DOI: 10.24996/ ijs.2017.58.4B.18

Iraqi Journal of Science
ISSN: 0067-2904

# Geochemistry and Depositional Conditions of the Cretaceous Oceanic Red Beds (CORBs) within the Shiranish Formation in North of Iraq

**Mohammed Jamal Ahmed*[1], Mazin Yousif Tamar-Agha[2], Thamer Abbas Alwan[2]**
[1] Department of Geotechnical Engineering, Faculty of Engineering, University of Koya, Irbil, Iraq.
[2]Department of Geology, College of Science, University of Baghdad, Baghdad, Iraq.

**Abstract**

Upper Cretaceous Oceanic Red Beds **(CORBs)** are pelagic sediment deposits that deposited in the Upper Cretaceous basin, with widespread in part of the world as well as in Iraq. This research investigates the deposition of cyclic marl and marly limestone **CORBs** of six selected sections at the active southern margin of the Tethys during the Late Campanian - Maastrichtian with petrography, microfacies, and depositional environment.

The measurement of carbonate content (CaCO3 %) in the rocks, 180 samples of all the geological sections were studied twice for each sample and the average readings were taken.

This examination proved the following major oxides wt. % concentrations domination $SiO_2$, CaO, Al2 O3 and Fe2O3 with average values of 33.10, 29.63, 5.10 and 3.67 respectively, with following minor elements ppm concentrations dominance Sr, Ni, V, Zn, Cu, Zr and Co with average values of 498.4, 257.6, 67.8, 38.2, 34.3, 25.5 and 20.4 respectively. Also this group of ratios $K2O/Al_2O_3$, $SiO_2$, $Al2O_3/TiO_2$, Ni/Co, V/Cr, Cu/Zn, Cr/Ni, V/Ni, and V/ (V+Ni) is used as an index of paleo oxygenation conditions, these ratios proved the oxidizing environments for the rock samples in the present study

The expense of the organic matter content (TOC) has shown low content of TOC % in most studied samples, with ranges values of 0.27 in all beds, 0.18 in only red marl beds, 0.29 only non-red marl beds, 0.20 in only red marly limestone beds, 0.36 only non-red marly limestone beds .

The Shiranish Formation (Late Campanian-Early Mastrichtian), composed of marl and marly limestone, rhythmically laminated. Relatively low contents of organic matter and the containing of some redox-sensitive trace elements support the interpretation of oxic bottom water conditions during the deposition of this formation, consisting of light grey, reddish, brownish, and pinkish laminated calcareous marl and marly limestone, is characterized by low TOC contents. The $C^{13}$ and $O^{18}$ values are indicate upon the diagenetic affective due to burial, and it means a detrital origin that may reflect local uplift and variations in weathering processes in the adjacent continental areas.

**Keywords:** Geochemistry, Depositional Conditions, Cretaceous Oceanic Red Beds and Shiranish Formation

* Email: mohammed.hamawndy@koyauni.org

# جيوكيميائية و ظروف ترسيب الطبقات المحيطية الحمراء للطباشيري في تكوين الشيرانش، شمال العراق

**محمد جمال أحمد*[1]، مازن يوسف تمر اغا[2]، ثامر عباس علوان[2]**

[1]قسم الهندسة الجيوتقنية، كلية الهندسة، جامعة كوية، اربيل، العراق.

[2]قسم علم الارض، كلية العلوم، جامعة بغداد، بغداد، العراق.

**الخلاصة**

ان الطبقات المحيطية الحمراء للعصر الطباشيري الأعلى المترسبة في بيئة بحرية عميقة (CORBs) ذات انتشار عالمي واسع النطاق في شمال بحر التيثيس، ومحدودية انتشاره في شمال العراق رواسب عميقة ترسبت في حوض الطباشيري ألأعلى. تركز هذا البحث في دراسة هذا النوع من الرسوبيات (CORBs) وتتابعاته الدورية في طبقات المارل والحجر الجيري المارلي ضمن تكوين الشيرانش (الكامباني المتأخر– الماسترخيتي المبكر) من ناحية الخصائص الرسوبية المعدنية والدراسة الجيوكيميائية والظروف البيئية الترسيبية.

قياس النسبة المئوية لمحتوى الكاربونيت (CaCO3 %) في الصخور المدروسة والتي تمت على 180 عينة صخرية بواقع 118 عينة لصخور الحجر الجيري المارلي و60 عينة لصخور المارل وعينتان من عروق اكاسيد الحديد. وزعت على 140، 10، 10، 10، 6، 4 عينة من المقاطع Q, Dr, D, Sm, Ch, GS على التوالي. وقد اثبتت هذه الدراسة ان ضخور الحجر الجيري المارلي وصخور المارل مختلفة في محتواها من الكاربونيت، كما يختلف محتواها في الصخور الحاوية على الطبقات الحمراء عن محتواها في الصخور الخالية من الطبقات الحمراء. أذ تراوحت بين 53,5 – 100 % في صخور الحجر الجيري المارلي، وبين 20,5 – 50,0 % في صخور المارل. من جانب آخر تراوحت هذه النسبة بين 52 – 100 % في الصخور الحاوية على الطبقات الحمراء، وبين 27,5 – 49,5 % في الصخور الخالية من الطبقات الحمراء.

الفحوصات الكيمياوية (XRF) اجريت على 352 عينة بواقع 180 عينة من مساحيق الصخور 172 عينة من القطع الصخرية. عينات مساحيق الصخور موزعة على 140، 10،10، 10، 6، 4 من المقاطع Q, Dr, D, Sm, Ch, GSعلى التوالي، بينما وزعت عينات القطع الصخرية كالآتي 65، 41,28، 16، 14، 8 من المقاطع Q, Dr, D, Sm, Ch, GS على التوالي. أثبتت هذه الدراسة هيمنة نسبة تراكيز الأكاسيد الرئيسية (%) التالية على مكونات عينات الصخور موضوعة البحث، حيث بينت نتائج هذه الفحوصات بأن معدلات تراكيز اكاسيد $Fe_2O_3$, $Al_2O_3$, CaO, $SiO_2$ هي 33,10، 29,63، 5,10، 3,67 على التوالي. أما نسبة معدلات تراكيز العناصر النادرة (ppm) فسجلتها فحوصات هذه الدراسة حيث كانت الغالبية للعناصر النادرة التالية السنترونتيوم ,(Sr) النيكل ,(Ni) الفناديوم ,(V) الزنك ,(Zn) النحاس ,(Cu) الزركون ,(Zr) والكوبلت (Co) وبمعدلات تراكيز 498,4، 257,6، 67,8، 38,2، 34,3، 25,5 و20,4 على التوالي. كذلك استخدمت في هذه الدراسة بعض النسب مثل $K_2O/Al_2O_3$, $SiO_2$, $Al_2O_3/TiO_2$, Ni/Co, V/Cr, Cu/Zn, Cr/Ni, V/Ni, V/ (V+Ni)كمؤشر للبيئة القديمة، حيث اثبتت هذه الدراسة من خلال قيم ونتائج هذه النسب ان البيئة السائدة للعينات موضوعة البحث هي بيئة اكسدة.

استخدم في حساب النسبة المئوية لمحتوى المواد العضوية (TOC %) في عينات هذه الدراسة اجهزة حديثة بتقنيات ودقة عالية. هذه الحسابات بينت المحتوى الواطئ من المواد العضوية (TOC %) حيث تراوحت قيم معدلاتها من 0,27 % في عموم صخور منطقة البحث، الى 0,18 % في عينات المارل الحمراء، و 0,29 % في عينات المارل غير الحمراء. بينما كانت معدلاتها 0,20 % في عينات الحجر الجيري المارلي الحمراء و 0,36 % في عينات الجيرية غير الحمراء .وعليه فان تكوين الشيرانيش (من أواخر الكامبانيان الى الماستريختي المبكر)، يتألف من مارل والحجر الجيري المارلي، بتطبقات متعاقبة. ذات

محتوى منخفض نسبيا من المواد العضوية واحتواء بعض العناصر النزرة الحساسة للأكسدة تدعم تفسير ظروف المياه القاعية المؤكسدة خلال ترسب هذا التكوين. مما ميز مكوناته المختلفة (الحجر الجيرية الرملي ا والحجر الجيري المارلي الرمادي الفاتح، المحمر، البني، والوردي) بمحتواها العضوي منخفض. ان معدلات قيم نظائر ($C^{13}$) و ($O^{18}$) تشير الى العمليات التحويرية الناتجة عن الدفن، وعليه فان الاصل المنقول ممكن ان يشير الى عمليات الرفع المحلية و تباين في عمليات التجوية في مناطق محاذية لليابسة.

## Introduction

This paper is focues on the Cretaceous Oceanic Red Beds (CORBs) within the Shiranish Formation, their depositional conditions and their importance in rebuilding marine environments as well as their characteristics and the geochemical relationships between CORBs sediments and other sediments that cover all studied sections. The geochemical analyses consisting of chemical analyses (XRF), carbonate content examine ($CaCO_3$wt. %), total organic carbon (TOC %) measurements, carbon isotopes ($C^{13}$) and oxygen isotopes ($O^{18}$).

Late Cretaceous period is characterized by the evolution of global change from anoxic to mostly oxic condition in the oceans which happened after the last universal oceanic anoxic event OAE2 [1]. Therefore, the change from anoxic to oxic bottom ocean environment during the Late Cretaceous was at least hemiglobally if not globally wide. The change to oxic bottom conditions occurred later in the southern Tethys than in the western Tethys, where it began during the late Turonian [2]. Also Late Cretaceous period is characterized by greenhouse condition, changes in sea level, with opening and closing of ocean basins due to the tectonic compression in the Tethyan belt [3, 4].

## Location of studied area

The studied area is situated in the northeastern part of Iraq. It is bounded by longitudes (45° 03´-45° 45´E) and latitudes (34° 55´ -35° 37´ N), and it is extending from Zakho City in the northwestern towards the Darbandikhan Lake in the southeastern. It falls within Sulaimaniya, and Erbil governorates. The study area is located on Sulaimaniya-Erbil road, 70 km West of Sulaimaniya city Figure- 1.

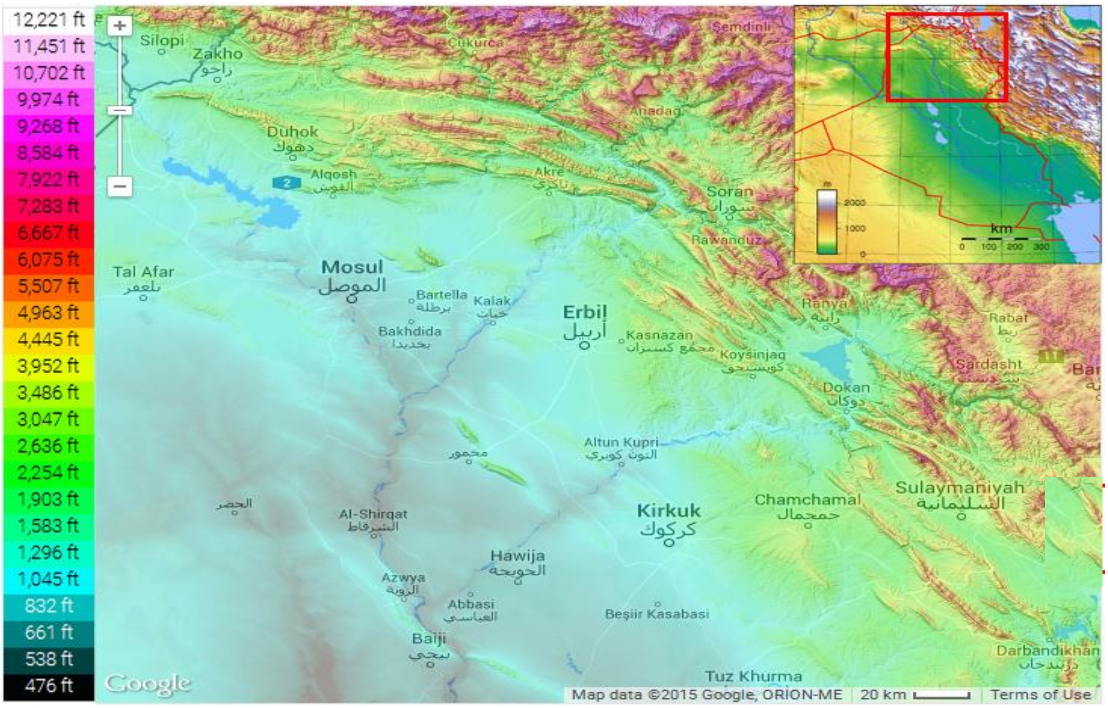


**Figure 1-** Geographical location map of the studied area(www.topomap.com).

## Geological framework

The exposed geological formations in the study area are mostly ranging in age from Middle Eocene age (Pila Spi Formation) to Late Campanian age (Bekhme Formation), and it includes several formations. It is exposed at the Unstable Shelf and is characterized by High Folded Zone and Zagros Suture Zone [5]. It is constituted by long and narrow anticlines; some of them exhibit different types

of faulting. The lithologies of these formations include limestone, dolostone, shale, marl, claystone, siltstone and sandstone. The Zagros Suture Zone consist of different igneous and metamorphic rocks; limestone, shale and mudstone. The Quaternary deposits include river terrace, alluvial fan, slope, valley fill, floodplain, and polygenetic deposits [6, 7] Figure- 2.
Cretaceous period is divided into groups and subgroups (sequences) [5]. In this research the formations that spread in the project area shown in Table- 1.

The Shiranish Formation is first defined by [8] from the High Folded Zone of north Iraq near the village of Shiranish Islam. In the type area, the Shiranish Formation is about 225m thick (9). It is composed of thinly bedded marly limestone at the lower part, blue marl at the upper part with beds of marly limestone. Shiranish Formation is rich in fossils especially Planktonic Foraminifera, and it contains limestone conglomerate in some areas such as Sinjar Area [9].

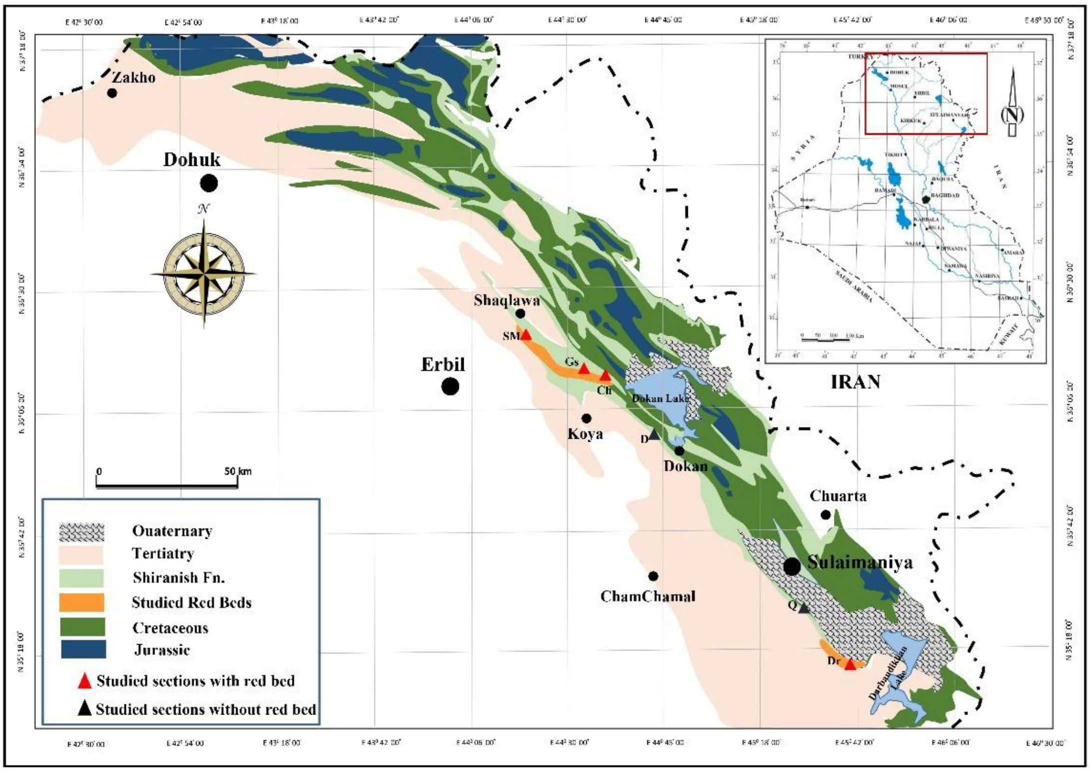


**Figure 2-**Geological map of the studied area showing the six studied sections [6, 7].

**Table 1-**Formations spread in the studied area.

| Sequence | Formation | Period | Age | Main Lithology |
|---|---|---|---|---|
| **Middle – Early Eocene Mid. Palaeocene – Early Eocene** | PilaSpi | Tertiary | Late Eocene | Chalky Limestone |
| | Avanah | | Middle Eocene | Limestone |
| | Gercus | | Middle Eocene | Clastic and Limestone |
| | Kolosh | | Palaeocene | Shale & Sandstone |
| **Late Campanian – Mastrichtian** | Tanjero | Cretaceous | Late Campanian-Maastrichtian | Marl &Marly Limestone |
| | Shiranish | | Late Campanian-Maastrichtian | Marl &Marly Limestone |
| | Bekhme | | Mastrichtian | Limestone |
| | Aqra | | Late Campanian | Limestone |
| | Kometan | | Santonian | Limestone |

**Analytical techniques**

All studied analysis the Vienna University Laboratories in Austria which includes making 24 thin sections (slides) for petrology study, 180 samples for carbonate content (CaCO3 %) examinations, 110 samples for X-Ray Diffraction (XRD) tests, 322 powder and rock samples for X-Ray Fluorescence (XRF) assays to all sections, making 20 thin sections (slides) from GS section for nannofossils study, 75 samples for Total Organic Content (TOC%) checking and 17 samples for stable isotopes C13 and O 18.

X-ray fluorescence (XRF) analysis for major and trace elements was carried out on171 samples (131, 10, 10, 6, 10, 4 samples from the GS, Ch, Sm, Dr, D, Q sections respectively). Bulk geochemistry was measured on powder pill with a sequential wavelength disperse X-ray fluorescence spectrometer (Spectro X-Lab 2000) with Pdanode calibrated to the SARM 46 standard (Pretoria, Republic of SA). The analytical uncertainty is below 5% for major elements and between 5-10% for trace elements. Bulk geochemical investigates depending on the results and XRF data were obtained from Principal Component Analysis (PCA). PCA is a statistical tool used to assess metal behavior in earth materials [10]. The PCA is applied to detect the concealed structure and associations of elements in the data set [11, 12].

Total Organic Content (TOC %) is determined on 75 powder samples, these samples are covered all types of lithology that studied. Using a Leco Multiphase Carbon Determinator LECO RC-412, at 550 °C and an after burner temperature of 800 °C.

Stable carbon and oxygen isotope compositions of bulk samples were determined using a Thermo Finnigan Delta Puls XL mass spectrometer equipped with a Gas- Bench II.

**Geochemistry of Shiranish CORBs**

The chemical data are obtained from various tests and chemical analysis of research samples those points from GS, Ch, Sm, D, Dr and Q sections. The major oxides (wt. %) distributions and its averages presence with distribution in all the sections can be observed through Table-2.

**Table 2-** The major oxides (wt. %) ranges and averages in all studied sections.

| Sections | Details | Al2O3 % | SiO2 % | Fe2O3 % | CaO % | K2O % | TiO2 % | P2O5 % | MnO % | Cr2O3 % |
|---|---|---|---|---|---|---|---|---|---|---|
| GS | Min. | 1.02 | 31.80 | 0.46 | 11.47 | 0.03 | 0.02 | 0.01 | 0.01 | 0.01 |
| | Max. | 15.47 | 41.10 | 7.17 | 50.38 | 3.30 | 0.40 | 0.14 | 0.40 | 0.35 |
| | Averages | **5.21** | **37.34** | **3.97** | **29.11** | **0.70** | **0.25** | **0.07** | **0.15** | **0.05** |
| Ch | Min. | 3.25 | 18.74 | 2.67 | 12.04 | 0.14 | 0.17 | 0.06 | 0.09 | 0.02 |
| | Max. | 11.42 | 26.15 | 4.2 | 36.51 | 0.81 | 0.28 | 0.1 | 0.37 | 0.1 |
| | Averages | **5.75** | **21.71** | **3.5** | **29.09** | **0.51** | **0.23** | **0.09** | **0.2** | **0.04** |
| Sm | Min. | 5.83 | 17.64 | 1.91 | 26.32 | 0.36 | 0.15 | 0.07 | 0.07 | 0.02 |
| | Max. | 2.81 | 22.16 | 4.89 | 39.82 | 1.27 | .055 | 0.12 | 0.12 | 0.08 |
| | Averages | **4.36** | **20.26** | **3.44** | **32.67** | **0.69** | **0.26** | **0.09** | **0.09** | **0.04** |
| D | Min. | 0.77 | 11.15 | 0.37 | 24.05 | 0.12 | 0.12 | 0.09 | 0.01 | 0.002 |
| | Max. | 8.03 | 23.35 | 3.12 | 51.44 | 0.67 | 0.24 | 0.15 | 0.22 | 0.011 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Averages** | **4.80** | **18.58** | **1.64** | **34.85** | **0.39** | **0.18** | **0.12** | **0.08** | **0.007** |
| **Dr** | **Min.** | 0.91 | 11.07 | 0.05 | 29.72 | 0.07 | 0.01 | 0.08 | 0.01 | 0.008 |
| | **Max.** | 3.06 | 17.31 | 2.08 | 36.14 | 0.61 | 0.14 | 0.10 | 0.11 | 0.043 |
| | **Averages** | **1.77** | **12.71** | **0.67** | **34.61** | **0.20** | **0.04** | **0.09** | **0.04** | **0.019** |
| **Q** | **Min.** | 4.99 | 20.58 | 4.21 | 14.77 | 0.01 | 0.34 | 0.06 | 0.06 | 0.018 |
| | **Max.** | 13.70 | 24.42 | 5.75 | 31.42 | 1.23 | 0.43 | 0.09 | 0.12 | 0.044 |
| | **Averages** | **7.52** | **22.59** | **4.90** | **24.29** | **0.82** | **0.38** | **0.08** | **0.10** | **0.026** |

The trace elements (ppm) distribution in studied samples from all the sections with its ranges and its averages presence can be observed through Table-3.

**Table 3-**The trace element (ppm) ranges and averages in all studied sections.

| Sections | Details | Co ppm | Nb ppm | Rb ppm | Sr ppm | U ppm | V ppm | W ppm | Zr ppm | Y ppm | Ce ppm | Cu ppm | Pb ppm | Zn ppm | Ni ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GS | Min | 2.6 | 0.5 | 1.1 | 133.6 | 0.03 | 23.5 | 0 | 1.4 | 6.5 | 7.6 | 16.9 | 0 | 4.7 | 26.8 |
| | Max. | 64.4 | 5.1 | 40.3 | 950 | 0.8 | 123.1 | 6 | 64.8 | 15.1 | 109 | 94.4 | 27.4 | 320.2 | 787.3 |
| | Averages | **22.2** | **3.3** | **16.7** | **478.9** | **0.5** | **69.5** | **0.5** | **27.7** | **9.0** | **11.5** | **35.1** | **1.95** | **41.1** | **274.4** |
| Ch | Min | 12 | 0 | 10 | 211 | 0 | 43 | 0 | 3 | 9 | 10 | 28 | 0 | 31 | 96 |
| | Max. | 205 | 0 | 34 | 676 | 0.2 | 134 | 4 | 58 | 22 | 14 | 47 | 7 | 47 | 551 |
| | Averages | **35.4** | **0** | **19** | **562.5** | **0.02** | **69.4** | **0.4** | **34.9** | **13.7** | **11.3** | **37.8** | **0.7** | **38.8** | **189** |
| Sm | Min | 9 | 0 | 12 | 433 | 0 | 41 | 0 | 20 | 9 | 10 | 28 | 0 | 25 | 89 |
| | Max. | 29 | 3.7 | 33 | 628 | 0.7 | 84 | 0 | 39 | 17 | 16 | 42 | 2.2 | 271 | 350 |
| | Averages | **17.7** | **0.7** | **22.5** | **566** | **0.12** | **60.1** | **0** | **29.8** | **13.1** | **12.1** | **35.5** | **0.34** | **68.3** | **217.6** |
| D | Min | 2 | 0 | 0 | 109 | 0 | 20 | 0 | 32 | 7 | 9 | 16 | 0 | 0 | 0 |
| | Max. | 13 | 0 | 35 | 1197 | 0 | 85 | 0 | 62 | 21 | 12 | 58 | 0.02 | 82 | 112 |
| | Averages | **6.8** | **0** | **23.2** | **760.3** | **0** | **50.1** | **0** | **46.4** | **12.3** | **10** | **41.1** | **0.002** | **31.3** | **46.3** |
| Dr | Min | 1 | 0 | 0 | 115 | 0 | 47 | 0 | 0 | 10 | 8 | 7 | 0 | 0 | 19 |
| | Max. | 111 | 0 | 21 | 198 | 0 | 69 | 0 | 9 | 17 | 15 | 18 | 0 | 0 | 166 |
| | Averages | **3.7** | **0** | **5.7** | **140** | **0** | **52.2** | **0** | **3.3** | **12.3** | **11.2** | **11.2** | **0** | **0** | **57.3** |
| Q | Min | 120 | 0 | 13 | 1081 | 0 | 41 | 0 | 33 | 10 | 7 | 38 | 0 | 45 | 15 |
| | Max. | 253 | 0 | 32 | 5774 | 0 | 92 | 0 | 72 | 22 | 17 | 61 | 10 | 60 | 139 |
| | Averages | **194.8** | **0** | **22.5** | **4027** | **0** | **67.8** | **0** | **47.3** | **14.5** | **11.5** | **47.3** | **2.5** | **51.5** | **89.3** |

The comparison between the occurrences and concentrations of major oxides (wt. %) and trace elements (ppm) their ranges and averages in the red marly limestone and non-red marly limestone beds are listed in Table- 4.

**Table 4-** The ranges and averages of main oxides, major elements (wt. %) and trace elements (ppm) in red and non-red bed marly limestones in all studied sections.

| Oxides (%) | RED MARLY LIMESTONE BEDS | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GS-Section | | | Ch-Section | | | Sm-Section | | | Dr-Section | | | D-Section | | | Q-Section | | |
| | Min. | Max | Ave | Min. | Max | Ave. | Min. | Ma | Ave. | Min. | Max. | Ave. | Min. | Max. | Ave | Min. | Max. | Ave. |
| $Al_2O_3$ | 1.22 | 7.21 | **3.43** | 3.25 | 6.86 | **4.25** | 2.81 | 5.83 | **3.67** | - | - | - | - | - | - | - | - | - |
| $SiO_2$ | 34.60 | 40.60 | **38.62** | 18.74 | 23.94 | **20.49** | 17.64 | 21.93 | **19.34** | - | - | - | - | - | - | - | - | - |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FeO** | 0.41 | 6.05 | **2.74** | 2.40 | 3.13 | **2.88** | 1.72 | 4.20 | **2.65** | - | - | - | - | - | - | - | - | - |
| **$Fe_2O_3$** | 0.46 | 6.72 | **3.05** | 2.67 | 3.48 | **3.20** | 1.91 | 4.67 | **2.94** | - | - | - | - | - | - | - | - | - |
| **CaO** | 16.28 | 46.54 | **34.87** | 30.50 | 36.51 | **33.89** | 26.32 | 39.82 | **35.68** | - | - | - | - | - | - | - | - | - |
| **$K_2O$** | 0.00 | 0.86 | **0.38** | 0.14 | 0.57 | **0.39** | 0.18 | 1.16 | **0.53** | - | - | - | - | - | - | - | - | - |
| **$TiO_2$** | 0.02 | 0.40 | **0.19** | 0.19 | 0.23 | **0.21** | 0.15 | 0.55 | **0.30** | - | - | - | - | - | - | - | - | - |
| **$P_2O_5$** | 0.03 | 0.11 | **0.08** | 0.08 | 0.10 | **0.09** | 0.07 | 0.12 | **0.10** | - | - | - | - | - | - | - | - | - |
| **MnO** | 0.08 | 0.22 | **0.16** | 0.18 | 0.24 | **0.21** | 0.07 | 0.12 | **0.10** | - | - | - | - | - | - | - | - | - |
| **$Cr_2O_3$** | 0.00 | 0.20 | **0.04** | 0.02 | 0.03 | **0.03** | 0.02 | 0.08 | **0.04** | - | - | - | - | - | - | - | - | - |
| **Elements (%)** | | | | | | | | | | | | | | | | | | |
| **Al** | 0.65 | 3.82 | **1.80** | 1.72 | 3.63 | **2.25** | 1.49 | 3.09 | **1.94** | - | - | - | - | - | - | - | - | - |
| **Si** | 16.17 | 19.0 | **18.1** | 8.76 | 11.18 | **9.57** | 8.24 | 10.25 | **9.04** | - | - | - | - | - | - | - | - | - |
| **$Fe^{+2}$** | 0.32 | 4.70 | **2.13** | 1.87 | 2.43 | **2.24** | 1.34 | 3.27 | **2.06** | - | - | - | - | - | - | - | - | - |
| **$Fe^{+3}$** | 0.32 | 4.70 | **2.13** | 1.87 | 2.43 | **2.24** | 1.34 | 3.27 | **2.06** | - | - | - | - | - | - | - | - | - |
| **Ca** | 11.64 | 33.26 | **24.9** | 21.80 | 26.09 | **24.22** | 18.81 | 28.46 | **25.50** | - | - | - | - | - | - | - | - | - |
| **K** | 0.00 | 0.71 | **0.31** | 0.12 | 0.47 | **0.32** | 0.15 | 0.96 | **0.44** | - | - | - | - | - | - | - | - | - |
| **Ti** | 0.01 | 0.24 | **0.11** | 0.11 | 0.14 | **0.13** | 0.09 | 0.33 | **0.18** | - | - | - | - | - | - | - | - | - |
| **P** | 0.01 | 0.05 | **0.03** | 0.03 | 0.04 | **0.04** | 0.03 | 0.05 | **0.04** | - | - | - | - | - | - | - | - | - |
| **Mn** | 0.06 | 0.17 | **0.12** | 0.14 | 0.19 | **0.17** | 0.05 | 0.09 | **0.08** | - | - | - | - | - | - | - | - | - |
| **Cr** | 0.00 | 0.14 | **0.02** | 0.01 | 0.02 | **0.02** | 0.02 | 0.06 | **0.03** | - | - | - | - | - | - | - | - | - |
| **Elements (ppm)** | | | | | | | | | | | | | | | | | | |
| **Co** | 4.80 | 59.8 | **16.0** | 12.00 | 16.0 | **14.2** | 8.9 | 28.6 | **16.7** | - | - | - | - | - | - | - | - | - |
| **Nb** | 2.20 | 3.6 | **3.01** | 1.60 | 5.0 | **2.8** | 0.0 | 3.7 | **1.1** | - | - | - | - | - | - | - | - | - |
| **Rb** | 5.00 | 24.30 | **10.2** | 10.00 | 20.0 | **12.0** | 10.0 | 26.3 | **15.4** | - | - | - | - | - | - | - | - | - |
| **Sr** | 169.30 | 668.6 | **523.9** | 610.4 | 675.5 | **629.7** | 432.4 | 721.0 | **610.7** | - | - | - | - | - | - | - | - | - |
| **U** | 0.00 | 0.80 | **0.49** | 0.20 | 0.6 | **0.44** | 0.0 | 0.7 | **0.2** | - | - | - | - | - | - | - | - | - |
| **V** | 34.20 | 108.5 | **50.1** | 43.00 | 58.0 | **50.8** | 32.3 | 83.8 | **46.62** | - | - | - | - | - | - | - | - | - |
| **W** | 0.00 | 4.0 | **0.17** | 0.00 | 0.0 | **0.0** | 0.0 | 0.1 | **0.02** | - | - | - | - | - | - | - | - | - |
| **Zr** | 7.80 | 34.6 | **20.9** | 3.00 | 44.0 | **25.4** | 20.4 | 30.2 | **24.45** | - | - | - | - | - | - | - | - | - |
| **Y** | 6.50 | 11.0 | **7.74** | 10.00 | 10.0 | **10.0** | 8.5 | 10.3 | **9.67** | - | - | - | - | - | - | - | - | - |
| **Ce** | 10.00 | 11.7 | **10.9** | 10.00 | 10.0 | **10.0** | 10.1 | 11.3 | **10.6** | - | - | - | - | - | - | - | - | - |
| **Cu** | 21.80 | 45.6 | **29.1** | 10.00 | 45.0 | **28.6** | 27.7 | 40.3 | **32.9** | - | - | - | - | - | - | - | - | - |
| **Pb** | 0.10 | 5.8 | **1.30** | 0.10 | 0.4 | **0.22** | 0.0 | 2.2 | **0.57** | - | - | - | - | - | - | - | - | - |
| **Zn** | 12.10 | 63.8 | **30.4** | 30.00 | 39.0 | **34.80** | 20.0 | 50.6 | **36.53** | - | - | - | - | - | - | - | - | - |
| **Ni** | 103.50 | 712.0 | **189.4** | 96.00 | 167.0 | **122.8** | 122.4 | 740.3 | **677.8** | - | - | - | - | - | - | - | - | - |

| **Oxides (%)** | **NON-RED MARLY LIMESTONE BEDS** | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **GS-Section** | | | **Ch-Section** | | | **Sm-Section** | | | **Dr-Section** | | | **D-Section** | | | **Q-Section** | | |
| | **Min.** | **Max.** | **Ave.** | **Min.** | **Max.** | **Ave.** | **Min.** | **Max.** | **Ave.** | **Min.** | **Max.** | **Ave.** | **Min.** | **Max.** | **Ave.** | **Min.** | **Max.** | **Ave.** |
| **$Al_2O_3$** | 2.96 | 5.15 | **3.9** | 3.46 | 3.46 | **3.46** | 5.21 | 5.21 | **5.21** | 0.91 | 3.06 | ***1.77*** | 0.77 | 5.47 | ***3.93*** | 4.220 | 7.180 | **5.463** |
| **$SiO_2$** | 31.80 | 39.2 | **37.8** | 19.7 | 19.65 | **19.65** | 19.27 | 19.27 | **19.27** | 11.07 | 17.31 | ***12.71*** | 11.15 | 21.69 | ***17.72*** | 20.58 | 23.50 | **21.97** |
| **FeO** | 0.54 | 3.92 | **2.9** | 2.66 | 2.66 | **2.66** | 2.48 | 2.48 | **2.48** | 0.04 | 1.87 | ***0.60*** | 0.33 | 2.38 | ***1.27*** | 3.79 | 5.17 | **4.46** |
| **$Fe_2O_3$** | 0.60 | 4.36 | **3.23** | 2.96 | 2.96 | **2.96** | 2.76 | 2.76 | **2.76** | 0.05 | 2.08 | ***0.67*** | 0.37 | 2.650 | ***1.41*** | 4.21 | 5.75 | **4.96** |
| **CaO** | 11.47 | 37.5 | **32.4** | 33.9 | 33.94 | **33.9** | 31.64 | 31.64 | **31.64** | 29.72 | 36.14 | ***34.61*** | 26.04 | 51.44 | ***37.03*** | 22.21 | 31.42 | **27.47** |
| **$K_2O$** | 0.10 | 0.76 | **0.35** | 0.14 | 0.14 | **0.14** | 0.67 | 0.67 | **0.67** | 0.07 | 0.61 | ***0.20*** | 0.12 | 0.76 | ***0.36*** | 1.02 | 1.23 | **1.09** |
| **$TiO_2$** | 0.11 | 0.29 | **0.20** | 0.17 | 0.17 | **0.17** | 0.21 | 0.21 | **0.21** | 0.01 | 0.14 | ***0.04*** | 0.01 | 0.21 | ***0.15*** | 0.34 | 0.43 | **0.38** |
| **$P_2O_5$** | 0.04 | 0.14 | **0.08** | 0.08 | 0.08 | **0.08** | 0.11 | 0.11 | **0.11** | 0.08 | 0.10 | ***0.09*** | 0.09 | 0.15 | ***0.12*** | 0.07 | 0.09 | **0.08** |
| **MnO** | 0.01 | 0.26 | **0.19** | 0.37 | 0.37 | **0.37** | 0.08 | 0.08 | **0.08** | 0.01 | 0.11 | ***0.04*** | 0.00 | 0.21 | ***0.07*** | 0.09 | 0.12 | **0.11** |
| **$Cr_2O_3$** | 0.00 | 0.06 | **0.05** | 0.02 | 0.02 | **0.02** | 0.03 | 0.03 | **0.03** | 0.01 | 0.04 | ***0.02*** | 0.00 | 0.01 | ***0.01*** | 0.02 | 0.02 | **0.02** |
| **Elements (%)** | | | | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Al** | 1.57 | 2.73 | **2.04** | 1.83 | 1.83 | **1.83** | 2.757 | 2.757 | **2.757** | 0.48 | 1.62 | ***0.94*** | 0.41 | 2.89 | ***2.08*** | .23 | 3.80 | **2.89** |
| **Si** | 14.86 | 18.3 | **17.6** | 9.18 | 9.180 | **9.18** | 9.01 | 9.01 | **9.01** | 5.17 | 8.09 | ***5.94*** | 5.21 | 10.13 | ***8.28*** | 9.62 | 10.98 | **10.27** |
| **$Fe^{+2}$** | 0.42 | 3.05 | **2.26** | 2.07 | 2.070 | **2.07** | 1.93 | 1.93 | **1.93** | 0.03 | 1.45 | ***0.47*** | 0.26 | 1.85 | ***0.99*** | 2.95 | 4.02 | **3.47** |
| **$Fe^{+3}$** | 0.42 | 3.05 | **2.26** | 2.07 | 2.070 | **2.07** | 1.93 | 1.93 | **1.93** | 0.03 | 1.45 | ***0.47*** | 0.26 | 1.85 | ***0.99*** | 2.95 | 4.02 | **3.47** |
| **Ca** | 8.20 | 26.8 | **23.15** | 24.3 | 24.26 | **24.3** | 22.61 | 22.61 | **22.61** | 21.24 | 25.83 | ***24.74*** | 18.61 | 36.76 | ***26.46*** | 15.87 | 22.5 | **19.63** |
| **K** | 0.08 | 0.63 | **0.29** | 0.12 | 0.12 | **0.12** | 0.56 | 0.56 | **0.56** | 0.06 | 0.51 | ***0.17*** | 0.10 | 0.63 | ***0.30*** | 0.85 | 1.02 | **0.91** |
| **Ti** | 0.07 | 0.17 | **0.12** | 0.10 | 0.10 | **0.10** | 0.13 | 0.13 | **0.13** | 0.01 | 0.08 | ***0.03*** | 0.01 | 0.13 | ***0.09*** | 0.21 | 0.26 | **0.23** |
| **P** | 0.02 | 0.06 | **0.03** | 0.04 | 0.04 | **0.04** | 0.05 | 0.05 | **0.05** | 0.03 | 0.04 | ***0.04*** | 0.04 | 0.07 | ***0.05*** | 0.03 | 0.04 | **0.04** |
| **Mn** | 0.01 | 0.20 | **0.14** | 0.29 | 0.29 | **0.29** | 0.06 | 0.06 | **0.06** | 0.01 | 0.09 | ***0.03*** | 0.00 | 0.16 | ***0.06*** | 0.07 | 0.09 | **0.08** |
| **Cr** | 0.00 | 0.04 | **0.04** | 0.02 | 0.02 | **0.02** | 0.02 | 0.02 | **0.02** | 0.01 | 0.03 | ***0.01*** | 0.00 | 0.01 | ***0.004*** | 0.012 | 0.014 | **0.013** |
| **Elements (ppm)** | | | | | | | | | | | | | | | | | | |
| **Co** | 3.30 | 24.5 | **20.16** | 0.01 | 0.01 | **0.01** | 10.4 | 10.4 | **10.40** | 1.00 | 11.3 | ***3.87*** | 2.40 | 12.00 | ***6.94*** | 19.20 | 25.40 | **22.30** |
| **Nb** | 2.80 | 3.70 | **3.04** | 0.0 | 0.0 | **0.0** | 0.0 | 0.0 | **0.00** | 0.00 | 0.0 | **0.00** | 0.00 | 0.00 | **0.00** | 0.00 | 0.00 | **0.00** |
| **Rb** | 4.10 | 20.5 | **11.07** | 10.3 | 10.3 | **10.3** | 20.4 | 20.4 | **20.40** | 4.00 | 20.0 | ***10.50*** | 17.50 | 24.10 | ***20.61*** | 20.00 | 30.70 | **23.77** |
| **Sr** | 312.9 | 950.0 | **558.9** | 653.0 | 653.0 | **653.0** | 620.0 | 620.0 | **620.0** | 115.00 | 198.0 | ***140.00*** | 203.00 | 1090.0 | ***33.4*** | 108.00 | 577.0 | **396.0** |
| **U** | 0.20 | 0.80 | **0.51** | 0.00 | 0.0 | **0.0** | 0.0 | 0.0 | **0.00** | 0.00 | 0.0 | **0.00** | 0.00 | 0.00 | **0.00** | 0.00 | 0.00 | **0.00** |
| **V** | 37.2 | 65.7 | **56.3** | 0.01 | 0.01 | **0.01** | 60.3 | 60.3 | **60.3** | 47.60 | 69.0 | ***52.33*** | 21.10 | 78.40 | ***44.81*** | 64.30 | 92.20 | **76.97** |
| **W** | 0.0 | 0.10 | **0.61** | 0.0 | 0.0 | **0.0** | 0.0 | 0.0 | **0.00** | 0.00 | 0.0 | **0.00** | 0.00 | 0.00 | **0.00** | 0.00 | 0.00 | **0.00** |
| **Zr** | 19.1 | 42.3 | **24.8** | 27.4 | 27.4 | **27.4** | 30.5 | 30.5 | **30.5** | 0.00 | 0.0 | **0.00** | 15.40 | 48.70 | ***36.11*** | 0.003 | 0.01 | **0.004** |
| **Y** | 7.4 | 10.5 | **8.19** | 10.4 | 10.4 | **10.4** | 10.2 | 10.2 | **10.2** | 10.20 | 11.1 | ***10.50*** | 10.10 | 10.60 | ***10.36*** | 10.30 | 10.60 | **10.47** |
| **Ce** | 10.1 | 11.7 | **10.8** | 10.0 | 10.0 | **10.0** | 10.2 | 10.2 | **10.2** | 10.20 | 10.8 | **10.47** | 10.00 | 10.90 | **10.41** | 10.30 | 10.60 | **10.43** |
| **Cu** | 23.3 | 40.8 | **31.4** | 39.0 | 39.0 | **39.0** | 39.5 | 39.5 | **39.5** | 10.10 | 10.8 | **10.45** | 10.50 | 45.20 | **36.19** | 38.30 | 51.00 | **42.87** |
| **Pb** | 0.0 | 3.6 | **1.72** | 0.0 | 0.0 | **0.0** | 0.0 | 0.0 | **0.00** | 0.00 | 0.0 | **0.00** | 0.00 | 0.00 | **0.00** | 0.00 | 0.00 | **0.00** |
| **Zn** | 17.4 | 50.2 | **34.8** | 34.4 | 34.4 | **34.4** | 40.0 | 40.0 | **40.0** | 0.00 | 0.0 | **0.00** | 17.70 | 120.90 | **57.1** | 48.60 | 60.60 | **54.13** |
| **Ni** | 103.9 | 250.4 | **266.7** | 133.5 | 133.5 | **133.5** | 140.0 | 140.0 | **140.0** | 10.30 | 166.3 | **49.73** | 11.80 | 75.80 | **38.2** | 96.40 | 139.6 | **114.5** |

The distribution of the major oxides shown that the major oxide CaO has the highest concentration among the oxides determined, with concentration around 34.5 %, which is not much higher than its concentration (around 31.5 %) in the non-red marly limestone samples Table-4. These high concentrations associated with high content of carbonate minerals. This oxide followed by $SiO_2$ with concentration around 26.2 % and 21.6 % for red and non-red marly limestone respectively; these concentrations are compatible with the presence of clay and silicate minerals in these deposits. Third higher concentration is $Al_2O_3$ with concentration around 4.0 % in both red and non-red marly limestone beds, presence of this oxide correlated with abundant of the clay minerals, followed by $Fe_2O_3$ with close concentrations (about 3.0 %) in both red and non-red marly limestone beds Table -4.

As for the distribution of trace elements (ppm), in red marly limestone beds, strontium (Sr) and nickel (Ni) are the two highest concentrations trace elements with average values around 544.7 and 327.0 ppm respectively, followed by vanadium (V), zinc (Zn), copper (Cu), zircon (Zr), cobalt (Co) and rubidium (Rb) with average values around 49.2, 33.6, 30.2, 23.6, 15.7 and 12.5 ppm respectively. The elements cerium (Ce), yttrium (Y) and niobium (Nb) have low concentrations with average values around 10.6, 9.2 and 3.3 ppm respectively, and concentrations that are limited or almost near to nothing for the rest of the minor elements that are examined Table-4.

The distribution of trace elements (ppm) in non-red marly limestone beds, the Table-4 shows that: strontium (Sr) and nickel (Ni) are the two highest concentrations trace elements with average values around 533.6 and 123.8 ppm respectively, followed by vanadium (V), zinc (Zn), copper (Cu), zircon (Zr), rubidium (Rb) and cobalt (Co) with average values about 58.1, 44.1, 37.8, 29.7, 17.6 and 12.8 ppm respectively (Table-4). The elements cerium (Ce), and yttrium (Y) have low concentrations with average values around 10.4, and 10.0 ppm respectively, and concentrations that are limited or almost near to nothing for the rest of the minor elements that are examined Table-4.

In the red and non-red marl beds the comparison between the occurrences and concentrations of major oxides, major elements (wt. %) and trace elements (ppm) their ranges and averages shown in Table-5. The distribution shown that the $SiO_2$ has the highest concentration among the oxides determined, with an average concentration around 36.58 %, which is not much higher than its concentration (around 35.97 %) in the non-red marl samples Table-5. These concentrations are compatible with the presence of clay and silicate minerals in these deposits. This oxide followed by CaO with concentration around 26.17 % and 22.03 % for red and non-red marl samples respectively. These high concentrations associated with high content of carbonate minerals. Other high-oxide concentration is $Al_2O_3$ with concentration around 6.6 % in both red and non-red marl beds, presence of this oxide correlated with abundant of the clay minerals, followed by $Fe_2O_3$ with close concentrations (about 4.1 %) in both red and non-red marly limestone beds Table-5.

In red marl beds the distribution of trace elements (ppm), are documented that the strontium (Sr) and nickel (Ni) are the two highest trace elements concentrations with average values around 404.9 and 284.1 ppm respectively, followed by vanadium (V), copper (Cu), zinc (Zn), zircon (Zr), cobalt (Co), rubidium (Rb) and cerium (Ce), with average values around 82.0, 36.8, 36.3, 29.5, 23.0, 21.7 and 10.6 ppm respectively. The elements yttrium (Y), niobium (Nb) and lead (Pb) have concentrations less than 10 ppm, with average values around 9.2, 3.7 and 2.2 ppm respectively, and concentrations that are limited or almost near to nothing for the rest of the trace elements that are examined Table-5.

The distribution of these trace elements (ppm) in non-red marl beds, the Table-5 shows that: strontium (Sr) and nickel (Ni) are the two highest trace elements concentrations with average values around 571.4 and 323.2 ppm respectively, followed by vanadium (V), zinc (Zn), copper (Cu), rubidium (Rb), zircon (Zr), cobalt (Co) and cerium (Ce) with average values about 85.8, 48.4, 42.1, 26.7, 25.3, 22.5 and 10.5 ppm respectively (Table-5). The elements yttrium (Y), niobium (Nb) and lead (Pb) have concentrations less than 10 ppm, with average values around 13.4, 3.7 and 2.0 ppm respectively, and concentrations that are limited or almost near to nothing for the rest of the trace elements that are examined Table-5.

**Table 5-** Main oxides, major elements (wt. %) and trace elements (ppm) with its ranges and averages in red and non-red bed marl in all studied sections.

| Oxides % | RED MARL BEDS | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GS-Section | | | Ch-Section | | | Sm-Section | | | Dr-Section | | | D-Section | | | Q-Section | | |
| | Min. | Max. | Ave. | Min | Max. | Ave. | Min. | Max. | Ave. | Min. | Max. | Ave. | Min. | Max. | Ave. | Min. | Max. | Ave. |
| $Al_2O_3$ | 5.67 | 7.21 | **6.40** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $SiO_2$ | 35.80 | 37.40 | **36.6** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| FeO | 3.33 | 4.21 | **3.85** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $Fe_2O_3$ | 3.70 | 4.68 | **4.28** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| CaO | 24.20 | 28.27 | **26.2** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $K_2O$ | 0.64 | 1.11 | **0.88** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $TiO_2$ | 0.24 | 0.30 | **0.28** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $P_2O_5$ | 0.07 | 0.08 | **0.08** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| MnO | 0.10 | 0.11 | **0.10** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $Cr_2O_3$ | 0.05 | 0.07 | **0.06** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Elements %** | | | | | | | | | | | | | | | | | | |
| Al | 3.00 | 3.82 | **3.39** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Si | 16.73 | 17.47 | **17.1** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $Fe^{+}$ | 2.59 | 3.27 | **2.99** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $Fe^{+3}$ | 2.59 | 3.27 | **2.99** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Ca | 17.30 | 20.20 | **18.7** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| K | 0.53 | 0.92 | **0.7** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Ti | 0.14 | 0.18 | **0.17** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| P | 0.03 | 0.03 | **0.03** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Mn | 0.08 | 0.09 | **0.08** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Cr | 0.03 | 0.05 | **0.04** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Elements ppm** | | | | | | | | | | | | | | | | | | |
| Co | 18.80 | 25.70 | **23.0** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Nb | 3.50 | 3.80 | **3.70** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Rb | 13.30 | 30.30 | **21.7** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Sr | 378.2 | 442.0 | **404.9** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **U** | 0.30 | 0.60 | **0.50** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **V** | 73.90 | 90.30 | **82.0** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **W** | 0.00 | 0.20 | **0.05** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Zr** | 24.70 | 31.50 | **29.5** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Y** | 7.80 | 10.10 | **9.20** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Ce** | 10.40 | 10.80 | **10.6** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Cu** | 32.70 | 40.90 | **36.8** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Pb** | 0.80 | 3.80 | **2.20** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Zn** | 27.80 | 43.50 | **36.6** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| **Ni** | 247.0 | 302.9 | **284.1** | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | **NON-RED MARL BEDS** | | | | | | | | | | | | | | | | | |
| | **GS-Section** | | | **Ch-Section** | | | **Sm-Section** | | | **Dr-Section** | | | **D-Section** | | | **Q-Section** | | |
| | **Min.** | **Max.** | **Ave.** | **M** | **Max.** | **Ave.** | **Min.** | **Max.** | **Ave.** | **Min.** | **Ma** | **Ave.** | **Min.** | **Max.** | **Ave.** | **Mi** | **Ma** | **Av** |
| **$Al_2O_3$** | 3.32 | 15.47 | **7.42** | 5.87 | 11.42 | **8.19** | 4.91 | 5.39 | **5.15** | - | - | - | 5.78 | 8.03 | **6.82** | - | - | - |
| **$SiO_2$** | 32.70 | 41.10 | **36.0** | 21.8 | 26.15 | **23.8** | 21.39 | 21.61 | **21.50** | - | - | - | 18.12 | 23.35 | **20.6** | - | - | - |
| **FeO** | 1.80 | 6.20 | **4.59** | 3.09 | 3.78 | **3.53** | 3.70 | 3.84 | **3.77** | - | - | - | 1.25 | 2.81 | **1.96** | - | - | - |
| **$Fe_2O_3$** | 2.00 | 6.89 | **5.10** | 3.43 | 4.20 | **3.92** | 4.11 | 4.27 | **4.19** | - | - | - | 1.39 | 3.12 | **2.18** | - | - | - |
| **CaO** | 13.64 | 36.61 | **22.0** | 12.0 | 29.05 | **21.9** | 28.69 | 28.94 | **28.82** | - | - | - | 24.05 | 35.05 | **29.8** | - | - | - |
| **$K_2O$** | 0.00 | 1.57 | **1.01** | 0.58 | 0.81 | **0.74** | 0.71 | 1.11 | **0.91** | - | - | - | 0.21 | 0.67 | **0.45** | - | - | - |
| **$TiO_2$** | 0.18 | 0.39 | **0.32** | 0.27 | 0.28 | **0.28** | 0.25 | 0.28 | **0.27** | - | - | - | 0.19 | 0.24 | **0.22** | - | - | - |
| **$P_2O_5$** | 0.01 | 0.09 | **0.07** | 0.06 | 0.10 | **0.08** | 0.07 | 0.08 | **0.08** | - | - | - | 0.09 | 0.14 | **0.12** | - | - | - |
| **MnO** | 0.08 | 0.34 | **0.12** | 0.09 | 0.16 | **0.13** | 0.08 | 0.10 | **0.09** | - | - | - | 0.01 | 0.22 | **0.10** | - | - | - |
| **$Cr_2O_3$** | 0.03 | 0.35 | **0.07** | 0.03 | 0.10 | **0.05** | 0.06 | 0.07 | **0.07** | - | - | - | 0.007 | 0.01 | **0.01** | - | - | - |
| **Elements %** | | | | | | | | | | | | | | | | | | |
| **Al** | 1.76 | 8.19 | **3.9** | 3.11 | 6.04 | **4.33** | 2.598 | 2.852 | **2.73** | - | - | - | 3.06 | 4.25 | **3.61** | - | - | - |
| **Si** | 15.28 | 19.20 | **16.8** | 10.2 | 12.22 | **11.1** | 9.99 | 10.10 | **10.04** | - | - | - | 8.47 | 10.91 | **9.62** | - | - | - |
| **$Fe^{+2}$** | 1.40 | 4.82 | **3.57** | 2.40 | 2.94 | **2.74** | 2.88 | 2.99 | **2.93** | - | - | - | 0.97 | 2.18 | **1.52** | - | - | - |
| **$Fe^{+3}$** | 1.40 | 4.82 | **3.57** | 2.40 | 2.94 | **2.74** | 2.88 | 2.99 | **2.93** | - | - | - | 0.97 | 2.18 | **1.52** | - | - | - |
| **Ca** | 9.75 | 26.16 | **15.7** | 8.60 | 20.76 | **15.6** | 20.51 | 20.7 | **20.6** | - | - | - | 17.19 | 25.05 | **21.3** | - | - | - |
| **K** | 0.00 | 1.30 | **0.84** | 0.48 | 0.67 | **0.61** | 0.59 | 0.92 | **0.76** | - | - | - | 0.17 | 0.56 | **0.37** | - | - | - |
| **Ti** | 0.11 | 0.23 | **0.19** | 0.16 | 0.17 | **0.16** | 0.15 | 0.16 | **0.16** | - | - | - | 0.14 | 0.14 | **0.14** | - | - | - |
| **P** | 0.00 | 0.04 | **0.03** | 0.03 | 0.04 | **0.04** | 0.07 | 0.08 | **0.08** | - | - | - | 0.04 | 0.06 | **0.05** | - | - | - |
| **Mn** | 0.06 | 0.26 | **0.09** | 0.07 | 0.12 | **0.10** | 0.06 | 0.08 | **0.07** | - | - | - | 0.008 | 0.17 | **0.07** | - | - | - |
| **Cr** | 0.02 | 0.24 | **0.05** | 0.02 | 0.07 | **0.03** | 0.04 | 0.05 | **0.04** | - | - | - | 0.005 | 0.01 | **0.01** | - | - | - |
| **Elements ppm** | | | | | | | | | | | | | | | | | | |
| **Co** | 11.9 | 49.90 | **30.8** | 0.00 | 28.00 | **16.75** | 20.00 | 20.00 | **20.0** | - | - | - | 0.001 | 13.00 | **7.47** | - | - | - |
| **Nb** | 0.50 | 5.10 | **3.7** | 0.00 | 0.00 | **0.00** | 0.00 | 0.00 | **0.00** | - | - | - | 0.00 | 0.00 | **0.00** | - | - | - |
| **Rb** | 6.9 | 40.30 | **24.9** | 23.3 | 34.00 | **28.0** | 20.60 | 30.20 | **25.4** | - | - | - | 24.60 | 30.00 | **28.3** | - | - | - |
| **Sr** | 133.6 | 707.7 | **418.5** | 252. | 605.0 | **455.5** | 450.0 | 540.0 | **495.0** | - | - | - | 665.0 | 1197.0 | **916.7** | - | - | - |
| **U** | 0.03 | 0.80 | **0.45** | 0.00 | 0.20 | **0.05** | 0.00 | 0.00 | **0.00** | - | - | - | 0.00 | 0.00 | **0.00** | - | - | - |
| **V** | 41.6 | 123.1 | **94.1** | 76.4 | 134.1 | **106.9** | 70.00 | 70.60 | **70.3** | - | - | - | 43.00 | 85.80 | **63.8** | - | - | - |
| **W** | 0.00 | 6.00 | **0.89** | 0.00 | 3.60 | **0.90** | 0.00 | 0.00 | **0.00** | - | - | - | 0.00 | 0.00 | **0.00** | - | - | - |
| **Zr** | 2.80 | 64.80 | **36.1** | 0.00 | 58.1 | **14.5** | 0.003 | 0.003 | **0.003** | - | - | - | 0.005 | 0.006 | **0.005** | - | - | - |
| **Y** | 6.50 | 15.10 | **10.5** | 10.4 | 21.6 | **15.7** | 10.30 | 10.50 | **10.4** | - | - | - | 10.30 | 20.40 | **16.9** | - | - | - |
| **Ce** | 7.60 | 11.30 | **10.6** | 10.1 | 11.4 | **10.53** | 10.30 | 10.70 | **10.5** | - | - | - | 10.20 | 10.40 | **10.4** | - | - | - |
| **Cu** | 20.1 | 57.70 | **40.9** | 39.3 | 47.0 | **42.0** | 30.70 | 40.30 | **35.5** | - | - | - | 40.00 | 58.00 | **50.0** | - | - | - |
| **Pb** | 0.00 | 7.90 | **2.22** | 0.00 | 7.30 | **1.83** | 0.00 | 0.00 | **0.0** | - | - | - | *0.00* | 0.001 | **0.00** | - | - | - |
| **Zn** | 10.20 | 83.90 | **46.9** | 43.6 | 47.3 | **44.6** | 50.00 | 50.20 | **50.1** | - | - | - | 49.60 | 56.80 | **52.1** | - | - | - |
| **Ni** | 154.5 | 791.7 | **383.7** | 157. | 550.2 | **285.9** | 300.0 | 300.2 | **300.1** | - | - | - | 20.50 | 112.4 | **63.1** | - | - | - |

These results were compared with the standard and identical results for its presence in the shale, limestone and deep sea carbonate according to [13-15] Table -6.

**Table 6-** Comparison of the present red bed results with standard results.

| Major Oxides (%) | This Study Red – Bed Sections | | | | (Wedepohl, 1961 1971 ,1991) & (Brumsack,2006) |
|---|---|---|---|---|---|
| | Carbonate | | | Marl | Average shale |
| | GS | Ch | Sm | GS | |
| $Al_2O_3$ | 3.42 | 4.25 | 3.77 | 6.40 | 16.7 |
| CaO | 34.87 | 33.89 | 35.04 | 26.17 | 2.20 |
| $Cr_2O_3$ | 0.04 | 0.03 | 0.04 | 0.06 | nd |
| $Fe_2O_3$ | 3.05 | 3.20 | 3.05 | 4.28 | 6.90 |
| $K_2O$ | 0.38 | 0.39 | 0.53 | 0.88 | 3.60 |
| MnO | 0.16 | 0.21 | 0.10 | 0.10 | nd |
| $P_2O_5$ | 0.08 | 0.09 | 0.09 | 0.08 | nd |
| $SiO_2$ | 38.62 | 20.49 | 19.69 | 36.58 | 58.9 |
| $TiO_2$ | 0.19 | 0.21 | 0.26 | 0.28 | 0.78 |
| | This Study Red – Bed Sections | | | | (Wedepohl, 1961 1971 ,1991) & (Brumsack,2006) |
| | Carbonate | | | Marl | Average shale |
| Ratios | GS | Ch | Sm | GS | |
| $SiO_2/Al_2O_3$ | 11.28 | 4.82 | 5.22 | 5.71 | 26.95 |
| $K_2O/Al_2O_3$ | 0.11 | 0.09 | 0.14 | 0.14 | 0.04 |
| $Al_2O_3/TiO_2$ | 17.99 | 20.07 | 14.60 | 22.86 | 11.96 |
| Ni/Co | 11.84 | 8.65 | 26.18 | 12.35 | 3.57 |
| V/Cr | 0.25 | 0.25 | 0.16 | 0.20 | 1.50 |

| Minor Elements (ppm) | This Study Red – Bed Sections | | | | (Wedepohl, 1961 1971 ,1991) & (Brumsack,2006) | |
|---|---|---|---|---|---|---|
| | Carbonate | | | Marl | Average shale | Average carbonate |
| | GS | Ch | Sm | GS | | |
| Ni | 189.4 | 122.8 | 447.3 | 284.10 | 68 | 20 |
| Cu | 29.10 | 28.60 | 32.58 | 36.75 | 45 | 4 |
| Zn | 30.35 | 34.80 | 35.78 | 36.60 | 95 | 20 |
| Rb | 10.24 | 12.00 | 15.35 | 21.7 | 140 | 3 |
| Sr | 523.9 | 629.7 | 592.2 | 404.95 | 300 | 610 |
| Y | 7.74 | 10.00 | 9.65 | 9.20 | 26 | 30 |
| Zr | 20.87 | 25.40 | 24.35 | 29.53 | 160 | 19 |
| Nb | 3.01 | 2.80 | 1.10 | 3.70 | 11 | 0.3 |
| Pb | 1.30 | 0.22 | 0.57 | 2.20 | 22 | 9 |
| U | 0.49 | 0.44 | 0.20 | 0.50 | 3.7 | 2.2 |
| Ti | 1700 | 1300 | 2600 | 1700 | 4600 | 400 |
| V | 50.05 | 50.80 | 48.02 | 81.95 | 130 | 20 |
| Cr | 680 | 200 | 400 | 400 | 90 | 11 |
| Co | 15.99 | 14.20 | 17.08 | 23 | 19 | 0.1 |
| Ce | 10.87 | 10.00 | 10.45 | 10.58 | 59 | 11.5 |

Generally there are clear differences between the results of this study and average shale values. In this study, there are obvious increases of the CaO, Ni, Cr, Sr, $K_2O/Al_2O_3$ and $Al_2O_3/TiO_2$ values than in the standard values, because most contains higher content of calcium carbonate. On the contrary, the values of $Al_2O_3$, $SiO_2$, $K_2O$, Zn, Zr, Rb, Pb, U, V, $SiO_2/Al_2O_3$ and V/Cr are higher in the average shale than in this study results. However other values when compared between the average shale and the results of this study are similar or close to each other (Table-6). Concerning minor elements, is higher in Cu, Co, Ni, Pb and U which is most likely caused by the occurrence of ferromanganese nodules in some parts of the profile.

The Figures- (3, 4) explain the positive and negative linear relationship between aluminum (Al) against some main elements in red and non-red bed samples in the studied area. It show a good positive linear relations between Al and the following major elements in both red and non-red $Fe^{+2}$, $Fe^{+3}$, K and Ti Figure-(3, 4). Also it shows reverse linear relations between Al and Ca and P, and without any relation between Al and Mn element Figure-(3, 4).

Also in both red and non-red bed samples the Figures -(5, 6) give details to the positive and reverse linear relations. It has been plot diagrams of the relationship between aluminum (Al) against some minor elements in red and non-red bed samples in the studied area. It show a good positive linear relations between Al and the following major elements in both red and non-red Co, Cr, Cu, Ni, Nb, Y and Zr Figure-(5, 6). Also it shows any relation between Al and the following minor elements Pb, U, Sr and W element Figure-(5, 6).

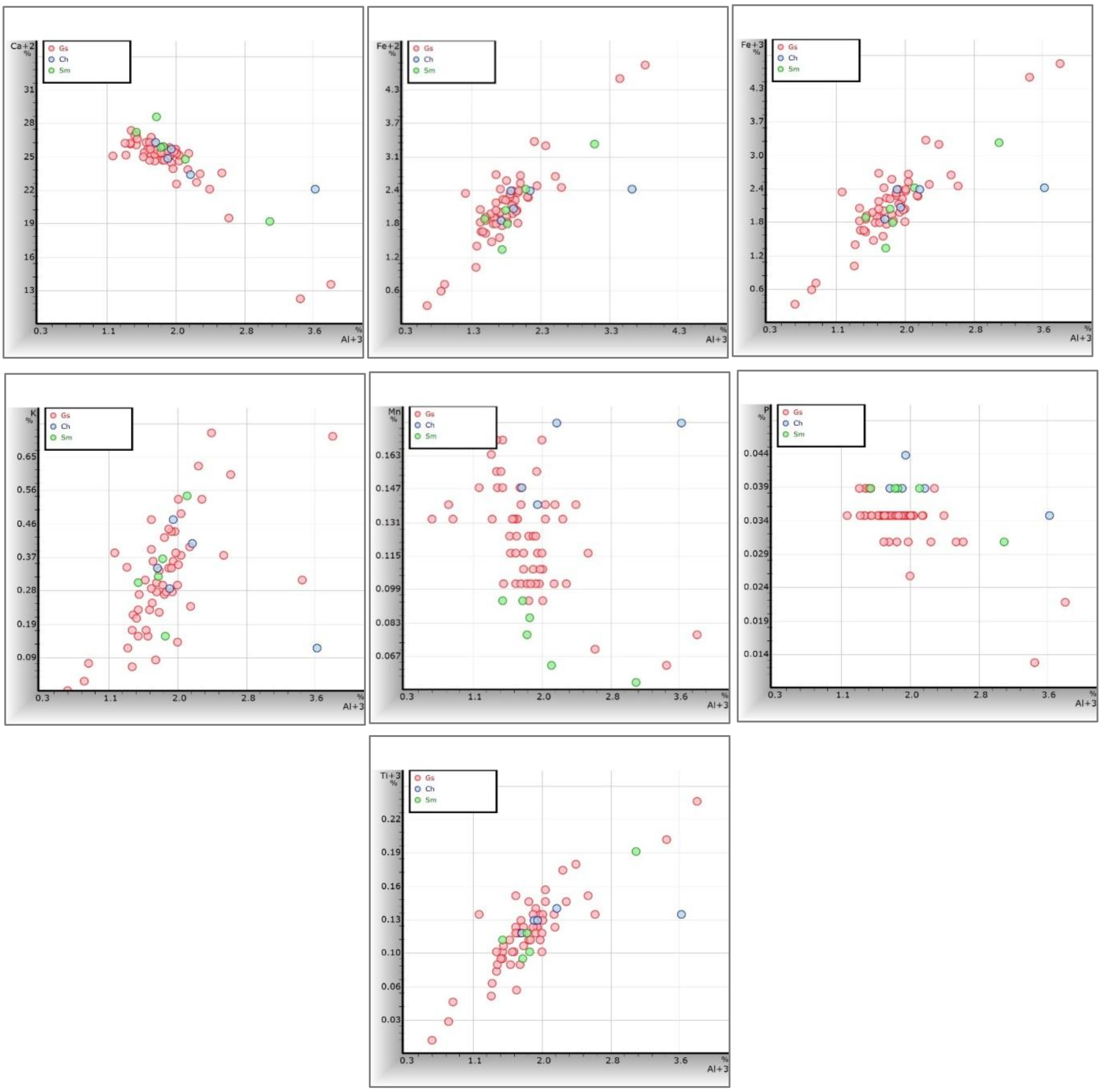


**Figure 3-**Major elements wt. % (Ca, $Fe^{+2}$, $Fe^{+3}$, K, Mn, P, and Ti) vs. Al; average values for red beds samples in the studied area

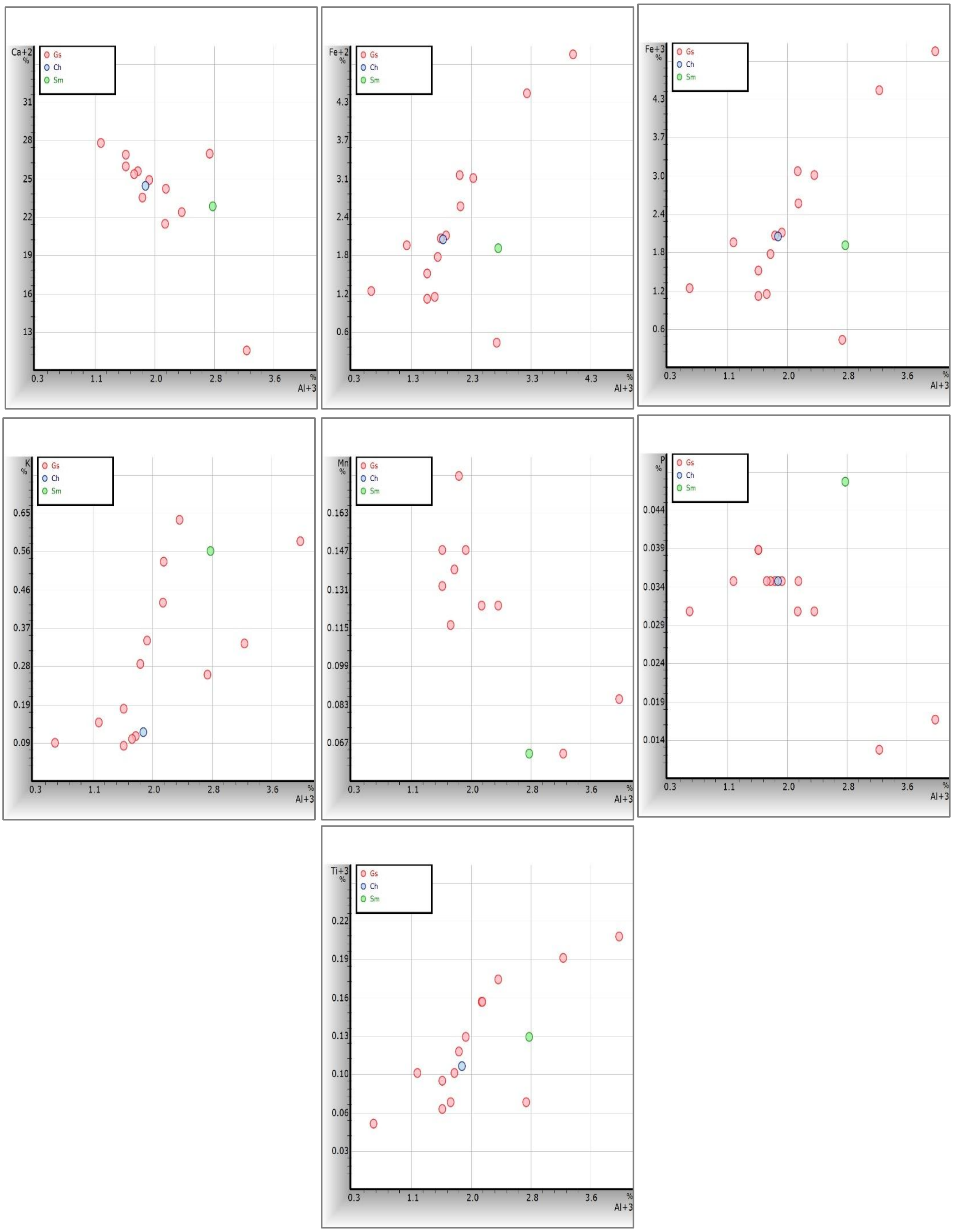


**Figure 4-** Major elements wt. % (Ca, Fe+2, Fe+3, K, Mn, P, and Ti) vs. Al; average values for non- red beds samples in the studied area.

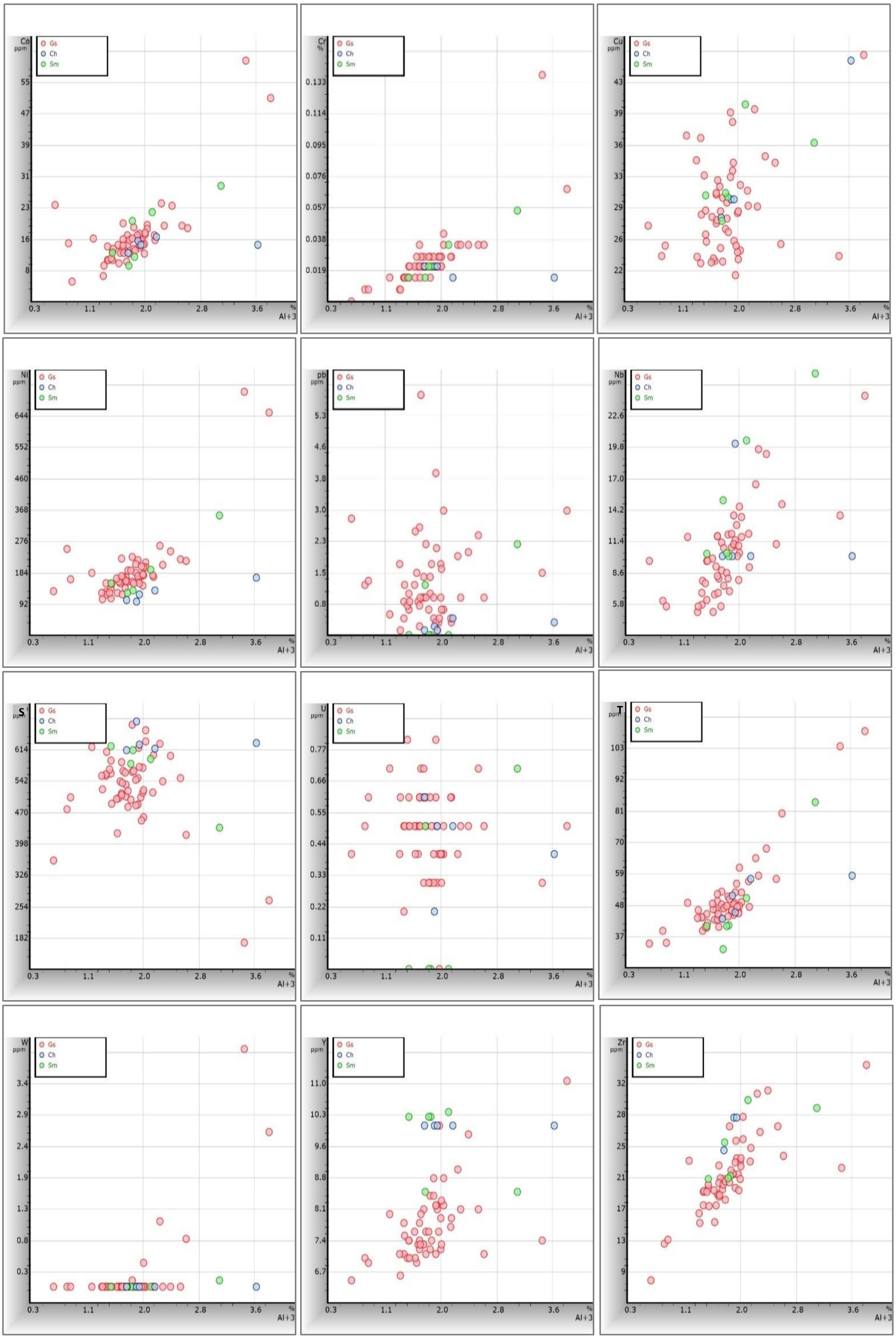

**Figure 5-** Trace elements (Co, Cr, Cu, Ni, Pb, Nb, Sr, U, W, Y, and Zr) vs. Al; average values for red beds samples in the studied area.

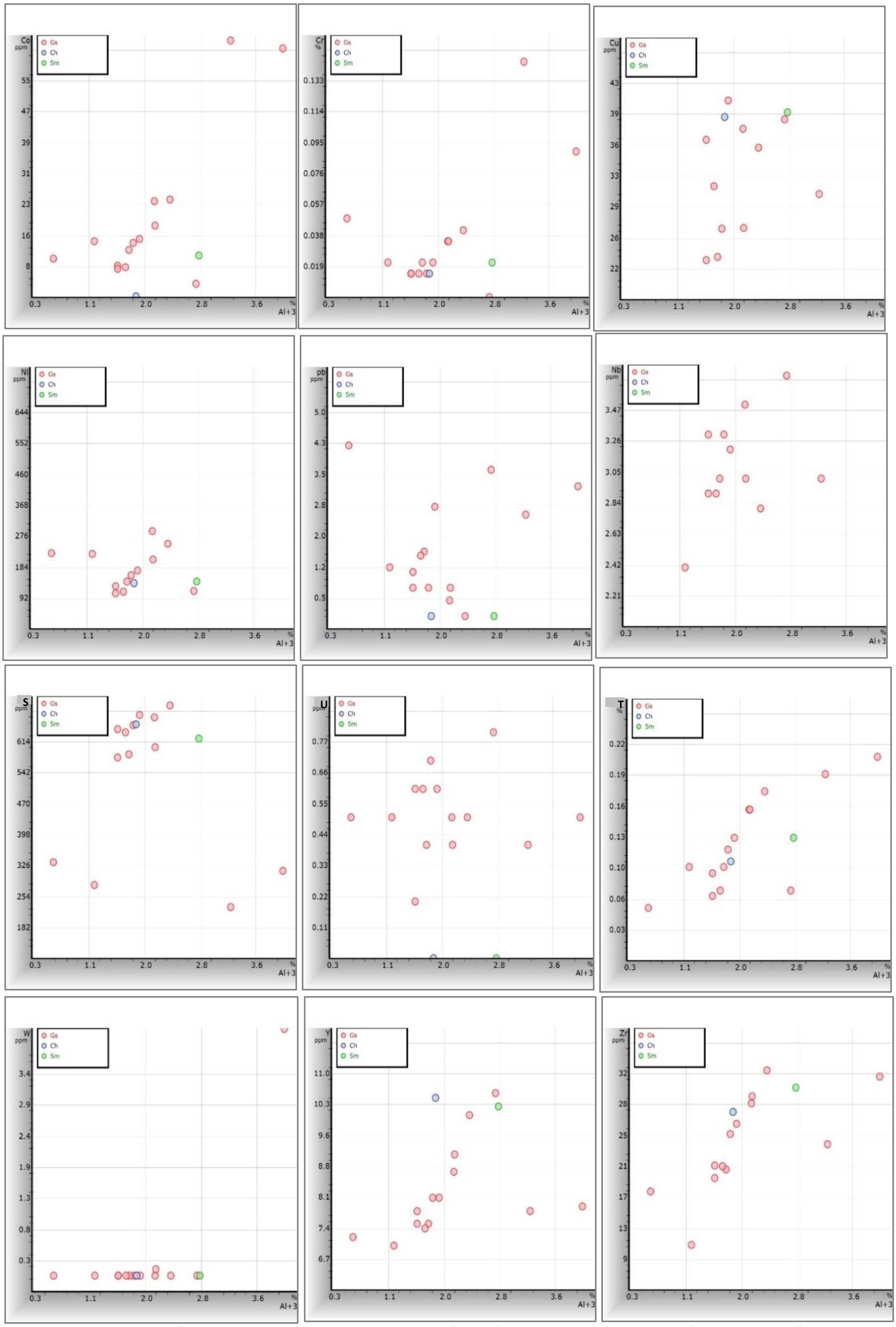


**Figure 6-** Trace elements (Co, Cr, Cu, Ni, Pb, Nb, Sr, U, W, Y, and Zr) vs. Al; average values for non-red beds samples in the studied area.

**Distribution of major and trace elements**

The minimum, maximum, and average concentrations of major oxides (wt. %), and minor elements (ppm) in all sections for the different types of rocks are listed in Table-7. The dominance of $SiO_2$ and CaO oxides on the rest oxides, which have been examined, $SiO_2$ % and CaO % are the higher concentrations they have values around 33.1 and 29.6 respectively in all studied samples, followed by $Al_2O_3$, $Fe_2O_3$ and FeO with average concentration values around 5.1, 3.7 and 3.3 respectively, whereas other tested oxides have averages concentration values less than 1.0 % ($K_2O$=0.61, $TiO_2$=0.24, MnO=0.13, $P_2O_5$=0.08 and $Cr_2O_3$=0.05 %). Also the Table-7 illustrates the concentrations of the minor elements (ppm) in same samples, it shows Sr and Ni elements have the two highest concentrations, they around 498.4 and 257.6 ppm, followed by V, Zn, Cu, Zr, Co, Rb and Ce with average values of 67.8, 38.2, 34.3, 25.5, 20.4, 17.4 and 10.7 ppm respectively, whereas other tested oxides have averages concentration values less than 10 ppm (Y=9.53, Nb=2.68, W=0.42 and U=0.39 ppm) Table-7.

**Table 7-**Major oxides (wt. %) and trace elements (ppm) with its ranges and averages in all studied sections.

| | Major Oxides (Wt. %) In All Sections | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Al2O3 % | SiO2 % | FeO % | Fe2O3 % | CaO % | K2O % | TiO2 % | P2O5 % | MnO % | Cr2O3 % |
| **Average** | **5.10** | **33.10** | **3.30** | **3.67** | **29.63** | **0.62** | **0.24** | **0.08** | **0.13** | **0.05** |
| **Minimum** | 0.77 | 11.07 | 0.04 | 0.05 | 11.47 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 |
| **Maximum** | 15.47 | 41.10 | 6.45 | 7.17 | 51.44 | 1.57 | 0.55 | 0.15 | 0.40 | 0.35 |

| | Major Elements (Wt. %) In All Sections | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Al % | Si % | $Fe^{+2}$ % | $Fe^{+3}$ % | Ca % | K % | Ti % | P % | Mn % | Cr % |
| **Average** | **2.69** | **15.47** | **2.57** | **2.57** | **21.18** | **0.52** | **0.14** | **0.03** | **0.10** | **0.03** |
| **Minimum** | 0.41 | **5.17** | **0.03** | **0.03** | **8.20** | **0.00** | **0.01** | **0.00** | 0.00 | 0.00 |
| **Maximum** | 8.19 | **19.20** | **5.01** | **5.01** | **36.76** | **1.30** | **0.33** | **0.07** | 0.31 | 0.24 |

| | Trace Elements (ppm) In All Sections | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Co ppm | Nb ppm | Rb ppm | Sr ppm | U ppm | V ppm | W ppm | Zr ppm | Y ppm | Ce ppm | Cu ppm | Pb ppm | Zn ppm | Ni ppm |
| **Average** | **20.4** | **2.68** | **17.4** | **498.4** | **0.39** | **67.8** | **0.42** | **25.5** | **9.53** | **10.7** | **34.3** | **1.43** | **38.2** | **257.6** |
| **Minimum** | 0.0 | 0.00 | 3.6 | 108.0 | 0.00 | 0.01 | 0.00 | 0.0 | 6.50 | 7.6 | 10.0 | 0.00 | 0.0 | 10.3 |
| **Maximum** | 64.4 | 5.10 | 40.3 | 1197.0 | 0.80 | 134.1 | 6.00 | 64.8 | 21.60 | 11.7 | 58.0 | 7.90 | 120.9 | 1740.3 |

The values of most redox-sensitive trace elemental abundances and geochemical ratios presented here show a systematic, decreasing trend along a depth. Samples from the studied interval (GS-section) are significantly enriched in the redox-sensitive trace elements such as U, V, Co, Cr and geochemical ratios Figure- 7.

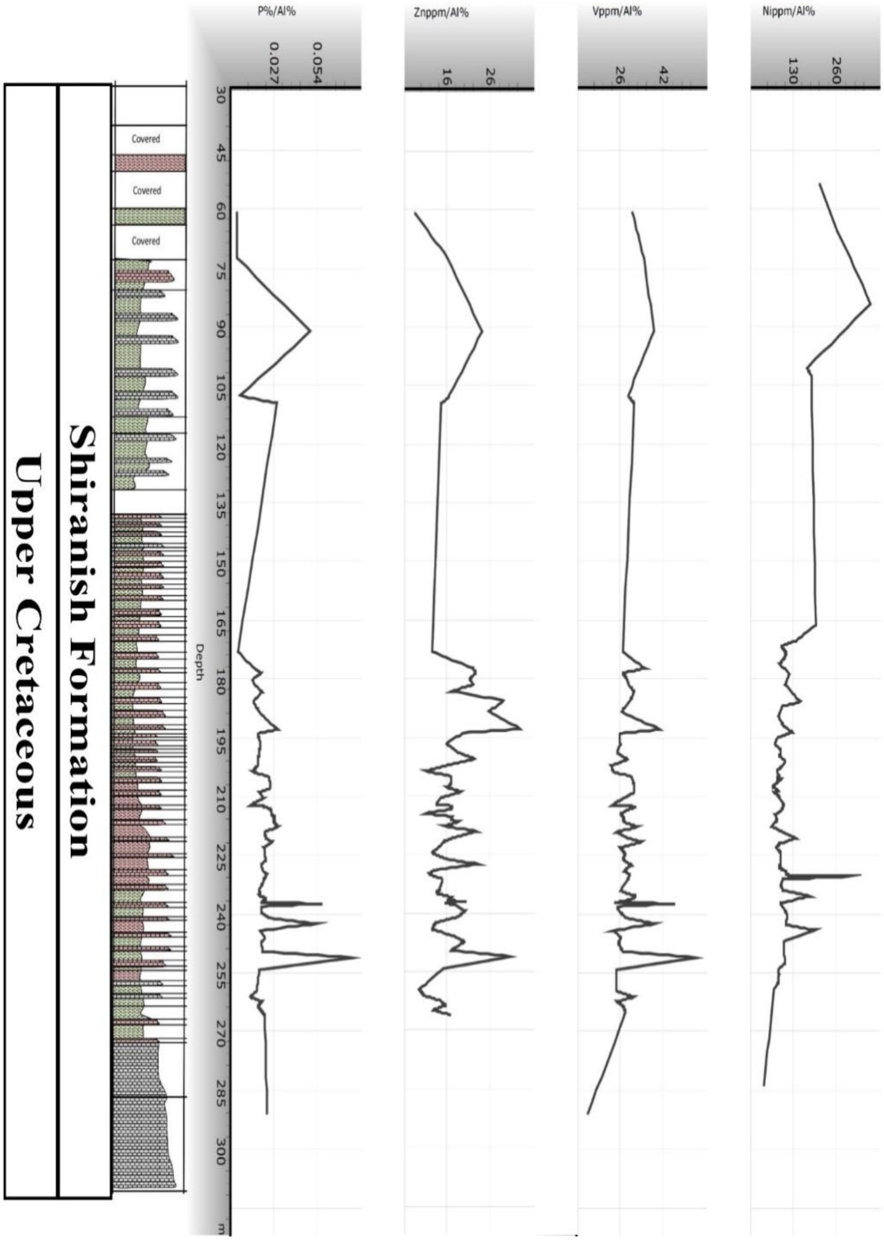


**Figure 7-** lithological section showing ratio elements for the Gs Section.

**Paleo-oxic conditions and trace elements enrichments**

Ni/Co, V/Cr, Cu/Zn, V/ (V+Ni), and Cr/Ni ratios have been used to evaluate paleoredox conditions [16, 17]. V/Cr and Ni/Co ratios have been used as an indicator of oxygen levels, and both Ni and Co occur in pyrite [18, 19].

The V/Cr ratio is used as an index of paleo oxygenation [19-21]. The incorporation of Cr is probably in the detrital fraction of sediments and it is possible that it substitutes for Al in the clay structure. Vanadium (V) may be bound to organic matter by the incorporation of $V^{+4}$ is generally found in sediments deposited in reducing environments. The V/Cr ratios of < 2 to infer to more oxidizing conditions, 2.0–4.25 for dysoxic conditions, and >4.25 for suboxic to anoxic conditions [17].

Generally, the results of Cr/Ni ratios values of all studied samples in all sections are compatible and very identical. Cr/Ni ratios values in the present study are with ranges that suggested the studied rock samples in the present study belong and under more oxidizing conditions. These data supports the evidence and ideas that adopt the presence of volcanic activity.

The high average concentrations of both elements in studied sediments, Cr around 234 ppm in marly limestone and 443 ppm in marl, the Ni average concentrations around 190 ppm in marly limestone and 335 ppm in marl, with strong positive correlation coefficient between both elements (Cr and Ni) with Co (Cr=0.88 very strong and Ni=0.49 strong). These relationships indicate a significant contribution of detrital from mafic and ultra-mafic igneous source rocks.

The Cross plot of vanadium versus nickel Figure-8, from GS and Ch red bed samples from studied area showing that the sediments had mixed marine and terrigenous source input and were deposited under oxic to dyoxic [22].

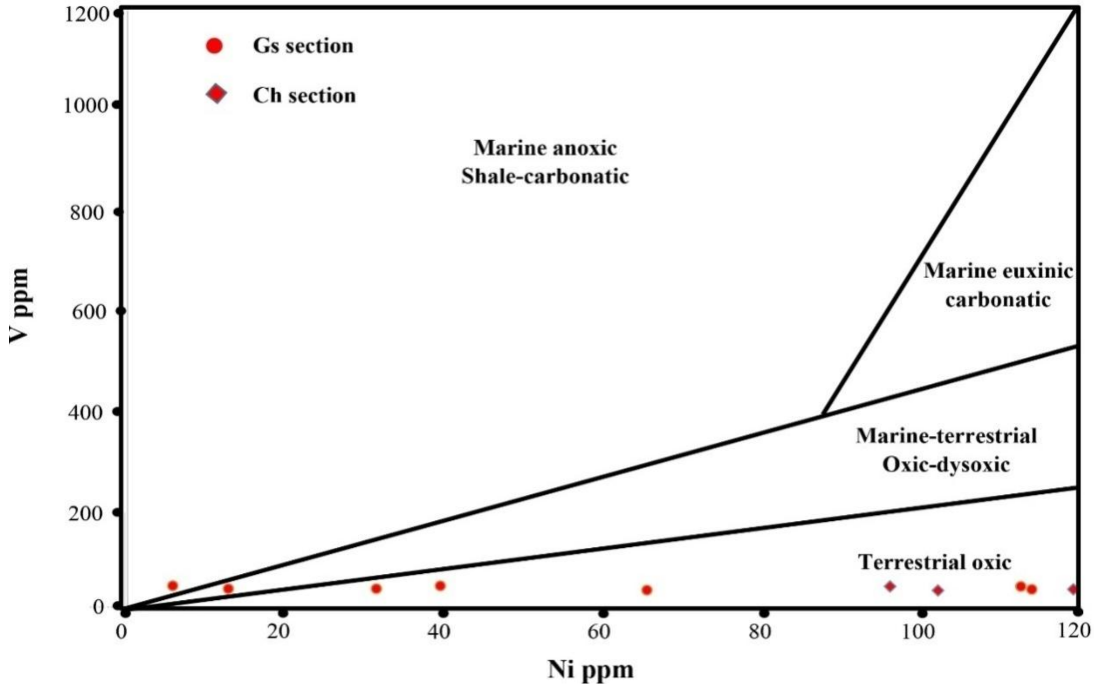


**Figure 8-** Cross plot of vanadium versus nickel of GS and Ch red beds samples from studied area [22].

**Total organic content measurements (TOC %)**

Total organic carbon (TOC %) was determined on powder samples using a Leco Multiphase Carbon Determinator LECO RC-412 at 550 °C and an afterburner temperature of 800 °C.

In this study the TOC % for all beds range from 0.10 to 1.13 with average value 0.27, for only marl and only marly limestone beds in all studied sections range from 0.16 to 0.92 and from 0.10 to 1.13 with average values of 0.27 and 0.26 respectively Table-8. In red and non-red marl bed samples the TOC % range from 0.17 to 0.18 and from 0.16 to 0.92 with average values of 0.18 and 0.29 respectively Table-8. Whereas the TOC % range from 0.12 to 0.28 and from 0.15 to 1.13, with average values of 0.20 and 0.36 in red and non-red marly limestone bed samples respectively Table- 8.

**Table 8-** Total Organic Carbone (TOC %) (ranges & averages) of all beds in all studied sections.

| Type of Lithology | Total Organic Carbone (TOC %) of All Bed Types In All Studied Sections | | |
|---|---|---|---|
| | Minimum | Maximum | Average |
| All Beds | 0.10 | 1.13 | 0.27 |
| Only Marl in All Sections | 0.16 | 0.92 | 0.27 |
| Only Marly Limestone in All Sections | 0.10 | 1.13 | 0.26 |
| Only Red Marl Beds | 0.17 | 0.18 | 0.18 |
| Only Non-Red Marl Beds | 0.16 | 0.92 | 0.29 |
| Only Red Marly Limestone Beds | 0.12 | 0.28 | 0.20 |
| Only Non- Red Marly Limestone Beds | 0.15 | 1.13 | 0.36 |

All ranges and averages in each section of the present study, are observed and noted in Table-8. In the present study the TOC % content in red beds (Shiranish CORBs beds) less than its presence in non-red beds Tables-(8, 9).

**Table 9-** Total Organic Carbone (TOC %) its ranges with its averages of red and non-red marl and marly limestone studied sections.

| Sections | Total Organic Carbone (TOC %) of All Bed Types In All Studied Sections | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Red Marl | | | Non-Red Marl | | | Red Marly Limestone | | | Non- Red Marly Limestone | | |
| | Minimum | Maximum | Average | Minimum | Maximum | Average | Minimum | Maximum | Average | Minimum | Maximum | Average |
| GS | 0.17 | 0.18 | **0.18** | 0.18 | 0.34 | **0.24** | 0.12 | 0.24 | **0.18** | 0.10 | 0.27 | **0.21** |
| Ch | - | - | - | 0.16 | 0.20 | **0.18** | 0.18 | 0.26 | **0.22** | - | - | - |
| Sm | - | - | - | 0.24 | 0.24 | **0.24** | 0.19 | 0.28 | **0.24** | 0.22 | 0.22 | **0.22** |
| Dr | - | - | - | - | - | - | - | - | - | 0.18 | 0.35 | **0.27** |
| D | - | - | - | 0.32 | 0.92 | **0.66** | - | - | - | 0.18 | 1.13 | **0.60** |
| Q | - | - | - | - | - | - | - | - | - | 0.15 | 0.20 | **0.18** |

The low organic carbon content in all profiles indicates a rapid recycling of TOC in oxic water with either an almost entire respiration of organic carbon in the water column and during early diagenesis or a primary oligotrophic environment. The Table-10 shows the distribution of TOC % due to its lithology Table-10.

**Table 10-**TOC % with lithology types of all bed in all studied sections.

| Carbonate content (wt. %) measurement with type of lithology | | |
|---|---|---|
| **Sections** | No. of Samples | Type of lithology |
| **GS** | 60 | Red Marly Limestone |
| | 80 | Non-Red Marly Limestone |
| **Ch** | 5 | Red Marly Limestone |
| | 5 | Non-Red Marly Limestone |
| **Sm** | 7 | Red Marly Limestone |
| | 3 | Non-Red Marly Limestone |
| **D** | 10 | Non-Red Marly Limestone |
| **Dr** | 6 | Non-Red Marly Limestone |
| **Q** | 4 | Non-Red Marly Limestone |

Through the results above, the highest content of total organic content (TOC %) presence in marly limestone rock (TOC %=1.13), whereas the higher value of TOC % in marl rock samples is 0.92 % Table-8. Using the relevant ratios with TOC% such as V/Ni ratio Tables-(11, 12 and 13), when V/Ni ratio greater than 3 indicates that the TOC % was deposited in a reducing environment, and when V/Ni less than 3 suggested the TOC% was deposited in oxidizing condition [22].

Therefore, in this study, all results for all studied samples that covered all studied sections, TOC % values less than 1, which suggest an oxidizing environment for the rock samples in the present study.

**Table 11-** Major Oxides (wt. %), trace elements (ppm) ratios in all (marl and marly limestone) beds in all studied sections.

| | Major Oxides (Wt. %),Trace Elements (ppm) Ratios In All Marl Beds In All Sections | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K_2O/Al_2O_3$ | $SiO_2/Al_2O_3$ | $Al_2O_3/TiO_2$ | Ni/Co | V/Cr | Cr/Ni | Cu/Zn | V/Ni | V/V+Ni |
| **Minimum** | 0.04 | 2.29 | 11.33 | 8.65 | 0.09 | 0.61 | 0.55 | 0.15 | 0.13 |
| **Maximum** | 0.26 | 11.68 | 23.48 | 27.17 | 1.30 | 3.63 | 2.25 | 2.10 | 0.48 |
| **Average** | **0.14** | **5.11** | **19.65** | **12.65** | **0.28** | **1.23** | **0.92** | **0.32** | **0.22** |
| **Average Shale** | **0.04** | **26.95** | **11.96** | **3.57** | **1.50** | **1.32** | **0.47** | **1.91** | **0.66** |
| | **Major Oxides (Wt. %),Trace Elements (ppm) Ratios In All Marly Limestone Beds In All Sections** | | | | | | | | |
| | **$K_2O/Al_2O_3$** | **$SiO_2/Al_2O_3$** | **$Al_2O_3/TiO_2$** | **Ni/Co** | **V/Cr** | **Cr/Ni** | **Cu/Zn** | **V/Ni** | **V/V+Ni** |
| **Minimum** | 0.02 | 3.27 | 7.13 | 3.22 | 0.05 | 0.12 | 0.26 | 0.02 | 0.05 |
| **Maximum** | 0.24 | 17.39 | 40.50 | 22.90 | 1.54 | 4.70 | 2.12 | 4.85 | 0.66 |
| **Average** | **0.11** | **9.66** | **19.37** | **11.32** | **0.34** | **1.37** | **0.99** | **0.50** | **0.26** |
| **Average Shale** | **0.04** | **26.95** | **11.96** | **3.57** | **1.50** | **1.32** | **0.47** | **1.91** | **0.66** |

**Table 12-** Major oxides (wt. %), trace elements (ppm) ratios in red and non-red marl beds in all studied sections.

| | Major Oxides (Wt. %),Trace Elements (ppm) Ratios In Red Beds Marl In All Sections | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K_2O/Al_2O_3$ | $SiO_2/Al_2O_3$ | $Al_2O_3/TiO_2$ | Ni/Co | V/Cr | Cr/Ni | Cu/Zn | V/Ni | V/V+Ni |
| **Minimum** | 0.11 | 4.97 | 13.63 | 11.09 | 0.18 | 1.20 | 0.87 | **0.25** | 0.22 |
| **Maximum** | 0.17 | 6.37 | 21.80 | 13.34 | 0.25 | 1.58 | 1.04 | **0.31** | 0.24 |
| ***Average*** | **0.14** | **5.76** | **17.95** | **12.43** | **0.21** | **1.38** | **0.95** | **0.29** | **0.23** |
| **Average Shale** | **0.04** | **26.95** | **11.96** | **3.57** | **1.50** | **1.32** | **0.47** | **1.91** | **0.66** |
| | **Major Oxides (Wt. %),Trace Elements (ppm) Ratios In Non-Red Beds Marl In All Sections** | | | | | | | | |
| | **$K_2O/Al_2O_3$** | **$SiO_2/Al_2O_3$** | **$Al_2O_3/TiO_2$** | **Ni/Co** | **V/Cr** | **Cr/Ni** | **Cu/Zn** | **V/Ni** | **V/V+Ni** |
| **Minimum** | 0.00 | 2.29 | 11.33 | 8.65 | 0.04 | 0.61 | 0.55 | 0.15 | 0.13 |
| **Maximum** | 0.26 | 11.68 | 23.48 | 27.17 | 1.30 | 3.63 | 1.57 | 2.10 | 0.48 |
| ***Average*** | **0.14** | **5.07** | **20.50** | **12.36** | **0.28** | **1.23** | **0.86** | **0.32** | **0.22** |
| **Average Shale** | **0.04** | **26.95** | **11.96** | **3.57** | **1.50** | **1.32** | **0.47** | **1.91** | **0.66** |

**Table 13-** Major oxides (wt. %), trace elements (ppm) ratios in red and non-red marly limestone Beds in all studied sections.

| | Major Oxides (Wt. %),Trace Elements (ppm) Ratios In Red Beds Marly Limestone In All Sections | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K_2O/Al_2O_3$ | $SiO_2/Al_2O_3$ | $Al_2O_3/TiO_2$ | Ni/Co | V/Cr | Cr/Ni | Cu/Zn | V/Ni | V/V+Ni |
| **Minimum** | 0.02 | 3.49 | 7.13 | 5.35 | 0.08 | 0.27 | 0.26 | 0.15 | 0.13 |
| **Maximum** | 0.20 | 15.37 | 28.56 | 19.32 | 0.67 | 2.14 | 1.84 | 0.53 | 0.35 |
| **Average** | **0.11** | **10.43** | **18.16** | **11.59** | **0.25** | **1.31** | **0.99** | **0.29** | **0.23** |
| **Average Shale** | **0.04** | **26.95** | **11.96** | **nd** | **1.50** | **nd** | **nd** | **nd** | **nd** |
| | **Major Oxides (Wt. %),Trace Elements (ppm) Ratios In Non-Red Beds Marly Limestone In All Sections** | | | | | | | | |
| | $K_2O/Al_2O_3$ | $SiO_2/Al_2O_3$ | $Al_2O_3/TiO_2$ | Ni/Co | V/Cr | Cr/Ni | Cu/Zn | V/Ni | V/V+Ni |
| **Minimum** | 0.03 | 3.27 | 12.41 | 2.60 | 0.49 | 0.81 | 0.37 | 0.11 | 0.10 |
| **Maximum** | 0.24 | 33.85 | 46.17 | 22.90 | 3.3 | 9.97 | 2.12 | 4.85 | 0.64 |
| **Average** | **0.11** | **8.71** | **23.00** | **10.15** | **1.94** | **1.86** | **0.93** | **0.92** | **033** |
| **Average Shale** | **0.04** | **26.95** | **11.96** | **nd** | **1.50** | **nd** | **nd** | **nd** | **nd** |

In Figure-9 displays the geochemical expression of GS section due to the Pindos Zone (Pindos Zone defined and considered as a deep ocean during the Cretaceous Period) and assists in addressing the relatively low TOC values recorded in this section. Obviously an inverse relationship between the TOC % and $C^{13}$ based on the results of the GS-section are noted stratigraphically upwards increasing in TOC % Figure-9. The reverse is the case under normal oxic conditions according to [22] Galarraga et al. 2008).

**Carbonate content determinations**

The carbonate content (CaCO3 %) of all samples was investigated by acidification and liberation of carbon dioxide using (ÖNORM L1084) device with a standard deviation of 5%. The results from semiquantitative XRD analysis and the carbonate determination show a good deal.

The comparison between the existences of the $CaCO_3$ % in the studied samples that covered red marl and red marly limestone with non-red marl and non-red marly limestone in all studied sections are listed in Table-14. In all beds it ranged from 20.50 to 100.00 with average value 54.60, for only marl and only marly limestone beds in all studied sections ranged from 22.50 to 73.50 and from 20.50 to 100.00 with average values of 41.01 and 64.09 respectively Table-14. While the $CaCO_3$ % in red and non-red marl bed samples are ranged from 44.50 to 51.50 and from 22.50 to 73.50 with average values of 40.60 and 0.29 respectively Table-14. Whereas the $CaCO_3$ % are ranged from 20.50 to 110.00 and from 30.25 to 89.50, with average values of 66.57 and 62.90 in red and non-red marly limestone bed samples respectively Table-14.

Through the above results the carbonate content ($CaCO_3$ %) presence in marly limestone rock samples show the highest value of 100.00 %, while in marl rock samples the maximum value of 73.50 % Table-14, Figure-9.

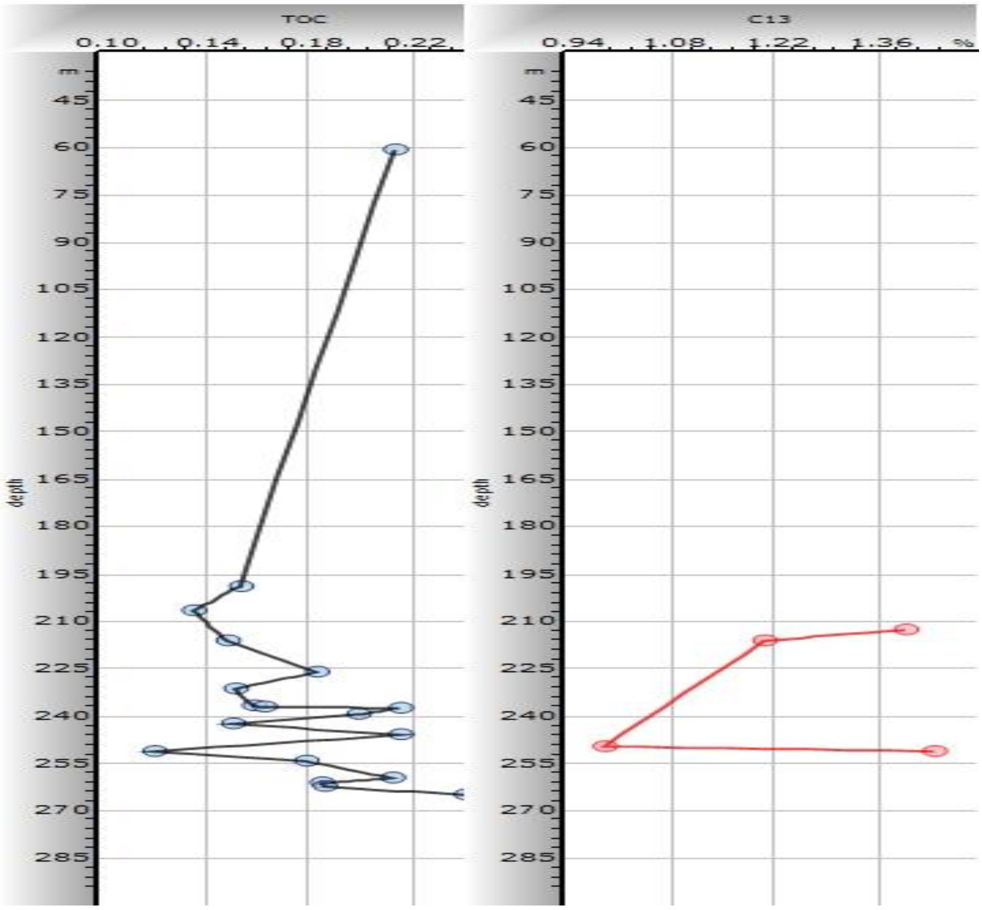


**Figure 9-** Lithology and chemostratigraphy of the GS section samples, based on Vasilios K., et al., 2010.

**Table 14-** Carbonate Content ($CaCO_3$ %) (ranges & averages) of all beds in all studied sections.

| Type of Lithology | Number of Samples (n) | Carbonate Content ($CaCO_3$ %) of All Bed Types In All Studied Sections | | |
|---|---|---|---|---|
| | | Minimum | Maximum | Average |
| All Beds | 180 | 20.50 | 100.00 | 54.60 |
| Only Marl in All Sections | 67 | 22.50 | 73.50 | 41.01 |
| Only Marly Limestone in All Sections | 96 | 20.50 | 100.00 | 64.09 |
| Only Red Marl Beds | 4 | 44.50 | 51.50 | 47.50 |
| Only Non-Red Marl Beds | 63 | 22.50 | 73.50 | 40.60 |
| Only Red Marly Limestone Beds | 65 | 20.50 | 100.00 | 66.57 |
| Only Non- Red Marly Limestone Beds | 31 | 30.25 | 89.50 | 62.90 |

All ranges and averages in each section of the present study are observed and noted in Table-14. In the present study the $CaCO_3$ % content in red beds (Shiranish CORBs beds) more than its presence in non-red beds Tables-(14, 15). The perceived increase in the carbonate content ($CaCO_3$) is a reflection of the abundance of calcite mineral in these deposits.

**Table 15-** Carbonate Content ($CaCO_3$ %) its ranges with its averages.

| Sections | Carbonate Content ($CaCO_3$ %) of All Bed Types In All Studied Sections | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Red Marl | | | Non-Red Marl | | | Red Marly Limestone | | | Non- Red Marly Limestone | | |
| | Minimum | Maximum | Average | Minimum | Maximum | Average | Minimum | Maximum | Average | Minimum | Maximum | Average |
| GS | 44.50 | 51.50 | 7.50 | 23.50 | 65.50 | 39.10 | 30.25 | 89.50 | 2.92 | 20.50 | 79.00 | 57.50 |
| Ch | - | - | - | 22.50 | 52.00 | 40.30 | 55.00 | 69.00 | 62.00 | 62.00 | 62.00 | 62.00 |
| Sm | - | - | - | 52.00 | 52.00 | 52.00 | 46.00 | 76.50 | 63.50 | 64.50 | 64.50 | 64.50 |
| Dr | - | - | - | - | - | - | - | - | - | 63.00 | 100.00 | 90.30 |
| D | - | - | - | 47.00 | 73.50 | 59.80 | - | - | - | 51.00 | 95.50 | 72.64 |
| Q | - | - | - | - | - | - | - | - | - | 38.00 | 52.00 | 46.50 |

**Stable isotopes tests**

Stable carbon and oxygen isotope compositions of bulk samples were determined using a Thermo Finnigan Delta Puls XL mass spectrometer, and results are calibrated against NBS19, CO1, and CO8 standard reference materials and are reported on the VPDB scale (Table-16 and Figure-10).

**Table 16-** Stable carbon ($\sigma C^{13}$) and oxygen ($\sigma O^{18}$) isotopes measurement.

| Sample No. | Stable Element Isotopes $\sigma C^{13}$ | | Stable Element Isotopes $\sigma O^{18}$ | |
|---|---|---|---|---|
| | First Run $\sigma C^{13}$ (1) | Second Run $\sigma C^{13}$ (2) | First Run $\sigma O^{18}$ (1) | Second Run $\sigma O^{18}$ (2) |
| GS 18 | 0.62 | 0.64 | -4.31 | -4.03 |
| GS 19 | 1.44 | 1.41 | -5.82 | -5.61 |
| GS 21 | 0.99 | 0.99 | -4.08 | -4.06 |
| GS 73 | 1.00 | 0.98 | -5.09 | -5.16 |
| GS 74 | 1.21 | 1.19 | -4.22 | -4.31 |
| GS 75 | 1.04 | 1.09 | -4.98 | -4.80 |
| GS 82 | 1.40 | 1.20 | -4.42 | -4.29 |
| GS 84 | 1.77 | 1.65 | -4.54 | -4.51 |
| GS 87 | 0.64 | 0.64 | -5.44 | -5.53 |
| CH 22 | 0.89 | 0.87 | -3.11 | -3.24 |
| CH 27 | 0.98 | 0.88 | -3.06 | -3.24 |
| SM 17 | 0.57 | 0.60 | -4.47 | -4.47 |
| SM 18 | 1.36 | 1.47 | -4.06 | -4.02 |
| SM 19 | 1.49 | 1.36 | -4.13 | -3.82 |
| D 9 | 1.23 | 1.18 | -3.78 | -3.77 |
| D 12 | 1.60 | 1.65 | -3.60 | -3.73 |
| D 14 | 1.42 | 1.47 | -3.72 | -3.69 |

The presence of smectite in studied samples suggested there is no diagenetic affective due to burial, and it means a detrital origin that may reflect local uplift and variations in weathering processes in the adjacent continental areas. The C13 and O18 values are generally constant around +1.2 and -4.3 respectively (Table-16), in upper Campanian and lower Maastrichtian red marl an marly limestone interbedded with light gray to light green marl and marly limestone.

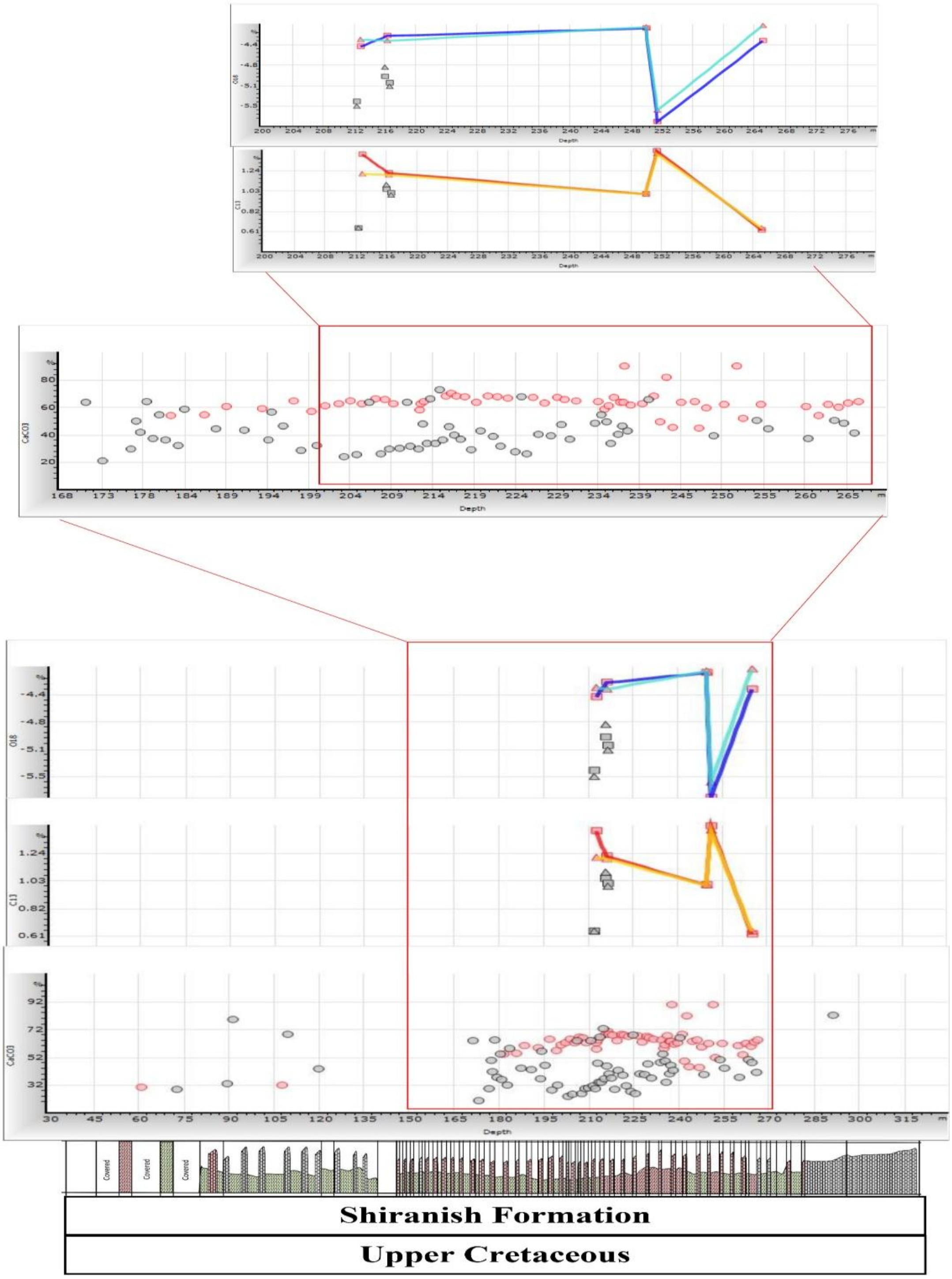


**Figure 10-** Lithological log of the Rødryggen section showing $CaCO_3$ % and TOC % with $C^{13}$ and $O^{18}$.

## Conclusions

The measurement of carbonate content ($CaCO_3$ %) in the rocks, 180 samples of all the geological sections were studied twice for each sample and the average readings were taken.

This examination proved the following major oxides wt. % concentrations domination $SiO_2$, CaO, $Al_2O_3$ and $Fe_2O_3$ with average values of 33.10, 29.63, 5.10 and 3.67 respectively, with following minor elements ppm concentrations dominance Sr, Ni, V, Zn, Cu, Zr and Co with average values of 498.4, 257.6, 67.8, 38.2, 34.3, 25.5 and 20.4 respectively. Also this group of ratios $K_2O/Al_2O_3$, $SiO_2$, $Al_2O_3/TiO_2$, Ni/Co, V/Cr, Cu/Zn, Cr/Ni, V/Ni, and V/ (V+Ni) is used as an index of paleo oxygenation conditions, these ratios proved the oxidizing environments for the rock samples in the present study

The expense of the organic matter content (TOC) has shown low content of TOC % in most studied samples, with ranges values of 0.27 in all beds, 0.18 in only red marl beds, 0.29 only non-red marl beds, 0.20 in only red marly limestone beds, 0.36 only non-red marly limestone beds .

The Shiranish Formation (Late Campanian-Early Mastrichtian), composed of marl and marly limestone, rhythmically laminated. Relatively low contents of organic matter and the containing of some redox-sensitive trace elements support the interpretation of oxic bottom water conditions during the deposition of this formation, consisting of light grey, reddish, brownish, and pinkish laminated calcareous marl and marly limestone, is characterized by low TOC contents.

The C13 and O18 values are generally constant around +1.2 and -4.3 respectively, in upper Campanian and lower Maastrichtian red marl an marly limestone interbedded with light gray to light green marl and marly limestone. The presence of smectite in studied samples suggested there is no diagenetic affective due to burial, and it means a detrital origin that may reflect local uplift and variations in weathering processes in the adjacent continental areas.

## References


1. Hu, X., Jansa, L., Wang, C., Sarti, M., Bak, K., Wagreich, M., Michalik, J. and Sotak, J. **2005.** Upper Cretaceous oceanic red beds (CORBs) in the Tethys: occurrences, lithofacies, age, and environments, *Cretaceous Research,* **26**: 3–20.
2. Chengshan W. et al. **2005.** Cretaceous Oceanic Red Beds (CORBs) in Southern Tibet: A Major Change from Anoxic to Oxic, Deep-Sea Environments.
3. Stampfli, G. M., and Borel, G. D., Marchant, R. and Mosar, J. **2002.** Western Alps geological constraints on western Tethyan reconstructions, *Journal of the Virtual Explorer,* **8**: 77–106.
4. Wagreich, M. and Faupl, P. **1994.** Palaeogeography and geodynamic evolution of the Gosau Group of the Northern Calcareous Alps (Late Cretaceous, Eastern Alps, Austria): *Palaeogeography, Palaeoclimatololgy, Palaeoecology,* **110**: 235–254
5. Jassim, S. Z. and Goff, J. C**. 2006.** *Geology of Iraq. Published by Dolin,* Prague and Moravian Museum, Srno. 341p.
6. Ma'ala K.A, **2008.** Geological map of the Sulaimaniya Quadrangle, sheet N1-38-3, scale 1:20000, GEOSURV.
7. Sissakian, V., K., **1998.** Geological map of Iraq, sheet No.1- 3-307 rd edition, Geol. Surv. Min., Invest. Baghdad, Iraq.
8. Henson, F. R. S. **I951.** Oil occurrences in relation to regional geology of the Middle East. *Geol. Soc. Tulsa, Digest,* **19**: 72-81.
9. Bellen, R. C. Van, Dunnington, H. V., Wetzel, R. and Morton, D. **1959.** Lexique Stratigraphique Internal Asie. Iraq. *Intern. Geol. Conger. Comm. Stratigr,* 3, Fasc. lOa, 333p.
10. Liu, W. X, Li, X. D., Shen, Z. G., Wang, D. C., Wai, O. W. H., and Li, Y. S. **2003.** Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environmental Pollution,* **121**; 377-388.
11. Simeonov, V., Massart, G., Andrew, G., and Tsakovski, S. **2000.** Assessment of metal pollution based on multivariate statistical modelling of ''hot spot'' sediments from the Black sea. *Chemosphere,* **41**: 1411-1417.
12. Krishna, K. A., Raman-Mohan, K., Murthy, N. N. **2011.** A multivariate statistical approach for monitoring of heavy metals in sediments: a case study from Wailpalli Watershed, Nalgonda District, Andhra Pradesh. *India. Research Journal of Environmental and Earth Sciences,* **3**(2): 103-113.

**13.** Turekian, K. K.,Wedepohl, K. H. **1961.** Distribution of the elements in some major units of the Earths crust. *Geol. Soc. Am. Bull*. **72**: 175–191.Wedepohl 1971; 1991

**14.** Brumsack, H.-J. **2006.** The trace metal content of recent organic carbon-rich sediments: implications for Cretaceous black shale formation. *Palaeogeography, Palaeoceanography, Palaeoecology,* **232**(2-4): 344-361.

**15.** Hallberg, R.O. **1976.** A geochemical method for investigation of palaeoredox conditions in sediments: Ambio. Special Report, 4, p. 139-147.

**16.** Jones, B., Manning, D. A. C. **1994.** Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. *Chem. Geol*. **111**: 111 –129.

**17.** Dypvik, H. **1984.** Geochemical compositions and depositional conditions of upper Jurassic and lower cretaceous Yorkshire clays. *England Geol. Mag*. **121**(5): 489–504.

**18.** Dill, H. **1986.** Metallogenesis of early Paleozoic graptolite shales from the Graefenthal Horst (Northern Bavaria-Federal Republic of Germany). *Econ. Geol*. **81**: 889–903.

**19.** Dill, H., Teshner, M., Wehner, H. **1988.** Petrography, inorganic and organic geochemistry of Lower Permian Carboniferous fan sequences (Brandschiefer Series) FRG: constraints to their palaeogeography and assessment of their source rock potential. *Chemical Geology,* **67**(3-4): 307-325.

**20.** Nagarajan, R., Madhavaraju, J., Nagendra1, R., Armstrong-Altrin, J. S., and Moutte, J. **2007.** Geochemistry of Neoproterozoic shales of the Rabanpalli Formation, Bhima Basin, Northern Karnataka, southern India: implications for provenance and paleoredox conditions. *Revista Mexicana de Ciencias Geologicas,* **24**(2): 150-160.

**21.** Galarraga, F., Reategui, K., Martïnez, A., Martínez, M., Llamas, J.F., Márquez, G. **2008**. V/Ni ratio as a parameter in palaeoenvironmental characterisation of non mature medium-crude oils from several Latin American basins. *J. Petrol. Sci.Eng.* **61**: 9–14.

**22.** Kafousia, N., Karakitios, V., and Jenkyns, H. C. **2010.** Preliminary data from the first record of the Toarcian Oceanic Anoxic Event in the sediments of the Pindos Zone (Greece). *Bulletin of the Geological society of Greece,* **43**(2): 627-633