Reconstruction of Paleo depth and Paleo temperature from C- O stable isotope records of Mishrif Formation, southern Iraq

Taher M. Taha*,1, Enaam J. Abdullah2
1Department of Applied Geology, College of Science, University of Tikrit, Tikrit, Iraq
2Department of Geology, College of Science, University of Baghdad, Baghdad, Iraq

Abstract
Stable isotopes $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in the carbonate rocks of the Mishrif Formation are examined here to define the depositional characters in the basin includes paleo temperatures and paleo depth.

The Mishrif formation (Cenomanian – Early Turonian) has extensive distribution in Iraq and Middle East. Mishrif Formation composed of organic detrital limestone. Four boreholes in four oilfields, Noor – well (11), Amarah – well (14), Buzurgan – well (24), Halfaya – well (8), in south east of Iraq have been studied.

The studied samples have negative δ$^{18}O$ isotope values studied well, with Average (-4.11‰), (-4.47‰), (-4.48‰), (-4.18‰) in the studied wells respectively. Carbon Isotope composition positive values in the study samples, with average (2.32‰), (1.84‰), (2.20‰), (2.24‰) are studied well respectively. The Stable isotope ($^{18}O/^{16}O$ and $^{13}C/^{12}C$) of Mishrif Formation provide the first records of paleotemperature for the (Cenomanian – Early turanian ) which indicate moderate during deposition.

The plot of depositional environment refers to warm water carbonate sediment and the bulk samples cluster tightly to small positive reflect modal isotope composition of dominant skeletal marine carbonate. The paleo-salinity (Z values) provide the marine deposits in studied samples. As the paleo-temperature was high temperature by (T values). The paleo depth he all studied samples in the four oilfields are fall in the same level which is in the upper part of Thermocline this indicate the moderate depth

Keywords: O and C isotopes, Paleo temperature, Paleo depth, Mishrif Formation.

*Email: taher.mahmood.taha@gmail.com
1- INTRODUCTION

Iraq is one of the most petroleum-rich countries in the Middle East, and is considered as the biggest in reserved oil which Contains one of the worlds most have hydrocarbon systems of the Middle–Upper Jurassic [1].

During early late cretaceous times, The decrease large part of the Arabian plate was covered by shallow subtropical seas resulting in deposition of thick limestone successions. Throughout the Middle East, these carbonates host a considerable part of the words total hydrocarbon reservoir [2] The Mishrif Formation is of Late Cenomanian age is the most important oil reservoir in the Mesopotamian Basin, southern Iraq.

Mishrif formation is one of the richest rock which forms up to 40% of Cretaceous oil reserves in Iraq [3]. It is deposit during Cenomanian-Early Turonian cycle as a part of the Wasia Group, (equivalent to Upper Sarvak in Iran) reservoirs [4] and the Natih formation in Oman [5, 6]. The Late Tithonian-Early Turonian Megasequence (AP8) was deposited in a large intra-shelf basin contemporaneous with a new phase of ocean floor spreading in the Southern NeoTethys. It can be divided into two subcycle: the Albian and the Cenomanian-Early Turonian sequences, thickens towards the east in the Tigris Subzone and the Foothill Zone.

Isotope geochemistry is increasingly used in environmental study to obtain pale-environmental condition, including pale-hydrology, pale-climate and the role of photosynthetic activity in the precipitation of carbonate [7]. Stable isotopes in the geosciences have emerged as a useful tool as thermometry to find the temperature history for surface and sub-surface environment. in carbonate rock and sediment a use based on measurement of the proportion of δ18O and δ13C analyses of the same sample and the result from these analyses are widely scattered [8]. The C- O isotope ratio compositions of coexisting sedimentary carbonates from the carbonates samples (Bulk samples) are expressed in the conventional δ notation.

Isotopic analysis was carried out on 30 carbonate Samples in order to aid in environmental interpretation as well as to establish geochemical similarities or differences among the carbonate facies. The aims of this paper are for determining the origin of carbonate rock and depositional environment using 18O and 13C stable isotopes.

2- LOCATION OF THE STUDY AREA

The study area includes Mishrif Formation investigation in selected oil fields Noor – well (11), Amarah – well (14), Buzurgan – well (24), Halfaya – well (8), which are bounded between (47°15’36”), (46°15’43”) longitude and (31°45’16”), (31°15’30”) latitude, where is located in Maysan Governorate, south eastern Iraq (Figure-1) in the Mesopotamian zone except Buzurgan oil fields where lies within Hemrin- Makhul sbzone from the low folded zone. This entire oilfield located in the south east of Iraq near the Iraqi – Iranian border and east Tigris River.

3- MATERIALS AND METHODS

Thirty (30) samples belong to Mishrif rock formation from four oilfield distributed in four boreholes have been Analysis of carbon and oxygen isotopic were carried out by Mass Spectrometry in Iso-Analytical Limited in UK.
The determination of the oxygen and carbon isotope composition in the carbonate rocks which formed of calcite, dolomite, siderite and magnesite minerals is not accurate when the carbonate minerals not separated physically. Chemical separation of the minerals depends on deferential reactions rates of various carbonate minerals by using phosphoric acid under different heat temperature [9]. The method of producing CO$_2$ from carbonates for stable C and O isotopic is analysed by reaction with phosphoric acid:

$$\text{CaCO}_3 + \text{H}_3\text{PO}_4 = \text{CaHPO}_4 + \text{CO}_2 + \text{H}_2\text{O}$$

Conventionally, the abundance of $^{13}$C and $^{18}$O isotopes in samples is reported in conventional notation ($\delta$) as part per thousand ($\%$) difference between an isotopic ratio ($^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O) in a sample compared with the ratio in the international standard.

Oxygen and Carbon isotopes are mostly calculated according to the PDB (Pee Dee Belemnite) carbonate international standard. So, the resulted Data ($\delta^{13}$C and $\delta^{18}$O) can be explained as the following equation:

$$\delta = \left( \frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000$$

Whereas:

$R = \text{ratio} \left( ^{13}\text{C} / ^{12}\text{C} \text{ or } ^{18}\text{O} / ^{16}\text{O} \right)$. The standard for carbonates is PDB [10].

Figure 1 - Location map of the study area
3-RESULTS AND DISCUSSION

- Oxygen Isotope

The temperature of precipitation and the oxygen isotopic composition of carbonate depends on the fractionation of both oxygen isotopes (δ18O) between water and carbonate which differs for each carbonate mineral species [11]. The δ18O of both limestones and dolomites decreases with increasing age [12].

The studied samples have negative δ18O isotope values studied well, as they show significant variation range, Noor oilfield Well-11 (-5.20 to -3.39 ‰), Amarah oilfield Well-14 (-5.65 to -4.10‰), Buzurgan oilfield Well-24 (-5.13 to -3.40‰), Halfaya oilfield Well-8 (-4.79 to -3.46‰) with Average (-4.11‰), (-4.47‰), (-4.48‰), (-4.18‰) in the studied wells respectively. (Table-1). The values are confirmed to the value records by Veizer and Hoefs (1976), these are compared with compiled data in an attempt to verify previously reported measurements of cretaceous rocks. Veizer and Hoefs (1976) were measured both O and C stable isotopes in both limestone and dolomite rocks Table-2, (Figure-2). Marine limestone that has been affected by a diagenetic process often show negative values, because of the type of the diagenetic processes which take place in fluids depletion in δ18O with according to sea water or at elevated temperature due to deep burial [13].

- Carbonate Isotope

The carbon isotopic composition derived from carbonates is mostly related to the isotopic composition of dissolved inorganic carbon (DIC) and only mostly depending on temperature (less than 0.1 ‰ / °C, [14], [15], [16]. Also, the carbon isotopic fractionation during precipitation is slightly different for the carbonate minerals, calcite being enriched by about 1.1‰ relative to DIC in the temperature range 10 – 40 °C [16], while the dolomite is heavier by about 2‰ relative to cogenetic calcite [17] δ13C of limestones and dolomites seems to be decreasing with increasing age [12].

Carbon Isotope composition values show enrichment in the study samples, it has positive value in the studied wells, and significant variation ranges, Noor oilfield Well-11 (-1.22 to 3.29‰), Amarah oilfield Well-14 (-1.26 to 3.40‰), Buzurgan oilfield Well-24 (0.96 to 3.21‰), Halfaya oilfield Well-8 (-2.31 to 3.52‰) with average (2.32‰), (1.84‰), (2.20‰), (2.24‰) in studied well respectively, that’s shown in the Table-1 and they are approximating to the value records by[12], these are compared with compiled data in an attempt to verify to previously reported measurements of cretaceous rocks. [12] Was measured both O and C isotopes in both limestone and dolomite rocks, Table-2, Figure-2.

Table 1-Show analytical results of 18O and 13C in studied borehole

| Depth  | 18O-PDB (%) | 13C-PDB (%) |
|--------|-------------|-------------|
| Noor oilfield Well-11 | | |
| 3334   | -5.20       | -1.22       |
| 3370   | -3.73       | 3.03        |
| 3400   | -3.39       | 3.29        |
| 3424   | -4.30       | 2.65        |
| 3448   | -3.77       | 2.64        |
| 3472   | -4.65       | 2.79        |
| 3532   | -3.81       | 2.75        |
| 3590   | -3.84       | 2.19        |
| 3662   | -4.29       | 2.77        |
| Min    | -5.20       | -1.22       |
| Max    | -3.39       | 3.29        |
| Average| -4.11       | 2.32        |
| Amarah oilfield Well-14 | | |
| 2896   | -5.65       | -1.26       |
| 2950   | -4.31       | 1.91        |
### Table 1-continued

| Depth | Mean $\delta^{18}$O-PDB (%) | Mean $\delta^{13}$C-PDB (%) |
|-------|-----------------------------|-----------------------------|
| 2307  | -4.29                       | 3.40                        |
| 3124  | -4.34                       | 2.33                        |
| 3148  | -4.32                       | 2.12                        |
| 3190  | -4.30                       | 2.04                        |
| Min   | -5.56                       | -1.26                       |
| Max   | -4.10                       | 3.40                        |
| Average | -4.47                   | 1.84                        |

#### Buzurgan oilfield Well- 24

| Depth | Mean $\delta^{18}$O-PDB (%) | Mean $\delta^{13}$C-PDB (%) |
|-------|-----------------------------|-----------------------------|
| 3736  | -5.13                       | 0.96                        |
| 3808  | -3.40                       | 2.29                        |
| 3868  | -4.65                       | 3.21                        |
| 3958  | -4.22                       | 2.16                        |
| 3982  | -4.57                       | 2.23                        |
| 4042  | -4.82                       | 2.33                        |
| Min   | -5.13                       | 0.96                        |
| Max   | -3.40                       | 3.21                        |
| Average | -4.48                   | 2.20                        |

#### Halfaya oilfield Well-8

| Depth | Mean $\delta^{18}$O-PDB (%) | Mean $\delta^{13}$C-PDB (%) |
|-------|-----------------------------|-----------------------------|
| 2842  | -4.79                       | -2.31                       |
| 2908  | -4.40                       | 2.74                        |
| 2962  | -4.27                       | 2.72                        |
| 2986  | -3.95                       | 2.84                        |
| 3016  | -4.35                       | 3.52                        |
| 3082  | -3.46                       | 3.44                        |
| 3148  | -3.96                       | 2.22                        |
| 220   | -4.23                       | 2.74                        |
| Min   | -4.79                       | -2.31                       |
| Max   | -3.46                       | 3.52                        |
| Average | -4.18                   | 2.24                        |

**Figure 2** - $\delta^{18}$O and $\delta^{13}$C for the Mishrif Formation relative to the Cretaceous period after Veizer (1976)
Table 2-list of $\delta^{18}$O and $\delta^{13}$C values in (PDB) after (Veizer and Hoefs, 1976)

| Cretaceous Age | $\delta^{18}$O | $\delta^{13}$C |
|----------------|---------------|---------------|
|                | -2.60         | 2.20          |
|                | -2.60         | 2.80          |
|                | -5.40         | 2.60          |
|                | -1.70         | 3.00          |
|                | -2.80         | 1.20          |

4-Relation between $\delta^{18}$O and $\delta^{13}$C

Marine limestone is generally, composed of a variety of skeletal and non-skeletal grain with a certain amount of matrix material, and diagenetic processes that readily altered the primary isotopic signatures [18]. [19] indicate a positive correlation between $\delta^{18}$O and $\delta^{13}$C has been observed in the early to middle Miocene.

The relationship between $\delta^{18}$O and $\delta^{13}$C values for Mishrif Formation in the present study are shown in a scatter diagram Figure-3, there is a weak correlation across the wells in (Buzrgan and Halfaya) oil field $R^2 = (0.10, 0.42)$ and moderate correlation in (Noor and Aamara) oil field $R^2 = (0.60, 0.87)$. Decrease in $^{13}$C with decreasing $^{18}$O in both limestones and dolomite. This is a frequently observed feature of sedimentary carbonate rocks. Since the decrease in $^{18}$O has age connotations, the decrease in $^{13}$C could have the same meaning [12]. The poor correlation between $\delta^{18}$O and $\delta^{13}$C indicating a lack of diagenetic influence on the carbon Isotope signature [20]. Depended on the weak correlation between $\delta^{18}$O and $\delta^{13}$C, we suggest that limestone from Mishrif carbonate formation exhibit primary Carbone isotope composition value and can use as a direct indicator for the composition of the sea water in the basin during Cenomanian – early Turanian Time.

Figure 3-Correlation between $\delta^{13}$C and $\delta^{18}$O.
5-Plote of $\delta^{18}$O and $\delta^{13}$C for depositional environment

Stable Carbone and oxygen isotope composition signal in carbonate sedimentary rock is a function for environmental conditions for sedimentation, $\delta^{18}$O composition functions for temperature of the water, whereas the $^{13}$C reflect the isotope composition of the dissolved inorganic carbon (DIC), which in turn is a complex function to the dissolved CO$_2$ in equilibrium with atmospheric CO$_2$ and the CO$_2$ formed by organic matter alteration or other source [21].

Carbonates underlying surfaces with long histories of subaerial exposure typically record substantially lowered carbon- and oxygen isotope values, which become progressively more positive with increasing depth or distance from the surface, respectively [13].

The most samples of Mishrif formation are grouped at the small positive (3.52) for both $\delta^{18}$O and $\delta^{13}$C, with extension small negative (-5.65) for both $\delta^{18}$O and $\delta^{13}$C. These values are comparable with the oxygen and carbon isotopic composition of the Permo-Triassic carbonate samples of South Pars in the Persian Gulf (-6.4 to -1.8 $\%_o$ for $^{18}$O and -0.8 to 2.5 $\%_o$ for $^{13}$C [22]). The samples have negative values for $\delta^{18}$O and positive values for $\delta^{13}$C across the study wells. The positive carbon isotopes used as indications of the closed and strongly evaporitic condition during the depositional period. At the same time, $^{12}$C-rich CO$_2$ preferentially escaped from the surface of sea water [23], and the same time the seawater become riches with $^{13}$C, also $^{13}$C enrichment in syngenetic dolomites of the seawater [24].

Plotted of $\delta^{18}$O and $\delta^{13}$C of samples show in Figures-(4, 5), the bulk samples cluster tightly to small positive reflect modal isotope composition of dominant skeletal marine carbonate, the former The positive value of bulk samples reflecting unaltered, reflecting cool bottom and upwelling water

Moderately positive value of carbonate is ,dominant calcite and come from full marine Formation [25]

(4, 5). 07708507557 typically fermentation, which is represented by algae mat, shown in Figur-[26] and [27] to discriminate between marine and freshwater limestone use the following equation: $Z$: $2.048(\delta^{13} C_{13} + 50) + 0.498(\delta^{18} O + 50)$

Where both $\delta^{13}$C and $\delta^{18}$O are expressed as $\%_o$ PBD. Carbonate rocks samples with Z value above 120 would be classified as marine, while with Z below 120 as freshwater. In the present study, the Mishrif carbonate samples have Z range from (122.22 - 132.36), (121.90 - 132.12), (126.71- 131.57) and (120.18 - 132.62) in the borehole (Noor, Aamara, Buzrgan, and Halfaya oilfield) respectively (Table-3). The results reflect marine deposits.

6- $\delta^{18}$O and $\delta^{13}$C for paleo temperature

Heavy isotope thermometry is an emerging tool to probe the temperature history of surface and subsurface environments based on measurements of the proportion of $^{13}$C and $^{18}$O isotopes bound to each other within carbonate minerals. Although most Heavy isotope geothermometer implicitly presumes carbonate crystals have attained lattice equilibrium (i.e., thermodynamic equilibrium for a mineral, which is independent of solution chemistry), several factors are other than temperature, including dissolved inorganic carbon (DIC) speciation may influence mineral isotopic signatures [28].

The temperature depends on the fractionation of oxygen isotopic composition in the carbonate dioxide water-carbonate system has been employed widely for paleotemperature measurement and this method applied at first by [29] based on observed the temperature of the solution from which carbonate is precipitatively reflected in oxygen isotope ration of the carbonate. Oxygen isotope ratio is the ideal indicator if the only temperature was responsible for the final $^{18}$O/$^{16}$O isotope ratio of the precipitated carbonate [30].

The calcite paleo temperature equation, can be used to calculate the "isotope temperature" of Formation of calcite. The [31] use the $\delta^{18}$O value of the water from which the calcite precipitated is known: $T=16.5 - 4.3 \delta + 0.14 \delta^2$

where T is the temperature in °C (based on a least-squares fit for a range of temperature values between 9 °C and 29 °C, with a standard deviation of ±0.6 °C, and $\delta$ is $\delta^{18}$O for a calcium carbonate sample. The paleo temperature of the Mishrif carbonate ranges from (32.70 - 42.67), (36.48 - 45.28), (32.76 - 42.24) and (33.08 - 40.31) in the studied oil field (Noor, Aamara, Bazrgan, and Halfaya) respectively. With some samples show high temperature (Table-3)
Figure 4-Plots of $\delta^{18}$O and $\delta^{13}$C after Nelson and Smith (1996)
7-Paleo depth and pale climate

Original $\delta^{18}$O vs MOW composition

The following equation for calculated ($\delta^{18}$Osw) values for Cretaceous sea water is given by:

$$\delta^{18}\text{Ovs (MOW)} = 1.03092 \times \delta^{18}\text{Ovs (PDB)} + 30.92$$

shows in general enrichment by $^{18}$O, sometimes low depletion in $^{18}$O (Table-3).

Carbon and oxygen isotopes in carbonate can act as an important tracer in geological studies. They can provide an important basis for analysis a significant scientific issue, such as climate change over geological time. Original oxygen and carbon isotope composition of sea water, and exogenous cycle of carbon, oxygen, and other element [32]. Under different climatic condition, Carbone and oxygen isotopes have different isotope abundance. Because they have a decrease in corrosion at a late
stage and good regional compatibility, they have been used as a good ideal material for palo-climate and paleo-environment studies [32].

The stable isotopic data from marine limestone can provide quantitative evidence for changes in global climate and oceanic circulation, and the Oxygen isotope data can indicate temperature and oceanic composition. There are some different process make the $^{18}$O composition of sea water vary with the time, which influence on the $\delta^{18}$O of the global ocean, and the local $\delta^{18}$O of seawater. The composition of oxygen isotopic in the oceanic water is vary from place to place in a manner that roughly parallels salinity, as a consequent of the isotope fractionation which occurs during the evaporation condensation of water [33].

The $\delta^{18}$O of the global ocean is primarily affected by the changes in the amount of glacier volume on the land [34](Shackleton,1967), and also by the changes in temperature-dependent isotopic exchange with the oceanic crust [35], [36]. The dominant factor influenced the $\delta^{18}$O of the global ocean is related to paleo climatic changes. The changes in the $\delta^{18}$O isotope ratio of ocean water between glacial and interglacial periods interfere with paleo- temperature determinations for marine carbonates. During glacial Periods the $^{18}$O/$^{16}$O isotope ratio of ocean water increased because of the storage of large amounts of $^{18}$O-deficient water in the Pleistocene icecap [29] which mean enrichment of $^{18}$O in the sea water during glacial period. [37] Stated that the enrichment of $^{18}$O through glacial and interglacial periods.[38] used $\Delta\delta^{18}$O for determination the paleo depth of water in equation:

$$
\Delta\delta^{18}O = \delta^{18}O_{\text{Calcite}} - \delta^{18}O_{\text{SMOW}}
$$

[25] Suggest that the $^{13}$C isotope is enriched in shallow water condition due to concentration of bicarbonate more than deep water. They pointed that increases of $\delta^{13}$C are accompanied with sea-level rise, while decreases in $\delta^{13}$C are accompanied to sea-level fall.

The present study has applied [38] used $\Delta\delta^{18}$O figure to determine the paleo-depth for Mishrif formation. The all studded samples in the four oilfield are fall in the same level which is in the upper part of Thermocline part Figure-6, this indicates the moderate depth

![Figure 6](image-url)

**Figure 6**-$\Delta\delta^{18}$O of determine paleo depth in the water column, after (Ando et al, 2010).

**Table 3**-Show result of Z value, infer marine influence and temperature of calcite precipitation and $\Delta\delta^{18}$O.

| Noor oilfield - well (11) |
|---------------------------|
| **Depth** | **Z** | **T** | $\delta^{18}$O_{SMOW} | $\Delta\delta^{18}$O |
| 3334 | 122.22 | 42.67 | -4.44 | -0.76 |
| 3370 | 131.65 | 34.48 | -2.92 | -0.80 |
| 3400 | 132.36 | 32.70 | -2.58 | -0.82 |
| 3424 | 130.58 | 37.56 | -3.51 | -0.79 |
8-conclusion

The Mishrif formation (Cenomanian – Early Turonian) has extensive distribution in Iraq and Middle East. Mishrif Formation composed of organic detrital limestone. Plotted of δ18O and δ13C of samples show), the bulk samples cluster tightly to small positive reflect modal isotope composition of dominant skeletal marine carbonate. The positive value of bulk samples reflecting unaltered, dominant calcite and come from full marine Formation. Depended on the weak correlation between δ18O and δ13C, we suggest that limestone from Mishrif carbonate formation exhibit primary Carbone isotope composition value. The paleo salinity (Z values) reflect marine deposits. Where’s paleotemperature (T values) for some samples shows high temperature. The paleodepth investigation indicates the moderate depth for studied boreholes.
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