Petroleum Res. J. Vol. 16 (2004); P. 65–76, 7 Figs.

Trace Elements and Stable Isotopes For The Abu Ghaylan Formation, Central Jabal Nafusah, NW Libya

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العناصر الشحيحة والنظائر الثابتة لتكوين أبوغيلان في وسط جبل نفوسة - شمال غرب ليبيا

محمود البكاي وعائشة شلغوم وسلامة رحومة

يتكشف تكوين أبو غيلان في الجزء الشمالي الأوسط من جبل نفوسة شمال غرب ليبيا بين وادي غان شرقاً إلى الرابطة غرباً، ولعوامل التعرية أكثر منها لأسباب الترسيب يختفي هذا التكوين في اتجاه الشرق بعد وادي غان.

ينتمي تكوين أبو غيلان للعصر الترياسي الأعلى والجوارسي المبكر ويمكن التعرف على هذا التكوين بمنطقة أبو غيلان وما جاورها لكونه محصوراً بين وحدتين من الصخور الرملية الحمراء هما تكوين أبوشيبة عند القاع وتكوين ككلة الفتاتي القاري من أعلى.

يتغير هذا التكوين جانبياً في اتجاه الغرب قرب كاف منطروس إلى سحنة مختلفة تسمى تكوين بئر الغنم. وتتشابه السحنات الصخرية لتكويني أبو غيلان وبئر الغنم، وكما ورد ذكره في عدة مراجع، مع رسوبيات الأرصفة الجيرية الضحلة.

من خلال المعلومات والنتائج المتحصل عليها من جهاز الأشعة السينية يمكن أن نعتبر أن تنظيم بلورات الدلومايت جيدة وأنه غير متعادل، أي أن نسبة جزيئاته من أكاسيد الكربونات إلى أكاسيد الماغنيسيوم غير متساوية.

بلغ متوسط قيمة نظائر الأكسجين الثابتة للدولومايت المتكوّن في رسوبيات أبو غيلان -1.66 بمقياس (PDB) بينما كان متوسط قيمة نظائر الكربون الثابتة له -0.28 (PDB). وتقل نظائر الأكسيجن الثابتة تدريجياً بازدياد العمق وهذا يعكس تزايد التصخر أثناء الردم أو دفن هذه الرسوبيات. ويحتوي الدولومايت في هذا التكوين عموماً على كميات ضئيلة من عناصر السترونشيوم والمنجنيز والصوديوم والحديد.

يمكن إستنتاج أنه هناك طريقتين ساهمتا في تكون الدولومايت أو إحلال الدولومايت محل الرسوبيات الأصلية لهذا التكوين وهما طريقة دخول ماء البحر إلى المستنقعات المالحة ليصبح سائل غني بالماغنيسيوم ومرور هذا السائل خلال الرسوبيات التي تعلوه ثم تبخر، أما الطريقة الأخرى فهي إختلاط المياه العذبة التي تمر خلال الرسوبيات إلى أسفل بمياه البحر المالحة المتسربة إلى الرسوبيات.

Abstract: *The Abu Ghaylan Formation is well exposed in north-centeral Jabal Nafusah, north-west Libya, between Wadi Ghan to the east and Ar Rabitah to the west. Abu Ghaylan Formation is missing towards the east owing to erosional factors rather than depositional.*

The Upper Triassic-Lower Jurassic stratigraphic section (Abu Ghaylan Formation) in the vicinity of Gharyan is easily distinguished at Abu Ghaylan and neighbouring areas where it lies between two red-coloured rock units, the Abu Shaybah Formation at

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the base and the continental clastics of the Kiklah Formation at the top.

The Abu Ghaylan unit further west grades into the Bir al Ghanam Formation near kaf Mantrus The lithofacies of the Abu Ghaylan as descriped in litrature, is analogous to the shallow shelf carbonates.

Two types of dolomite can be differentiated petrographically based on crystal size and precursor facies. The data gathered from XRD analysis suggest that the Abu Ghaylan dolomite types seem to be mainly non-stoichiometric and well-ordered.

Stable carbon and oxygen data are reported from dolomite and calcite from the Abu Ghaylan Formation. Surface dolomite samples have a mean $\delta^{18}O$ value of -1.66 per mil, and a mean $\delta^{13}C$ value of -0.28 per mil (all values are relative to PDB). Oxygen isotopic ratios become progressively lighter by depth, and reflect progressive lithification of the Abu Ghaylan sediments during burial.

The lack of significants in both carbon and oxygen isotopes from estimated values for the Upper Triassic-Lower Jurassic carbonate precludes meteoric influence during Abu Ghaylan diagenesis. Abu Ghaylan dolomites generally have low trace elements (Sr, Mn, Na and Fe) concentration.

Two mechanisms were involved in the formation of the Abu Ghaylan's dolomite; they are hypersaline reflux and mixed water.

INTRODUCTION

Abu Ghaylan Formation (Christie, 1955) in its outcrop is limited to the area between Wadi Ghan in the east and Ar Rabitah to the west of Jabal Nafusah (Fig. 1), north-western Libya. Locally thin section of Abu Ghaylan is exposed just east of Suk Al Ahad (Fatmi and Sbeta, 1991).

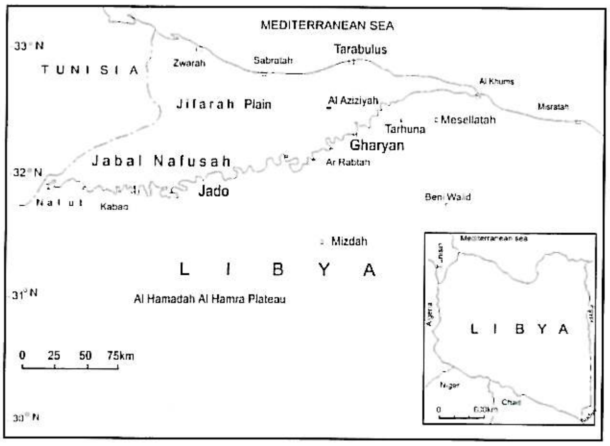

Fig. 1. Location map.

Abu Ghaylan Formation is missing towards the east (Fig. 2) owing to erosional factors rather than depositional (Desio *et al*, 1963; Burollet, 1963a and b; Magnier, 1963). This formation passes to the west into the Bir al Ghanam Formation, which is composed mainly of gypsum. The thickness of the Abu Ghaylan carbonates in the type section at Abu Ghaylan area is about fifty eight meters. It is composed mainly of light-coloured white to buff to light brown dolomite and dolomitic limestone. The lower twenty meters (Fig. 3) are highly fractured and recemented to form breccia (Fig. 4). Above the most fractured band a narrow layer of dolomitized oolitic limestone contains numerous small ghosts or indeterminate fossils.

The middle part is compact, recrystallized and yellowish massive dolomite. At the top the carbonate rocks are interbedded with clay, the upper most layers, however, being very hard, compact and oolitic. A trace of chert was found in this formation in Abu Ghaylan area which increases towards the west (south of Kaf Takut) forming a permanent resistant band.

Abu Ghaylan Formation occupies an intermediate position in the scarp face. It is easily distinguished at Abu Ghaylan and the neighbouring areas, where it lies unconformably between two red-coloured rock units, the Abu Shaybah Formation at base and the Kiklah Formation at top.

Owing to the lack of well-preserved fossils as a result of extensive dolomitization, the age of the Abu

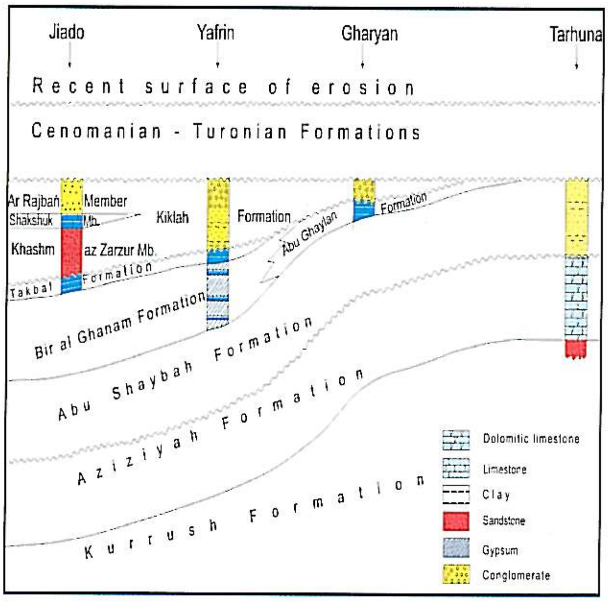

Fig. 2. Stratigraphic cross-section [(not to scale), after Fatmi and Sbeta, 1991].

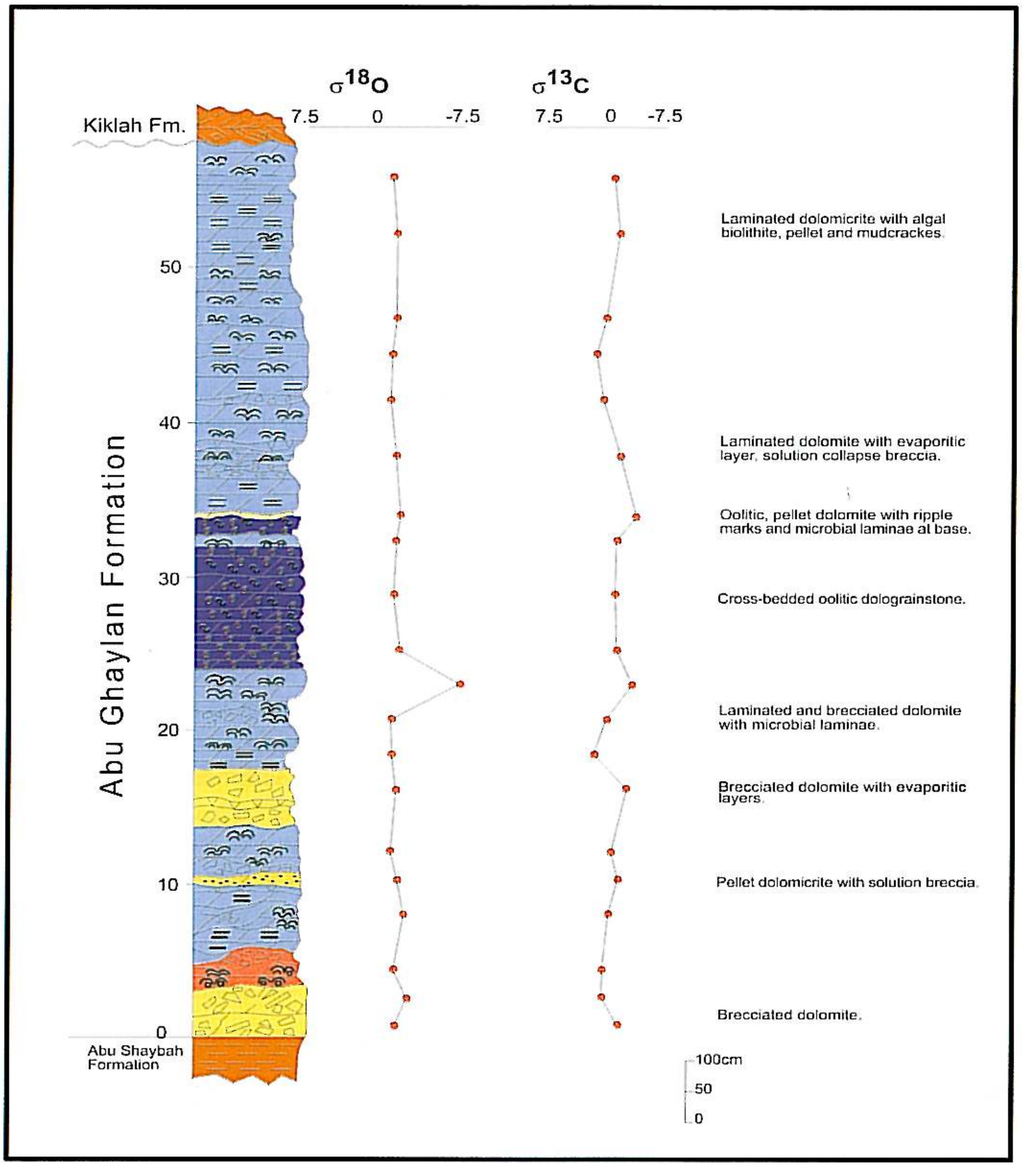

Fig. 3. Columnar section of the Abu Ghaylan Formation at Abu Ghaylan- Gharyan new road, in central Jabal Nafusah.

Fig. 4. General view of the Abu Ghaylan Formation showing collapse breccia. Photo was taken along the road approximately 1km west of Abu Ghaylan Police Station.

Ghaylan Formation is interpreted on the basis of its stratigraphic position. The Abu Ghaylan Formation and a part of the Bir al Ghanam Formation at top and the Abu Shaybah Formation were dated as Carnian (Christie, 1955), on the other hand the overlying middle and upper members of the Bir al Ghanam Formation are of Upper Triassic-Lower Jurassic age. Therefore, the age of the Abu Ghaylan Formation can be assigned to the time lapse between the Carnian and the Bajocian (Burollet, 1960 and El Hinnawy and Chesitev, 1975).

PETROGRAPHY

The extensive dolomite sequence of the Abu

Ghaylan Formation is fine crystalline and light-coloured white to buff to light gray brown in colour. Breccia with vertical fractures, microbial laminae and some dissolution vugs are distinctive characteristics.

Petrographically, the dolomites of the Abu Ghaylan Formation can be divided into two main types on the basis of crystals size and original sediments or precursor facies.

Type-I dolomite (Fig. 5) is very fine and is volumetrically dominated, non-ferroan and consists of dense interlocking, anhedral or nonplanar-a crystals less than 10 µm in size, with irregular intercrystalline boundaries. Type-I dolomite is non-mimetically replaced precursor mudstone or pellets and/or microbial mudstone/wackestone. The texture is mainly xenomorphic.

Type-II dolomite (Fig. 6) is non-ferroan commonly mimetic, preserving textural details of the precursor limestone (poorly to well-sorted bi-oolitic and oolitic packstone/grainstone), as well as depositional fabrics. Crystals of this type of dolomites which are present close to pore spaces are zoned with cloudy cores and clean rimes.

Calcite cement exhibits large, blocky crystals observed in some filling pore spaces, notably with irregular contacts with dolomite crystals. Some zones of the dolomite crystals are dissolved out and are replaced by calcite (calcitization or dedolomitization).

GEOCHEMISTRY

It has been shown that the geochemistry of dolomites, including their major and trace elements concentration and isotopic composition, is an essential complement to geologic and petrographic studies (Veizer, 1983).

Most diagenetic carbonates represent the alteration products of sedimentary phases that were originally crystallized from seawater. Over the past two decades, studies of modern seawater and sediment samples as well as ancient fossils permit the estimation of the trace element and stable isotopic composition of equilibrium marine carbonates for a given time (*e.g.* M'Rabet, 1981; Veizer, 1983; DePaolo and Ingram, 1985).

Abu Ghaylan formation extends westward and grades into Bir al Ghanam Formation. The latter sediments are mainly composed of massive gypsum and anhydrite and minor sandstone and clay. Bir al Ghanam Formation is thickening westwards where it was deposited in a continuously sinking shallow, mostly closed, sedimentary basin varying between lagoonal gypsum facies to open marine environment carbonate facies (Banerjee, 1980). Some samples were collected at the Bir al Ghanam village and adjacent areas for geochemical analysis.

Results of these analyses exhibit that the collected samples from the shale and carbonate beds of the

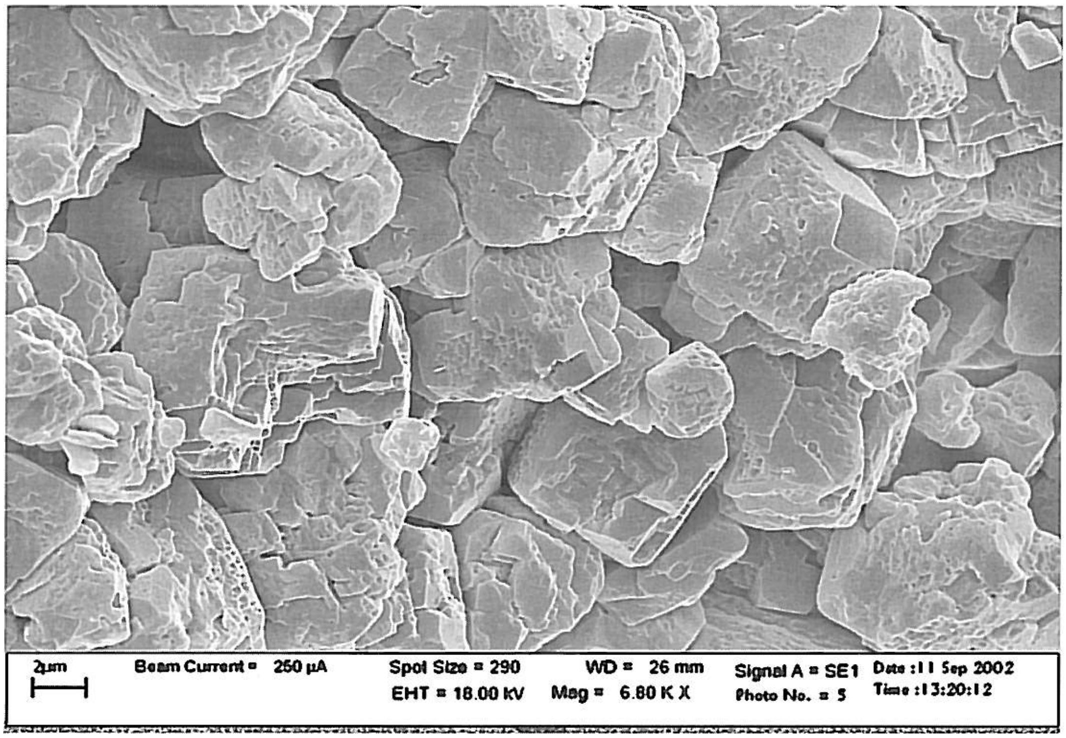

Fig. 5 Scanning electron photomicrograph of Type-I Dolomite.

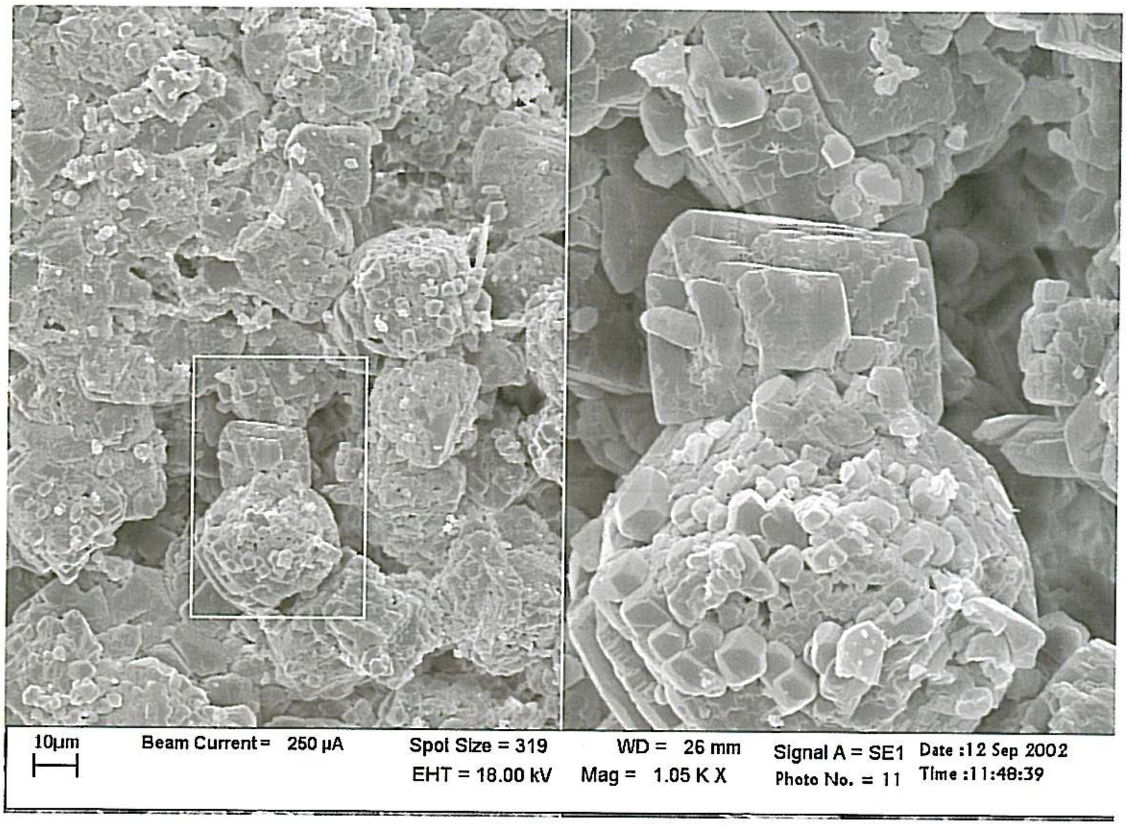

Fig. 6. Scanning electron photomicrograph of Type-II Dolomite.

Bir al Ghanam Formation are fair to good source rock with an average value of 1-3% total organic carbon (TOC) content. These sediments need further investigation in order to know their potential and their extention at subsurface which is expected to form a good source in the Jifarah Basin.

Stoichiometry and Crystal Order

As discussed by many authers such as Hardy and Tucker (1988); Tucker and Wright (1990), many if not most, natural dolomites are non-stoichiometric, i.e they do not have the ideal molar ratio of $CaCO_3/MgCO_3$ of 50/50. Stoichiometry of the Abu Ghaylan dolomite is determined by XRD analysis of whole rock powder . The $CaCO_3$ content was calculated using Lumsden's (1979) equation "Mole % $CaCO_3$= Md+B"; where M is (333.3), B is (-911.99) and d is the observed d-spacing (Å). This technique is also used in order to provide more information on the ordering of the dolomite crystals by dividing the intensity of peak (015) over peak (110). The greater the ratio of the highest of the ordering peak 015 to diffraction peak 110, the higher the degree of order (Tucker and Wright, 1990).

XRD data can be useful to distinguish between different types of dolomite within one carbonate formation, but with some overlap (Hardy & Tucker,1988), by plotting relationships between the ordering ratio versus the mole % $CaCO_3$ for all types of dolomite (Fig. 7a). Two types of dolomite can be recognized based on stoichiometry and ordering ratio from the data gathered from XRD analysis, the Abu Ghaylan dolomite types seem to be mainly non-stoichiometric and well-ordered.

The mole % $CaCO_3$ of very fine crystalline (Type-I) dolomite ranges from $Ca_{0.47}$ $Mg_{0.53}$ to $Ca_{0.45}$ $Mg_{0.46}$ with an average mole % $CaCO_3$ 50.1, and its ordering ratio ranges from 0.58 to 0.83 with an average of 0.71. However, mole % $CaCO_3$ of type-II dolomite ranges from $Ca_{0.46}$ $Mg_{0.54}$ to $Ca_{0.53}$ $Mg_{0.47}$ with an average mole % $CaCO_3$ 49.1, and its ordering ratio ranges from 0.46 to 0.95 with an average of 0.73.

Trace Elements

Trace elements concentration within the different dolomite types of the Abu Ghaylan Formation is determind by Atomic Absorption at Petroleum Research Centre Labs.

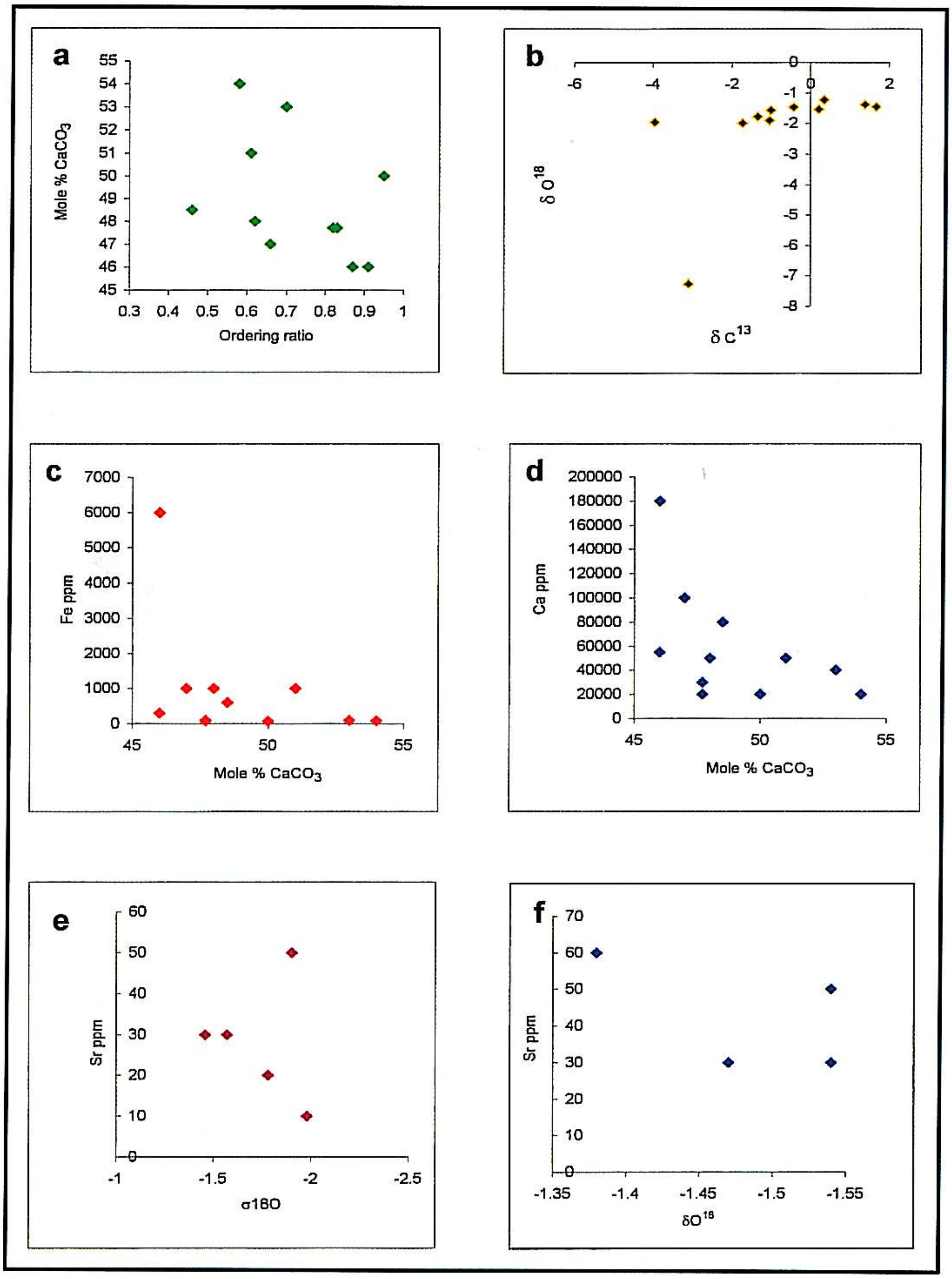

Fig. 7 Relationships between mole % Ca CO$_3$, trace elements, stable isotopes and stoichometry of the Abu Ghaylan dolomites.

Strontium

Strontium has received more attention in recent years than any other trace element in order to use it in the interpretation of formation of dolomite and diagenetic environment (Land, 1980).

The strontium concentration of the Abu Ghaylan Formation is generally low. Table (1) reports trace element concentrations in the Abu Ghaylan dolomites and in other dolomites reported in the literature.

The Sr concentration of Type-I dolomite of the Abu Ghaylan ranges from 10-30 ppm with an average of 20 ppm.

Type-II dolomite which replaced packstone and grainstone, has slightly higher Sr concentration. It ranges from 10-50 ppm, with an average of 28 ppm.

Table 1. Correlation of trace element concentrations in the Upper Triassic–Lower Jurassic Abu Ghaylan dolomites (this study) and various other dolomites reported in the literature:

Locality and Reference (s)	Formation (age) and dolomite type (s)	Sr (ppm)	Na (ppm)	Mn (ppm)	Fe (ppm)
Egypt Holail *et al,* 1988	El Heiz Formation (Cenomanian dolom.)	120	650	1900	-
	El Hefhuf Formation (Campanian dolom.)	103	425	720	-
U.S.A. Moore *et al*,1988	Smackover Fm. (U. Jurassic)				
	Evaporitic dolomite	261-490	512-990	89-172	416-1200
	Early coarse dol.	42-69	117-185	42-137	51-114
	Early fine dolomite	40-89	129-212	59-710	58-2663
	Late- zoned replacive dolomite	53-83	112-192	110	689
	Late saddle dolomite	93-139	256-399	418-1571	3631-36294
Tunisia M'Rabet (1981)	Central Tunisia (L. Cretaceous)				
	Dolomite associated with quartz	0-65	390-1370		11600-68100
	Dolomite associated with evaporite	6-175	440-1940		3000-11900
	Dolomite associated with palaekarst	0-90	440-950		2000-22600
	Dolomite associated with lacustrin	0-150	380-980		600-10800
U.S.A.Zenger and Dunham, 1988	Subsurface cores (Siluro-Devonian)				
	Saddle dolomite	8	759	117	250
	Medium to coarse dol.	4	884	75	134
	Fine dolomite	8	832	74	154
	Coarse to fine dol.	4	1165	52	593
	Medium to coarse dolomite	9	1053	73	314
Tunisia Soussi and M'Rabet, 1994	Central Tunisia (Jurassic)				
	Burial dolomite	0-50	65-2025	38-382	255-8290
Libya (this study)	Abu Ghaylan Fm., U. Triassic-L. Jurassic				
	Dolomite Type-I	0	238	34	320
	Dolomite Type-II	8	300	50	414

Sodium

Sodium concentration in diagentic phases is used in order to obtain more information about the salinty of the diagenetic fluids during preciptation and accordingly the mechanism responsible for dolomitization (Land,1980; Shukla,1988; Humphery, 1988).

Sodium in the Abu Ghaylan dolomites is generally low and its concentration is slightly lower in type-I (compared to Type-II dolomite). It ranges from 130-320 ppm in Type-I, with an average of 238 ppm. Na concentration ranges from 110 to 680 ppm in type-II dolomite, with an average 300 ppm.

Manganese

Mn contents in Type-I dolomite of the Abu Ghaylan sediments are low, ranging from 15 to 50ppm, having an average of 34 ppm, Type-II ranges from 40-60 ppm, having an average of 50ppm.

Iron

Concentration of iron may provide information on the oxidation-reduction state of the diagentic environment. The low concentration probably represents preciptation from oxidizing diagentic water (Humphery, 1988 and many others).

Fe concentrations in Type-I dolomite ranges from 90 to 1000 ppm, with an average of 320 ppm, whereas Type-II is simlar to Type-I and it ranges from 70 to 1000 ppm with an average of 414 ppm.

Stable Isotopes

Whole-rock samples from Abu Ghaylan sediments were analysed for ^{18}O and ^{13}C isotopes. All isotopic measurments reported here are in per mil PDB values.

Average $\delta^{18}O$ and $\delta^{13}C$ of the fine crystalline dolomite Type-I are -1.4% and +0.91% respectively. $\delta^{18}O$ varies from -1.54 to -1.23% and $\delta^{13}C$ from +0.22 to +1.68% (Fig. 7b).

Type-II dolomite is similar to Type-I in terms of $\delta^{18}O$, but has depleted values in $\delta^{13}C$ compared to Type-I dolomite. Average $\delta^{18}O$ of this dolomite is -1.74 and it ranges from -1.46 to -1.98%. $\delta^{13}C$ values of dolomite Type-II range from -1.72 to -0.43%, with an average of -1.11% (Fig. 7b).

Calcites from Abu Ghaylan deposits show a widespread distribution of $\delta^{18}O$ (between -7.26 to -1.95%) and less variable of $\delta^{13}C$ (between -3.96 to -3.1%, Fig. 7b).

DISCUSSION AND INTERPRETATION

The origin of large scale ancient dolomite has been a controversial subject. Pervasively dolomitized ancient sequences such as the Abu Ghaylan Formation contrast with Holocene dolomites, which are extremely limited in both areal extent and occurrences throughout the world. No modern analogue exists for these extensive, thick, ancient dolomites.

The lack of a comparable present day analogue limits the application of information to develop models for ancient dolomites. Also, it has not yet proved possible to synthesise dolomite in laboratory at conditions which approxinate the earth·s surface (low temperature; see Usdowski, 1994).

In considering models for thick, extensive dolomites in the past, a source for magnesium and a mechanism to pump the dolomitizing fluid through thick sediments must be found.

Land (1985) has pointed out that seawater is the only natural source for extensive dolomitization on the earth's surface. Sea water may be the ultimate source of Mg for many regionally extensive dolomite sequences. Dolomites are susceptible to varying source and composition, which may produce new textures and compositions on precursor phases (Banner, 1986; Gregg and Shelton, 1990; Kupecz *et al*, 1993; Nielson *et al*, 1994). Early diagenetic dolomites in many ancient carbonate platforms were formed by seawater, modified seawater and mixed meteoric-marine water (Adams and Rhodes, 1960; Mckenzie *et al*, 1980; Land, 1985; Machel and Mountjoy, 1986; Hardie, 1987; James *et al*, 1993; Sun, 1994).These early diagenetic dolomites are subsequencely altered, because they are intially metastable, calcium-rich phase (Land,1985). Many examples of alteration have been recognized in recent years (Banner *et al*, 1988; Kupecz *et al*,1993).

This study represents the first attempt of analysing trace elements and stable isotope composition of Upper Triassic-Lower Jurassic rocks from the Nafusah escarpment in north-west Libya and may shed light on the proceses of dolomitization of the Abu Ghaylan Formation in this area.

Type-I dolomite is very fine and non-plannar (Fig. 5). The absence of vugs and moldes that formed in the subsurface environments and dissolved core of some dolomite grains is typical of dolomite formed under near-surface low temperature. The non-ferroan character and low Fe content (Fig. 7c) of dolomite Type-I is further support for near-surface oxidizing conditions.

The sedimentary structures associated with the fine crystalline Type-I dolomite such as microbial laminae, layers of evaporite and solution collapse breccia suggest that this type is an early dolomite formed in supratidal-intertidal environment under the influence of refluxing brines. This type of dolomite is associated with evaporites, therefore, it is more variable in calcium contents (Fig. 5d), and the XRD for Type-I indicates that it is an early diagenetic dolomites precipitant from solution with relatively high Mg/Ca ratios which were probably evaporitic (reflux model).

The suggested model is consistent with the early timing and low Fe and Mn contents (average 320ppm and 34 ppm respectively).

Petrographic observation such as absence of exposure and invasion of meteoric water features in this type of dolomites does not favour mixing zone origin. Moreover, oxygen isotope composition of this dolomite is higher than the general values estimated for marine calcite (0% to +2%) proposed by Hudson (1977). Therefore, Type-I dolomite is interpreted as being formed by the hypersaline reflux model.

Dense mosaics of fine crystalline (5-70m) planar-a and planar-s dolomite Type-II (Fig. 6) is typical of dolomites formed under near-surface low temperature (average C) saline to hypersaline conditions (Gregg and Sibley, 1984; Machel and Mountjoy, 1987; Zenger and Dunham, 1988; Gregg and Shelton, 1990). They are commonly mimetic, preserving textural details of the precursor limestones (Fig. 6) as well as primary depositional fabrics where these are not overprinted. Their isotopic composition is close to those values estimated for dolomites precipitated from sea water (Muntjoy and Amthor, 1994).

Type-II dolomite is moderately to highly ordered and non-stoichiometric, showing that this dolomite type was precipitated at an early stage from solution of low Mg/Ca ratio, which was probably more humid and non-evaporitic, suggesting mixed marine-meteoric fluids as the diagenetic solution for the Type-II dolomite formation (Badiozamani, 1973).

Type-II dolomite has low Sr content (average 28ppm). Dolomite which formed from aragonite, high-Mg calcite and low-Mg calcite during the early stages has high Sr contents (500-600ppm), this may indicate that the dolomite has been precipitated from hypersaline solution process (Tucker, 1982; 1983; Tucker and Wright, 1990). The Sr content of dolomite type-II does not favour hypersaline model. Instead, it favours a mixing zone solution which usually has Sr contents of 70-300 ppm (Rodgers *et al*, 1982; Tucker and Wright, 1990) and would support a high-Mg calcite precursor rather than aragonite (Veizer, 1978, 1983). Furthermore, the mimetic_textures of completely dolomitized ooides should have heavy isotopic composition if the precursor was aragonite.

Low Fe and Mn contents noted in dolomite type-II (average 44ppm and 50ppm respectively) clearly indicates diagenesis dominated by meteoric water under oxidizing conditions during dolomitization. On the others hand, marine and hypersaline dolomites clearly contain high Na concentrations, as would expected from precipitation of these diagentic environments.

Type-II dolomite contains low Na (average 298ppm) which falls within the range of dolomite whose origin is ascribed to mixed-water precipitation (Humphrey, 1988).

The isotopic compostion of Type-II dolomite which ranges from -1.98% to -1.46% ^{18}O and from -1.72% to -0.43% ^{13}C might suggest less variable fluid compositions than for Type-I dolomite. Therefore, Type-II dolomite probably was formed in a mixing zone of σ^{18}O and σ^{13}C-enriched seawater and σ^{18}O and σ^{13}C-depleted freshwater at low temperature ranges from 49°C to 52°C (average 51°C) assumuing σ_w = o%. The positive correlation between Sr contents and oxygen isotope values for Type-II dolomite (Fig. 7e) compared to the same relation for Type-I (Fig. 7f) may reflect lower salinity (M'Rabat, 1981) related to meteoric influences. Furthermore, oxygen isotope values of this dolomite are comparable to other values for dolomites attributed to a mixed water origin, such as Holocene dolomites from Jamaica (Land, 1973) and Upper Cretaceous dolomites from Egypt (Holail *et al*, 1988).

Finally, the strongly negative σ^{18}O (-7.26%) and moderately light σ^{13}C (-3.96%) of a calcite which survived dolomitization are consistent with calcite precipitation during later stage under the influence of fresh water.

ACKNOWLEDGEMENTS

Field work and sample processing of this research were funded by the Petroleum Research Centre (PRC) of the National Oil Corporation (NOC). Authors would like to extend their sincere thanks to Mr Osama Burshan and Miss Fowzia Lahmar for their patience during SEM performance.

We are grateful to Mr Jalal Siefanasar for his assistance and performance of XRD analysis.

We would like to thank all colleagues and friends in the Exploration and Exploitation Research Department of the PRC for their help and support.

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