

RELATIONSHIPS BETWEEN SEDIMENTARY ENVIRONMENT VIA GEOCHEMISTRY AND MINERALOGY IN SARVAK FORMATION, ZAGROS OIL FIELDS, SW OF IRAN

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Abstract

The Sarvak Formation was deposited in the Zagros foreland basin and which was formed during the Albian to Cenomanian. This formation is a part of the Bangestan group comprising of a thick series of carbonate rocks and is one of the main hydrocarbon reservoirs in the south-west of Iran. The subsurface sedimentary sequence of the Sarvak Formation has been studied using cores taken from Gachsaran, Mansuri, and Kupal (55 samples) oil fields. Based on major (Ca, Mg) and minor (Mn, Fe, Na, Sr) elements and the rate of change in the carbon and oxygen isotope, aragonite was main carbonate mineralogy. Sr/Na concentrations which range from 1.29 to 7, show that carbonate of the Sarvak formation situated in warm water aragonite limestone. The elemental composition in Zagros oil fields carbonates also demonstrates that they have stabilized in a non-marine diagenesis environment. Variation of Sr/Ca vs. Mn values in Zagros oil field suggests that diagenetic alteration occurred in a semi-closed to open geochemical system. Changes in Mn, Fe, and V, show regenerated environment (without sulfate with Eh) with medium to low pH condition. These chemical indicators suggest variable paleo redox conditions in the Sarvak Formation.

Keywords: *Geochemistry; Oxygen and carbon isotope; Trace and major elements; Sarvak Formation; Zagros oil fields.*

1. Introduction

Sarak formation is one of the carbonate units of Bangestan Group ^[1] which belong to the Lower to Upper Cretaceous period (Albian-Turonian) ^[2] and is considered as one of the oil reservoir rocks in Zagros ^[3-4]. There are several porosity systems which allow heterogeneous Petrophysical properties in the carbonate reservoir rocks ^[4-5]. Hence, the relative percentage and type of pores and their distributions are strongly effective in producing indexes and carbonate reservoirs simulation ^[6-7]. Tectonically, Zagros area is a part of a foreland basin predominantly filled with thick sedimentary sequences of clastic and carbonate compositions ^[8]. Sarvak Formation was deposited on platforms and within the intra-shelf basin in the passive margin of the Arabian Plate ^[9-11]. In Ab-teymoor oil field, Ghabeishavi *et al.* ^[12] concluded that Ilam and Sarvak Formations deposited in carbonate ramp areas. Lasmi and Kavoosi ^[13] specified four sedimentary sequences stratigraphy for Sarvak Formation in Lorestan area. Different authors have studied the Sarvak formation of the outcrops in the Zagros area ^[2,3-4,9,14], but the present study has selected the Sarvak formation in the Zagros oil field. The present study investigates the original mineralogy and the digenetic environment of the Sarvak limestone in these oil fields using geochemistry methods (major and trace elements, oxygen, and carbon isotopes), and compares these data with modern tropical ^[15-16] and temperate carbonates ^[17-19].

1.1. Geological settings

Sarak formation has expanded in Fars, Khuzestan, and Lurestan ^[20]. In Bangestan Anticline (section type) Sarvak formation having a thickness of more than 830m has been noticed which consists of medium to thick layers and massive fossiliferous limestones. Gachsaran, Mansuri, and Kupal oil fields are located in the Dezful embayment (Fig.1).



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1.2. Previous work

Many researchers [1] believe that the Sarvak Formation is formed with carbonate. At first, James and Wynd [1] studied Sarvak Formation, and consequently other researches were conducted on Zagros bio-stratum such as Bangestan group and the result of these researches showed that the age of Sarvak Formation goes back to Cenomanian. Lasmi and Kavooosi [45] specified four sedimentary sequences of stratigraphy for Sarvak Formation in Lurestan area and recognized that the age of Sarvak Formation is from Cenomanian to Turonian in this area. By studies conducted on sedimentary environment and diagnosis of Sarvak Formation in Izeh Zone, Asadi *et al.* [9] found that the sedimentation of Sarvak Formation has occurred in four sedimentary environments: Open marine, shale, lagoon, and tidal flats. Afghah and Dehghanian [24] in their studies of microfacies Sarvak Formation in Fars province specified that the age of Sarvak Formation goes back to Cenomanian in this area. Asadi *et al.* [9] specified dissimilarities of oxygen versus carbon isotope in Sarvak limestone which indicates marine Phreatic and Meteoric diagenesis in Mish anticline.

Asghari and Adabi [22], spatially studied the chemical Variations of Sr/Ca and $\delta^{18}\text{O}$ values versus Mn and showed that carbonates in Sarvak were affected by meteoric diagenesis in an almost closed system.

Obtaining operational method of the processes; is only possible through geochemical studies of sediments. Study of trace elements, especially in the rocks, could be used to determine the salinity, temperature, depth, and also other paleo-environmental traits [25]. From the element point of view chemical facies can be applied as an index for genesis and diagenesis of sediments.

Changes in the mineral compositions of a formation can be noticed which depends on parameters and different processes such as sedimentation rate, depositional environment, and paleo-climatic conditions, lithological and diagenetic effects [26]. Studies of each of these processes can be useful and effective for explanation of carbonate composition and their changes in the formation [25, 27]. The elements Ca, Mg, Fe, Mn, Sr, and Na in the carbonates rocks are essential to understand carbonate mineralogy, salinity, environmental setting, substitution of elements and temperatures [28].

2. Material and methods

Whole-rock powders of all samples (A dentist drill with a stainless steel circular bit was used to collect micrite samples) were dissolved in 1N HCl for 2 hours at room temperature (these conditions minimized the alternation of the clays and oxides of the rocks) and 55 samples with less than 10% insoluble residue were collected from Kupal (Well No.48, 15 Samples), Mansuri (Well No.54, 17 Samples) and Gachsaran (Well No.55, 23 Samples) oil fields and analyzed by atomic absorption spectrometer (AAS) for Ca, Mg, Sr, Na, Mn and Fe contents, Precision was $\pm 0.5\%$ for Ca and Mg and ± 5 ppm for Sr, Na, Mn and Fe [29]. All powdered samples were analyzed with a Micro mass, for oxygen and carbon isotopes. The precision of data is $\pm 0.1\%$ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, and these values were reported relative to PDB (Tab.1 to 3).

Table 1. Geochemical analysis of selected samples based on stratigraphic column in the Gachsaran oil field

Sample No.	Mg%	Ca%	Sr ppm	Mn ppm	Na ppm	Fe ppm	V ppm	Ni ppm	Cr ppm	Co ppm	Mo ppm	$\delta^{13}\text{C}$ ‰ PDB	$\delta^{18}\text{O}$ ‰ PDB
1	0.1	37.09	1025	175	583	367	56	47	5	2	11	1.73	-4.35
2	0.093	37.43	1530	183	461	523	62	35	3	4	17	1.82	-4.63
3	0.202	37.26	1348	210	628	286	47	55	2	3	8	2.04	-4.18
4	0.148	38.15	1120	188	512	548	41	51	4	2	10	1.95	-5.52
5	0.273	37.26	2183	173	752	394	55	26	4	4	13	1.83	-4.23
6	0.231	36.13	2428	195	830	481	81	38	3	6	17	1.99	-4.17
7	0.15	37.42	1360	240	825	479	68	49	2	2	15	2.52	-4.11
8	0.17	35.31	2184	184	763	536	42	58	2	3	11	1.76	-4.38
9	0.11	36.39	2344	210	611	392	56	34	4	4	9	1.86	-4.08
10	0.145	36.37	1655	158	739	372	58	38	6	4	8	2.01	-4.37

Sample No.	Mg%	Ca%	Sr ppm	Mn ppm	Na ppm	Fe ppm	V ppm	Ni ppm	Cr ppm	Co ppm	Mo ppm	$\delta^{13}\text{C}$ ‰ PDB	$\delta^{18}\text{O}$ ‰ PDB
11	0.22	38.08	1034	178	565	287	61	41	7	4	9	1.87	-5.351
12	0.183	37.51	1563	217	584	671	32	54	11	6	11	1.83	-4.18
13	0.254	37.24	1478	234	211	465	37	46	4	2	7	1.94	-4.16
14	0.248	39.25	1287	185	341	359	43	44	3	2	14	1.93	-4.27
15	0.17	39.42	1083	193	544	276	47	42	2	4	8	2.55	-4.84
16	0.146	39.37	1163	241	737	364	73	57	2	7	10	1.83	-4.31
17	0.141	38.2	2011	195	641	461	56	26	5	5	10	1.81	-5.26
18	0.124	38.56	1547	169	779	657	78	39	5	3	13	2.39	-4.16
19	0.151	39.74	1394	183	517	584	86	46	3	3	15	2.36	-4.51
20	0.136	38.02	1952	187	497	367	64	35	2	2	16	2.54	-4.73
21	0.217	41.36	1879	215	655	255	56	51	4	4	10	1.88	-5.11
22	0.129	36.25	1623	194	441	407	39	43	4	2	9	2.11	-5.85
23	0.248	36.25	1761	204	826	603	47	58	7	5	11	1.98	-4.62

Table 2. Geochemical analysis of selected samples based on stratigraphic column in the Kupal oil field

Sample No.	Mg%	Ca%	Sr ppm	Mn ppm	Na ppm	Fe ppm	V ppm	Ni ppm	Cr ppm	Co ppm	Mo ppm	$\delta^{13}\text{C}$ ‰ PDB	$\delta^{18}\text{O}$ ‰ PDB
1	0.172	38.14	2107	184	621	541	43	37	9	4	5	2.26	-4.11
2	0.142	37.05	1835	217	527	553	32	21	7	4	7	2.14	-4.37
3	0.237	36.2	1082	238	280	616	15	36	4	3	11	2.2	-4.57
4	0.151	39.76	1417	225	411	495	28	42	2	4	8	2.55	-4.23
5	0.052	38.14	1712	195	402	572	64	27	8	2	6	1.86	-4.32
6	0.072	37.75	1816	187	785	656	57	22	4	2	9	1.74	-4.18
7	0.175	38.33	1017	192	765	409	33	34	5	2	11	2.45	-4.21
8	0.081	37.42	1652	211	667	631	82	41	3	4	8	2.17	-4.51
9	0.15	38.11	1739	196	730	610	41	39	2	6	8	2.68	-5.47
10	0.14	38.74	1648	243	454	557	39	17	2	4	10	2.41	-5.16
11	0.28	38.53	1180	219	486	216	48	23	5	2	13	2.17	-5.23
12	0.14	39.57	2217	223	494	474	52	26	11	4	10	2.56	-5.86
13	0.26	39.20	2437	194	517	405	19	33	7	4	12	1.96	-4.41
14	0.23	38.77	1520	247	574	483	24	51	9	2	7	1.75	-4.84
15	0.16	38.02	1083	206	448	491	18	28	5	3	9	2.37	-4.29

Table 3. Geochemical analysis of selected samples based on stratigraphic column in the Mansuri oil field

Sample No.	Mg%	Ca%	Sr ppm	Mn ppm	Na ppm	Fe ppm	V ppm	Ni ppm	Cr ppm	Co ppm	Mo ppm	$\delta^{13}\text{C}$ ‰ PDB	$\delta^{18}\text{O}$ ‰ PDB
1	0.174	37.8	1060	211	576	283	27	47	7	3	8	1.82	-4.23
2	0.148	41.23	1445	237	451	361	41	22	8	2	11	1.73	-4.11
3	0.08	37.64	1024	204	534	247	33	30	4	6	14	2.46	-4.25
4	0.12	38.55	835	197	470	172	21	55	2	4	17	2.7	-4.72
5	0.144	39.51	1830	227	764	276	17	37	9	7	13	1.97	-4.51
6	0.112	37.35	1710	241	621	363	56	41	4	11	12	2.02	-4.27
7	0.221	39.21	1950	187	557	341	70	48	3	4	18	2.11	-4.31
8	0.209	41.61	2210	213	741	212	44	39	2	5	9	2.35	-4.75
9	0.279	39.25	1022	227	790	357	25	55	2	7	12	1.65	-4.86
10	0.172	39.93	1135	189	186	252	38	45	8	10	5	1.72	-4.27
11	0.25	37.25	1540	201	897	368	62	38	10	7	7	1.86	-5.26
12	0.192	38.37	1793	215	523	357	71	77	9	5	11	1.75	-5.37
13	0.105	36.4	1834	236	637	196	18	23	11	11	14	1.74	-5.29
14	0.248	38.43	1367	241	472	265	23	49	7	3	17	1.86	-5.77
15	0.273	37.65	1411	195	512	283	17	25	4	7	13	2.66	-4.11
16	0.231	38.02	1382	186	663	354	49	47	2	9	11	1.67	-4.07
17	0.15	39.76	1955	217	412	395	55	26	2	2	9	1.89	-5.21

3. Discussion

Evaporation of sediments and the abundance of carbonate rocks are an indicator of hot weather [30]. The ratio of Mg/Ca increases with increase in salinity with preferential replacement of Mg and Sr. Instead of Ca; other elements can be used as indicators to the carbonate sediments, [31]. Analysis of 55 samples of selected carbonated rocks from the AAS is listed in Table 1 to 3. By referring to Table 1 to 3, it appears that Ca/Mg ratio varies from 136.48 to 733.46. At this range it changes in trends of elements was observed. This trends can be related to orogenic phases and depth of sedimentary environment, and therefore changes in depositional conditions. The ratio of Mg/Ca (Fig.2.a) and Sr/Na (Fig.2.b) shows salinity parameter, which according to the degree of salinity can control the process of Dolomitization [32]. As a result of low altitude, considering its lowness, dolomitization has taken place. The Na values increase with percentage aragonite [33]. Na is unrelated to Sr ($R^2 = 0.0736$) because Na values show low salinity of fluid.

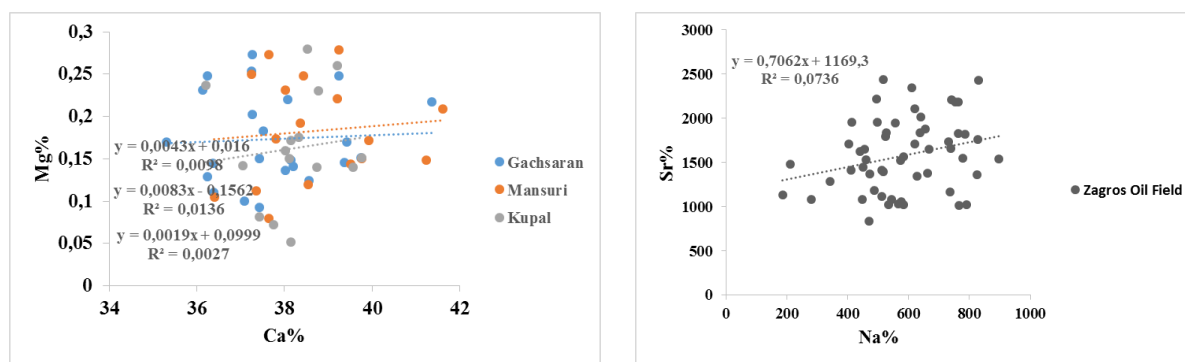


Figure 2 (a). Variability of Mg% vs. Ca% and positive trend during Sarvak deposition and shows lowness degree of dolomitization. (b). Ratio of Sr vs. Na shows the degree of salinity and lowness of dolomitization

Strontium (Sr) value changes from 1017 to 2437 ppm. The Sr content varies due to carbonate mineralogy. Sr increases with increasing aragonite content and decreases with increasing calcite content [32]. Concentrations of Sr have also been directly related to the increase in water temperature [34]. The concentration of Sr in recent temperate carbonates ranges from 1642 to 5007 ppm, whereas in recent tropical carbonate sediments range from 8000 to 10,000 ppm. Decrease in Sr values in Sarvak Formation, compared with Sr in recent tropical abiotic aragonite is due to meteoric diagenesis.

The values of manganese (Mn) in carbonate samples from the Gachsaran, Mansuri, and Kupal Oil Fields range from 158 to 247 ppm. The amount of Iron (Fe) in these areas change from 172 to 671 ppm. In modern warm-water aragonite, Mn and Fe concentrations are less than 20 ppm. In the Gachsaran, Mansuri and Kupal Oil Field, Mn is interpreted to reflect the meteoric diagenesis and high depositional rates.

Al-Aasm and Veizer [35] consider carbonate samples with Mn contents higher than 70 ppm can be altered. The Mn values of samples fall within the range of calcite precipitated at equilibrium with sea water in addition to modern marine carbonates (i.e., <50 ppm as reported by Veizer, [36]). Low Mn concentrations may also be related to a limited source of Mn to a wide platform [9].

Sr/Mn ratio versus Mn plot (Fig.3) used as useful criteria for estimating solubility of limestone; the solubility of aragonite and high-Mg calcite and their conversion into low-Mg calcite, which causes significant reduction of Sr values and increase in Mn concentration. The high Sr/Mn content in Sarvak limestone has been affected by non-marine diagenesis, with a high rate of rock-water interaction in a semi-closed to open system. Variation of Mn versus Sr illustrates that the Sr concentrations (1017–2437 ppm) from samples of Zagros areas are moderate. Sr values decrease from modern to ancient limestone's and dolomites [34]. Modern shallow marine abiotic aragonite is characterized by high Sr values (up to 10,000 ppm), while

abiotic calcite consists lower amounts of Microfacies and Geochemistry of Middle Cretaceous Sarvak Formation in Zagros Basin, Izeh Zone, SW of Iran's [9].

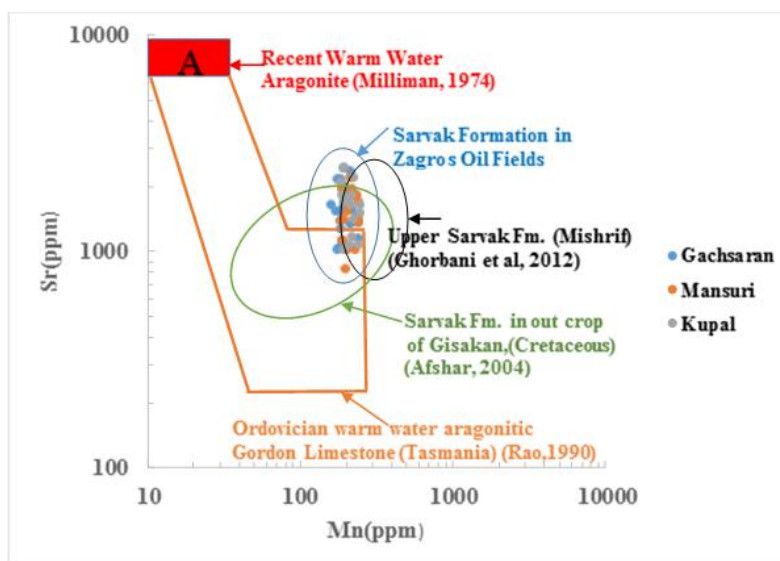


Figure 3. Sr and Mn variation in the Sarvak formation. Some sample fall out of Tasmania aragonite fields due to less meteoric diagenesis in carbonate of Sarvak

The concentration of Na in the Sarvak Formation samples from the Zagros oil field ranges from 186 to 826 ppm. Modern and ancient tropical carbonates differ from their non-tropical counterparts by their Sr/Na ratio and Mn contents [4]. Modern tropical aragonitic sediments have low Mn, and high Sr/Na ratio (from 3 to ~5); in contrast, modern temperate bulk carbonates have high Mn, and low Sr/Na ratios (~1). Sub-polar Permian cold-water fossils and the sub-polar bulk cold-water lime stones also have a Sr/Na ratio of ~1. In the Sarvak limestone, Sr/Na concentrations range from 1.29 to 7.00; Sr/Na ratio shows the carbonate limestone of Sarvak formation is modern, warm water aragonite sediments (Fig.4).

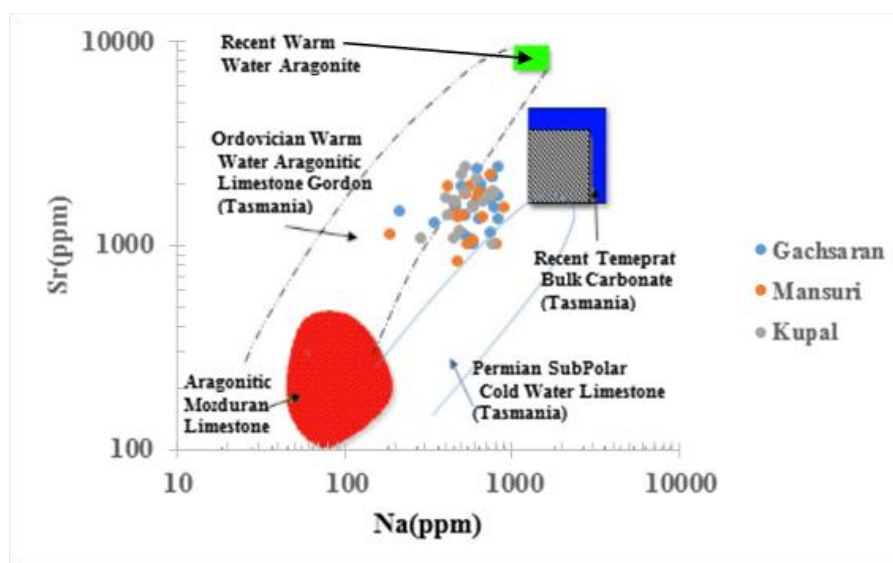
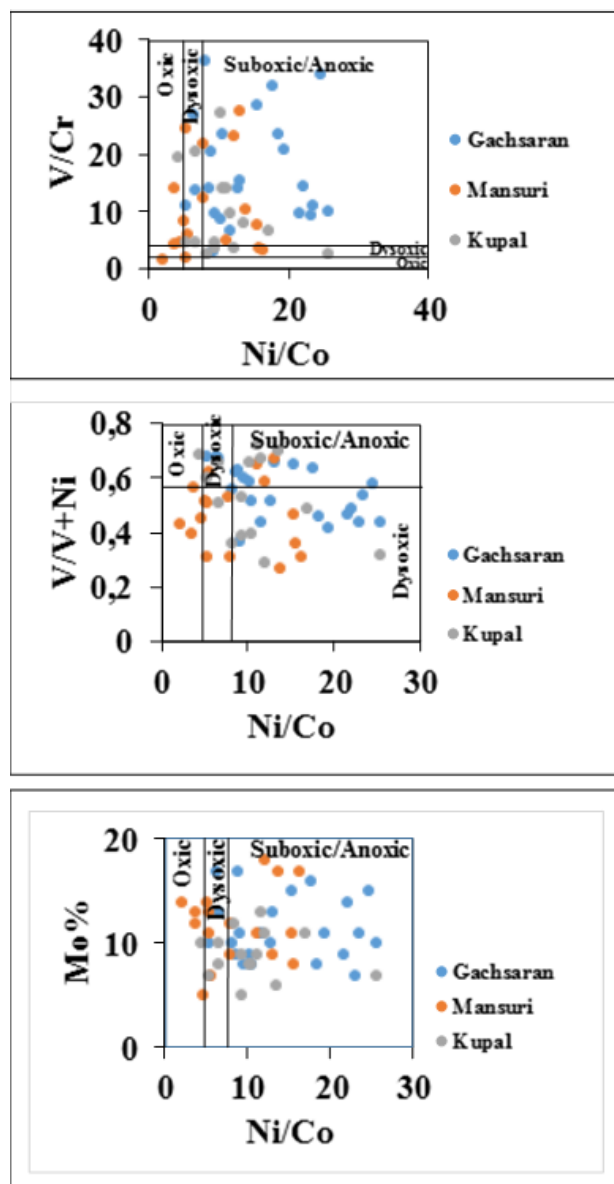


Figure 4. Sr and Na variations shows the all data of carbonate limestone in Sarvak formation falls into the aragonite fields due to similar mineralogy

Changing Mn, Fe, and V in all the samples belonging to group 3 domain (Mn<800, Fe<37500, V<320) (Hunt & Wilde, [37]) shows regenerated environment (without sulfate with Eh)

and medium to low condition of pH. In some samples there are some non-consistency in elements distribution and environmental conditions due to mineralogy which is sensitive to the concerned elements [25,37].

V/Cr [38] and Ni/Co [1] has been used as indicators of oxygen levels [25]. Hatch & Leventhal [39] ascribed V/(V + Ni) ratios to depositional environment. Both Ni and V occur in highly Stable structures preferentially preserved under anaerobic conditions (Lewan & Maynard 1982). Cr seems to be associated only with the terrigenous fraction [38], not influenced by redox conditions, and thus high V/Cr values (>2) are thought to indicate anoxic conditions. High Ni/Co ratios are thought to be associated with anoxic conditions [40]. V also may occur absorbed onto clay minerals [41]. In this study, based on pale-redox indicators [42], a good agreement is not noticed in the interpretations of redox conditions (Fig. 5) using thresholds established by Jones and Manning [40] for Ni/Co and V/Cr (Fig. 5a). However, V/(V+Ni) ratios predict lower oxygen conditions than either Ni/Co or V/Cr for all samples.



In fact, for most of the Sarvak samples, V/(V+Ni) predicted suboxic/anoxic conditions, whereas Ni/Co (Fig. 5b) and V/Cr predicted suboxic/anoxic to dysoxic. There seems to be a coupling of Mo with Ni/Co suggesting similar controls on accumulation (Fig. 5c). Figure 5c shows the Sarvak samples have Mo contents <200 ppm, plot within dysoxic to suboxic/anoxic ranges. In V/Cr and Ni/Co a lot of the samples in sub-oxic/anoxic part which is because of the highness of ratio of V/cr and may be this substance being absorbed by the organic substances and this by itself shows presence or amount of organic substances, but the Mo/Ni is non-mobile substance and therefore shows the ratio better. On the whole, these samples are because of sensitivity of the substances to the environmental conditions. This is different from those indicated by other indicators. Ranges of V/(V + Ni) are from Hatch & Leventhal [39], and for V/Cr and Ni/Co are from Jones & Manning [40]. However, the present data in this paper does show less variability between units that would be consistent with deposition under paleoenvironmental conditions. Thus, it may be reasonable to use these ratios and ranges in a relative sense and should be applied cautiously due to differences between basins of different geologic ages and geographic settings [25].

Figure 5. Paleoredox indicators of Sarvak Formation in Zagros oil field (a) V/Cr vs. Ni/Co; (b) V/(V+Ni) vs. Ni/Co; and (c) Mo vs. Ni/Co. Ni/Co ranges for V/Cr and Ni/Co are from Jones & Manning [40]; ranges for V/(V+Ni) are from Hatch & Leventhal [39]

The variations of Mn versus Sr content (normalized to Ca) in Fig.6 reveal the openness of the diagenetic system, the amounts of water–rock interaction, and Redox conditions of the system [43–44]. Sr value on the vertical axis shows the amount of rock–water interaction and is a measurement for the openness of the system. The Mn contents on the horizontal axis indicate the Redox conditions of the system during precipitation. Sarvak Formation carbonates in Zagros oil field falls into the LMC area and is a Semi-closed to open system. The intensity of water rock interaction is related to the position of the platform [9]. The dip shallow ramp section (Sarvak formation in Bangestan anticline) was heavily altered.

Base on Sr/Na ratio versus Mn (Fig.7), all samples are >1 and fall within the recent warm-water aragonite field, which is due to similar mineralogy.

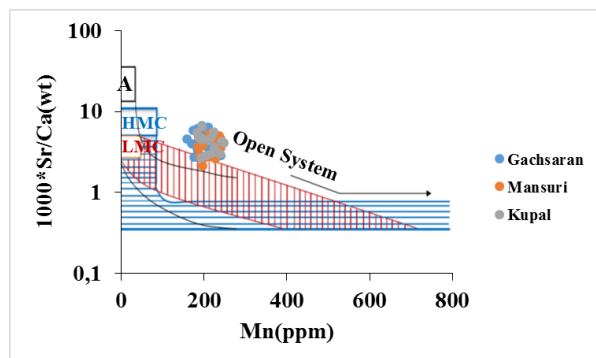


Figure 6. Mn and Sr/Ca variations in the Gachsaran, Kupal and Mansuri oil field shows this formation were affected by meteoric phreatic fluids in Semi-closed to open system

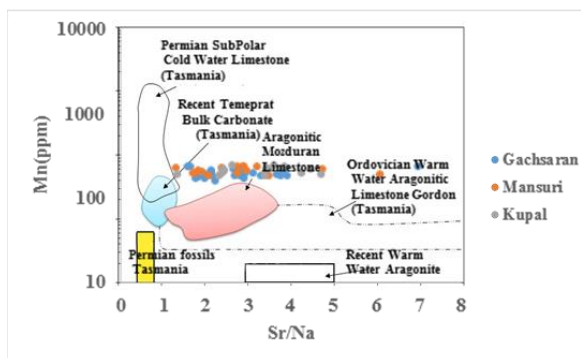


Figure 7. Mn and Sr/Na variations in Sarvak limestones, Sr/Na ratio of all samples are >1, indicating original aragonite mineralogy

Isotopic analysis indicates that $\delta^{18}\text{O}$ values range from -5.86 to -4.07‰ PDB and $\delta^{13}\text{C}$ values range from -1.659 to 2.7‰ PDB in Sarvak Formation limestone in Zagros oil fields. The cross plot of $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ values (Fig.8.a) from the carbonates of Sarvak formation, in Zagros oil fields, shows alteration by meteoric diagenesis in warm and arid climate with a little thickness of soil and Semi-closed to open system.

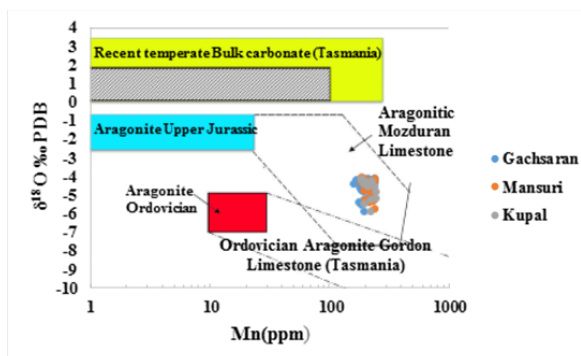
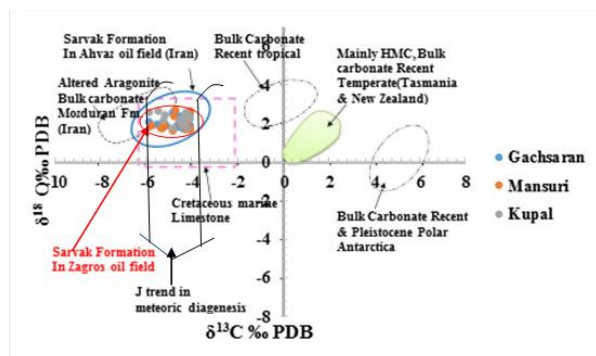


Figure 8. (a) Cross-plot of carbon and oxygen isotope data from the Sarvak Formation in the Gachsaran, Kupal and Mansuri oil field. All samples fall in cretaceous marine limestone with meteoric diagenesis. (b) Variations of $\delta^{18}\text{O}$ value versus Mn. Note the most of Sarvak samples fall in aragonite Mozduran limestone because of similar mineralogy

The Mn values show a slight increase in lighter $\delta^{18}\text{O}$ values (Fig.8.b). This trend indicates that most of the samples were affected by non-marine water during diagenesis in semi-reduced to reduced condition. The very heavy $\delta^{18}\text{O}$ values and very low Mn concentration of a few micrite samples may indicate less altered original aragonite mineralogy. As micrite is assumed to be least affected by non-marine waters, due to their low permeability, the relatively heavy $\delta^{18}\text{O}$ values and high Mn concentration in some other micrite, compared to most of the bulk

samples, and may suggest calcite mineralogy. In recent temperate bulk carbonates, the Mn concentration range up to 300 ppm.

4. Conclusion

Now a day's geochemistry by the elements and isotope, in the rocks without fossil or indicators play a suitable role in recognition of sedimentary condition and diagenesis evolution. The present study reveals that geochemical distribution in different locations of the Zagros Range shows individual trends. In this study, Results of geochemical studies of the Sarvak Formation in Gachsaran, Mansuri and Kupal oil fields can be summarized. The Sarvak formation (Albian to Cenomanian), as unit of Folded Zagros Zone, consisting of a series of sedimentary rocks of which is limestone dominated. The lithological characteristics and sedimentary structures of the Sarvak limestone, suggest the transgressive periods conditions in a foreland basin. Various plots of traces (Mn, Fe, Na, and Sr) and majors (Ca, Mg) elements, oxygen, and carbon isotope values show that the original carbonate mineralogy was dominantly aragonite in this formation. Sr/Mn, Sr/Ca, $\delta^{13}\text{C}$ / $\delta^{18}\text{O}$ and Mn/ $\delta^{18}\text{O}$ Ratios indicate that Sarvak limestone was affected by non-marine diagenesis in warm and arid climate with a little thickness of soil and high rate of rock-water interaction in a Semi-closed to open system. Sr/Na ratio shows the carbonate limestone of Sarvak formation in moderate warm water aragonitic sediments. In the Gachsaran, Mansuri and Kupal Oil Fields, Mn is interpreted to reflect the meteoric diagenesis and high depositional rates. Changes in Mn, Fe show a regenerated environment (without sulfate with Eh) and medium to low condition of ph.

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