Review Article

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Geochemistry and diagenetic evidence of middle-late Permian deposits, Northern Iran

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Abstract

This study provides a evaluation of the initial carbonate mineralogy, and diagenetic condition of the Ruteh Formation, a middle-late Permian carbonate sequence, in the Emarat section in Central Alborz, northern Iran. 200 samples were examined for petrographical contents and thirty-four samples were collected for geochemical analysis. The high Sr and Na contents, Sr/Na>1, and the presence of dolomites and dissolution fractures are indicative aragonite early mineralogy. The diagenetic process in the Ruteh Fm. are an indication of the marine, meteoric and burial diagenetic environments. The original carbonate texture in the Ruteh Fm. are Severely affected by diagenetic process. The data obtained from the values of the Major (Ca and Mg), minor (Sr, Na, Fe, and Mn), oxygen and carbone isotopes show the initial aragonite composition of the Ruteh Fm. deposited in a subtropical shallow water. An open diagenetic system was indicated by changes in the values of Sr / Ca and δ18O vs. Mn. The shallow burial diagenetic temperature of the Ruteh carbonate was approximate 28.6°C with the maximum diagenetic temperature of 53.4°C.

Keywords: *Alborz, Permian, Ruteh Formation, Geochemistry, Diagenesis.*

1. Introduction

The 2,000 km long Alborz Basin in northern Iran is a polyorogenic folded belt (Fig.1a), extending eastward from the Lesser Caucasus to the Paropamamisus Mountains in northern Afghanistan (Alavi 1996). Devonian to Middle Triassic succession in the Alborz, often limestone and basaltic lava, have characteristics of a continental shelf succession to belive have formed on the passive margin of Paleotethys divergent margin (Stampfli et al. 1991). Alborz Basin belongs to the southern margin of the Cimmerian continent (Sengor 1984), which separated from Gandiana in the late Permian (Fig 1b, and characterized by by sedimentary resources, such natural gas, phosphate, lead, and bauxite deposits. The Permian deposits in Alborz Basin are divided into Lower (Asselian-Sakmarian), Middle (Kubergandian- Midian) and Upper (Djulfian-Darshamian). The Lower Permian is mainly made up of two terrigenous units separated by a- mostly carbonate lithesome in the middle. It was introduced as Dorud Formation by Assereto (1963). Later, Jenny and Stampfli (1978)

Introduced Dorud Group which spans the uppermost Carboniferous to the lowest Permian deposits. Assereto (1963) named the middle Permian deposits as the Ruteh Limestone. The upper Permian limestone of Alborz Zone was named Nessen Glaus introduced Formation by Glaus (1964). The Ruteh Fm. is the most important and widespread representive of the Permian system in Iran (Stöcklin 1971).

Although biostratigraphic studies have been carried out for many decades on the Permian sections, no geochemical analyses have been conducted in the Ruteh Fm. in northern Alborz. Therefore, the main objective of this research is geochemical analysis emphasizing the original carbonate mineralogy and find out the paleotemperature at the Emarat section in the northern Alborz.

2. Geological Setting

The geographic coordinates of the study section are 52° 21' 42" longitude and 36° 11' 15" latitude. It is located in the center of Emarat anticline, 30 km south of Amol City, Mazandaran Province, Alborz Basin, Northern Iran (Fig. 1c). Emarat structure is a dom shaped anticline, with11km in length and 8km in width. The Dorud Formation is outcroping on the central portion of the structurre (Fig.1d). It consists of thin-bedded micritic limestone, chertic and dolomitic limestone. The Ruteh Fm. is 642 m thick in the Emarat anticline, and conains thiny bedded limestone, cherty and dolomitic limestone. Its lower and upper boundaries are disconformable with Dorud and Nessan formations, respectively. The Ruteh Fm. is the most important and widespread representative of the Permian System in the Alborz Basin. The base of the Ruteh Fm. is correlated to the major 'break Up unconformity' associated with the spreading of the Iran from the Arabian Plate (Şengor 1984). The Ruteh Fm. is believed to the correlate with Dallan Formation, Jamal Formation, and Surmaq Formation in Zagros, Central Iran, and Abadeh regions, respectively (Fig 2). At the end of the Ruteh Formation, there is a major global regression

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known as the “Dongwu Movement” that is caused by a widespread paraconformity marked by bauxite deposits in the basal part of the Lopingian in Iran. The Ruteh Fm. ranges is early Guadalpian to early Lopingian in age. The Guadalupian Epoch also represented a brief changes from an icehouse to a greenhouse condition (Chen et al. 2013).

3. Material and methods

Field observations were complemented with the petrographic examination of 200 surface samples for phases of limestone. The compositional and textural features of the concretions, as well as the microscopic aspects of the Ruteh carbonate, were investigated by petrographic analysis with a polarizing microscope.

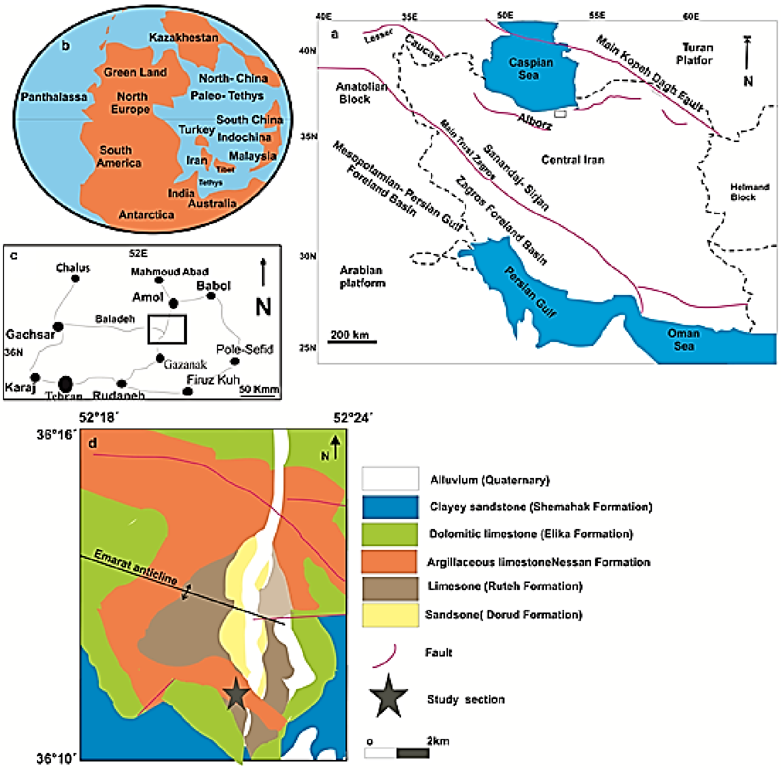


Fig 1. a) Palaeogeographic reconstruction during the Late Permian (after Scotese 2002); b) Location of Alborz in Iran; c) geographical locations of the study section; d) Geological map of the Emarat anticline

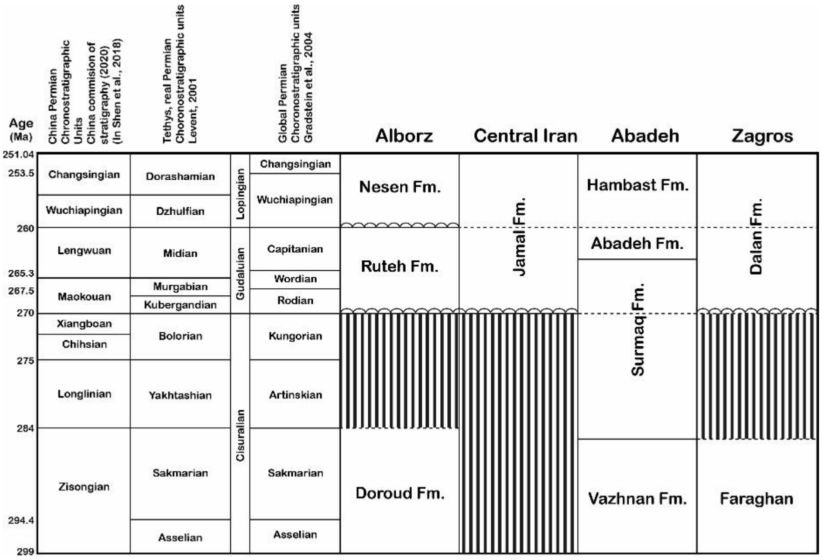


Fig 2. Permian lithostratigraphic units of Iran (Aghanabati, 2012).

The textural classification follows the classifications of Dunham (Dunham 1962). The thirty-four of powdered samples were analyzed by Atomic Absorption Spectrometer at the Kansaran Binalood Company, Iran. Sampling was taken from non weathered surfaces by microdrill. Data accuracy were ±0.5% for Ca and Mg and ±5 ppm for Sr, Na, Mn, and Fe (Scholle and Ulmer-Scholle 2006).

The oxygen and carbon isotopes were analyzed by 15 samples at the Central Science Laboratory, University of Ottawa, Canada. Fifteen mg of the powdered samples were allowed to react with anhydrous phosphoric acid in reaction tubes under vacuum at 25°C for 24h. The CO_2 extracted from each sample was analyzed for $\delta^{18}O$ and and $\delta^{13}C$ by Mass Spectrometry. The precision of data was ±0.001‰ for both $\delta^{18}O$ and $\delta^{13}C$ and these values were reported relative to PDB and in standard δ -notation.

4. Results and discussion

The microscopic analysis showed that the diagenetic processes in the Ruteh carbonates were bioturbation, micritization, compaction, replacement, cementation, dissolution, and dolomitization (Fig 3).

4.1. Cementation

The Ruteh Fm. contains marine to meteoric and burial cement (Figures. 3a to d). Fibrous and bladed cement occurs as isopachous fringe and it makes the first generation of cement around allochems in inner ramp environment. This cement can also be seen in intraparticle porosities. Syntaxial cement was observed beside echinoid spines. Equant, drusy, and blocky cement were also founded in other layers.

4.2. Dissolution

Vuggy porosity was very common in the Ruteh Fm. (Fig 3f). Most of them were filled by later- stage calcite cement. Bioclast molds of bivalve and gastropod, fracture or vein filling cement are present in these carbonates. Shallow carbonates are affected by meteoric diagenesis for two reasons: 1) the aggregation of carbonate above sea level; 2) exposes platform carbonates during falling in sea level (Scholle and Ulmer-Scholle 2006). Aragonite and magnesian calcites are stable phases in the marine environment, but they are very unstable in other environments. In freshwater lakes, vadose or phreatic zones, Low-Mg calcite is the stable phase. The dissolution of metastable phases may often occure as selective, and originally aragonitic parts of shells may be dissolved, while magnesian calcites may remain intact.

4.3. Compaction

Petrographic studies analyses express that the Ruteh limestones often before dolomitization have been affected by compaction (Fig 3g). The compaction (extensive chemical compaction) caused the development of solution seams and stylolites, which pass initial crystals, but no latter crystals are seen on them. Most of the develop at the surface of the layers and between the facies. Therefore, Therefore, the amount of clay and energy of the environment has a strong impact in the amount of compaction.

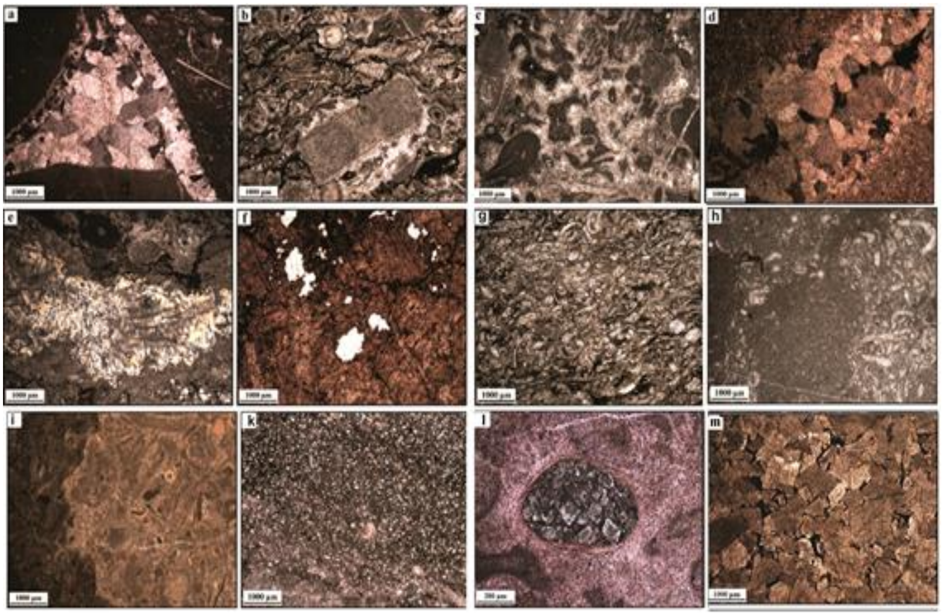


Fig 3. Diagenetic operation that affected Permian carbonates of the Emarat section. a) Drusy cement, sample 21, plane polarized light; b) Synthaxial overgrowth cement, sample 25, plane polarized light; c) Equant cement, sample 32, plane polarized light; d) Blocky cement, sample 7, plane polarized light; e) Silicification, sample 84, plane polarized light; f) Vuggy porosity, sample 33, crossed polarized light; g) Compaction, sample 134, crossed polarized light; h) Bioturbation, sample 21, crossed polarized light; i) Micritization, sample 1, crossed polarized light; k) Type 1 fine crystalline dolomite (dolomicrosparite), sample 56, crossed polarized light; l) Type 2 medium crystalline dolomite (dolosparite), sample 188, crossed polarized light; m) Type 3 coarse crystalline planar-c (cement) dolomite, sample 92, crossed polarized light.

4.4. Replacementation (Silicification)

Replacementation is different in both crystal size and mineralogy (for example silica cement). In the grain supported texture of the Doroud Formation, silicification process is observed among small cavities (Fig. 4e) which is more common in the upper and lower parts of the Ruteh Formation. It is likely that the silica required for the silicification process in this formation could have been due to the supply and availability of silica forming fluid from neighboring formations. The dissolution / precipitation process, such as silicification, are effected by mineralogy and s ultrastructure of shells, the content of organic matter, and the character and matrix (Butts 2014).

4.5. Micritization

In micritization, skeletal and non-skeletal components of the rock are crushed to micrite so that the walls of grains or fossils are not recognizable (Perkins and Halsey,1971; Alexanderson 1972; Bathurst 1974; Kobluk and Risk 1977). In the present study, two important factors of micritization were identified: partial micritization (Fig 3i); 2), and the complete micritization. Algae and fingi are are the most important cause of micritization (Perkins and Halsey 1971, Flügel 2010).

4.6. Bioturbation

Bioturbation means the mixing and disruption of sediment by organisms (Fig 3h). This process occurs in loose sediments and is extremely abundant in deep marine environments with high organism density and low sedimentation rate (Flügel 2010). Important creatures are worms that live and feed in sediments, eat sludge, and disperse sediments with homogeneous texture, but digestive organisms, such as crustaceans, cause large mixing of sediments and loss of primary sedimentary texture. Most of the cavities and disruption are filled by these organisms or sediments themselves (Scholle and Ulmer-Scholle 2003). The frequency and type of this process depend on the sedimentation rate, the nature of the seafloor sediments, the oxygen content, the pore water, and the abundance of nutrients (Flügel 2010). Belley et a.l (2008) reported that Changes in environmental conditions as decrease the amount of dissolved oxygen and increase nutrients have negative influcence on biological activity and diversity.

4.7. Dolomitization

Tidal flat facie in the Emarat section has most selective dolomitization (Figs 3 k, l and m). Dolomitization is higher in aragonites than in calcite (Sibley and Gregg. 1987; Gaines 1980). Sibley and Gregg (1987) recognized three different types of dolomite fabrics. The most important factors in their classification are: the shape of crystal boundaries, and sorting, and degree of preservation of precursor fabrics (mimic or non-mimic). Three dolomites are observed in study section are as follows:

4.7.1. Dolomicrosparite (Fine Crystalline Dolomite)

Dolomicrosparite contains of unimodal subhedral to anhedral crystals at lower precipitation temperatures. The most important type of porosity in these dolomite are Vuggy and channel. This type of dolomite is the result of a replacement process in calcite crystals at temperatures below 60° C (Gregg and Shelton 1990; Adabi 2009).

4.7.2. Dolosparite (Medium Crystalline Dolomite)

This dolomite consists of anhedral and euhedral polymodal mosaics of medium (70–250 µm). An increase in the degree of alteration caused a change in the fabric of dolomites from dolomicro sparite to dolosparite. They often have have cloudy cores and clear rims (Sibley 1982; Kyser et al. 2002).

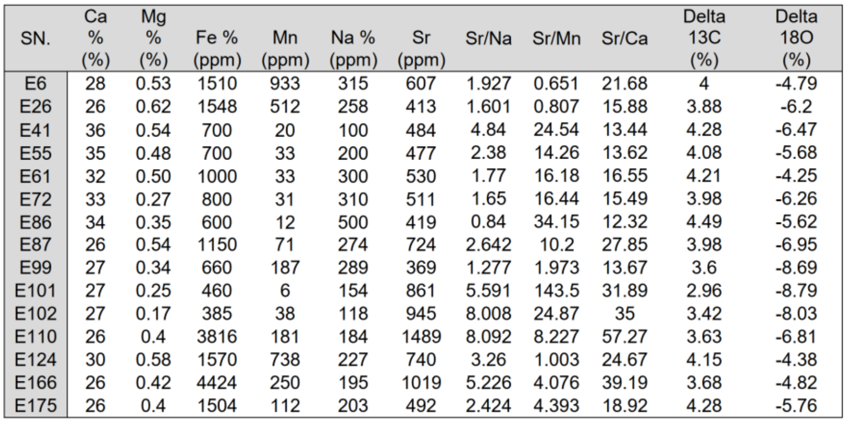
4.7.3. Coarse Crystalline Dolomite

Coarse crystalline dolomite has polymodal euhedral dolomite, with lining voids, vugs, and fractures. The crystal sizes, depending upon the size of the void in which it was precipitated, ranging from 100 to 500 µm. Since they are found in moldic and vuggy porosities; it can be concluded that they are a production a deep burial environment of late- stage diagenesis.

5. Geochemistry

Elemental evidence was used to compare carbonate mineralogy of the Ruteh Fm. with new tropical shallow-marine aragonite (Milliman 1974). The results indicate original aragonite mineralogy and close to open diagenetic systems for Mid-Late Permian carbonates of the Ruteh Fm. (Table 1).

Table 1. Variation of major and minor elements, δ18O and δ13C values, ratios and average quantity of studied samples in the Ruteh Formation.



SN.	Ca % (%)	Mg % (%)	Fe % (ppm)	Mn (ppm)	Na % (ppm)	Sr (ppm)	Sr/Na	Sr/Mn	Sr/Ca	Delta 13C (%)	Delta 18O (%)
E6	28	0.53	1510	933	315	607	1.927	0.651	21.68	4	-4.79
E26	26	0.62	1548	512	258	413	1.601	0.807	15.88	3.88	-6.2
E41	36	0.54	700	20	100	484	4.84	24.54	13.44	4.28	-6.47
E55	35	0.48	700	33	200	477	2.38	14.26	13.62	4.08	-5.68
E61	32	0.50	1000	33	300	530	1.77	16.18	16.55	4.21	-4.25
E72	33	0.27	800	31	310	511	1.65	16.44	15.49	3.98	-6.26
E86	34	0.35	600	12	500	419	0.84	34.15	12.32	4.49	-5.62
E87	26	0.54	1150	71	274	724	2.642	10.2	27.85	3.98	-6.95
E99	27	0.34	660	187	289	369	1.277	1.973	13.67	3.6	-8.69
E101	27	0.25	460	6	154	861	5.591	143.5	31.89	2.96	-8.79
E102	27	0.17	385	38	118	945	8.008	24.87	35	3.42	-8.03
E110	26	0.4	3816	181	184	1489	8.092	8.227	57.27	3.63	-6.81
E124	30	0.58	1570	738	227	740	3.26	1.003	24.67	4.15	-4.38
E166	26	0.42	4424	250	195	1019	5.226	4.076	39.19	3.68	-4.82
E175	26	0.4	1504	112	203	492	2.424	4.393	18.92	4.28	-5.76

Based on the geochemical analysis, the mean values of Sr, Na, Mn, and Fe contents in the 15 sample were 672 ppm, 242 ppm, 210.5 ppm, and 1388 ppm, respectively. Kaufman et al. (1993) used Mn/Sr ratio<2~3 as criterion for selecting carbonate samples in which the isotopic values are considered to be proxy for those of seawater. Variation of Sr/Mn versus Mn also supports the conclusions that Ruteh the carbonate effected by close to open diagenesis system (Fig 4a). The low Sr/Mn shows higher alteration and more meteoric diagenetic effects with higher water/rock interaction. The condensation of Sr in new tropical carbonate sediments ranges from 8000 to 10000 ppm, whereas in new temperate carbonates range from 1642 to 5007 ppm. The Sr content varies mainly due to carbonate mineralogy. The contents of Sr increase with increasing of aragonite content and decreases with water depth. Abiotic calcite has a maximum of about 1000 ppm Sr. The concentration of Sr in Permian limestone samples ranges from 419 to 1489 ppm (Table 1). The average value of Sr is about 672 ppm. High Sr values of these samples support aragonite mineralogy.

The diagenetic process in limestones is a wet dissolution and redeposition (Bathurst 1974). After aragonite and high-Mg calcite were dissolved and converted to stable low-Mg calcite, the Sr values are reduced and the Mn value is increased. The lower Sr values of the micritic samples in comparison with newtropical carbonate sediments show diagenetic alteration, due to the replacement of aragonite by calcite (Al-Aasm and Packard 2000). The Sr versus Mn values shows that most samples fall within aragonite field of Mozduran with the orginal aragonite mineralogy (Fig 4b). The concentration of Mn in the Permian limestone samples changes from 6 to 933 ppm. The average value of Mn is 210.5 ppm (Table 1). The Sr–Mn changes indicates that the samples are close to the aragonite fields of Mozduran and Gordon limestone. The Mn and Fe condensationsdensations are <20 ppm in modern warm-water aragonite (Morse and Mackenzie 1990). The high value of Mn and Fe in the samples reveals the effect of meteoric diagenesis (Morse and Mackenzie 1990).

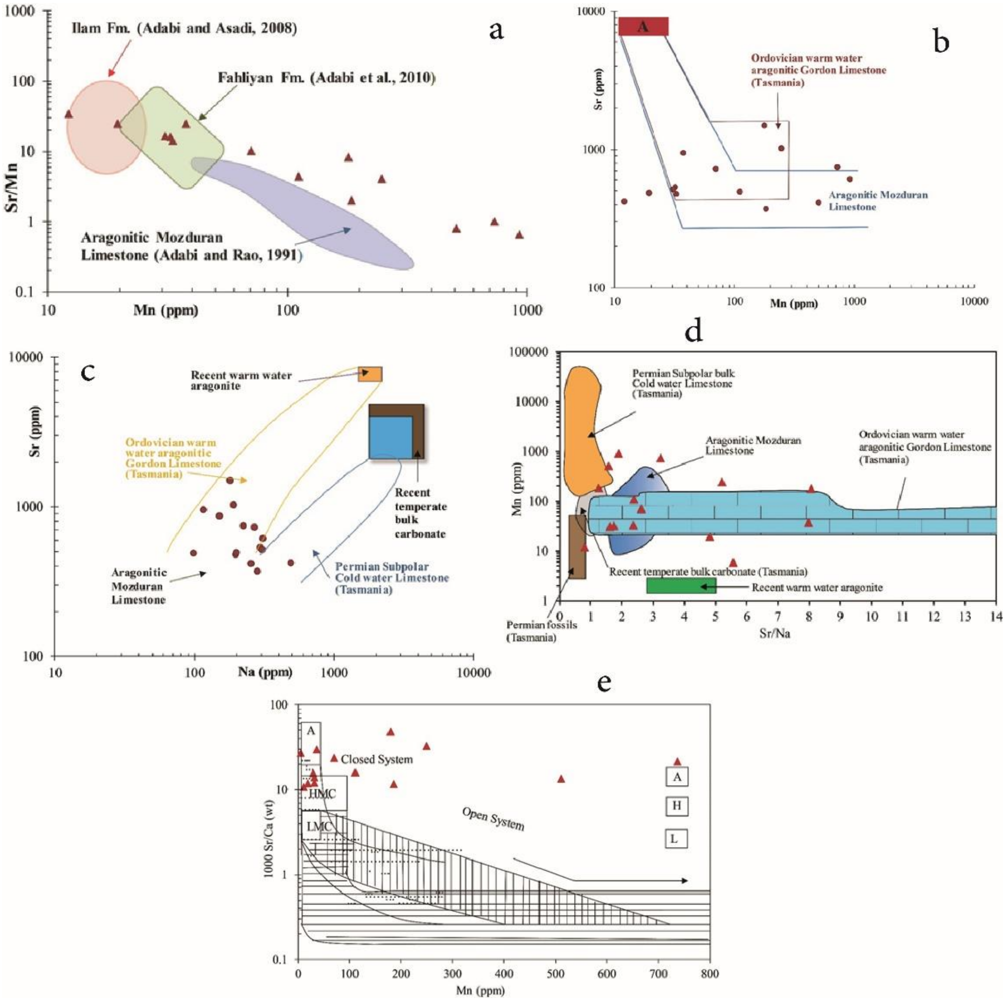


Fig 4. a) Mn and Sr/Mn fluctuations in the Ruteh FM.; b) Sr and Mn fluctuation in Ruteh lFm.; c) Sr and Mn fluctuation in Ruteh Fm. Note to similar mineralogy between the Ruteh carbonate and Mozduran carbonate; d) Sr and Na fluctuation in the Ruteh Fm.; e) Mn, and Sr/Na fluctuation in the Ruteh Fm.

Variation of Sr/Mn versus Mn also support conclusion that the Ruteh carbonate is also effected by close to open diagenesis system. The low Sr/Mn indicate higher alteration and more meteoric diagenetic effects with higher water/rock interaction (Bathurst 1975).

The condensation of Na in new tropical abiotic aragonite varies from 1500 to 2700 ppm (average 2500 ppm; which related to salinity, biological fractionation, kinetics, mineralogy and water depth. The quantity of Na in Permian limestone samples range from 100 to 500 ppm. The mean amount of Na is about 242 ppm. The high Na condensation can be related to high salinity. Due to diagenetic alteration, the Na contents are lower than those of new warm water carbonate. The plot of Sr–Na amount (Fig 4c) indicates that most samples are close to the warm-water sub-tropical aragonite fields of Ordovician Gordon Limestone (Tasmania). The samples fall in the aragonite field of the Mozduran Formation (Fig 4d).Sr/Na ratio and Mn contents are the most difference between new and ancient tropical carbonates with their non-tropical carbonate (Winefield et al. 1996). The new tropical aragonitic sediments have low Mn from 3 to ~5 (mean 4). In contrast, new temperate carbonates have high Mn and low Sr/Na ratios<1 to ~1 (Rao 1996).

In the Permian Formation of the Emarat section, Sr/Na ratio ranges from 0.84 to 8.09. The average Sr/Na ratio is 3.45. This amount is within the range of new warm-water aragonitic carbonates (Milliman 1974) and Ordovician warm water aragonitic Gordon Limestone (Tasmania) Changes in Sr / Na versus Mn indicate that most limestone samples are located in or near the subtropical aragonite. The diagram of Sr/Ca ver. Mn indicates that limestones should have been stabilized by fluids in the close diagenetic system (Brand and Veizer 1980). The variability of Sr / Ca vs. Mn shows that samples of Ruteh Fm. with meteoric diagenesis in a near-open system are affected by low to high water / rock interactions (Fig 4e).

6. Oxygen and Carbon Isotopes

The $\delta^{18}O$ quantity in the Ruteh Fm. range from -8.79 to -4.25‰ PDB (Average -6.2‰ PDB), whereas $\delta^{13}C$ values range from 2.96 to 4.49‰ PDB (Average 3.9 ‰ PDB). Most samples fall has a similar age. Bivariate diagram of trace elements ver. oxygen isotope values were employed to clear the initial mineralogy and diagenetic environment. Sr ver. $\delta^{18}O$ (Fig 5a) and $\delta^{13}C$ (Fig 5b) variations show that most samples fall within or close to open to the warm-water sub-tropical aragonite field of the Mozduran Formation.

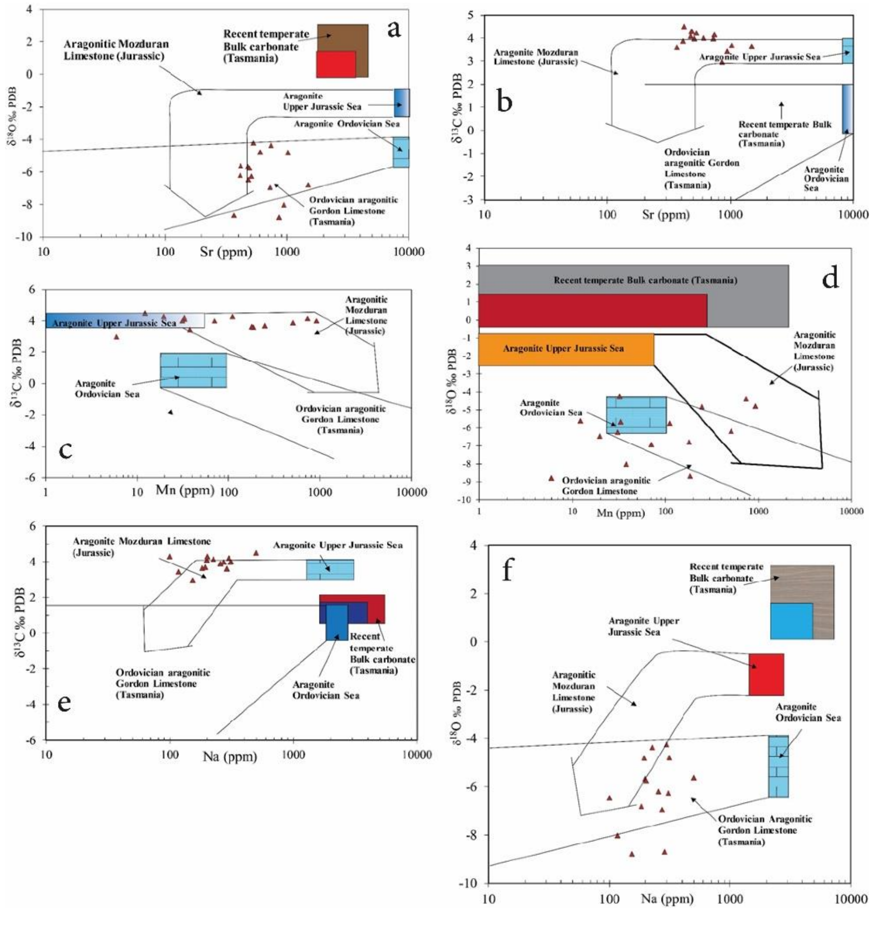


Fig 5. a) Sr and $\delta^{18}O$ changes in the Ruteh Fm.; b) Sr and $\delta^{18}C$ changes in the Ruteh Fm.; c) collation of $\delta^{18}O$ and $\delta^{13}C$ quantity of he Ruteh carbonates with altered aragonite bulk carbonate Mozduran Fm. of upper Jurassic (Iran) (Adabi and Rao 1991), Gordon limestone Late Orvovician (Tasmania) (Adabi and Rao 1991) and aragonite bulk carbonate recent tropical (Rao 1991); d) Mn and $\delta^{18}C$ variations in the Ruteh Fm. ; e) Mn and $\delta^{18}O$ variations in the Ruteh Fm.; f) Na and $\delta^{18}C$ variations in the Ruteh Formation.

The carbon and oxygen isotopes data for the section are illustrated in Fig 5c. Trace elements ver, oxygen and carbon isotop confirm the original carbonate mineralogy (aragonite) (Figs 5d, e and f). Paleotemperature calculation, based on the heaviest δ^{18}O (-4.25 ‰ PDB) value in the micritic samples of the Permian, where δ18O for Permian seawater is -2.8 ‰ SMOW, and the formula of Anderson and Arthur (1982), T°C = 16.4-14* (δc - δw) + 0.13* (δc - δw)2, show that shallow burial temperature should have been around 28.6°C during deposition of the Permian Formation deposits. Where T, δc, and δw are temperature (in°C), the isotopic ratio of CO2 orginated from the carbonate, the isotopic ratio of CO2 in equilibrium with formation water, respectively. This temperature shows an initial aragonite mineralogy, such as the present deposits of the Persian Gulf, of the Emarat anticline which deposited in a shallow-marine sub-tropical environment. This commentary is supported by the trace element and petrographic evidence. Accordingly, the Permian deposits in the Emarat anticline was deposited in shallower parts of the basin in the central Alborz area. However, it is important that very small value of the altered carbonate can cause significant errors in determining the temperature of diagenesis. The lightest oxygen isotope of -8.79 is used to determine the maximum diagenetic temperature. The maximum diagenetic temperature for the limestone in region is 53.4°C.

7. Conclusions

The Ruteh Fm. is an indicator of a shallow warm-water deposits of the mid-late Permian, overlaid by the Dorud sandstone and is covered by the Nesen Formation. The main diagenetic processes were cementation, dissolution, and dolomitization that changed the original texture of the carbonates.

Three different types of dolomite have been generated from dolomitization in several stages, dolomicrospaite, dolosparit and coars crystalline plannar-C (cement) dolomite. Geochemical petrographic studies indicate an open metoric diagenetic system with high water/rock interaction and also that aragonite was the initial mineralogy in the Ruteh deposits. The δ^{18}O content shows that the diagenetic temperature was about 28.6°C during Ruteh sedimentation. The maximum diagenetic temperature based on the lightest δ^{18}O values of limestone was 53.4°C.

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