Arab J Geosci (2015) 8:9407–9421
DOI 10.1007/s12517-015-1863-y

ORIGINAL PAPER

Biomarkers and inorganic geochemical elements of Late Jurassic-Early Cretaceous limestone sediments from Banik Village in the Kurdistan Region, Northern Iraq: implications for origin of organic matter and depositional environment conditions

Mohammed Hail Hakimi · Ibrahim M. J. Mohialdeen · Wan Hasiah Abdullah · William Wimbledon · Yousif M. Makeen · Khairul Azlan Mustapha

Received: 2 December 2014 / Accepted: 24 February 2015 / Published online: 10 March 2015

Abstract Late Jurassic-Early Cretaceous limestone sediments from Banik Village in the Kurdistan Region, Northern Iraq, were analysed based on a combined investigation of elemental composition and biomarker characterisation. These investigations were used to define the origin, type of organic matters and their relation to the environment conditions during deposition. The bulk geochemical characteristics indicated that the Late Jurassic-Early Cretaceous limestone sediments were deposited in a marine environment with calcium-rich seawater. Their biomarkers provide evidence for a major contribution by aquatic organic matter with a minor terrigenous organic matter contribution. This is confirmed by normal alkanes, hopanoids, steroids and related compounds of the saturated hydrocarbons. Moreover, the salinity stratification and relatively reducing bottom water conditions are evidenced in the Late Jurassic-Early Cretaceous limestone sediments, as identified from Sr/Br, V/Ni and Pr/Ph ratios. The occurrence of gammacerane biomarker in the analysed samples is also a strong indicator of reducing and salinity stratification during deposition. Therefore, a stratified water column with salinity and relatively anoxic bottom water conditions contribute to organic matter (OM) preservation.

Keywords Late Jurassic-Early Cretaceous limestone · Biomarkers · Inorganic geochemistry · Depositional condition · Banik Village · Kurdistan Region

Introduction

The Kurdistan Region is an oil-rich area and has become the largest oil-producing portion of north Iraq. The Late Jurassic-Early Cretaceous sediments are widespread and occur in Northern Iraq. The dataset used herein is from the Banik Village, Duhok Governorate, Kurdistan Region (Fig. 1a). The study area occupies the Northern part of the Kurdistan Region, which lies between latitudes 37° 13′ 33.4″ N and longitudes 42° 58′ 2.6″ E (Fig. 1b) and has attracted the interest of numerous researchers. The Banik Village is located at about 25 km northeast of Zakho City in the Kurdistan Region. The area is situated within the highly folded zone of Iraq (Buday 1980; Edilbi 2010). The Banik section also lies in a rugged terrain where the section of Jurassic rocks is exposed along a relatively narrow valley in which Banik Village lies (Fig. 1c). The exploration successes in the Kurdistan Region of north Iraq have attracted the attention of many petroleum researchers and explorers. However, a detailed geochemical

M. H. Hakimi (✉)
Geology Department, Faculty of Applied Science, Taiz University, 6803 Taiz, Yemen
e-mail: ibnalhakimi@yahoo.com

I. M. J. Mohialdeen
Department of Geology, School of Science, University of Sulaimani, Kurdistan, Iraq

W. H. Abdullah · Y. M. Makeen · K. A. Mustapha
Department of Geology, University of Malaya, 50603 Kuala Lumpur, Malaysia

W. Wimbledon
Department of Earth Sciences, University of Bristol, Bristol, England

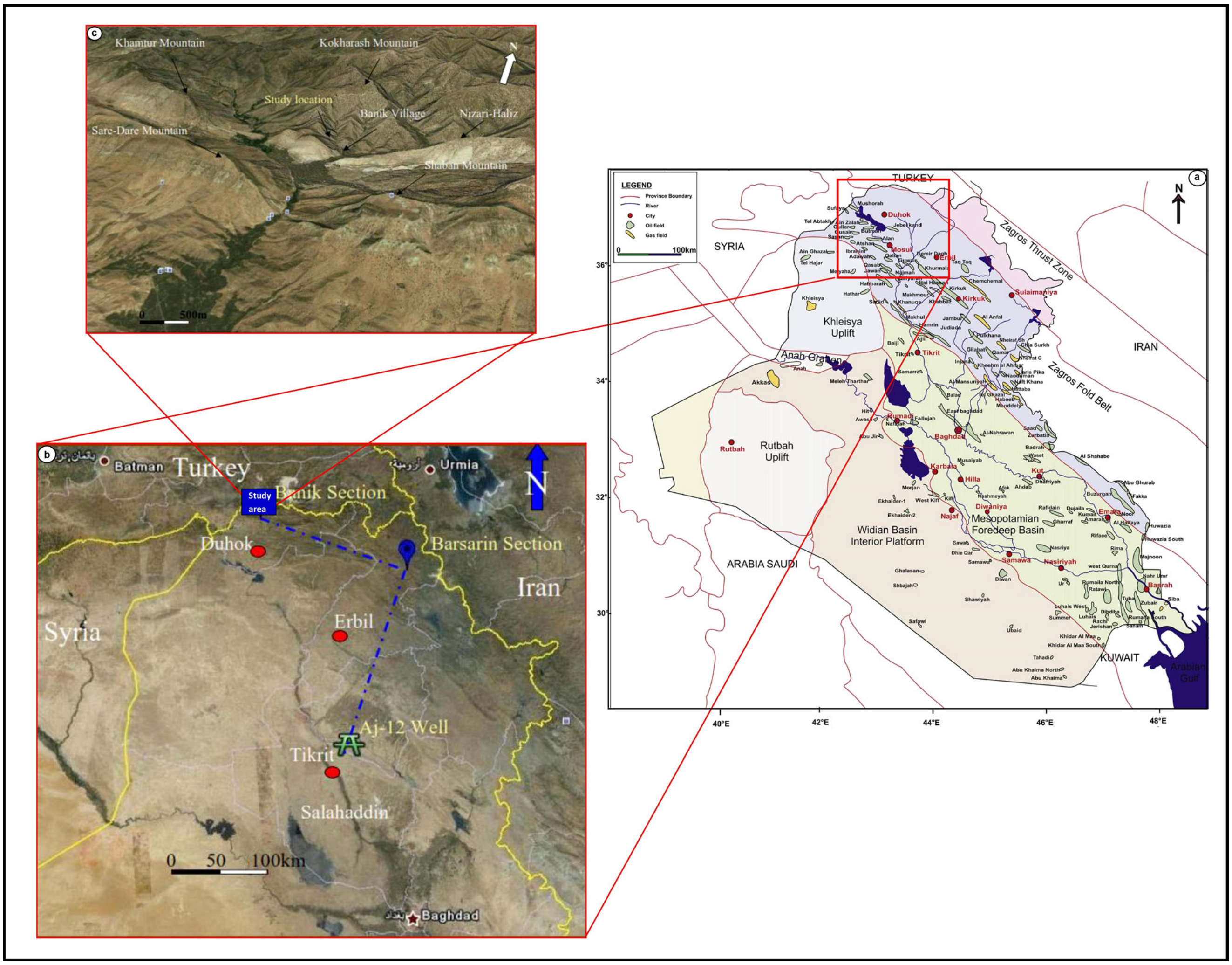


Fig. 1 **a** Location map for the northeast Arabian Peninsula in Iraq, which shows the Zagross Fold Belt with oil and gas field locations in the Iraqi Kurdistan (compiled and modified using the map from Al-Ameri and Zumberge 2012). **b** Location map of the studied section from Banik Village in the Kurdistan Region. **c** Satellite image of area around Banik Village (modified after Edilbi 2010)

characterisation of the Late Jurassic-Early Cretaceous sediments in the Banik Village has not been reported to date in any of the previews literature; thus, there is poor knowledge on the organic facies variation and distributions. Integrating organic and inorganic geochemistry provides a multi-scale view and increases knowledge about the organic matter type, source inputs, depositional environment conditions, mineralogy and chemical composition of sedimentary strata. The present study focuses on the geochemical characteristics of the Late Jurassic-Early Cretaceous limestone sediments from the Banik Village in the Kurdistan Region, Northern Iraq, so as to provide an overview on the origin of organic matter and depositional environment conditions. The organic and inorganic geochemical data involved total sulfur (TS) contents, bitumen extractions, biomarker distributions and major trace element composition. Biomarker distribution is widely applied and successfully used to interpret deposit environment conditions and the thermal maturity for organic matter preserved in sediments (Peters and Moldowan 1993; Peters et al. 2005). The biomarker investigations can also give more detailed information needed to answer exploration questions on source input and conditions of depositional environment of organic matter. Thus, we report herein results from an investigation on limestone sediments using detailed biomarker characteristics, coupled with inorganic geochemical elements.

Sampling and experimental methods

A total of ten outcrop limestone samples were collected from Late Jurassic-Early Cretaceous sequence in the Banik Village within the Kurdistan Region from Northern Iraq (Fig. 2). Since weathering is always a factor of concern for geochemical analyses of outcrop sediments, the weathered rock surfaces were removed by digging in each sampling point. The samples then were scrubbed and exhaustively cleaned with

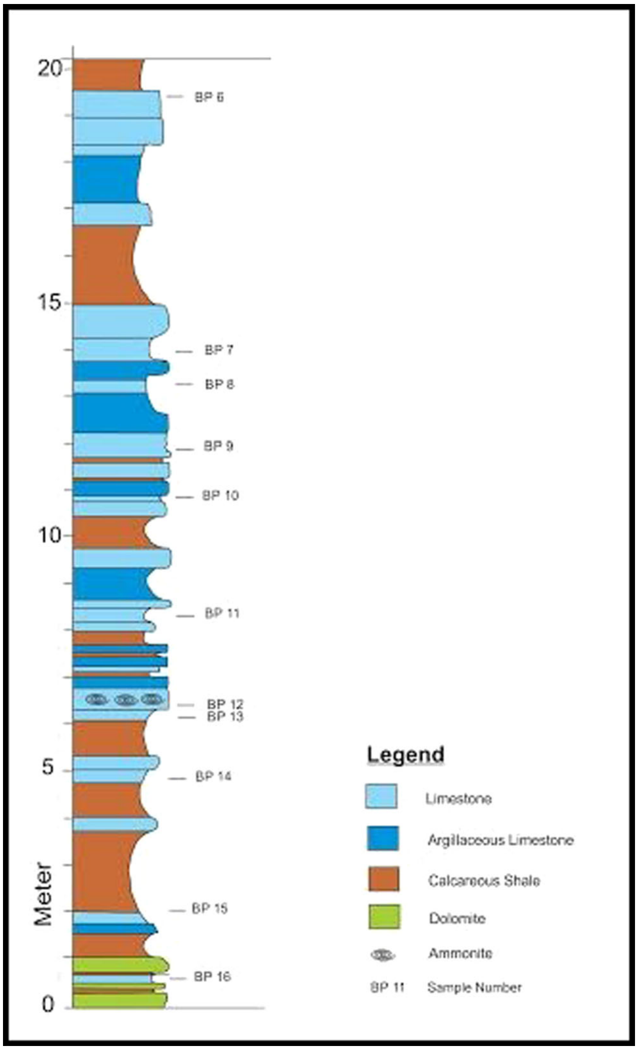


Fig. 2 Sedimentary log of the studied Jurassic-Early Cretaceous limestone sediments from Banik Village in the Kurdistan Region, Northern Iraq

distilled water to remove traces of superficial dirt and plant growth, then dried at 35 °C for 12 h. Most of organic and inorganic geochemical analyses were performed on limestone samples and conducted at the Geochemistry Laboratories of the Department of Geology in the University of Malaya.

Extraction and fractionation

The whole limestone samples were extracted (after fine grinding) with a mixture of dichloromethane (DCM) and methanol (CH_3OH) (93:7) for 72 h using a Soxhlet apparatus. The bitumen fractions of the limestone extracts were fractionated using liquid column chromatography on silica gel below alumina. Elution with petroleum ether produced the aliphatic hydrocarbon fraction, elution with DCM produced the aromatic hydrocarbon fraction and elution with CH_3OH produced the polar compounds. Aliphatic fractions were dissolved in hexane and analysed by a gas chromatography–mass spectrometry (GC-MS) instrument.

Gas chromatography–mass spectrometry

GC-MS was carried out using a HP 5975B MSD system in full scan (50–550 amu) modes. The GC was HP-5MS column and temperature programmed from 40 to 300 °C at a rate of 4 °C/min, and then held for 30 min at 300 °C. GC-MS analysis was performed on a HP 5975B MSD mass spectrometer with a gas chromatograph attached directly to the ion source (70-eV ionisation voltage, 100-mA filament emission current, 230 °C interface temperature). The selected ion monitoring capabilities of the data acquisition system permitted specific ions to be monitored, such as *n*-alkanes (TIC), terpanes and hopanes (m/z 191), and steranes (m/z 217) (Amijaya et al., 2006; Korkmaz and Kara Gülbay 2007; Hakimi et al. 2011). Relative abundances of triterpenes and steranes were calculated by measuring peak heights in the m/z 191 and m/z 217 fragmentograms, respectively.

Inorganic geochemistry analyses

The whole crushed samples also were used for the analysis of major oxides and trace elements. X-ray fluorescence spectrometer (XRF) analysis was performed on the powdered sample using PANalytical Axios mAX 4kW sequential XRF spectrometer. The oxides of major elements and trace elements were identified from the non-destructive wavelength dispersive X-ray fluorescence spectrometer. In order to determine the low concentration of trace and rare earth elements, about 0.50 g of each sample was weighed in a Teflon beaker and dried at 105 °C overnight. The samples were moistened with a few millilitres of deionised water; 5 ml of nitric acid (HNO_3) was slowly added and placed on a hotplate at 150 °C until it reaches near dryness and allowed to cool; 10 ml of hydrofluoric acid (HF) was slowly added followed by 4 ml of perchloric acid ($HClO_4$). The samples were decomposed on a hotplate at approximately 200 °C until it reaches near dryness with a crystalline mush. After cooling, the samples were digested with 10 ml of 5 M HNO_3 in a fume hood. The solutions were diluted with deionised water to 50 ml in a volumetric flask. All the digested samples were diluted up to 100 times with ultimate pure water (UPW). Standard solutions of the elements with an analyte concentration of 10 ppm were used for calibration with a minimum detection limit of less than 1 ppb. The trace and rare earth elements were determined using Agilent Technologies 7500 series inductively coupled plasma mass spectrometer (ICP-MS). The whole samples were subsequently used for the analysis of TS content using multi EA 2000 CS equipment.

Results and discussion

Molecular geochemistry characterisation

n-Alkanes and isoprenoids

The normal alkane and acyclic isoprenoid ratios of saturated hydrocarbon fractions of the extracts were determined based on distributions in *m*/*z* 85 of the GC-MS fragmentation (Fig. 3a). The chromatograms display full site of C_{13}–C_{33} *n*-alkanes and isoprenoid hydrocarbons (Fig. 3a). The *n*-alkane distribution shows a unimodal distribution, with a predominance of short (*n*-C_{14}–*n*-C_{20}) to middle (*n*-C_{21}–*n*-C_{25}) chain *n*-alkanes with the presence of significant waxy alkanes (+ *n*-C_{25}) and thus gave low to moderate carbon preference index (CPI) values (Table 1). This *n*-alkane distribution supports high marine-derived organic matter contribution with terrigenous organic matter input (Ebukanson and Kinghorn 1986; Murray and Boreham 1992; Peters et al. 2005; Hakimi et al. 2012 2014).

Acyclic isoprenoids occur in significant amount in the terms of pristane and phytane isoprenoids (Fig. 3a). The analysed samples have pristane/phytane (Pr/Ph) ratios in the range of 0.60–1.84 (Table 1), indicating suboxic to anoxic conditions during deposition of the sediments. There are also significant differences in the amounts of *n*-alkanes compared to isoprenoids (Fig. 3a), thus giving relatively high pristane/*n*-C_{17} and low phytane/*n*-C_{18} ratios in the range of 0.42–1.50 and 0.28–0.58, respectively (Table 1). CPI index is also calculated to provide some insights into the source input of the organic matter (Peters et al. 2005). Late Jurassic-Early Cretaceous limestone sediments in the Kurdistan Region contain relatively low to moderate CPI values of 0.85–1.25 (Table 1).

Hopanoid and steroid biomarkers

The distributions of hopanoids, steroids and related compounds are commonly studied using GC-MS by monitoring the ions *m*/*z* 191 and *m*/*z* 217 mass chromatograms, respectively (Fig. 3b, c), and the identified peaks are listed in Appendix A.

The *m*/*z* 191 mass chromatograms of the saturated hydrocarbon fractions of all the analysed samples show that the hopanoids are dominated by the presence of C_{30} hopane, C_{29} norhopane, 17α (H)-trisnorhopane (Tm) and a considerable quantity of homohopanes (C_{31}–C_{35}) and tricyclic terpanes (Fig. 3b). However, the relative abundance of C_{29}-norhopane is generally higher than that of C_{30}-hopane in most of the studied samples (Fig. 3b), with C_{29}/C_{30} 17α (H)-hopane ratios in the range of 0.81–1.53 (Table 1). This is frequently associated with carbonate-rich rocks which agree with the lithofacies of the limestone samples. The enhanced norhopane C_{29} input may also be associated with land plant input (Rinna et al. 1996). Tm (C_{27} 17a(H)-22,29,30-trisnorhopane) and Ts (C_{27} 18a(H)-22,29,30-trisnorneohopane) are well known to be influenced by maturation, type of organic matter and lithology (e.g. Seifert and Moldowan 1978 1979; Moldowan et al. 1985). The investigated samples have varying Tm/Ts values in the range of 0.19–0.43 (Table 1), indicating that the samples contain a mixture of land- and aquatic-derived organic matter.

The homohopane distributions are dominated by the C_{31}-homohopane and decrease with increasing carbon number (Fig. 3b). Homohopanes (C_{31}–C_{35}) are believed to be derived from bacteriohopanetetrol as well as from other hopanoids in bacteria (Ourisson et al. 1984). However, the C_{31}-22R hopane/C_{30} hopane ratio is used to distinguish between different depositional environments (Peters et al. 2005). This ratio is generally higher than 0.25 for marine environments whereas lower than 0.25 for lacustrine settings (Peters et al. 2005). C_{31}-22R hopane/C_{30} hopane ratios of the extract samples are in the range of 0.29–0.40, indicating that the studied limestone sediments were interpreted to be deposited principally in marine environment.

The concentration of tricyclic terpanes is relatively higher than that of tetracyclics in most of the samples analysed (represented by C_{24} tetracyclic/C_{26} tricyclic; Table 1). The samples also have relatively low C_{24} Te/C_{26} and C_{24}/C_{23} tricyclic terpane values and relatively low C_{26}/C_{25} tricyclic ratios (Table 1). Gammacerane also presents in small amounts in most of the samples (Fig. 3b), and the studied samples display variable gammacerane index (gammacerane/C_{30} hopane) in the range of 0.14–0.21 (Table 1). This is believed to have the existence of relatively high salinity stratified water column during deposition (Sinninghe Damsté et al. 1995; Ten Haven et al. 1988). This is evidenced by inorganic geochemical elements, which lead to the high Sr/Br ration and total sulfur contents (Tables 1 and 2).

The distribution of steroids is characterised by the *m*/*z* 217 ion chromatograms (Fig. 3c). Steroids are another group of important biomarkers that are derived from sterols found in higher plants and algae, but rare or absent in prokaryotic organisms (Seifert and Moldowan 1978 1979; Huang and Meinschein 1979; Volkman 1986). Steranes and diasteranes are present in high quantities in saturated hydrocarbon fractions of the analysed samples (Fig. 3c). The relative proportions of each of the regular steranes (C_{27}, C_{28} and C_{29}) can vary greatly from sample-to-sample, depending upon the type of organic matter input to the sediment. Relative abundances of C_{27}, C_{28} and C_{29} regular steranes and the ratios of C_{29}/C_{27} regular sterane, C_{27}+C_{28}/C_{29} sterane, diasterane/sterane and sterane/hopane are calculated, and the results are given in Table 1. The analysed samples show a high proportion of C_{29} (38.8–48 %) and C_{27} (34.42–45.63 %) compared to C_{28} (12.3–18.5 %) steranes as shown in Table 1. The samples also have low diasterane/sterane and relatively high C_{29}/C_{27} regular sterane ratios in the range of 0.43–0.82 and 0.88–1.41, respectively (Table 1). The low diasterane/sterane ratios further suggest carbonate-rich sediments.

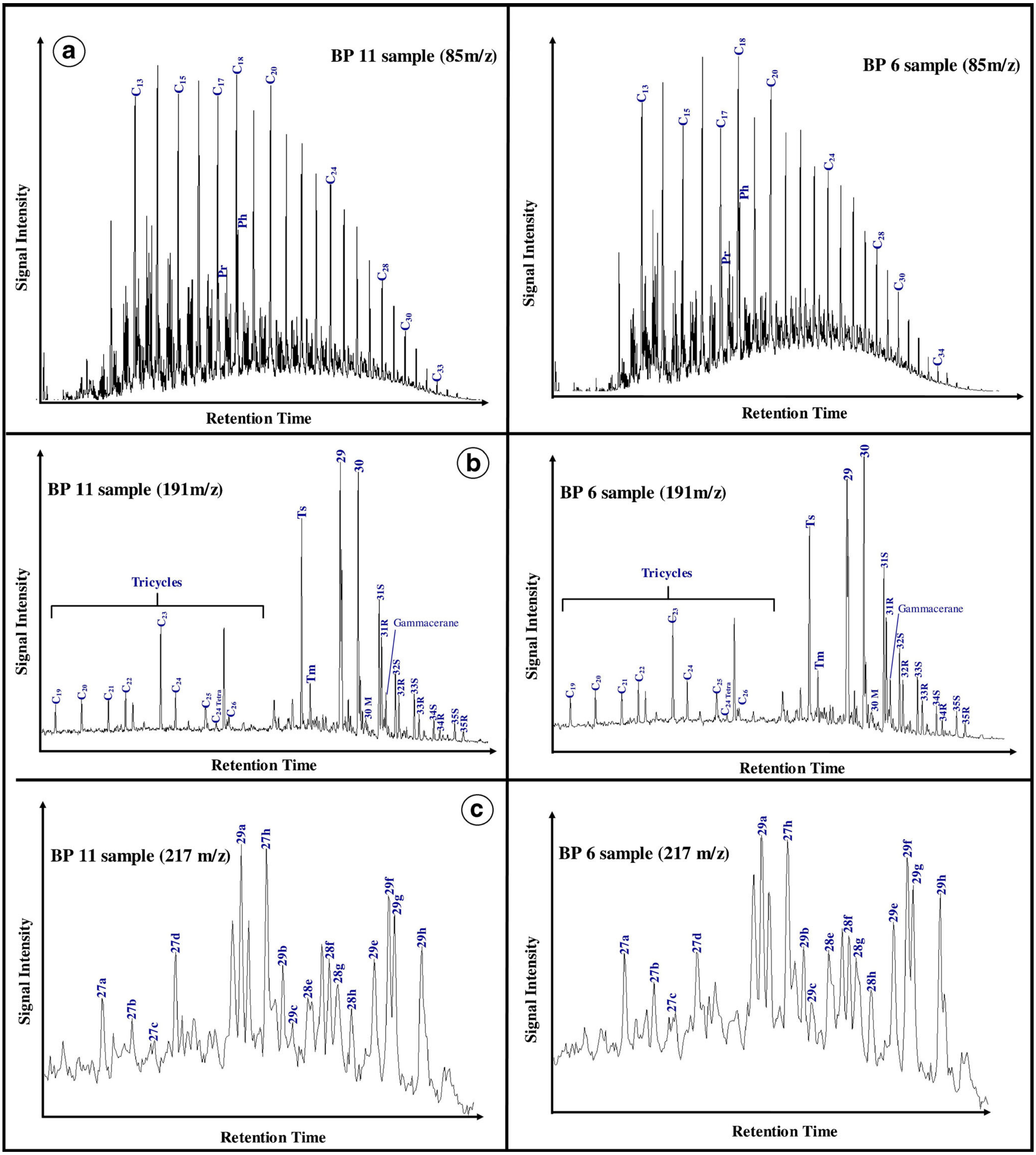


Fig. 3 Mass fragmentograms of **a** *m*/*z* 85, **b** *m*/*z* 191 and **c** *m*/*z* 217 of saturated hydrocarbons for representative two limestone extracts

Inorganic geochemistry characterisation

Total sulfur content

The total sulfur contents in sediments may provide insight into the depositional environment and microbial sulfate reduction (Berner and Raiswell 1983; Berner 1984; Mohialdeen, et al. 2013). High sulfur organic matter content is inferred to be derived from source deposited in highly reducing hypersaline marine (Huang and Pearson 1999), while the low sulfur concentrations are typical for a freshwater lacustrine environment (e.g. Berner and Raiswell 1983). Total sulfur is considered as a

Table 1 *n*-alkane, isoprenoids and biomarker ratios of the limestone extracts from Banik Village in the Kurdistan Region calculated from *m*/*z* 85, *m*/*z* 191 and *m*/*z* 217 mass fragmentograms, respectively, illustrating source organic matter and depositional environment conditions

Section	Sample ID	TS (wt%)	Normal alkanes and isoprenoids				Triterpenes and terpanes (*m*/*z* 191)											Steranes and diasteranes (*m*/*z* 217)								
							Hopane					Tricyclic (T) and tetracyclic (Te) terpanes						Regular steranes (%)			C_{29}/ C_{27}	C_{29} 20S/ 20S+20R	C_{29} ββ/ ββ+αα	C_{27}/ C_{27}+C_{29}	Diasterane/ sterane	Hopane/ sterane
			Pr/ Ph	Pr/*n* C_{17}	Ph/*n* C_{18}	CPI	C_{32} 22S/ (22S+22R)	C_{29}/ C_{30}	C_{31R}/ C_{30}	G/ C_{30}	Tm/ Ts	MC_{30}/ HC_{30}	$C_{22}T$/ $C_{21}T$	$C_{26}T$/ $C_{25}T$	$C_{24}Te$/ $C_{26}T$	$C_{24}T$/ $C_{23}T$	$C_{21}T$/ $C_{23}T$	C_{27}	C_{28}	C_{29}						
Banik Village	BP 6	2.13	1.62	1.40	0.44	0.88	0.60	0.81	0.40	0.14	0.41	0.06	1.04	0.63	0.40	0.38	0.35	44.26	16.94	38.80	0.88	0.43	0.55	0.47	0.49	1.3
	BP 7	1.27	1.32	1.50	0.58	1.01	0.61	0.93	0.37	0.18	0.33	0.06	1.05	0.50	0.63	0.35	0.32	42.92	17.70	39.38	0.92	0.42	0.55	0.48	0.43	1.1
	BP 8	1.02	1.33	1.20	0.44	0.93	0.63	1.53	0.35	0.20	0.19	0.12	0.96	0.77	0.50	0.18	0.48	41.00	18.50	40.50	0.99	0.4	0.47	0.50	0.82	1.2
	BP 9	3.41	0.62	0.62	0.54	0.95	0.62	0.90	0.40	0.17	0.30	0.07	1.29	0.50	0.71	0.36	0.31	41.86	16.28	41.86	1.00	0.44	0.53	0.50	0.43	1.4
	BP 10	5.53	0.60	0.42	0.28	0.92	0.61	1.06	0.33	0.16	0.42	0.07	1.33	0.58	0.43	0.36	0.30	39.02	16.26	44.72	1.15	0.41	0.58	0.53	0.48	1.3
	BP 11	5.64	0.67	0.56	0.52	0.97	0.62	1.02	0.36	0.17	0.36	0.07	1.25	0.60	0.83	0.37	0.30	34.42	17.21	48.37	1.41	0.46	0.52	0.58	0.54	1.3
	BP 12	0.88	1.51	0.98	0.35	0.85	0.62	1.15	0.31	0.18	0.40	0.08	2.36	0.70	0.71	0.63	1.38	45.63	12.30	42.06	0.92	0.40	0.55	0.48	0.51	1.1
	BP 13	1.04	1.84	1.30	0.44	1.19	0.64	1.36	0.32	0.16	0.23	0.09	1.35	0.42	0.80	0.23	0.38	39.92	16.21	43.87	1.10	0.42	0.54	0.52	0.59	1.0
	BP 14	0.78	1.08	1.00	0.43	1.03	0.62	1.32	0.39	0.21	0.31	0.09	1.08	0.55	0.83	0.31	0.38	44.44	14.18	41.38	0.93	0.39	0.56	0.48	0.60	1.0
	BP 15	1.41	1.31	1.30	0.52	1.25	0.62	1.06	0.29	0.16	0.43	0.06	1.03	0.62	0.75	0.36	0.41	37.77	15.45	46.78	1.24	0.43	0.54	0.55	0.56	1.3

TS total sulfur content (wt%), *Pr* pristane, *Ph* phytane, *CPI* carbon preference index, *(1)* $\{2(C_{23}+C_{25}+C_{27}+C_{29})/(C_{22}+2[C_{24}+C_{26}+C_{28}]+C_{30})\}$, *$C_{29}/C_{30}$* C_{29} norhopane/C_{30} hopane, *G/C_{30}* gammacerane/C_{30} hopane, *Ts* (C_{27} 18a(H)-22,29,30-trisnorneohopane), *Tm* (C_{27} 17a(H)-22,29,30-trisnorhopane), *C_{31R}/C_{30}* C_{31} regular homohopane/C_{30} hopane, *$C_{30}M/C_{30}H$* C_{30} moretane/C_{30} hopane

Table 2 Major (wt%) and trace element (ppm) compositions of the Jurassic-Early Cretaceous limestone sediments from Banik Village in the Kurdistan Region, Northern Iraq

Section	Sample ID	Major elements (wt%)											Trace elements (ppm)						
		SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	Al/Si	Ti/Al	V	Ni	Sr	Ba	Sr/Ba	V/Ni	V/(V+Ni)
Banik Village	BP 6	17.12	11.63	0.99	4.52	56.49	5.18	0.95	0.07	0.15	0.68	0.08	950	320	1430	650	2.20	2.97	0.75
	BP 7	10.27	6.40	0.77	5.37	75.26	0.59	0.31	0.05	0.08	0.62	0.12	1780	640	1020	630	1.62	2.78	0.74
	BP 8	10.14	7.29	0.91	5.31	74.80	0.61	0.36	0.03	0.07	0.72	0.12	945	320	1367	645	2.12	2.95	0.75
	BP 9	8.97	5.80	0.70	3.52	77.20	0.59	0.32	0.03	0.07	0.65	0.12	930	225	620	330	1.88	4.13	0.81
	BP 10	5.97	4.16	0.45	2.23	84.60	0.67	0.26	–	0.05	0.70	0.11	1140	230	795	455	1.75	4.96	0.83
	BP 11	7.70	5.35	0.52	2.34	81.41	0.63	0.35	–	0.04	0.69	0.10	1210	210	760	530	1.43	5.76	0.85
	BP 12	9.73	5.39	0.65	2.84	79.42	0.58	0.30	0.04	0.30	0.55	0.12	1130	650	1010	615	1.64	1.74	0.63
	BP 13	32.31	22.99	1.77	8.71	30.64	0.75	1.78	0.09	0.12	0.71	0.08	450	180	550	285	1.93	2.50	0.71
	BP 14	12.91	8.28	0.87	8.07	67.96	0.70	0.50	0.04	0.08	0.64	0.11	560	240	613	480	1.28	2.33	0.70
	BP 15	9.23	4.55	0.32	2.76	49.50	0.85	0.37	0.02	0.06	0.49	0.07	420	210	520	589	0.88	2.00	0.67
Average		12.44	8.18	0.79	4.57	67.73	1.11	0.55	0.05	0.10	0.65	0.10	951.5	322.5	868.5	520.90	1.67	3.21	0.74

more strong measure of the degree of marine influence than the organic or pyritic sulfur in sediments. According to Sykes (2004), an adopted 0.5 % sulfur content was the highest concentration of sulfur in the entire non-marine sediments. As such, total sulfur values >0.5 % are taken to indicate some degree of marine influence, while values of 0.5–1.5 % and >1.5 % are classified as slightly and strongly marine influenced. The TS (wt%) content of the studied limestone samples ranges from 0.78 to 5.64 wt% (Table 1), thus showing that the samples were deposited under marine environment. Moreover, a high TS value is an indication of low oxygen bottom water conditions (Huang and Pearson 1999). These interpretations are supported further by the geochemistry of trace elements and biomarker environment indicators (Tables 1 and 2).

Major and trace elements

The origin and/or state of preservation and factors controlling the accumulation of organic matter and relation to paleoenvironmental conditions can be partly addressed by examining its bulk inorganic geochemical compositions (Moosavirada et al. 2011; Mohialdeen and Raza 2013; Shu et al. 2013; Jia et al. 2013). Inorganic geochemical results of studied limestone samples, including major oxides and trace elements along with the several widely used geochemical ratios, are tabulated in Table 3.

Major oxides (CaO, SiO_2, Al_2O_3) The major oxide elements CaO, SiO_2, Al_2O_3 and Fe_2O_3 are the dominant constituents with an average of 67.73, 12.44, 8.18 and 4.57 wt%, respectively (Table 2). The carbonate input (CaO) showed highest concentrations in the studied samples (Table 3). This suggests that the samples were deposited in calcium-rich water (Stach et al. 1982). The high Ca concentration is explained by calcite carbonate minerals consistent with limestone sediments (Fig. 2). This also could be referred to the location of the depositional basin is more the depocenter of the basin.

SiO_2 and Al_2O_3 showed slightly highest concentrations in the studied samples (Table 2), which is consistent with the occurrence of quartz and clay minerals. The Al/Si ratios are low (0.49–0.72), allowing to suggest that Si has another source besides clay minerals, as inferred by Fu et al. (2011). The slightly high concentrations of SiO_2 and Al_2O_3 elements could be referred to the input of detrital matter (Ross and Bustin 2009). This is supported by relatively high titanium (Ti) element with an average 0.79 (Table 2) and very good correlations between Ti and SiO_2 and Al_2O_3 elements (Fig. 4).

Iron Fe_2O_3 is also an important component in the studied samples (avg. 4.57 wt%) and has known association with Fe sulfides (pyrite and marcasite). This is further suggest by the presence of pyrite within the Late Jurassic-Early Cretaceous limestone sediments (Mohialdeen 2008; Mohialdeen et al. 2013).

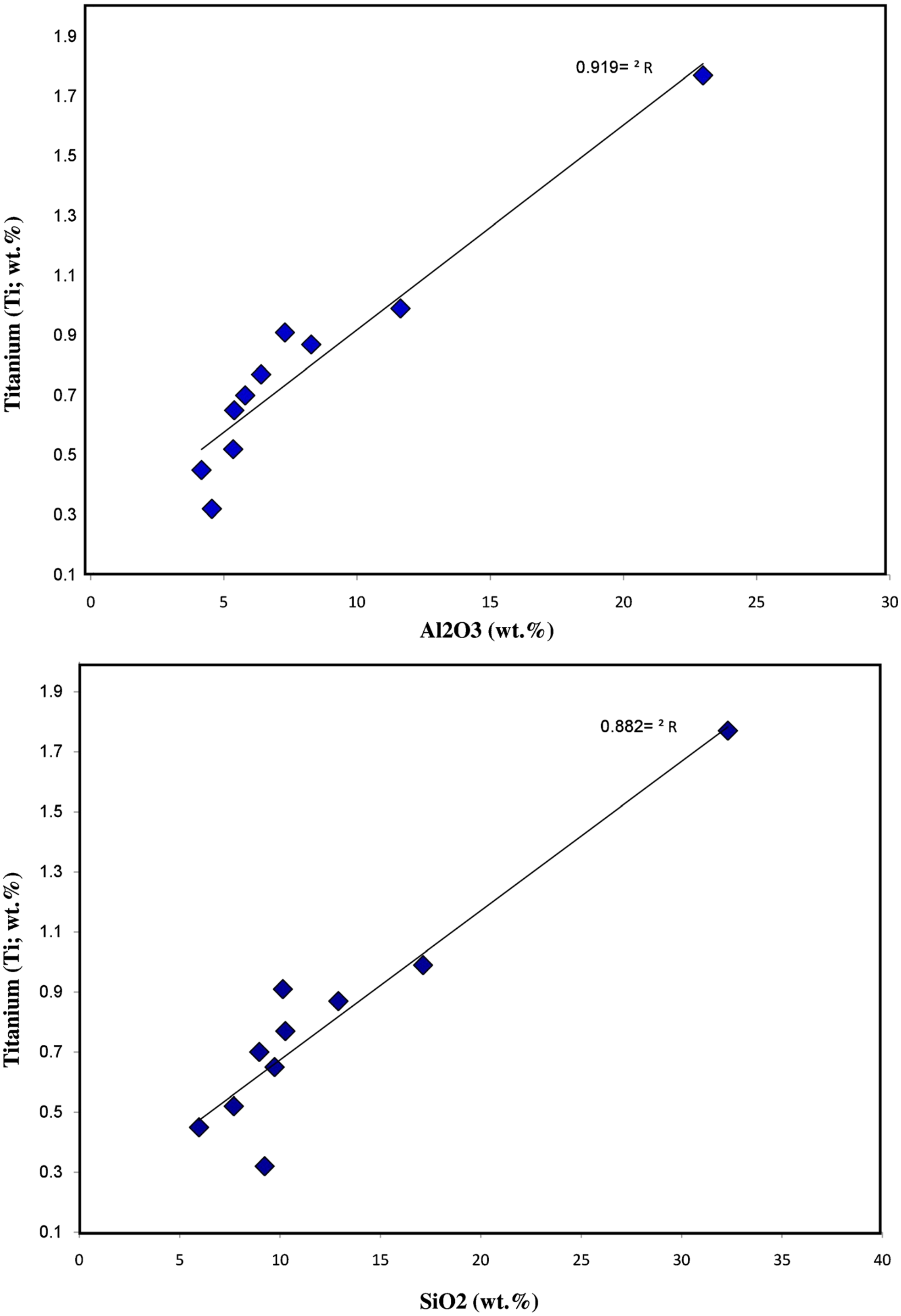


Fig. 4 Relationship between major elements of titanium (Ti) and SiO_2 and Al_2O_3 elements for investigated limestone sediments from Banik Village in the Kurdistan Region, Northern Iraq

Phosphorus Phosphorus contents also are detected in the Late Jurassic-Early Cretaceous limestone sediments (Table 2). The studied samples have low to moderate concentrations of phosphorus (P) in the range of 0.04–0.30, reflecting mixed organic matter input and leading to the formation of a reducing depositional environment favourable for preservation of organic matter (Shu et al. 2013). This is confirmed by organic matter input and conditions as indicated by biomarkers distributions (Table 1).

Vanadium and nickel Vanadium and nickel are important trace elements to indicate the redox conditions during deposition as vanadium (V) is usually enriched in comparison with nickel (Ni) in anoxic marine environments (Barwise 1990; Peters and Moldowan 1993; Bechtel et al. 2001; Galarraga et al. 2008). According to Galarraga et al. (2008), a V/Ni ratio greater than 3 indicates that the sediments were deposited in a reducing environment, while V/Ni ratios ranging from 1.9 to 3 indicate deposition under suboxic conditions with precursor organic matter of mixed origin. The V/Ni ratios for the analysed samples are in the range of 1.74–5.76, thus showing suboxic to anoxic conditions during deposition. More so, high V/(V+Ni) ratios (0.63–0.85) and sulfur contents (1.01–2.70 wt%) in the studied samples denote that these samples contain carbonate-rich sediments that were deposited under suboxic to anoxic conditions (Fig. 5).

Strontium and barium Strontium and barium are two trace elements that are regarded as empirical indicators of paleosalinity (Liu et al. 1984; Deng and Qian 1993; Wang 1996). A high Sr/Ba ratio reflects high salinity, and a low Sr/Ba ratio indicates low salinity (Deng and Qian 1993). The studied samples have relatively high Sr/Ba ratio (average 1.67), indicating high saline water during deposition, thus have influenced by seawater. This is consistent with high total sulfur content values (>0.5). The Sr/Ba versus V/Ni ratios diagram (Fig. 6a) also reflects relatively high salinity stratification and relatively reducing conditions during deposition of the Late Jurassic-Early Cretaceous limestone sediments. This founding is also consistent with the presence of gammacerane biomarker (Fig. 6b), as gammacerane occurs in reducing and high salinity stratification during deposition (Sinninghe Damsté et al. 1995; Peters et al. 2005).

Maturity of organic matter

In this study, the biomarker maturity parameters were used to assess the level of thermal maturity of organic matter within studied limestone sediments of the Kurdistan in the Northern Iraq (Mackenzie et al. 1980; Waples and Machihara 1991). The biomarker maturity ratios are C_{32} hopane 22S/(22S+22R), moretane/hopane, C_{29} sterane ββ/(ββ+αα) and 20S/(20S+20R) (Table 1). The ratios of 22S/(22S+22R) for C_{32} hopanes are between 0.60 and 0.63 (Table 1), suggesting that they have already reached oil window (Seifert and Moldowan 1986). The ratios of C_{29} sterane ββ/(ββ+αα) and 20S/(20S+20R), maturity ratios of the studied samples, are 0.47–0.58 and 0.39–0.46, respectively (Table 1), mostly either at or close to thermal equilibrium, consistent with their generation from early-mature to mature source rocks (Seifert and Moldowan 1978 1981) as shown in Fig. 7. This is supported by moretane/hopane ratios consistent with low relative abundance of C_{30} moretane (Fig. 3b). Moretane converts to C_{30} hopane with increasing thermal maturity (Seifert and Moldowan 1986), and thus, moretane decreases as thermal maturity increases. The ratio of moretane to their corresponding hopanes decreases with increasing thermal maturity, from about 0.8 in immature sediments to about 0.15–0.05 in mature source rocks and oils (Mackenzie et al. 1980; Seifert and Moldowan 1986). The limestones of the Iraq Kurdistan have moretane/hopane ratio in the range of 0.06 to 0.12, suggesting the samples have entered peak oil window maturity.

Origin of organic matter and paleodepositional conditions

In this study, organic geochemical (biomarker distributions) and inorganic data (major and trace elements) have been used

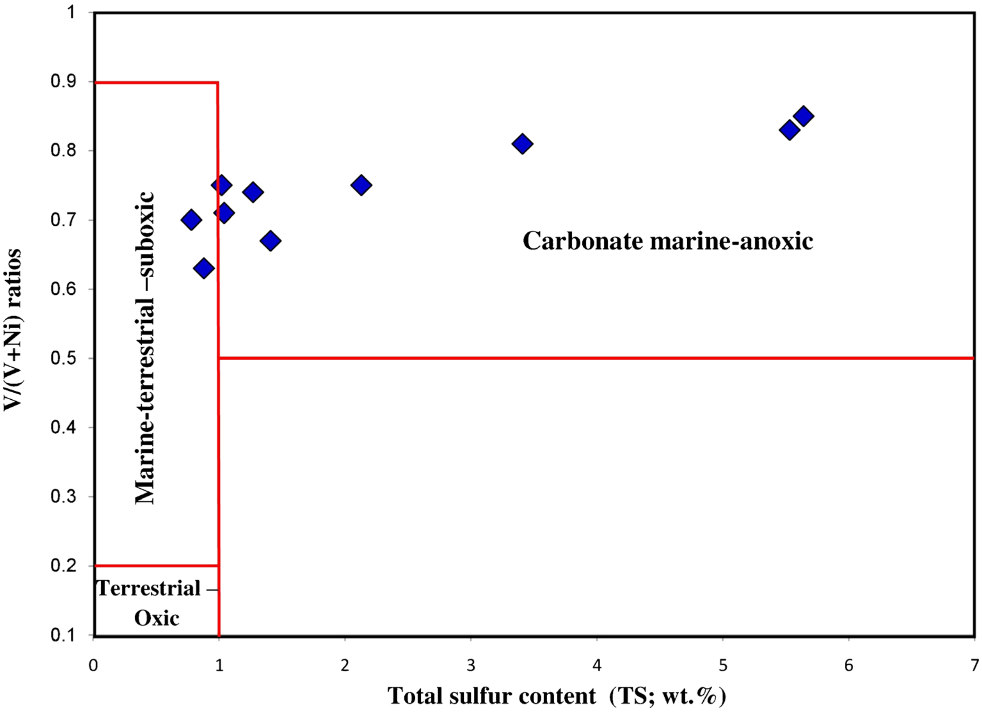


Fig. 5 V/(V+Ni) versus sulfur content (TS; wt. %) of studied limestone samples from Banik Village in the Kurdistan Region, Northern Iraq

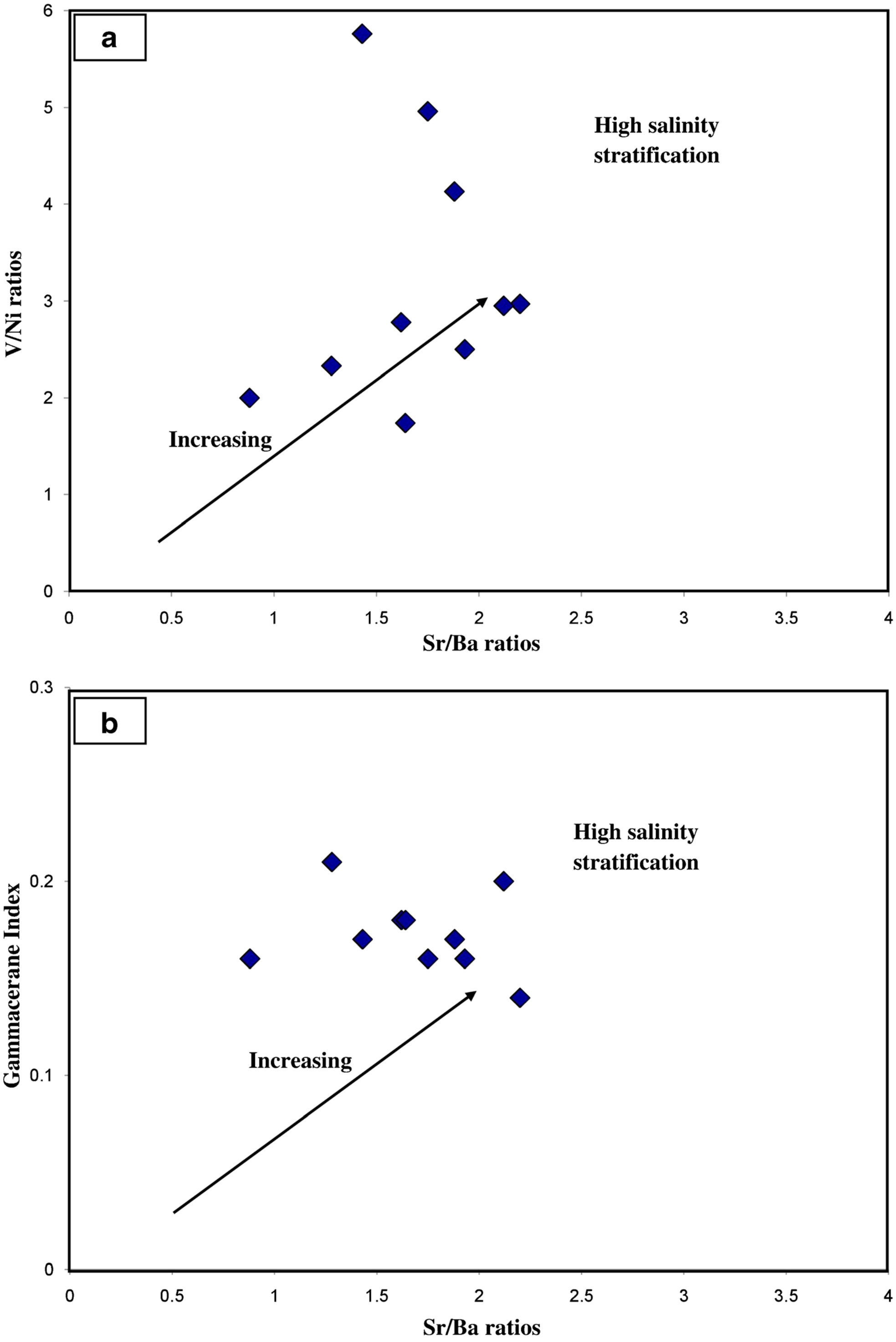


Fig. 6 The diagrams of Sr/Ba ratio versus V/Ni ratio (**a**), and gammacerane index (**b**) for the limestone sediments of the Banik Village in the Kurdistan Region (adopted after Jia et al. 2013)

to describe source input of organic matter and depositional environment conditions of limestones within the Late Jurassic-Early Cretaceous sequence in the Kurdistan Region, Northern Iraq.

The origin of organic matter was primarily examined through normal alkanes, hopanoids, steroids and related compounds (Waples and Machihara 1991; Hunt 1996; Peters et al. 2005). The *n*-alkane distribution patterns of saturated hydrocarbons can be used to define organic matter input from different producers (Brassell et al. 1978). The long-chain *n*-alkanes (>*n*-C_{23}) are characteristic biomarkers for higher terrestrial plants (Eglinton and Hamilton 1967), whereas the short-chain *n*-alkanes (<*n*-C_{20}) are predominantly found in algae and microorganisms (Peters et al. 2005). The *n*-alkane patterns

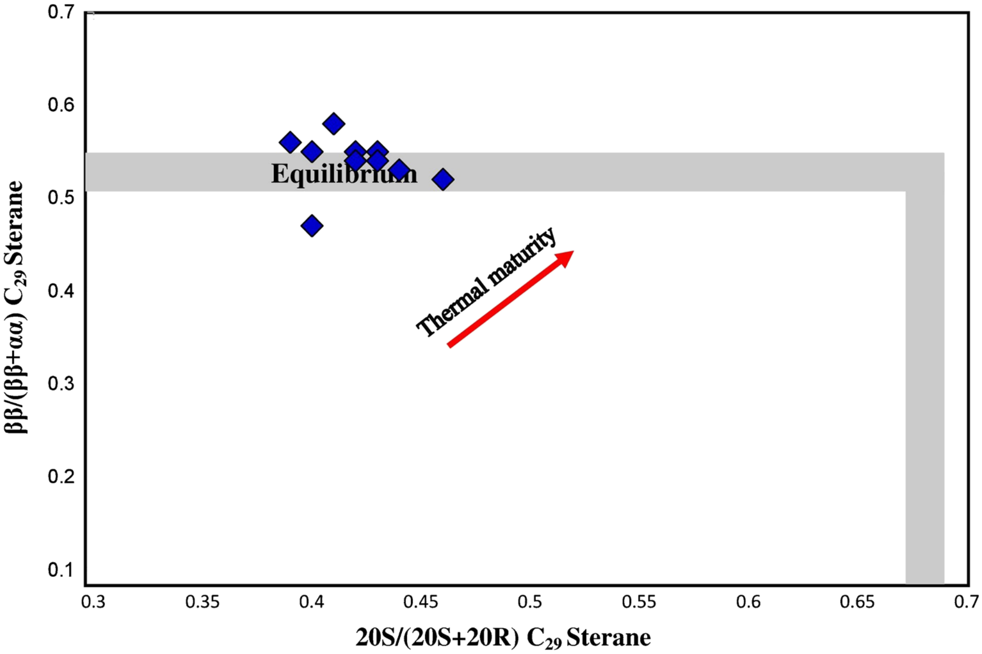


Fig. 7 A range of thermal maturity based on two maturity-related biomarker parameters [C_{29} 22S/(22S+22R) and C_{29} ββ/(ββ+αα)] for the studied limestone extracts

of studied sediments are predominance by a short (n-C_{15}–n-C_{20}) to middle (n-C_{21}–n-C_{25}) chain n-alkanes with the presence of significant waxy alkanes (+n-C_{25}) as shown in Fig. 3a. The n-alkane distributions are consistent with a dominant source of marine-derived organic matter, although receiving a minor terrigenous organic matter input (Ebukanson and Kinghorn 1986; Murray and Boreham 1992; Peters et al. 2005; Hakimi et al. 2012 2014). These interpretations are supported by low to moderate CPI values (0.85–1.25) (Table 1). The Pr/Ph ratios are in the range of 0.60–1.84 (Table 1), thus also further suggesting mixed organic matter with high contribution of aquatic organic matter deposited under suboxic to anoxic marine conditions (Didyk et al. 1978; Peters et al. 2005). The mixed organic matter type and conditions have also been interpreted using Pr/C_{17} and Ph/C_{18} ratios (Fig. 8). The influence of marine under reducing

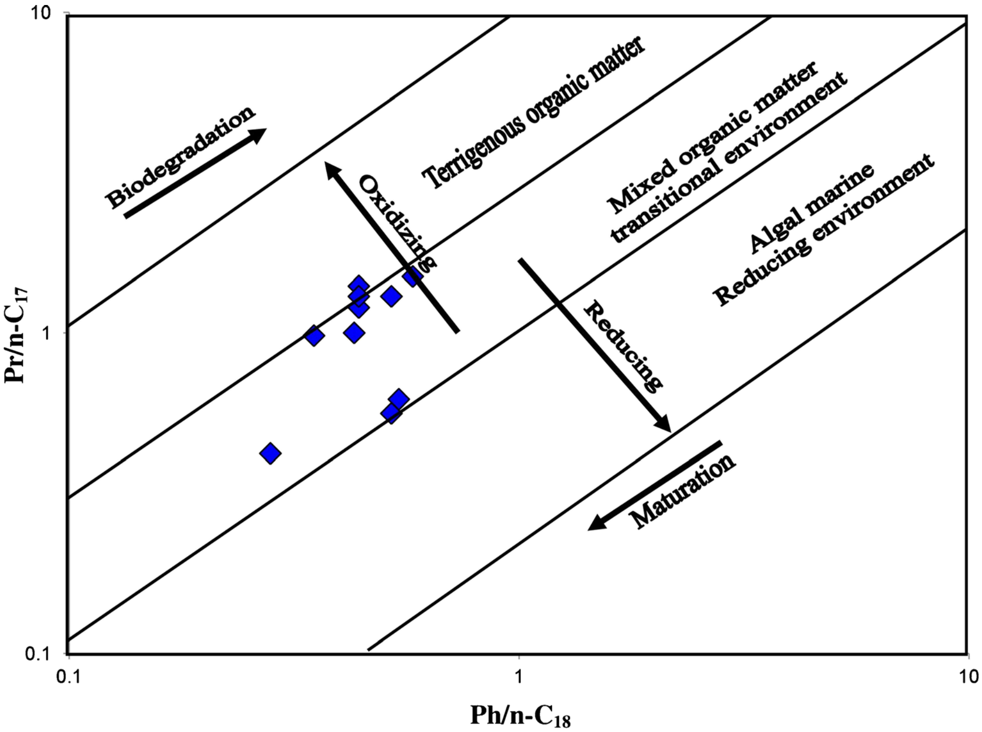


Fig. 8 Phytane to n-C_{18} alkane (Ph/n-C_{18}) versus pristane to n-C_{17} alkane (Pr/n-C_{17}) showing depositional conditions and type of organic matter of the analysed limestone samples from Banik Village in the Kurdistan Region, Northern Iraq

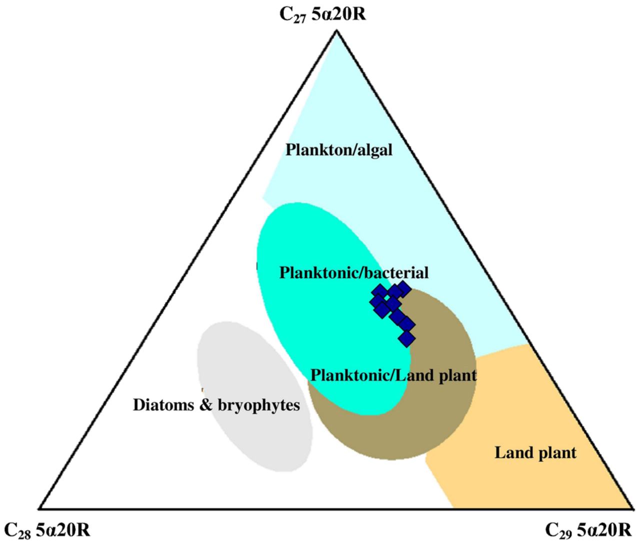


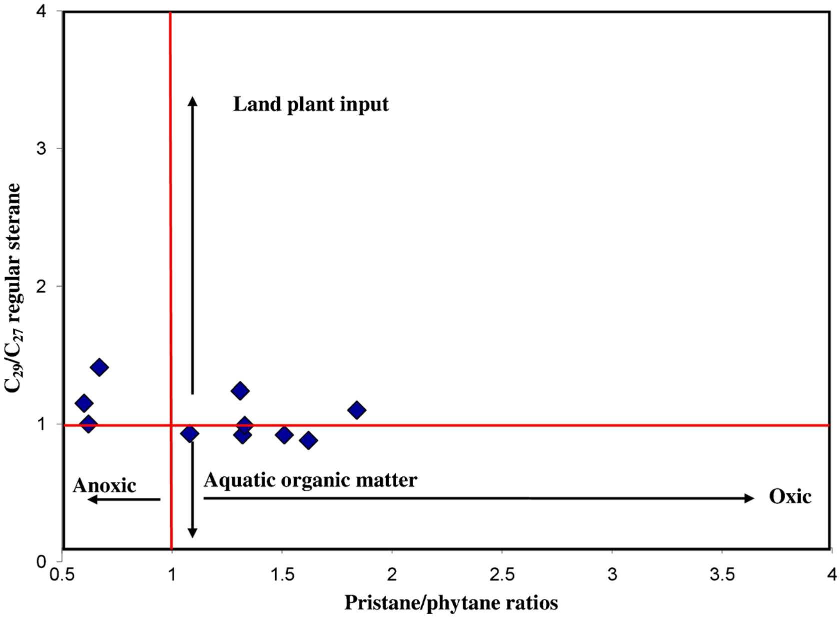
Fig. 9 Ternary diagram of regular steranes (C_{27}–C_{29}) indicating the relationship between sterane compositions and organic matter input, showing that the analysed limestone extracts from Banik Village in the Kurdistan Region, Northern Iraq (modified after Huang and Meinschein 1979)

condition is also consistent with the high sulfur content (0.77–5.64 wt%) and the presence of gammacerane biomarker that were identified in m/z 191 mass fragmentograms (Fig. 3b).

The studied sample extracts have relatively high tricyclic terpanes compared to tetracyclic (Fig. 3b), consistent with a high contribution of an aquatic organic matter (Zumberge 1987). The presence of a relatively high C_{23} tricyclic terpanes (Fig. 3b) and low C_{26}/C_{25} tricyclic terpane ratios (Table 1) is also indicative of a mixed marine organic matter (Aquino Neto et al. 1983; Marynowski et al. 2000). The high contributions of planktonic-bacterial organic matter is also demonstrated by the relative distribution of C_{27}, C_{28} and C_{29} steranes in m/z 217 chromatograms of the samples (Fig. 9). In most studied samples, the C_{27} and C_{29} steranes predominate over the C_{28} steranes (Table 1), reflecting a high contribution of aquatic planktonic-bacterial organic matter with a minor terrigenous organic matter input (Peters and Moldowan 1993; Peters et al. 2005), as indicated by regular sterane ratio ternary diagram (Fig. 9; Huang and Meinschein 1979) and corroborated by C_{29}/C_{27} sterane ratios (Fig. 10).

The reducing marine depositional environmental conditions of the Late Jurassic-Early Cretaceous limestone sediments in the Kurdistan Region, Northern Iraq, have also been interpreted using geochemistry of major and trace elements. The high carbonate input (CaO) element with terrestrial detritus elements (e.g., SiO_2, Al_2O_3 and TiO_2) in significant amounts further confirms that the Late Jurassic-Early Cretaceous limestone sediments were deposited in calcium-rich seawater (Stach et al. 1982) with detrital materials input (Ross and Bustin 2009). The calcium-rich seawater has also been confirmed by high Sr trace elements (Table 2). Palaeo conditions during sedimentation of Late Jurassic-Early Cretaceous limestone sediments can also be evaluated from their trace element data such as V, Ni, Sr and Ba (Harris et al. 2004; Sageman and Lyons 2004; MacDonald et al. 2010; Fu et al. 2011). Some standard ratios such as V/Ni and Sr/Ba are most used as palaeo condition indicators in this study

Fig. 10 Cross-plots of pristane/phytane ratios versus C_{29}/C_{27} regular steranes of the studied limestone samples, showing that limestones contain high contribution of aquatic planktonic-bacterial organic matter with a minor terrigenous organic matter input



(Table 2). The high Sr/Ba and V/Ni ratios (avg. 1.67 and 3.21, respectively) reflect enhanced salinity stratification and anoxic conditions during deposition of the Late Jurassic-Early Cretaceous limestone sediments in the Kurdistan Region, Northern Iraq (Fig. 6a).

Conclusions

An integrated biomarker characterisation and inorganic geochemical elements of the Late Jurassic-Early Cretaceous limestone sediments in the Kurdistan Region, Northern Iraq, to infer origin, type and preservation of organic matter in relation to paleodepositional conditions have revealed the following:

1. The limestone sediments were deposited in a marine environment with calcium-rich seawater under suboxic to anoxic conditions as supported by biomarker environment characteristics and inorganic elements.
2. The saturated fractions of the limestone extracts are characterised by a predominance of short (n-C_{15}–n-C_{20}) to middle (n-C_{21}–n-C_{25}) chain *n*-alkanes with the presence of significant waxy alkanes (+n-C_{25}), low to moderate CPI values (0.88–1.25), relatively low Pr/Ph ratios (0.60–1.84) and high concentrations of regular sterane C_{27}, as well as the presence of tricyclic terpanes, which is consistent with reducing marine environment which designifies a dominant contribution of aquatic organic matter. A small amount of terrigenous organic matter input is present based on the *n*-alkane distributions and significant concentrations of regular sterane C_{29}.
3. The dominant major elements identified in the limestones are CaO (avg. 67.73 wt%) followed by SiO_2 (avg. 12.44 wt%), Al_2O_3 (avg. 8.18 wt%) and Fe_2O_3 (avg. 4.57 wt%). The assemblages and modes of occurrence supported the calcium-rich seawater origin. Minor detrital material input is also evidenced based on the significant amounts of SiO_2 and Al_2O_3 elements and relatively high T) element (avg. 0.79 wt%).
4. Based on the assessment of Sr, Ba, V and Ni trace elements and their ratios, a stratified water column with salinity and low oxygen bottom water conditions within the Late Jurassic-Early Cretaceous limestone sediments are evidenced and again, indicative of a relatively reducing marine condition.

Acknowledgments The authors are most grateful to the Department of Geology in the University Malaya for providing geochemistry facilities to complete this study.

Appendix A

Table 3 Peak assignments for *n*-alkane hydrocarbons in the gas chromatograms of saturated fractions in the *m/z* 191 (I) and 217 (II) mass fragmentograms compound abbreviation

(I) Peak no.		
Ts	18α(H),22,29,30-trisnorneohopane	Ts
Tm	17α(H),22,29,30-trisnorhopane	Tm
29	17α,21β(H)-nor-hopane	C_{29} hop
30	17α,21β(H)-hopane	Hopane
30M	17 β,21α (H)-moretane	C_{30} mor
29M	17β (H),2lα (H)-30-norhopane (normoretane)	Normoretane
31S	17α,21β(H)-homohopane (22S)	C_{31}(22S)
31R	17α,21β(H)-homohopane (22R)	C_{31}(22R)
32S	17α,21β(H)-homohopane (22S)	C_{32}(22S)
32R	17α,21β(H)-homohopane (22R)	C_{32}(22R)
33S	17α,21β(H)-homohopane (22S)	C_{33}(22S)
33R	17α,21β(H)-homohopane (22R)	C_{33}(22R)
34S	17α,21β(H)-homohopane (22S)	C_{34}(22S)
34R	17α,21β(H)-homohopane (22R)	C_{34}(22R)
35S	17α,21β(H)-homohopane (22S)	C_{35}(22S)
35R	17α,21β(H)-homohopane (22R)	C_{35}(22R)
(II) Peak no.		
a	13β,17α(H)-diasteranes 20S	Diasteranes
b	13β,17α(H)-diasteranes 20R	Diasteranes
c	13α,17β(H)-diasteranes 20S	Diasteranes
d	13α,17β(H)-diasteranes 20R	Diasteranes
e	5α,14α(H), 17α(H)-steranes 20S	ααα20S
f	5α,14β(H), 17β(H)-steranes 20R	αββ20R
g	5α,14β(H), 17β(H)-steranes 20S	αββ20S
h	5α,14α(H), 17α(H)-steranes 20R	ααα20R

References

Amijaya H, Schwarzbauer J, Littke R (2006) Organic geochemistry of the Lower Suban coal seam, South Sumatra Basin, Indonesia: palaeoecological and thermal metamorphism implications. Org Geochem 37:261–279

Aquino Neto FR, Trendel JM, Restle A, Connan J, Albrecht P (1983) Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleum. In: Bjorøy M (ed) Advances in organic geochemistry 1981. Wiley, New Jersey, pp 659–667

Barwise AJG (1990) Role of nickel and vanadium in petroleum classification. Energy Fuels 4:647–652

Bechtel A, Gratzer R, Sachsenhofer RF (2001) Chemical characteristics of Upper Cretaceous (Turonian) jet of the Gosau Group of Gams/Hieflau (Styria, Austria). Int J Coal Geol 46:27–49

Berner RA, Raiswell R (1983) Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. Geochim Cosmochim Acta 47:855–862

Berner RA (1984) Sedimentary pyrite formation: an update. Geochim Cosmochim Acta 48:605–615

Brassell S.C, Eglinton G, Maxwell JR, Philp RP (1978) Natural background of alkanes in the aquatic environment. In: Hutzinger, L.H., van Lelyveld, O., Zoeteman, B.C.J. (Eds.), Pergamon, Oxford, pp. 69–86

Buday, T (1980) The regional geology of Iraq. In: Stratigraphy and paleogeography, vol. I. GEOSURV, Baghdad, 445pp

Deng HW, Qian K (1993) Analysis on sedimentary geochemistry and environment. Science Technology Press, Gansu, pp 15–85 (in Chinese)

Didyk BM, Simoneit BRT, Brassell SC, Eglinton G (1978) Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature 272:216–222

Ebukanson EJ, Kinghorn RRF (1986) Maturity of organic matter in the Jurassic of southern England and its relation to the burial history of the sediments. J Pet Geol 93:259–280

Edilbi ANF (2010) Stratigraphy and petroleum potential of Chia Gara Formation (Tithonian-Berriasian) in selected sections in North Iraq, M.Sc thesis, Unpublished, University of Salahdeen, 126p

Eglinton G, Hamilton RG (1967) Leaf epicuticular waxes. Science 156: 1322–1344

Fu X, Wang J, Zeng Y, Cheng J, Tano F (2011) Origin and mode of occurrence of trace elements in marine oil shale from the Shengli River Area, Northern Tibet, China. Oil Shale 28(4):487–506

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

Hakimi MH, Wan HA, Shalaby MR (2011) Organic geochemical characteristics and depositional environments of the Jurassic shales in the Masila Basin of Eastern Yemen. GeoArabia 16:47–64

Hakimi MH, Abdullah WH, Shalaby MR (2012) Molecular composition and organic petrographic characterization of Madbi source rocks from the Kharir Oilfield of the Masila Basin (Yemen): palaeoenvironmental and maturity interpretation. Arab J Geosci 5: 817–831

Hakimi MH, Abdullah WH, Shalaby MR, Alramisy GA (2014) Geochemistry and organic petrology study of Kimmeridgian organic-rich shales in the Marib-Shabowah Basin, Yemen: origin and implication for depositional environments and oil-generation potential. Mar Pet Geol 50:185–201

Harris NB, Freeman KH, Pancost R, White TS, Mitchell GD (2004) The character and origin of lacustrine source rocks in the Lower Cretaceous synrift section, Congo Basin, west Africa. AAPG Bull 88:1163–1184

Huang H, Pearson MJ (1999) Source rock palaeoenvironments and controls on the distribution of dibenzothiophenes in lacustrine crude oils, Bohai Bay Basin, Eastern China. Org Geochem 30:1455–1470

Huang WY, Meinschein WG (1979) Sterols as ecological indicators. Geochim Cosmochim Acta 43:739–745

Hunt JM (1996) Petroleum geochemistry and geology. W.H. Freeman, New York

Jia J, Bechtel A, Liu Z, Susanne AI, Strobl PS, Reinhard FS (2013) Oil shale formation in the Upper Cretaceous Nenjiang Formation of the Songliao Basin (NE China): implications from organic and inorganic geochemical analyses. Int J Coal Geol 113:11–26

Korkmaz S, Kara Gülbay R (2007) Organic geochemical characteristics and depositional environments of the Jurassic coals in the eastern Taurus of Southern Turkey. Int J Coal Geol 70:292–304

Liu YJ, Cao LM, Li ZL, Wang HN, Chu TQ, Zhang JR (1984) Element geochemistry. Science Press, Beijing, pp 283–372 (in Chinese)

MacDonald, R., Hardman, D., Sprague, R., Meridji, Y., Mudjiono, W., Galford, J., Rourke, M., Dix, M., Kelto, M (2010) Using elemental geochemistry to improve sandstone reservoir characterization: a case study from the Unayzah A interval of Saudi Arabia, SPWLA 51st Annual Logging Symposium, June 19–23, 1–16 p

Mackenzie AS, Patience RL, Maxwell JR, Vandenbroucke M, Durand B (1980) Molecular parameters of maturation in the Toarcian shales, Paris Basin, France-I. Changes in the configurations of acyclic isoprenoid alkanes, steranes, and triterpanes. Geochim Cosmochim Acta 44:1709–1721

Marynowski L, Narkiewicz M, Grelowski C (2000) Biomarkers as environmental indicators in a carbonate complex, example from the Middle to Upper Devonian, Holy Cross Mountains, Poland. Sediment Geol 137:187–212

Mohialdeen, I.M.J (2008) Source rock appraisal and oil-source correlation for the Chia Gara Formation, Kurdistan-north Iraq. PhD thesis, College of Science, University of Sulaimani, pp. 15e35

Mohialdeen IMJ, Raza SM (2013) Inorganic geochemical evidence for the depositional facies associations of the Upper Jurassic Chia Gara Formation in NE Iraq. Arab J Geosci 6:4755–4770

Mohialdeen IMJ, Hakimi MH, Al-Beyati FM (2013) Geochemical and petrographic characterization of Late Jurassic-Early Cretaceous Chia Gara Formation in Northern Iraq: palaeoenvironment and oil-generation potential. Mar Petrol Geol 43:166–177

Moldowan JM, Seifert WK, Gallegos EJ (1985) Relationship between petroleum composition and depositional environment of petroleum source rocks. Am Assoc Pet Geol Bull 69:1255–1268

Moosavirada SM, Janardhanab MR, Sethumadhava MS, Moghadamc MR, Shankara M (2011) Geochemistry of lower Jurassic shales of the Shemshak Formation, Kerman Province, Central Iran: provenance, source weathering and tectonic setting. Chem Erde 71:279–288

Murray AP, Boreham CJ (1992) Organic geochemistry in petroleum exploration. Australian Geological Survey Organization, Canberra. pp, 230

Ourisson G, Albrecht P, Rohmer M (1984) The microbial origin of fossil fuels. Sci Am 251:44–51

Peters KE, Moldowan JM (1993) The biomarker guide: interpreting molecular fossils in petroleum and ancient sediments. Prentice-Hall Inc, Englewood Cliffs, New Jersey

Peters KE, Walters CC, Moldowan JM (2005) The biomarker guide: biomarkers and isotopes in petroleum exploration and earth history, vol 2. Cambridge University Press, Cambridge

Rinna J, Rullkötter J, Stein R (1996) Hydrocarbons as indicators for provenance and thermal history of organic matter in late Cenozoic sediments from Hole 909C, Fram Strait: Proceedings of the Ocean Drilling Program, Scientific Results 151, 407–414

Ross DJK, Bustin RM (2009) Investigating the use of sedimentary geochemical proxies for palaeoenvironment interpretation of thermally mature organic-rich strata: examples from the Devonian–Mississippian shales, Western Canadian Sedimentary Basin. Chem Geol 260:1–19

Sageman BB, Lyons TW (2004) Geochemistry of fine grained sediments and sedimentary rocks. In: Holland HD, Turekian KK (eds) Treatise on geochemistry. Elsevier, New York, pp 115–158

Seifert WK, Moldowan JM (1978) Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. Geochim Cosmochim Acta 42:77–95

Seifert WK, Moldowan JM (1979) The effect of biodegradation on steranes and terpanes in crude oils. Geochim Cosmochim Acta 43: 111–126

Seifert WK, Moldowan JM (1981) Palaeoreconstruction by biological markers. Geochim Cosmochim Acta 45:783–794

Seifert, W.K., Moldowan, J.M (1986) Use of biological markers in petroleum exploration. In: Johns RB. editor. vol. 24. Amsterdam: Methods in geochemistry and geophysics book series, p. 261–90

Shu T, Dazhen T, Hao X, Jianlong L, Xuefeng S (2013) Organic geochemistry and elements distribution in Dahuangshan oil shale, southern Junggar Basin: origin of organic matter and depositional environment. Int J Coal Geol 115:41–51

Sinninghe Damsté JS, Kenig F, Koopmans MP, Koster J, Schouten S, Hayes JM, de Leeuw JW (1995) Evidence for gammacerane as an indicator of water column stratification. Geochim Cosmochim Acta 59:1895–1900

Stach E, Mackowsky MT, Teichmuller M, Taylor GH, Chandar D, Teichmuller R (1982) Stach's textbook of coal petrology, 3rd edition. Gebruder Borntraeger, Berlin, 535 pp

Sykes R (2004) Peat biomass and early diagenetic controls on the paraffinic oil potential of humic coals, Canterbury Basin, New Zealand. Pet Geosci 10:283–303

Ten Haven, H.L., de Leeuw, J.W., Rullkötter, J., Sinninghe Damsté, J.S., Schenck, P.A., Palmer, S.E., Zumberge, J.E., Fleet, A.J., Kelts, K., Talbot, M.R (1988) Application of biological markers in the recognition of palaeohypersaline environments. Lacustrine Petroleum Source Rocks. Geol Soc Spec Publ Lond. 123pp

Volkman JK (1986) A review of sterol biomarkers for marine and terrigenous organic matter. Org Geochem 9:83–89

Wang AH (1996) Discriminant effect of sedimentary environment by the Sr/Ba ratio of different existing forms. Acta Sedimentol Sin 14:168–173

Waples DW, Machihara T (1991) Biomarkers for geologists: a practical guide to the application of steranes and triterpanes in petroleum geology. American Association of Petroleum Geologists Methods in Exploration 9, Tulsa, Oklahoma

Zumberge JE (1987) Terpenoid biomarker distributions in low maturity crude oils. Org Geochem 11:479–496