornell University, USA. For C- and O-isotopic determinations, powdered samples were treated with  $\text{H}_3\text{PO}_4$  at 25 °C for 3 days to release  $\text{CO}_2$ . The released gas was measured for  $^{13}\text{C}$  and  $^{18}\text{O}$  by mass spectrometer, using the reference gas BSC (Borborema Skarn Calcite) calibrated against NBS-18 have a value of  $-23.20\%$  and  $-5.01\%$ , respectively; and for NBS-19 have  $-2.20\%$  and  $1.95\%$ , respectively. The isotopic results for both C and O are reported as per mil (‰) notation relative to Vienna Pee Dee Belemnite (V-PDB). The uncertainties of the isotope were 0.03‰ for C and 0.06‰ for O, founded on multiple analyses of standard dolomite.

The REE concentrations of the representative carbonate samples were measured by inductively coupled mass spectrometry (ICP-MS) at ALS international laboratory in Spain. Internationally recognized standard materials GBM908-10 and MRGeo08 were used as references. The analytical accuracy ranges from 2% to 12% and precision varies from 1% to 8%. The REE ratios are compared with that of shallow and deep water marine carbonates. The REE concentrations are normalized to PAAS (Taylor and McLennan, 1985).

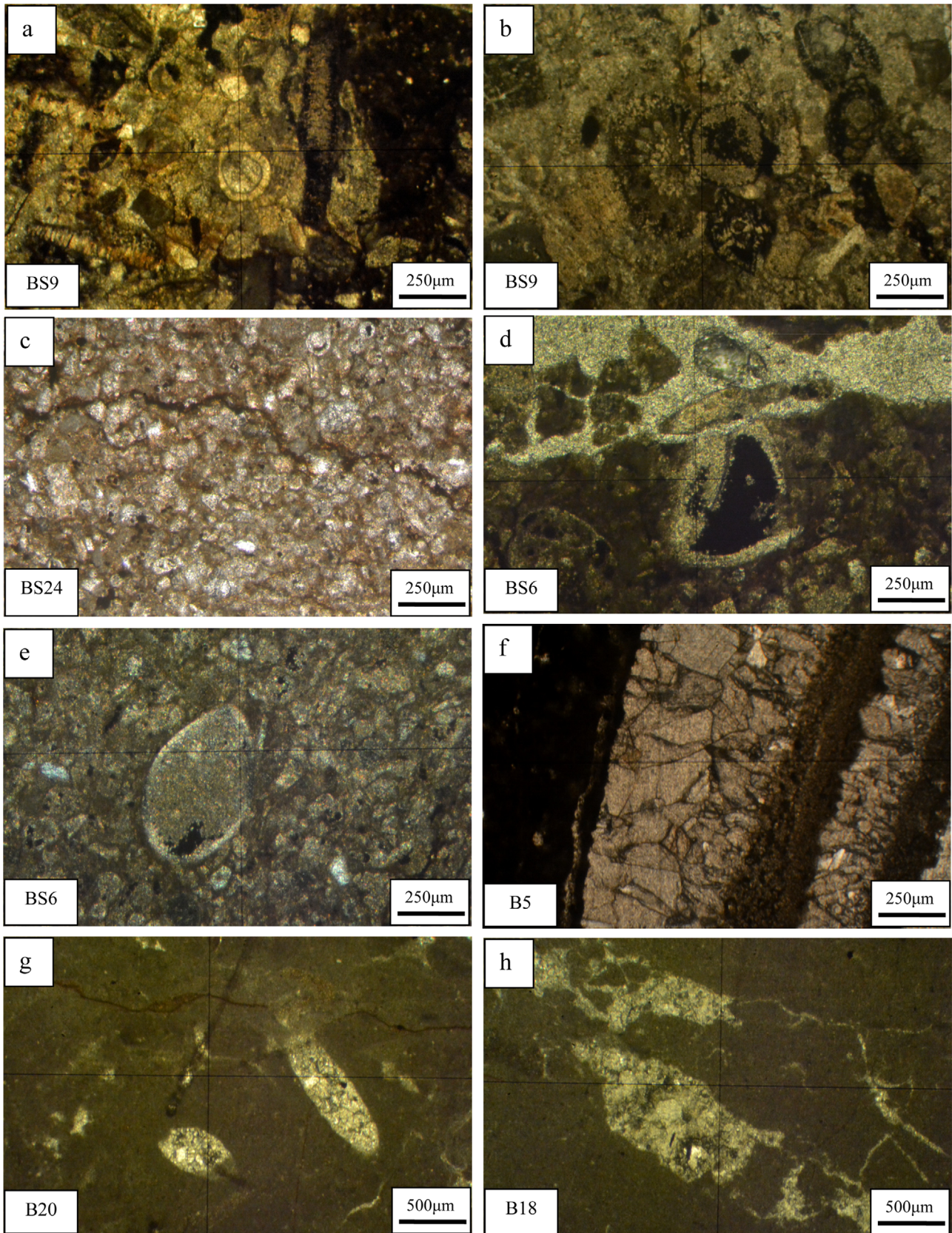
## 4. RESULTS

### 4.1. Petrography

Petrographic description of the Baluti carbonates has been documented based on carbonate classification of Dunham (1962). The bioclasts are the most abundant type of the allochems in Baluti carbonates. They are observed as both intact and fragmented fossils. The size of the bioclast varies from 0.01 mm to several millimeters. In the two studied sections, skeletal grains are well-preserved; however in some places these fossils were obliterated

<u>Diagenetic events</u>	<u>Early (marine meteoric)</u>	<u>Middle</u>	<u>Late</u>
Syntaxial rim cement	—————		
Compaction	—————		
Micritization	—————		
Neomorphism	—————		
Early dolomitization	—————		
Dissolution		—————	
Blocky calcite cement			—————
Silicification			———

**Fig. 3.** Paragenetic sequence of carbonates from Baluti Formation in Northern Thrust Zone summarizing major diagenesis processes.



**Fig. 4.** (a) Packing density and squeezing of bioclast grains, micrite envelop surrounding the skeletal bioclasts; (b) Micrite envelop surrounding the skeletal bioclasts, and crinoids are syntaxially replaced; (c) Irregular microstylolites; (d and e) Neomorphozed lime mud and late diagenetic dolomitization and dissolution process generating secondary porosity (moldic porosity); (f) Late cementation of diagenetic processes (blocky calcite cement); (g) Dolomite texture with microstylolite; (h) Dolomite and vugs filling (early dolomitization).

by the diagenetic processes such as dolomitization, neomorphism, micritization, cementation, and compaction (Fig. 3). The skeletal grains are mostly benthic foraminifers, red algae, echinoderms and mollusk (Figs. 4a and b). Non-skeletal clasts are generally less abundant than skeletal, but their population is high in localized areas. Micritization of the allochems is common (especially in bioclasts).

Four petrographic types have been distinguished: grainstone, packstone, wackestone, and mudstone. Grainstone microfacies are commonly rich in nodosaria, echinoderms and benthic foraminifers (Figs. 4a and b). These bioclasts are mainly cemented by sparry calcite, although some of sparite is dolomitized by diagenetic processes (Fig. 4c). This microfacies are observed in the lower part of the Sararu section. The second microfacies are packstone, a main framework grains are gastropods, echinoderms, crinoids and foraminifers. Dissolution processes are dominant phenomenon that gives a moldic porosity, beside to neomorphosed (Figs. 4d and e). Blocky calcite cement is common (Fig. 4f), and early dolomitization was observed. Some voids and cavities are filled with sparry calcite. This microfacies is present in the carbonate of the Sararu section and in lower part of the Sarki section. Wackestone microfacies are subjected to more intense dissolution processes. Most of the bioclast framework grains are brachiopods and foraminifers that are broken and fragmented to separate particles which float in the micritic matrix. These bioclasts are subjected to dolomitization (Figs. 4g and h). This type is recorded in the carbonate of Sararu section. Mudstone is a mud-supported microfacies was subjected to dissolution and neomorphism with blocky calcite cement. It also contains a considerable amount of fine-grained quartz. This microfacies is commonly observed in the carbonate of Sarki section.

## 4.2. Oxygen and Carbon Isotopes

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values for the Baluti carbonates (mainly dolomitic limestone especially in Sarki section) are given in Table 1 and also presented graphically as a  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  cross-plot (Fig. 5). The  $\delta^{18}\text{O}$  ranging from  $-5.36\text{‰}$  to  $-3.16\text{‰}$  (average =  $-4.12\text{‰}$ ) and  $\delta^{13}\text{C}$  from  $-2.94\text{‰}$  to  $-0.96\text{‰}$  (average =  $-1.75\text{‰}$ )

for Sararu, whereas  $\delta^{18}\text{O}$  ranging from  $-3.69\text{‰}$  to  $-0.39\text{‰}$  (average =  $-2.08\text{‰}$ ) and  $\delta^{13}\text{C}$  from  $-5.34\text{‰}$  to  $-2.70\text{‰}$  (average =  $-4.02\text{‰}$ ) for Sarki. Positive correlation trend between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values is observed especially in Sararu carbonates ( $r = 0.96$ ,  $n = 6$ ).

## 4.3. Rare Earth Elements

The REE contents are generally lower in carbonate rocks than in shales, which proposed that the marine carbonates (exhibit seawater-like REE pattern with LREE depletion, negative  $\text{Ce}_{\text{SN}}$  and positive  $\text{La}_{\text{SN}}$  anomalies; De Baar, 1991; Bau and Dulski, 1996; Nagarajan et al., 2011) contain less REE than clastic materials (with non-seawater-like REE patterns; Piper, 1974; Armstrong-Altrin et al., 2003; Nothdurft et al., 2004).

Sararu and Sarki carbonate samples exhibit large variations in  $\Sigma\text{REE}$  content (31.9–63.71 ppm with an average = 44.26 ppm and 19.31–27.24 ppm with an average = 22.30 ppm, respectively; Table 2). Generally, the carbonate samples from Sararu have higher REE contents than Sarki. PAAS-normalized REE patterns of the Baluti carbonate rocks are obvious in Figure 6. They exhibit (1) non-seawater-like REE patterns, (2) positive Gd anomalies (average = 1.112 for Sararu and 1.114 for Sarki); (3) super chondritic Y/Ho ratio of 31.48 for Sararu and 31.73 for Sarki, and (4) average  $\text{Ce}/\text{Ce}^*$  values of 0.994 for Sararu and 0.964 for Sarki, both of which are close to 1 as shown in Table 2 and Figure 6. Similarly, most of the Sararu carbonate samples show very weak positive to no Eu anomalies ( $\text{Eu}/\text{Eu}^* = 1.034$ ) and weak negative for Sarki carbonate ( $\text{Eu}/\text{Eu}^* = 0.928$ ; Table 2).

The  $(\text{La}/\text{Yb})$  values (Table 2) ranges from 1.074 to 1.254 with an average 1.155 for Sararu and from 0.849 to 1.772 with an average 1.137 for Sarki.

## 5. DISCUSSION

### 5.1. Diagenesis

The porosity and permeability of the studied carbonates were strongly affected by the diagenetic processes that modified the original textural framework as well as chemical compositions.

**Table 1.** Carbon and oxygen isotopic data (as standard deviation with reference to V-PDB) of carbonate rocks from Baluti Formation (Kurdistan Region)

Sample ID	$\delta^{18}\text{O}_{\text{VPDB}}$	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$	Sample ID	$\delta^{18}\text{O}_{\text{VPDB}}$	$\delta^{13}\text{C}_{\text{VPDB}}$	$\delta^{18}\text{O}_{\text{SMOW}}$
BS1	-3.16	-0.96	27.60	B1	-3.60	-4.00	27.15
BS2	-3.19	-1.03	27.57	B2	-1.59	-4.07	29.22
BS3	-3.73	-1.41	27.01	B3	-3.69	-5.34	27.06
BS4	-5.36	-2.80	25.33	B4	-2.36	-4.10	28.43
BS5	-5.11	-2.94	25.59	B5	-0.39	-2.70	30.46
BS6	-4.19	-1.36	26.54	B6	-0.86	-3.90	29.97
average	-4.12	-1.75	26.61	average	-2.08	-4.02	28.72

**Table 2.** Rare earth element (REE) concentrations (ppm) in carbonates from the Baluti Formation

Sample no.	Sararu section							Sarki section					PAAS	
	BS.1	BS.2	BS.3	BS.4	BS.5	BS.6	average	B1	B2	B3	B4	B5		average
La	9	5.3	9.9	12	6.7	6.4	8.22	4.6	2.4	3.6	3.5	3.7	3.56	38.20
Ce	20.4	14.4	21.1	26.1	15.8	12.9	18.45	10.95	7.5	8.17	8	8.19	8.56	79.60
Pr	2.47	1.53	2.55	3.26	1.94	1.65	2.23	1.36	1.37	1.06	1.04	1.07	1.18	8.83
Nd	9.9	6.1	10.1	13	7.7	6.6	8.90	5.6	6.8	4.3	3.9	4.6	5.04	33.90
Sm	1.83	1.22	1.89	2.54	1.48	1.32	1.71	1.28	1.71	0.99	0.77	1.22	1.19	5.55
Eu	0.37	0.25	0.37	0.51	0.32	0.27	0.35	0.22	0.27	0.2	0.15	0.21	0.21	1.08
Gd	1.69	1.08	1.56	2.12	1.25	1.11	1.47	1.08	1.2	0.77	0.64	1.07	0.95	4.66
Tb	0.22	0.15	0.24	0.29	0.18	0.16	0.21	0.16	0.13	0.13	0.09	0.13	0.13	0.77
Dy	1.38	0.88	1.34	1.71	1.03	0.92	1.21	0.88	0.59	0.74	0.55	0.73	0.70	4.68
Ho	0.26	0.16	0.25	0.32	0.2	0.17	0.23	0.16	0.08	0.12	0.09	0.13	0.12	0.99
Er	0.65	0.4	0.67	0.87	0.53	0.48	0.60	0.43	0.2	0.35	0.29	0.35	0.32	2.85
Tm	0.09	0.05	0.09	0.12	0.08	0.07	0.08	0.06	0.02	0.05	0.04	0.05	0.04	0.41
Yb	0.53	0.34	0.65	0.76	0.43	0.44	0.53	0.4	0.1	0.29	0.22	0.28	0.26	2.82
Lu	0.08	0.04	0.09	0.11	0.07	0.06	0.08	0.06	0.01	0.04	0.03	0.04	0.04	0.43
Y	8.2	5.1	8	9.8	6.1	5.5	7.12	4.7	2.5	3.7	3	4.4	3.66	
ΣREE	48.87	31.90	50.8	63.71	37.71	32.55	44.26	27.24	22.38	20.81	19.31	21.77	22.30	175.94
(La/Yb) <sub>SN</sub>	1.254	1.151	1.124	1.166	1.150	1.074	1.16	0.849	1.772	0.916	1.174	0.976	1.137	–
(La/Nd) <sub>SN</sub>	0.807	0.771	0.870	0.819	0.772	0.861	0.82	0.729	0.313	0.743	0.796	0.714	0.63	–
(Nd/Yb) <sub>SN</sub>	1.554	1.492	1.293	1.423	1.490	1.248	1.41	1.165	5.657	1.233	1.475	1.367	1.63	–
Y/Ho	31.54	31.88	32.00	30.63	30.50	32.35	31.48	29.38	31.25	30.83	33.33	33.85	31.73	–
Er/Nd	0.066	0.066	0.066	0.067	0.069	0.073	0.067	0.077	0.029	0.081	0.074	0.076	0.064	–
Eu/Eu*	0.991	1.026	1.015	1.035	1.108	1.050	1.034	0.881	0.888	1.079	1.006	0.865	0.928	–
Ce/Ce*	0.998	1.167	0.969	0.963	1.011	0.916	0.994	1.010	0.954	0.965	0.967	0.950	0.964	–
Pr/Pr*	1.020	0.960	1.026	1.038	1.032	1.048	1.023	1.017	1.053	1.046	1.093	1.016	1.043	–
Gd/Gd*	1.201	1.135	1.037	1.121	1.091	1.088	1.112	1.071	1.190	0.956	1.101	1.229	1.114	–

Ce/Ce\* = Ce<sub>SN</sub>/(La<sub>SN</sub> × Pr<sub>SN</sub>)<sup>0.5</sup>; Eu/Eu\* = Eu<sub>SN</sub>/(Sm<sub>SN</sub> × Gd<sub>SN</sub>)<sup>0.5</sup>; Pr/Pr\* = [Pr/(0.5Ce + 0.5Nd)]<sub>SN</sub>; Gd/Gd\* = [Gd/(0.33Sm + 0.67Tb)]<sub>SN</sub>.

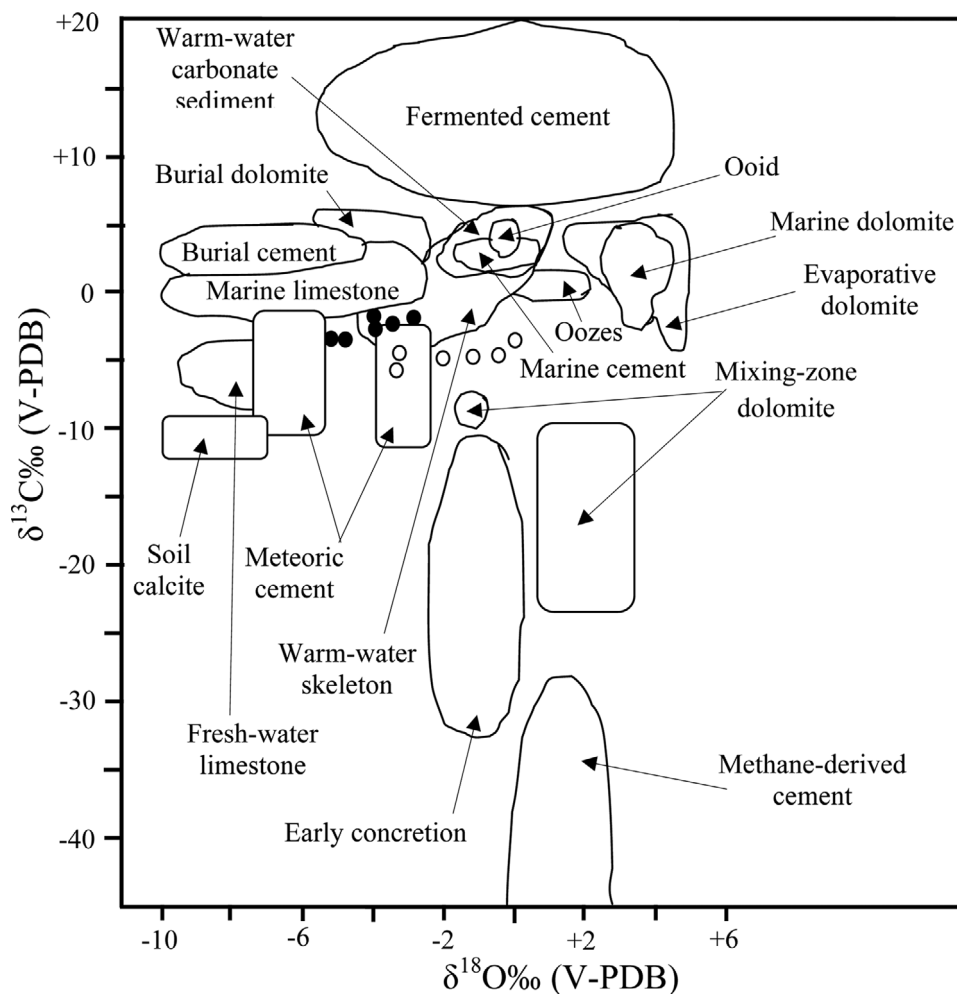
One of the most important diagenetic processes is micritization which can be observed as envelopes surrounding the skeletal bioclasts (Figs. 4a and b). It can be regarded as a primary diagenetic process, associated with algae and fungi for the void formation followed by micritization during later stage (Bathurst, 1972). The chemical compaction is represented by pressure solution structures of microstylolites that are marked by the existence of clay and other fine-sized minerals. Based on Logan and Semeniuk (1976) classification, smooth and irregular low peak amplitude types are recognized (Figs. 4c and g). The overgrowth of the syntaxial rim cement represents the change from marine phreatic to fresh water phreatic (Fig. 4b). The carbonates of Baluti are highly neomorphosed; for instance, the micritic groundmass in mud-dominated facies is neomorphosed to coarse calcite crystals (Figs. 5d and e).

Dissolution process can occur at any burial history of the carbonate rocks which are generally characterized by non-selective dissolution forming pores. These types are commonly called moldic, caverns, and channels depending on the size (Choquette and Pray, 1970) as shown in Figure 4f. The carbonates are highly

dolomitized and the two genetic types are distinguished: early diagenetic consists of very fine to fine crystalline planar e-dolomite mosaic (Figs. 4g and h); and late diagenetic is characterized by medium to coarse crystalline planar e-dolomite replacement dolomite (Fig. 4d).

## 5.2. Oxygen and Carbon Isotopic Variations

The δ<sup>18</sup>O values for the Baluti carbonate are low in relative to a typical marine δ<sup>18</sup>O value of 0‰. This finding suggests the δ<sup>18</sup>O values of this carbonate have been controlled by equilibrium with water that is dominated by fresh water, rather than seawater (Poulson and John, 2003). The isotopic composition of the Baluti carbonate shows a pattern of strongly variable δ<sup>13</sup>C (–5.34‰ to –0.96‰) and δ<sup>18</sup>O values (–5.36‰ to –0.39‰) that is typical for cement with the meteoric origin (Rahimpour and Bone, 2001). The depletion of <sup>13</sup>C and <sup>18</sup>O compared to those of marine water denotes the Baluti carbonates were subjected to extensive meteoric diagenesis. Armstrong-Altrin et al. (2009) suggested the humid paleoclimate for the Upper Miocene of southern India depending



**Fig. 5.** Bivariate plots of  $\delta^{18}\text{O}$  (V-PDB) and  $\delta^{13}\text{C}$  (V-PDB) for the Baluti carbonates. Fields are after Hudson (1977) and Nelson and Smith (1996).

on the negative  $\delta^{18}\text{O}$  values of the carbonate rocks. Accordingly, the study suggests the humid paleoclimate for the Baluti carbonates (Upper Triassic). Depending on the main palynomorph groups, Hanna (2007) concluded that the climate during the deposition of the upper portions of the Baluti was continually changing between humid and arid.

The stable oxygen isotope ( $\delta^{18}\text{O}$ ) of a precipitated carbonate depends mainly on the composition of the isotope, salinity and temperature of the host fluid (Friedman and O'Neil, 1977; Hudson, 1977; Leeder, 1982). The  $\delta^{18}\text{O}$  values show statistically positive correlation with  $\delta^{13}\text{C}$  values (especially for Sararu,  $r = 0.959$ ); such +ve relationship indicates that these carbonates were changed by diagenesis (Marshall, 1992; Buonocunto et al., 2002). Diagenesis often leads to more negative  $\delta^{18}\text{O}$  values in marine carbonates (Land, 1970; Allan and Matthews, 1977), because cementation and recrystallization occur in fluids depleted in  $\delta^{18}\text{O}$  (e.g., meteoric water) compared with seawater, or at elevated temperatures (e.g., burial conditions).

The negative values of oxygen isotope reveal either introducing of

meteoric water during diagenesis or increasing of temperature; and the carbon fluctuations show the existence of organic matter or  $\text{CO}_2$  production by various organic reactions (Armstrong-Altrin et al., 2009). The modern marine carbonates generally have  $\delta^{13}\text{C}$  values between 0‰ and 4‰ (Moore, 2001). The variation in  $\delta^{13}\text{C}$  values are related to the degrees of carbonate alteration, and the source and amount of  $\text{CO}_2$  due to the oxidation of organic carbon appended to the pore waters during cementation and recrystallization (Marshall, 1992; Maliva and Dickson, 1997; Armstrong-Altrin et al., 2009).

The carbon isotopic ratios are considered to be more robust during diagenesis than oxygen isotopes; therefore they provide better constraints on the original composition of the near-surface water of the Tethys Ocean (Muttoni et al., 2014). The Upper Triassic marine carbonates are marked by positive  $\delta^{13}\text{C}$  values, for Russia from 0‰ to +3.5‰ (Zakharov et al., 2000); and for Greece from -0.8‰ to +3.2‰, for Italy from +0.2‰ to +3.5‰ and for Albania from +2.6‰ to +3.6‰ (Muttoni et al., 2014). Carbon isotope values for the Upper Triassic Baluti carbonates



range between  $-0.96\text{‰}$  and  $-5.34\text{‰}$  (Table 1). The negative data of the Baluti carbonates is not consistent with the coeval global positive values.

Because shallow marine deposits may have experienced periodic subaerial exposure during sea-level oscillations, it is important to address the possibility of post-depositional fresh water alterations which can generate negative  $\delta^{13}\text{C}$  values (Oehlert and Swart, 2014). Hudson (1977) proposed that during sea-level fall the sediments are exposed to fresh water emanating from low limestone island, although for most of the time remained in the phreatic zone and the new cement have a  $\delta^{13}\text{C}$  of  $-5\text{‰}$  and  $\delta^{18}\text{O}$  of  $-4\text{‰}$  reflecting its fresh water origin.

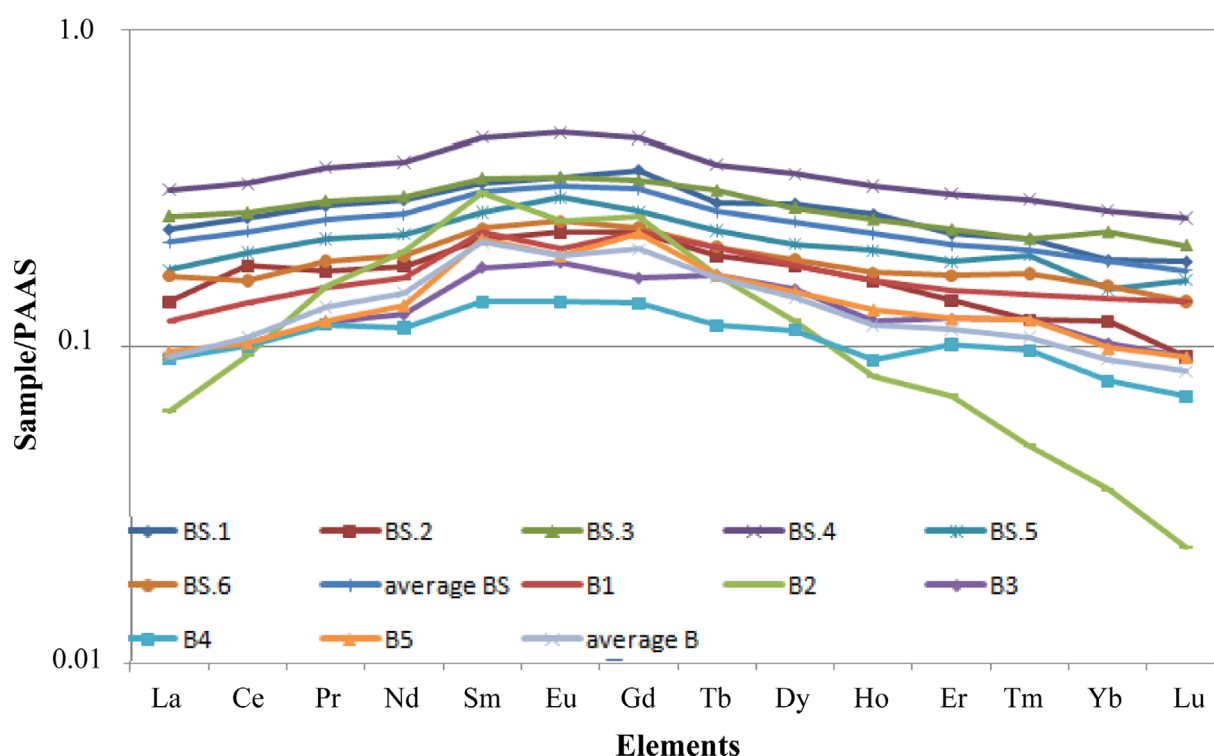
The results of current study are plotted in a  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  diagram (Hudson, 1977); the samples were plot in the fields of warm water skeletons and meteoric cement (Fig. 5) which reveals the alteration during diagenesis. The depleted  $\delta^{18}\text{O}$  values in the study carbonates are due to cementation under mainly burial and/or meteoric conditions rather than by direct precipitation of marine cements as in several tropical carbonates. The negative  $^{18}\text{O}$  values observed in the older carbonates are commonly attributed to post-depositional isotope exchange with meteoric waters (Keith and Weber, 1964).

### 5.3. Rare Earth Elemental Characteristics

The Eu/Eu\* ratio of the Baluti carbonate samples ranges from

0.991 to 1.108 (average = 1.034) for Sararu and from 0.865 to 1.076 (average = 0.928) for Sarki (Table 2). Generally, the slightly +ve Eu anomalies in REE patterns (particularly for Sararu) which are unusual in seawater probably resulted by the diagenetic changes in the carbonate rocks (Brand and Veizer, 1980; Abedini and Calagari, 2015; Singh et al., 2016) and increased by hydrothermal processes (German et al., 1999; Madhavaraju and Lee, 2009). The slightly -ve Eu anomalies in the Baluti carbonate (particularly for Sarki section) reveal that the terrigenous part of these samples was probably derived from felsic rocks, which are characterized by LREE enrichment and negative Eu anomaly (Armstrong-Altrin et al., 2003; Dai et al., 2016). This confirm with the source rocks of Baluti shales that suggested by Tobia and Mustafa (2016).

Several studies have been carried out on the application of Ce in the marine phases for determining paleoceanographic conditions (German and Elderfield, 1990; Nath et al., 1997). The deficit of Ce in oceanic water results from redox changes of Ce relative to other REEs (Elderfield, 1988). Ce/Ce\* ratios in Sararu ranges from 0.96 to 1.17, with an average = 0.99 (n = 6) while in Sarki ranges from 0.95 to 1.01, with an average = 0.96 (n = 5). The slightly negative Ce anomalies in the study carbonates (Table 2 and Fig. 6) are less than those of deep-sea carbonates of the Indian Ocean (Nath et al., 1992), sediments of Arabian Sea (Nath et al., 1997), and Maastrichtian shallow-marine carbonates of the Cauvery Basin, southern India (Madhavaraju and Ramasamy,



**Fig. 6.** Post-Archean Australian Shale (PAAS) normalized REE patterns for the Baluti carbonates (BS for Sararu and B for Sarki).

**Table 3.** Average values of the carbonate sediments of the Baluti Formation (this study) compared to the values of shallow and deep water marine carbonate sediments

Ratios & elements	Baluti Formation <sup>(a)</sup>		Shallow marine carbonate <sup>(b)</sup>	Arabian sea carbonate sediments <sup>(c)</sup>	Indian ocean carbonate Sediments <sup>(d)</sup>	Yellowish limestone <sup>(e)</sup>
	Sarki	Sararu				
REE (ppm)	44.26	22.30	73 ± 20	78 ± 40		25.55 ± 9.914
(La/Yb) <sub>n</sub>	1.16	1.14	1.82 ± 0.46	0.85 ± 0.2	0.166 ± 0.953	0.71 ± 0.15
(Nd/Yb) <sub>n</sub>	1.41	1.63	1.51 ± 0.30	0.85 ± 0.17	0.83 ± 0.13	0.42 ± 0.09
(Dy/Yb) <sub>n</sub>			1.25 ± 0.17	1.12 ± 0.11	1.37 ± 0.05	1.19 ± 0.11
Y/Ho	31.48	31.73		34.14 ± 1.64		31.11 ± 9.17
Er/Nd	0.067	0.064	0.07 ± 0.02	0.11 ± 0.02		0.2 ± 0.02
Eu/Eu*	1.034	0.928	0.58 ± 0.11	1.15 ± 0.08	> 1	1.88 ± 1.009
Ce/Ce*	0.994	0.964	0.76 ± 0.16	0.84 ± 0.06	0.56	0.57 ± 0.05
Gd/Gd*	1.112	1.114		1.09 ± 0.04		0.98 ± 0.20

<sup>(a)</sup>This study; <sup>(b)</sup>Madhavaraju and Ramasamy (1999); <sup>(c)</sup>Nath et al. (1997); <sup>(d)</sup>Nath et al. (1992); <sup>(e)</sup>Nagarajan et al. (2011).

1999; Table 3). Both Ce concentrations and anomalies can probably be explained by variations in terrigenous sediments in the Baluti carbonates in addition to the diagenesis processes. The absence of -ve Ce anomaly in Sararu (1.17; sample No. 2) is controlled by the lithological input and diagenesis that play an important role in incorporation of REE (especially Ce). Armstrong-Altrin et al. (2001) suggested that diagenetic process which might have a good role in eliminating a -ve Ce anomaly in the carbonate rocks.

The influence of LREE/HREE fractionation in marine environments can be described by the Er/Nd ratio (German and Elderfield, 1989). The elevated Er/Nd ratios of carbonates indicate the seawater signature preserved by the marine sediments. The ratio (Er/Nd) is about 0.27 in normal seawater (De Baar et al., 1988). Both detrital materials and diagenetic processes can lead to the discretionary concentration of Nd relative to Er and may reduce the Er/Nd values to < 0.1 (German and Elderfield, 1990; Bellanca et al., 1997; Abedini and Calagari, 2015). Er/Nd values for study carbonates range from 0.066 to 0.073 (average = 0.067) for Sararu and from 0.029 to 0.081 (average = 0.064) for Sarki which indicate the influence of detrital materials and diagenetic processes in the distribution of Er and Nd in the carbonates (Table 2).

The Gd/Gd\* ratios of the carbonate of the current study is confirm with the range of modern shallow seawater (1.05 to 1.30) as stated by De Baar et al. (1985) and Zhang and Nozaki (1998). The super chondritic Y/Ho ratios of the Baluti carbonates (Table 2) are less than the values of seawater (~44–74) as stated by Bau (1996), this is my be due to the diagenesis processes. The La/Yb values (Table 2) fall within the range postulated for terrigenous input (1.0–1.3) by Sholkovitz (1990) and Condie (1991).

Several studies have used the REE distribution in sediments to infer their tectonic setting (McLennan and Taylor, 1991; Verma and Armstrong-Altrin, 2013). These studies show that sediments deposited in the continental margins are characterized by LREE enrichment. These margins can be classified in to passive and

active types. Tobia and Mustafa (2016) suggest an active continental margin rather than passive tectonic environment for the shales of Baluti Formation based on the lower LREE and higher Eu/Eu\* ratio relative to the average of PAAS.

## 6. CONCLUSIONS

(1) The Baluti carbonates yielded significantly low  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values compared to other carbonates deposited under isotopic equilibrium with seawater. Therefore, the Baluti carbonates were likely influenced by meteoric diagenesis in an open diagenetic system near phreatic zone.

(2) The positive correlation between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  suggests that the isotopic compositions of the Baluti carbonates have been modified after deposition. The petrographic data also indicate extensive meteoric diagenetic effects under shallow burial conditions which is consistent with the obtained ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) stable isotope data.

(3) The  $\delta^{13}\text{C}$  data for the Upper Triassic Baluti Formation is not consistent with the global data represented by the Upper Triassic marine carbonates in the Tethyan Ocean which have marked positive  $\delta^{13}\text{C}$  values.

(4) The Ce anomaly and Er/Nd ratio indicate that the carbonates of Baluti Formation were influenced by the detrital materials and diagenetic processes.

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## REFERENCES

- Abedini, A. and Calagari, A.A., 2015, Rare earth element geochemistry of the Upper Permian limestone: the Kanigorgeh mining district, NW Iran. *Turkish Journal of Earth Sciences*, 24, 365–382.
- Ader, M., Macouin, M., Trindade, R.I.F., Hadrien, M.H., Yang, Z., Sun, Z., and Besse, J., 2009, A multilayered water column in the Ediacaran Yangtze platform: Insights from carbonate and organic matter paired  $\delta^{13}\text{C}$ . *Earth and Planetary Science Letters*, 288, 213–227.
- Ali, M.Y., 1995, Carbonate cement stratigraphy and timing of diagenesis in a Miocene mixed carbonate-clastic sequence, offshore Sabah, Malaysia: constraints from cathodoluminescence, geochemistry, and isotope studies. *Sedimentary Geology*, 99, 191–214.
- Allan, J.R. and Matthews, R.K., 1977, Carbon and oxygen isotopes as diagenetic and stratigraphic tools: data from surface and subsurface of Barbados, West Indies. *Geology*, 5, 16–20.
- Allan, J.R. and Matthews, R.K., 1982, Isotope signatures associated with early meteoric diagenesis. *Sedimentology*, 29, 797–817.
- Armstrong-Altrin, J.S., Lee, Y.I., Verma, S.P., and Worden, R.H., 2009, Carbon, oxygen, and strontium isotope geochemistry of carbonate rocks of the Upper Miocene Kudankulam Formation, Southern India: implications for paleoenvironment and diagenesis. *Chemie der Erde*, 69, 45–60.
- Armstrong-Altrin, J.S., Madhavaraju, J., Sial, A.N., Kasper-Zubillaga, J.J., Nagarajan, R., Flores-Castro, K., and Rodriguez, J.L., 2011, Petrography and stable isotope geochemistry of the Cretaceous El Abra Limestones (Actopan), Mexico: implication on diagenesis. *Journal of the Geological Society of India*, 77, 349–359.
- Armstrong-Altrin, J.S., Verma, S.P., Madhavaraju, J., Lee, Y.I., and Ramasamy, S., 2003, Geochemistry of Upper Miocene Kudankulam Limestones, southern India. *International Geology Review*, 45, 16–26.
- Armstrong-Altrin, S.J., Ramasamy, S., and Makhnach, A., 2001, Stable isotopes geochemistry and evidences for meteoric diagenesis in Kudankulam Formation, Tamil Nadu. *Journal of the Geological Society of India*, 57, 39–48.
- Avigad, D., Sandler, A., Kolodner, K., Stern, R.J., McWilliams, M., Miller, N., and Beyth, M., 2005, Mass-production of Cambro-Ordovician quartz-rich sandstone as a consequence of chemical weathering of Pan-African terranes: environmental implications. *Earth and Planetary Science Letters*, 240, 818–26.
- Bathurst, R.G., 1972, *Carbonate Sediments and Their Diagenesis: Developments in Sedimentology 12* (2<sup>nd</sup> edition). Elsevier, Amsterdam, 657 p.
- Bau, M., 1996, Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contributions to Mineralogy and Petrology*, 123, 323–333.
- Bau, M. and Dulski, P., 1996, Anthropogenic origin of positive gadolinium anomalies in river waters. *Earth and Planetary Science Letters*, 143, 245–255.
- Bellanca, A., Masetti, D., and Neri, R., 1997, Rare earth elements in limestone/marlstone couplets from the Albian–Cenomanian Cismon section (Venetian region, northern Italy): assessing REE sensitivity to environmental changes. *Chemical Geology*, 141, 141–152.
- Bellen, R.C., Dunnington, H.V., Wetzel, R., and Morton, D., 1959, *Lexique Stratigraphique Internal Asie, Iraq*. International Geological Congress, Fasc. 10a, Paris: International Commission on Stratigraphy (in French), 311 p.
- Brand, U. and Veizer, J., 1980, Chemical diagenesis of a multicomponent carbonate system-1: trace element. *Journal of Sedimentary Petrology*, 50, 1219–1236.
- Buday, T., 1980, *The Regional Geology of Iraq*, Stratigraphy and Paleontology. Dar Al-Kutb Publishing House, Mosul, 335 p.
- Budd, D.A. and Land, L.S., 1990, Geochemical imprint of meteoric diagenesis in Holocene ooid sands, Schooner Cays, Bahamas: correlation of calcite cement geochemistry with extant groundwaters. *Journal of Sedimentary Petrology*, 60, 361–378.
- Buonocunto, F.P., Sprovieri, M., Bellanca, A., D'Argenio, B., Ferreri, V., Neri, R., and Ferruzza, G., 2002, Cyclostratigraphy and high frequency carbon isotope fluctuations in Upper Cretaceous shallow-water carbonates, southern Italy. *Sedimentology*, 49, 1321–1337.
- Choquette, P.W. and Pray, L.C., 1970, Geologic nomenclature and classification of porosity in sedimentary carbonates. *American Association of Petroleum Geologists Bulletin*, 54, 207–250.
- Condie, K.C., 1991, Another look at rare earth elements in shales. *Geochimica et Cosmochimica Acta*, 55, 2527–2531.
- Coniglio, M., Myrow, P., and White, T., 2000, Stable carbon and oxygen isotope evidence of Cretaceous sea-level fluctuations recorded in septarian concretions from Pueblo, Colorado, USA. *Journal of Sedimentary Research*, 70, 700–714.
- Dai, S., Graham, I.T., and Ward, C.R., 2016, A review of anomalous rare earth elements and yttrium in coal. *International Journal of Coal Geology*, 159, 82–95.
- De Baar, H.J.W., 1991, On cerium anomalies in the Sargasso Sea. *Geochimica et Cosmochimica Acta*, 55, 2981–2983.
- De Baar, H.J.W., Bacon, M.P., and Brewer, P.G., 1985, Rare earth elements in the Pacific and Atlantic oceans. *Geochimica et Cosmochimica Acta*, 49, 1943–1959.
- De Baar, H.J.W., German, C.R., Elderfield, H., and Van Gaans, P., 1988, Rare earth element distributions in anoxic waters of the Cariaco Trench. *Geochimica et Cosmochimica Acta*, 52, 1203–1219.
- Dunham, R.J., 1962, Classification of carbonate rocks according to depositional texture. In: Ham, W.E. (ed.), *Classification of Carbonate Rocks*. American Association of Petroleum Geologists, Tulsa, p. 108–121.
- Elderfield, H., 1988, Tracer in the ocean – the oceanic chemistry of the rare-earth elements. *Philosophical Transactions of the Royal Society A*, 325, 105–126.
- Elderfield, H. and Pagett, R., 1986, Rare earth elements in ichthyoliths: variations with redox conditions and depositional environments. *Science of the Total Environment*, 49, 175–197.
- Fairchild, I.J., Marshall, J.D., and Bertrand-Sarfati, J., 1990, Stratigraphic shifts in carbon isotopes from Proterozoic stromatolitic carbonates (Mauritania): influences of primary mineralogy and diagenesis. *American Journal of Science*, 290, 46–79.
- Friedman, I. and O'Neil, J.R., 1977, *Compilation of stable isotope fractionation factors of geochemical interest*. U.S. Geological Survey, Professional Paper 440K, 12 p.
- Gao, G., Dworkin, S.I., Land, L.S., and Elmore, R.D., 1996, Geochemis-

- try of late Ordovician Viola limestone, Oklahoma: implications for marine carbonate mineralogy and isotopic compositions. *The Journal of Geology*, 104, 359–367.
- German, C.R. and Elderfield, H., 1989, Rare earth elements in Saanich Inlet, British Columbia, a seasonally anoxic basin. *Geochimica et Cosmochimica Acta*, 53, 2561–2571.
- German, C.R. and Elderfield, H., 1990, Application of the Ce anomaly as a paleoredox indicator: the ground rules. *Paleoceanography*, 5, 823–833.
- German, C.R., Hergt, J., Palmer, M.R., and Edmond, J.M., 1999, Geochemistry of a hydrothermal sediment core from the OBS vent-field, 21°N East Pacific Rise. *Chemical Geology*, 155, 65–75.
- Hanna, M.T., 2007, Palynology of the upper part of Baluti Formation (Upper Triassic) and the nature of its contact with the Sarki Formation (Lower Jurassic) at Amadiya district, Northern Iraq. Ph.D. Thesis, Mosul University, Mosul, 120 p.
- Hudson, J.D., 1977, Stable isotopes and limestone lithification. *Journal of the Geological Society*, 133, 637–660.
- Jacobsen, S.B. and Kaufman, A.J., 1999, The Sr, C and O isotopic evolution of Neoproterozoic seawater. *Chemical Geology*, 161, 37–57.
- Jassim, S.Z. and Goff, J.C., 2006, Phanerozoic development of the Northern Arabian Plate. In: Jassim, S.Z. and Goff, J.C. (eds.), *Geology of Iraq*. Dolin, Prague, p. 15–34.
- Jiang, L., Worden, R.H., and Cai, C.F., 2014, Thermochemical sulfate reduction and fluid evolution of the Lower Triassic Feixianguan Formation sour gas reservoirs, northeast Sichuan Basin, China. *American Association of Petroleum Geologists Bulletin*, 98, 947–973.
- Kato, Y., Nakao, K., and Isozaki, Y., 2002, Geochemistry of Late Permian Triassic pelagic cherts from southwest Japan: implications for an oceanic redox change. *Chemical Geology*, 182, 15–34.
- Keith, M.L. and Weber, J.N., 1964, Carbon and oxygen isotopic composition of selected limestones and fossils. *Geochimica et Cosmochimica Acta*, 28, 1787–1816.
- Kumar, B., Sharma, S.D., Sreenivas, B., Dayal, A.M., Rao, M.N., Dubey, N., and Chawla, B.R., 2002, Carbon, oxygen and strontium isotope geochemistry of Proterozoic carbonate rocks of the Vindhyan Basin, central India. *Precambrian Research*, 113, 43–63.
- Land, L.S., 1970, Phreatic versus vadose meteoric diagenesis of limestones: evidence from a fossil water table. *Sedimentology*, 14, 175–185.
- Land, L.S., 1986, Limestone diagenesis – some geochemical considerations. In: Mumpton, F.A. (ed.), *Studies in Diagenesis*. US Geological Survey Bulletin, 1578, p. 129–137.
- Latorre, C., Quade, J., and McIntosh, W.C., 1997, The expansion of C4 grasses and global change in the late Miocene: stable isotope evidence from the Ameritas. *Earth and Planetary Science Letters*, 146, 83–96.
- Leeder, M.R., 1982, *Sedimentology*. Chapman and Hall, London, 344 p.
- Logan, B.W. and Semeniuk, V., 1976, Dynamic metamorphism, process and products in Devonian carbonate rocks, Canning Basin, Western Australia. *Geological Society of Australia, Special Publication*, 6, 138 p.
- Madhavaraju, J., Gonzalez-Leon, C.M., Lee, Y.I., Armstrong-Altrin, J.S., and Reyes-Campero, L.M., 2010, Geochemistry of the Mural Formation (Aptian–Albian) of the Bisbee Group, Northern Sonora, Mexico. *Cretaceous Research*, 31, 400–414.
- Madhavaraju, J., Kolosov, I., Buhlak, D., Armstrong-Altrin, J.S., Ramasamy, S., and Mohan, S.P., 2004, Carbon and oxygen isotopic signatures in Albian–Danian limestones of Cauvery Basin, Southeastern India. *Gondwana Research*, 7, 519–529.
- Madhavaraju, J. and Lee, Y.I., 2009, Geochemistry of the Dalmiapuram Formation of the Uttatur Group (Early Cretaceous), Cauvery basin, southeastern India: implications on provenance and paleo-redox conditions. *Revista Mexicana de Ciencias Geológicas*, 26, 380–394.
- Madhavaraju, J. and Ramasamy, S., 1999, Rare earth elements in limestones of Kallankurich-chi Formation of Ariyalur Group, Tiruchirappalli Cretaceous, Tamil Nadu. *Journal of the Geological Society of India*, 54, 291–301.
- Maliva, R.G. and Dickson, J.A.D., 1997, Ulster white limestone formation (Upper Cretaceous) of Northern Ireland: effects of basalt loading on chalk diagenesis. *Sedimentology*, 44, 105–112.
- Marshall, J.D., 1992, Climatic and oceanographic isotopic signals from the carbonate rock record and their preservation. *Geological Magazine*, 129, 143–160.
- McLennan, S.M. and Taylor, S.R., 1991, Sedimentary rocks and crustal evolution: tectonic setting and secular trends. *Journal of Geology*, 99, 1–21.
- Moghazi, A.M., 2003, Geochemistry and petrogenesis of a high-K calc-alkaline Dokhan volcanic suite. South Safaga area, Egypt: the role of late Neoproterozoic crustal extension. *Precambrian Research*, 125, 116–178.
- Moore, C.H., 2001, Carbonate Reservoirs: Porosity Evolution and Diagenesis in a Sequence Stratigraphic Framework: Developments in Sedimentology. Elsevier, Amsterdam, 460 p.
- Morad, S. and Eshete, M., 1990, Petrology, chemistry and diagenesis of calcite concretions in Silurian shales from central Sweden. *Sedimentary Geology*, 66, 113–134.
- Murray, R.W., Buchholtz, M.R., Brink, M.R., Gerlach, D.C., Russ, G.P., and Jones, D.L., 1991, Rare earth, major and trace elements in chert from the Franciscan complex and Monterey group, California: assessing REE sources to fine grained marine sediments. *Geochimica et Cosmochimica Acta*, 55, 1875–1895.
- Muttoni, G., Mazza, M., Mosher, D., Katza, M.E., Kent, D.V., and Balini, M., 2014, A Middle–Late Triassic (Ladinian–Rhaetian) carbon and oxygen isotope record from the tethyan Ocean. *Palaogeography, Palaeoclimatology, Palaeoecology*, 399, 246–259.
- Nagarajan, R., Sial, A.N., Armstrong-Altrin, J.S., Madhavaraju, J., and Nagendra, R., 2008, Carbon and oxygen isotope geochemistry of Neoproterozoic limestones of the Shahabad Formation, Bhima basin, Karnataka, southern India. *Revista Mexicana de Ciencias Geológicas*, 25, 225–235.
- Nagarajan, R., Madhavaraju, J., Armstrong-Altrin, J.S., and Nagendra, R., 2011, Geochemistry of Neoproterozoic limestones of the Shahabad Formation, Bhima Basin, Karnataka, southern India. *Geosciences Journal*, 15, 9–25.
- Nath, B.N., Bau, M., Ramalingeswara Rao, B., and Rao, C.M., 1997, Trace and rare earth elemental variation in Arabian Sea sediments through a transect across the oxygen minimum zone. *Geochimica et Cosmochimica Acta*, 61, 2375–2388.
- Nath, B.N., Roelandts, I., Sudhakar, M., and Plueger, W.L., 1992, Rare

- earth element patterns of the Central Indian Basin sediments related to their lithology. *Geophysical Research Letters*, 19, 1197–1200.
- Nelson, C.S. and Smith, A.M., 1996, Stable oxygen and carbon isotope fields for skeletal and diagenetic components in New Zealand Cenozoic non tropical carbonate sediments and limestones: a synthesis and review. *New Zealand Journal of Geology and Geophysics*, 39, 93–107.
- Nothdurft, L.D., Webb, G.E., and Kamber, B.S., 2004, Rare earth element geochemistry of Late Devonian reefal carbonates, Canning Basin, western Australia: confirmation of a seawater proxy in ancient limestones. *Geochimica et Cosmochimica Acta*, 68, 263–283.
- Oehlert, A.M. and Swart, P.K., 2014, Interpretation carbonate and organic carbon isotope covariance in the sedimentary record. *Nature communications*. DOI: 10.1038/ncomms5672
- Piper, D.Z., 1974, Rare earth elements in the sedimentary cycle, a summary. *Chemical Geology*, 14, 285–304.
- Poulson, S.R. and John, B.E., 2003, Stable isotope and trace element geochemistry of the basal Bouse Formation carbonate, southwestern United States: implications for the Pliocene uplift history of the Colorado plateau. *Geological Society of American Bulletin*, 115, 434–444.
- Rahimpour-Bonab, H. and Bone, Y., 2001, Isotopic signature of the diagenetic fluids and cement in the Tortachilla limestone, South Australia. *Iranian International Journal of Science*, 2, 33–54.
- Santos, R.V., Souza, De Alvarenga, C.J., Babinski, M., Ramos, M.L.S., Cukrov, N., Fonseca, M.A., Sial, A.N., Dardenne, M.A., and Noce, C.M., 2004, Carbon isotopes of Mesoproterozoic–Neoproterozoic sequences from Southern São Francisco craton and Araçuaí Belt, Brazil: paleographic implications. *Journal of South America Earth Sciences*, 18, 27–39.
- Scott, R.W., 2002, Albian caprinid rudists from Texas re-evaluated. *Journal of Paleontology*, 76, 408–423.
- Sharland, P.R., Archer, R., Casey, D.M., Davies, R.B., Hall, S.H., Heward, A.P., Horbury, A.D., and Simmons, M.D., 2001, Arabian plate sequence stratigraphy. *GeoArabia Special Publication 2*, Gulf PetroLink, Bahrain, 371 p.
- Shields, G.A., 1999, Working towards a new stratigraphic calibration scheme for the Neoproterozoic–Cambrian. *Eclogae Geologicae Helvetiae*, 92, 221–233.
- Sholkovitz, E.R., 1990, Rare earth elements in marine sediments and geochemical standards. *Chemical Geology*, 88, 333–347.
- Singh, A.K., Tewari, V.C., Sial, A.N., Khanna, P.P., and Singh, N.I., 2016, Rare earth elements and stable isotope geochemistry of carbonates from the mélange zone of Manipur ophiolitic complex, Indo-Myanmar Orogenic Belt, Northeast India. *Carbonates and Evaporites*, 31, 139–151.
- Sissakian, V.K., 2000, Geological map of Iraq (1:1000000) sheet no.1 (3<sup>rd</sup> edition). GEOSURV, Baghdad.
- Srivastava, P., 2001, Paleoclimatic implications of pedogenic carbonates in Holocene soils of the Gangetic Plains, India. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 172, 207–222.
- Stern, R.J., 1994, Arc assembly and continental collision in the Neoproterozoic East African Orogen: implications for consolidation of Gondwanaland. *Annual Reviews of Earth Planetary Sciences*, 22, 319–51.
- Taylor, S.R. and McLennan, S.H., 1985, The geochemical evolution of the continental crust. *Reviews of Geophysics*, 33, 241–265.
- Tobia, F.H. and Mustafa, B.H., 2016, Geochemistry and mineralogy of the Al-rich shale from Baluti Formation, Iraqi Kurdistan region: implications for weathering and provenance. *Arabian Journal of Geosciences*, 9, 757.
- Veizer, J. and Demovič, R., 1973, Environmental and climatic controlled fractionation of elements in the Mesozoic carbonate sequence of the Western Carpathians. *Journal of Sedimentary Petrology*, 43, 258–271.
- Verma, S.P. and Armstrong-Altrin, J.S., 2013, New multi-dimensional diagrams for tectonic discrimination of siliclastic sediments and their application to Precambrian basins. *Chemical Geology*, 355, 117–133.
- Wright, V.P., 1990, Equatorial aridity and climatic oscillations during the Carboniferous, Southern Britain. *Journal of the Geological Society*, 147, 359–363.
- Yoshioka, H., Asahara, Y., Tojo, B., and Kawakami, S., 2003, Systematic variations in C, O, and Sr isotopes and elemental concentrations in Neoproterozoic carbonates in Namibia: implications for a glacial to interglacial transition. *Precambrian Research*, 124, 69–85.
- Zakharov, Y.D., Ukhaneva, N.G., Ignatyev, A.V., Afanasyeva, T.B., Bur Yi, G.I., Panasenko, E.S., Popov, A.M., Puniua, T.A., and Cherbadzhi, A.K., 2000, Latest Permian and Triassic carbonates of Russia: new palaeontological finding, stable isotopes, Ca-Mg ratio, and correlation. In: Yin, H., Dickins, J.M., Shi, G.K., and Tong, J. (eds.), *Persian–Triassic Evolution of Tethys and Western Circum Pacific*. Elsevier Science B.V., p. 141–171.
- Zhang, J. and Nozaki, Y., 1998, Behavior of rare earth elements in seawater at the ocean margin: a study along the slopes of the Sagami and Nankai troughs near Japan. *Geochimica et Cosmochimica Acta*, 62, 1307–1317.
- Zhao, Y.Y., Zheng, Y.F., and Chen, F., 2009, Trace element and strontium isotope constraints on sedimentary environment of Ediacaran carbonates in Southern Anhui, South China. *Chemical Geology*, 265, 345–362.