Silicification in the Cyrenaican Miocene Carbonate-Evaporite Sequence, NE Libya: Origin, Occurrence, Facies, and Sea Level Relationship

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ABSTRACT

This work investigates the distribution, occurrence, and origin of silica in the Cyrenaican Miocene shallow marine carbonates along a 135 km strike section, and its relation to the depositional facies and the sequence stratigraphic framework. Twenty-nine detailed measured stratigraphic field sections, 14 gamma-ray profiles, and four carbon stable isotope curves were used to define the Cyrenaican Miocene detailed facies relationships and their sequence stratigraphic context. The Ar-Rajmah Group Cyrenaican Miocene facies consists of red algal reefs, bioclastic packstones, oolitic grainstones, and microbialites that are associated with evaporites and siliciclastics. These facies are arranged within two second order supersequences that comprise six third order sequences. A total of 503 rock samples were collected for thin section petrographic analysis and x-ray fluorescence (XRF) geochemical analysis.

As observed in the field, silica is very common in the ramp crest oolitic grainstone facies and peritidal microbialite facies, but rare in the subtidal red algal and bioclastic packstone facies. The silica commonly occurs as chert nodules of reddish-bluish light gray color in the ramp-crest and peritidal facies and is whitish light gray color in the subtidal facies. In addition, the silica forms in up to 20 cm thick, discontinuous layers in the porous mixed microbial-oolitic grainstone facies.

In thin section, the silica forms as disseminated silica, microquartz, and chalcedonic quartz. It replaces matrix, grains, cements, and even forms authigenic fan-shaped chalcedonic cement that filled up pore spaces. In the paragenetic sequence of the Cyrenaican Miocene, silicification always comes as the last replacement process after dolomitization, dedolomitization, and gypsum replacement.

All studied silica samples are length slow while the gypsum plate is inserted in the XPL position. A study of all 503 samples did not reveal any evidence of a biogenic origin for the silica. However, the XRF analysis of the same samples did reveal a linear rela-

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tionship between aluminium and silicon (R^2 = 0.8143). The relationship, as empirically determined, is Al (wt. %) = 0.1646 * Si (wt. %) + 0.11405.

In the Cyrenaican Miocene carbonate-evaporite sequence, the diagenetic silica occurrence and distribution are strongly facies controlled and have no correlation with the sequence stratigraphic surfaces or systems tracts. Also, the silica originated from continental weathering rather than being biological, as evidenced by the strong direct proportional geochemical relationship between the silicon and aluminum, as well as the petrographic analysis.

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ABSTRATCT
This work investigates the distribution, occurrence, and origin of silica in the Cyrenaica Miocene shallow marine carbonates, along a 135 km strike section, and its relation to the depositional facies and the sequence stratigraphic framework. Twenty-nine detailed measured stratigraphic field sections, 14 gamma-ray profiles, and 4 carbon stable isotope curves were used to define the Cyrenaican Miocene detailed facies relationships and their sequence stratigraphic context. The Ar-Rajmah Group Cyrenaican Miocene facies consists of red algal reefs, bioclastic packstones, oolitic grainstones, and microbialites that are associated with evaporites and siliciclastics. These facies are arranged within two 2nd order supersequences that comprise six 3rd order sequences. 503 rock samples were collected for thin section petrographic analysis and XRF geochemical analysis. As observed in the field, silica is very common in the ramp crest oolitic grainstone facies and peritidal microbialite facies, but rare in the subtidal red algal and bioclastic packstone facies. The silica commonly occurs as chert nodules of reddish-bluish light gray color in the ramp-crest and peritidal facies and whitish light gray color in the subtidal facies. In addition, the silica forms in up to 20 cm thick, discontinuous layers in the porous mixed microbial-oolitic grainstone facies.
In thin section, the silica forms as disseminated silica, microquartz, and chalcedonic quartz. It replaces matrix, grains, cements, and even forms authigenic fan-shaped chalcedonic cement that filled up pore spaces. In the paragenetic sequence of the Cyrenaican Miocene, silicification always comes as the last replacement process after dolomitization, dedolomitization, and gypsum replacement. All studied silica samples are length slow while the gypsum plate is inserted in the XPL position. A study of all 503 samples did not reveal any evidence for biogenic origin for the silica. However, the XRF analysis of the same samples did reveal a linear relationship between aluminium and silicon ($R^2 = 0.8143$). The relationship is Al (wt. %) = 0.1646* Si (wt. %) + 0.11405 as empirically determined. In Cyrenaican Miocene carbonate-evaporite sequence the diagenetic silica occurrence and distribution is strongly facies controlled and has no correlation with the sequence stratigraphic surfaces or systems tracts. Also the silica origin is continental weathering rather than being biological as proposed by the strong direct proportional geochemical relationship between the Si and Al, as well as the petrographic analysis.

INTRODUCTION

The studied Miocene shallow marine carbonate sequences of the Ar-Rajmah Group outcrops are in the Cyrenaica, NE Libya, Central Mediterranean (Fig. 1). The exposures extend along a north-south strike profile for more than 130 km. This work examines the distribution, occurrence, and origin of silica in the Cyrenaican Miocene shallow marine carbonates and its relation to the depositional facies and the sequence stratigraphic framework. For this purpose a multi-disciplinary approach was advised to include field and lab data analysis. The analyzed field data was sedimentological, stratigraphic, and gamma-ray profiles, whereas the lab data was thin sections and XRF scans of the outcrop collected samples. Analyses and integration of these filed and lab datasets analyses made it possible to reconstruct the nature of the silicification events in the shallow sequences of the Cyrenaican Miocene carbonate platform.The Ar-Rajmah Group is made up of red algal reefs, bioclastic packstones, oolitic grainstones, and microbialites associated with evaporites and siliciclastics (Amrouni et al, 2013; El-Hawat and Abdulsamad, 2004; Francis and Issawi, 1977; Klen, 1974; Rohlich 1974). These facies are arranged within two 2nd order supersequences that together made up of six 3rd order sequences (Amrouni et al, 2013; Amrouni et al, 2014; Amrouni et al, 2015s; Amrouni, 2015; Amrouni et al, 2016s).

GEOLOGICAL SETTING

Cyrenaican, northeast Libya is a part of stable foreland basin in the Central Mediterranean region (Ziegler, 1988 and Esteban, 1996 edited by Franseen et.al. 1996). The Cyrenaica area of northeast Libya includes two major tectonic provinces, the Al-Jabal Al -Khdar Uplift to the north and the Cyrenaica Platform in the south. Additionally, the Soluq and Marmarica Troughs represent western and eastern indentations on the margin of the Cyrenaica Platform (Hallett, 2002).
The exposed surface rocks of the Cyrenaican platform range from Cretaceous to Late Miocene (El-Hawat and Abdulsamad, 2004). The Miocene Ar-Rajmah Group includes the Benghazi Formation, and Wadi Al-Qattarah in Al-Jabal Al-Khdar Uplift, and the Benghazi Formation, Al-Sceleidima Formation and Msus Formation in Soluq Trough area. The Wadi Al-Qattarah Formation lateral equivalents are the Al-Sceleidima Formation and Msus Formation.

METHODS

The research methodology was based on the integration of the field and lab data analysis to understand the distribution, occurrence, and origin of silica and its relation to the depositional facies and the sequence stratigraphic framework in the Cyrenaica Miocene shallow marine carbonates, along a 135 km strike section. The field work explained the detailed regional facies relationships within their sequence stratigraphic framework. The facies analysis, depositional environments, and sequence stratigraphic correlations were done through measuring 29 detailed stratigraphic sections over a distance of 130 km laterally, 14 spectral gamma-ray profiles were constructed using a hand-held gamma-ray scintillometer at 0.5 m intervals. The lab work includes petrographic and diagenetic studies of 503 hand samples, thin sections, and $\delta^{13}C$ whole-rock stable isotope analyses. The carbon stable isotopes plotted curves were tied to the field measured outcrop stratigraphic sections and gamma ray vertical profiles.
Microscopy was done, documented by photomicrographs, on thin sections to indentify the main facies components and diagenetic alterations. The Ar-Rajmah Group carbonate platform in Cyrenaica is made up of coralline red algae, bioclastic packstone, oolitic grainstones, evaporites, microbialites, and siliciclastic quartz sandstone and green shale. Thin sections were analyzed for 503 samples to indentify the silica distribution, occurrence, and origin, and its relation to the depositional facies. In addition, 146 samples, the 74 m thick measured section A1 at 0.5 m interval, were analysed for trace and major elements by using the ED-XRF Niton-XL3t-950-GOLDD+, run at 330 seconds with four different energy settings and varying filters for detection of up to 40 elements. The silicon (Si) and aluminium (Al) major elements are implemented in this study to define the silica origin in the Cyrenaican Miocene shallow carbonate sequences.

RESULTS

Depositional facies and sequence stratigraphic framework

The two 2nd order depositional supersequences (97 m maximum thickness) of the Cyrenaican Miocene Ar-Rajmah Group has six 3rd order sequences that contain nine carbonate facies and two siliciclastics facies (Amrouni et al, 2013; Amrouni et al, 2014; Amrouni et al, 2015s; Amrouni, 2015; Amrouni et al, 2016s). The depositional facies are grouped into peritidal facies, ramp crest facies and subtidal facies. The peritidal facies include: evaporites, microbialites (stromatolites, thrombolites, and laminites), pelletal wackestone/packstone, porites reefs and bioclastic packstone, very fine to fine quartz sandstone, 6) green shale. The ramp crest facies is oolitic grainstones. The subtidal facies include: bioclastic carbonates, reworked bioclastic carbonates, red algae reefs, and reworked red algae (Fig. 2).

Silica occurrence and distribution from field and lab observations

Based on field observations, silica is very common in the oolitic grainstone facies (Fig. 3) and microbialite facies of ramp crest and peritidal environments respectively. However, silica is rare in the red algal facies and bioclastic packstone facies of subtidal environment. The silica occurs in two forms as chert nodules of up to 10 cm in diameter and as discontinuous layers of up to 20cm thick. Silica chert nodules in the ramp-crest and peritidal facies are of reddish-bluish light gray color and in the subtidal facies are of whitish light gray color. In addition, the silica discontinuous layers occur only in the porous mixed microbial-oolitic grainstone facies and are of reddish-bluish light gray color.
In thin section, silica has different forms. It replaces matrix, grains, and cements fill up pores. The silica forms as disseminated silica replacing carbonate matrix and grains, microquartz replacing fibrous cements, and authigenic fan-shaped chalcedonic quartz cement that filled up pore spaces (Fig. 4). The paragenetic sequence of the Cyrenaican Miocene indicates that the diagenetic silica always comes as the last replacement process after dolomitization, dedolomitization, and gypsum replacement.

Aluminium (Al) and silicon (Si) relationship

The microscopically studied silica samples are all length slow while the gypsum plate is inserted in the XPL position. Also, the petrographic study of all 503 samples (sections A1, P1, E1, and H1-H2) show no evidence for biogenic origin for the silica. However, the XRF analysis of section A1 of the same samples did reveal a strong positive linear relationship ($R^2 = 0.8143$) between two major elements (Fig. 5) aluminium (Al) and silicon (Si). The relationship is Al (wt. %) = 0.1646*Si (wt. %) + 0.11405 as empirically determined.

Silica origin and its sequence stratigraphic context

In Cyrenaican Miocene carbonate-evaporite sequence the diagenetic silica occurrence and distribution is strongly facies controlled and has no correlation with the sequence stratigraphic surfaces or systems tracts. Also the silica origin is continental weathering rather than being biological as proposed by the strong direct proportional geochemical relationship between the Si and Al, as well as the petrographic analysis.

DISCUSSION

Facies and depositional sequences

The depositional facies of the Cyrenaica Miocene Ar-Rajmah Group depositional sequences includes nine carbonate facies and two siliciclastics facies that are grouped into peritidal facies, ramp crest facies and subtidal facies. The vertical and lateral arrangement of these depositional facies from landward peritidal facies to seaward ramp crest facies to relatively deeper marine subtidal facies indicates that these facies belongs to the carbonate ramp system that characterized by gentle slope dipping towards the sea side (Ahr, 1973; Tucker, 1996; and Schlager, 2005; Amrouni et al, 2013; Amrouni et al, 2014; Amrouni et al, 2015s; Amrouni, 2015; Amrouni et al, 2016s). These facies associations formed two 2nd order supersequences (Fig. 2) that include six 3rd order sequences (Amrouni et al, 2013; Amrouni et al, 2014; Amrouni et al, 2015s; Amrouni, 2015; Amrouni et al, 2016s).

Silica distribution, occurrence, origin, and its relation to the depositional facies and the sequence stratigraphic framework

Silica was documented in all depositional facies of the Cyrenaican Miocene carbonate sequence of the Ar-Rajmah Group. However, silica is common in the porous ramp crest oolitic grainstone facies (Fig. 3) and the microbial supratidal facies and rare in the porous subtidal red algal and bioclastic facies. The silica occurs as chert nodules and discontinuous layers of reddish-bluish light gray color in ramp crest and peritidal facies, whereas in the subtidal facies occurs as whitish light gray color chert nodules. The silica dominance in the landward porous peritidal and ramp crest depositional facies, and rarity in the seaward porous depositional subtidal facies might indicate that the source of silica was from the landside through rivers, but not from the open seaside.
The petrographic study of the different silica forms indicates that silica formed as a replacement diagenetic product rather than being direct grainy siliciclastic deposits. The studied diagenetic silica replaces matrix, grains, cements, and filled up pores (i.e. Flügel, 2004; and Scholle and Ulmer-Scholle, 2003) to form a disseminated silica replacing carbonate matrix and grains, microquartz replacing fibrous cements, and authigenic fan-shaped chalcedonic quartz cement to fill up pore spaces (Fig. 4). Also, the diagenetic silica was the last replacement process after dolomitization, dedolomitization, and gypsum replacement. In addition, silica samples are all length slow while the gypsum plate is inserted in the XPL position; length slow silica indicates replacement after evaporites (Tucker, 1996). Furthermore, there was no evidence for biogenic origin of the silica from all 503 samples of sections A1, P1, E1, and H1-H2 that studied under the microscope. All these petrographic observations and the absence of the silty size silica grains indicate that silica was carried and transported as soluble material dissolved in water, but not by wind.
From geochemical point of view, the XRF analysis of section A1 (Fig. 5) of the same samples indicates a significant strong positive linear relationship ($R^2 = 0.8143$) between two major elements aluminium (Al) and silicon (Si). The mathematical formula for this relationship is Al (wt. %) = 0.1646*Si (wt. %) + 0.11405 as empirically determined. The Al is a continental weathering product, Al/Si ratio is utilized as a proxy for chemical weathering (Hoang et al., 2010; Croudace and Rothwell, 2015), physical erosion and flux of siliciclastic material to the ocean (Clift et al., 2014) . Also, the XRF data analysis is implemented in the paleogeographic and stratigraphic studies (Röhl and Abrams, 2000; Tjallingii et al., 2007; Clemens et al., 2008, Clift et al., 2014). This significantly strong proportional relationship ($R^2 = 0.8143$) between the continental weathering product aluminium (Al), always not affected by the biogenic carbonates (Croudace and Rothwell, 2015), and the silica (Si) in the Cyrenaican Miocene shallow marine carbonate sequences indicates that both silica and aluminium were produced by the same chemical weathering process and from the same source. Therefore, in Cyrenaican Miocene carbonate-evaporite sequence the diagenetic silica occurrence and distribution is strongly facies controlled and has no correlation with the sequence stratigraphic surfaces or systems tracts. Also, the silica origin is chemical continental weathering rather than being biological as proposed by the strong direct proportional geochemical relationship between the Si and Al, as well as the petrographic analysis.

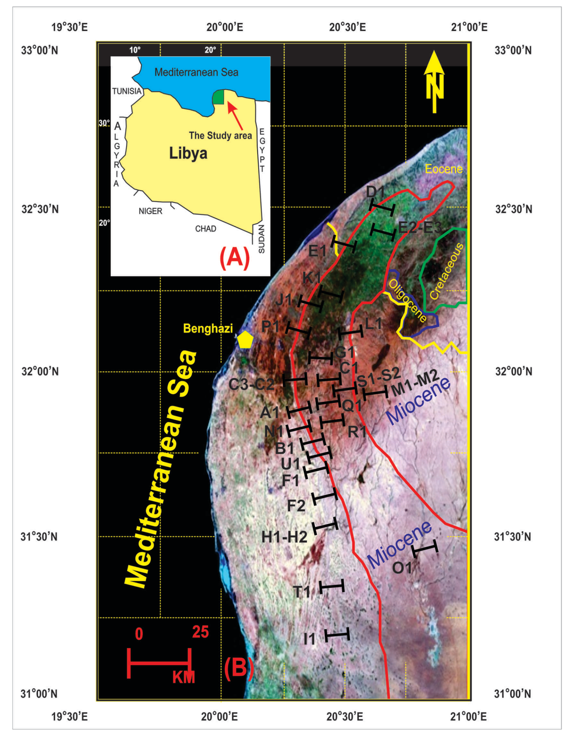

Fig.1 (A) Location map of the study area in Cyrenaica, northeastern Libya. (B) Landsat image of NE Libya showing the geological boundaries of Cretaceous- Tertiary rocks. The geological boundaries are based on the IRCs sheet-Benghazi (Klen, 1974) and sheet-Soluq (Francis and Issawi, 1977) that were later modified by (El-Hawat et al., 1987).

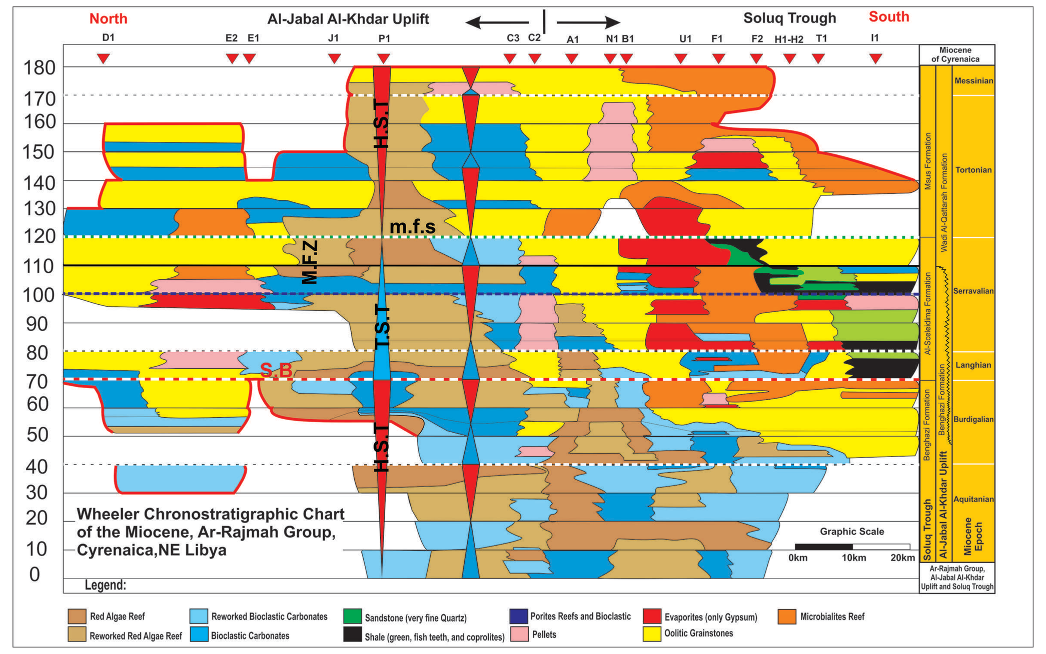

Fig.2 Wheeler chronostratigraphic diagram of the Cyrenaica Miocene, Ar-Rajmah Group, NE Libya. It shows the sequence stratigraphic framework that built based on the integration of the outcrop measured sections-gamma ray curves-and-carbon-oxygen isotopes curves (Amrouni et al, 2014; Amrouni et al, 2015s; Amrouni, 2015; Amrouni et al, 2016s).

Fig.3 Silica chert replacing the ramp crest oolitic grainstone facies.

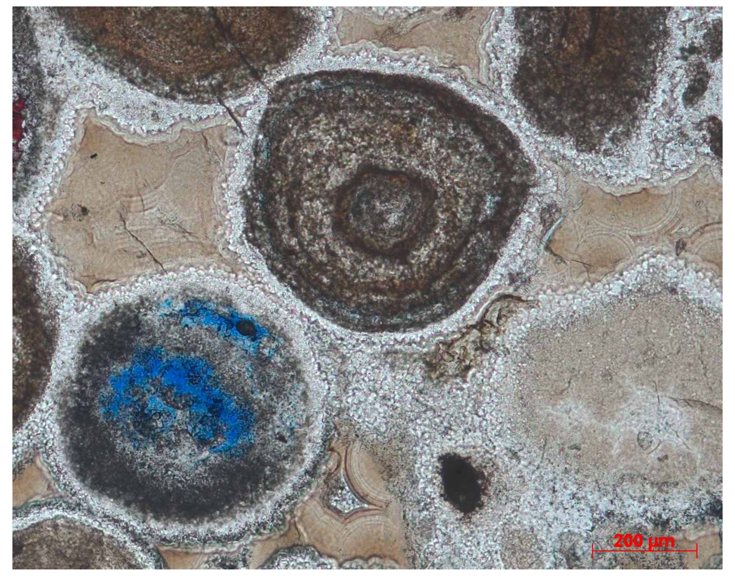

Fig.4 The silica forms as disseminated silica replacing carbonate matrix and grains, microquartz replacing fibrous cements, and authigenic fan-shaped chalcedonic quartz cement that filled up pore spaces in the oolitic grainstone facies.

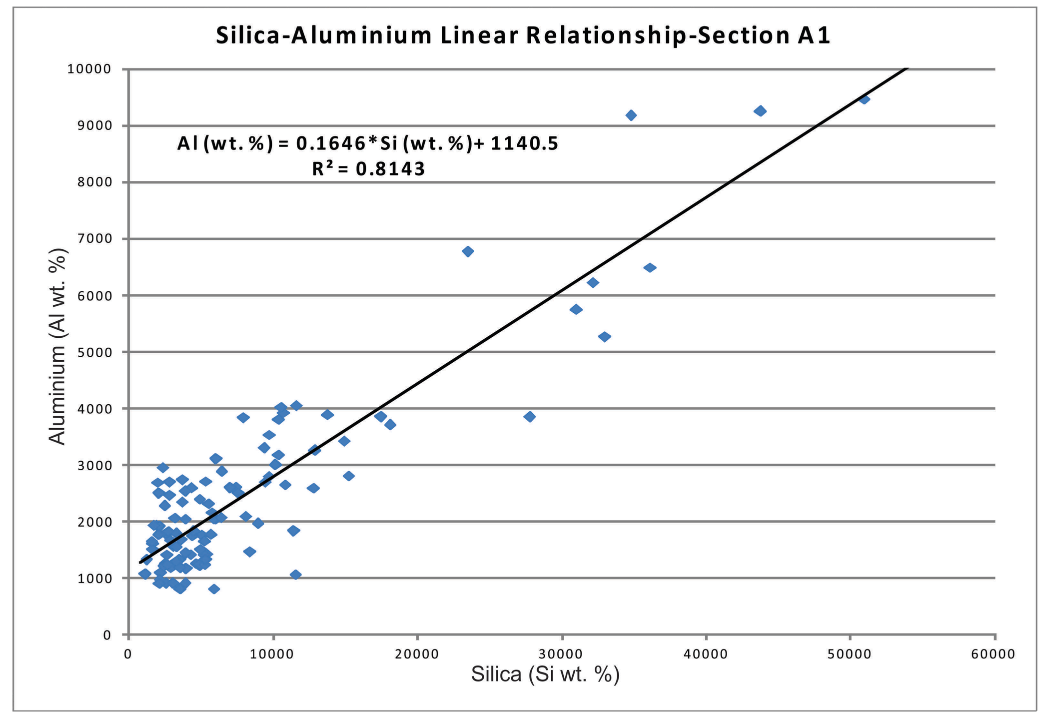

Fig.5 XRF analysis of 146 of the stratigraphic section A1 of the same samples indicates a strong positive linear relationship ($R^2 = 0.8143$) between two major elements aluminium (Al) and silicon (Si). The relationship is Al (wt. %) = 0.1646*Si (wt. %) + 0.11405 as empirically determined.

CONCLUSIONS

This multi-disciplinary sedimentological, stratigraphic, petrographic, and geochemical study proposed an explanation for the distribution, occurrence, and origin of silica in the Cyrenaica Miocene shallow marine carbonates and its relation to the depositional facies and the sequence stratigraphic framework. This Cyrenaican Miocene carbonate platform is made up of two 2nd order supersequences, six 3rd order sequences and eleven depositional facies deposited in a ramp setting. The silica is facies controlled, common in the landward peritidal microbial and ramp crest oolitic grainstone facies, and rare in the seaward subtidal red algal and bioclastic facies. It occurs in the field as chert nodules and discontinuous layers.
The silica is of diagenetic origin, replaced the carbonate cement, matrix, grains and filled pore spaces as disseminated silica, microquartz cements, and authigenic fan-shaped chalcedonic quartz pore fill cement. The silica source in the Cyrenaican Miocene carbonate sequences is not biogenic as indicated by the petrographic study of 503 samples. However, the geochemical XRF data analysis proposed that the silica is a chemical weathering product as indicated by the strong positive relationship ($R^2 = 0.8143$) between the aluminium (Al) and silica (Si). This suggests that silica was emplaced in the carbonates with Al.
In conclusion, the silica is diagenetic in the Cyrenaican Miocene carbonate-evaporite sequences. It was the product of chemical continental weathering and was carried in river waters as a soluble material to the shorelines of the Cyrenaica region in the Mediterranean Sea. Later when the geochemical environment conditions were favourable, the silica replaced the carbonates and evaporites to form chert nodules and discontinuous chert layers in the studied outcrops of the Cyrenaican Miocene platform.

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