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Dolomitization mechanism in the Chorgali formation, Pakistan: Evidence from field observations, Petrography, Mineralogical, and SEM analysis

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Keywords
Dolomitization
Petrographic study
Geochemical characteristics
Chorgali Formation

ABSTRACT

The subject of dolomite formation has always put researchers in the challenge. In this study, the origin of the dolomites of the Chorgali Formation near Chorgali Pass was explored through field observation, petrographic characteristics, mineralogical and geochemical analysis. Analytical analyses used in the present studies include XRD, SEM-EDS, and stable isotopes studies. The dolomites were categorized into three major genetic types based on their textural and structural features showing their distinct origins. These dolomites are named fine crystalline dolomite (Df), medium crystalline dolomite (Dm), and coarse crystalline dolomite (Dc). The analytical approaches linked with field observations and petrographic examinations identified that; the first type of dolomites (i.e., Df) is related to the early stage of diagenesis and contain the presence of mineral dolomite (40%), gypsum (27%), quartz (17%) and albite (16%) and are low stochiometric low ordered in character as recognized by XRD results. The SEM-EDS analysis identified low Mg, Ca, O, Na, Si, and Fe concentrations. Further, the stable isotopes (δ18O) values for Df (i.e., -5.95 to -396‰V-PDB) are less depleted. Moreover, Dm and Dc revealed 100% mineral dolomite and are stochiometric ordered dolomites. High concentrations of Mg, Ca and O are observed in Dm and Dc respectively. Stable isotopes (δ18O) result in exhibiting highly depleted values for Dm (-7.947‰V-PDB) and Dc (-9.227 to -8.302‰V-PDB) showing its formation with the elevated temperature at depth. In addition, δ13C values of Df, Dm, and Dc lie in the range of the original marine signature of Eocene times.

1. INTRODUCTION

The study area lies in Survey of Pakistan (SOP) toposheet no. 43-C/11 at Latitude 33° 27' 05″ N and Longitude 72° 41' 02″ E (Figure 1). The rocks exposed in the study area are ranging in age from Eocambrian to Pleistocene (Jaswal et al., 1997). The rocks of Eocene age include Margala Hill Limestone, Chorgali, Kuldana formations, whereas Murree Formation represents Miocene age. According to Shah, (2009) and Shah and Khan, (2016) the formation is mainly contained of dolomite, dolomitic limestone, and shale. It is well known that the Chorgali Formation is performing as a reservoir in many oil fields (Kadri, 1995; Benchilla et al., 2002a). Previous work is mainly focused on the outcrop-based sedimentology and depositional environment of the Chorgali Formation (Mujtaba et al., 1989; Jurgan and Abbas, 1991; Mujtaba, 2001; Awais et al., 2019). The present study deliberates inclusive investigations of the dolomitization evolution mechanism in the Chorgali Formation near Chorgali Pass Pakistan.

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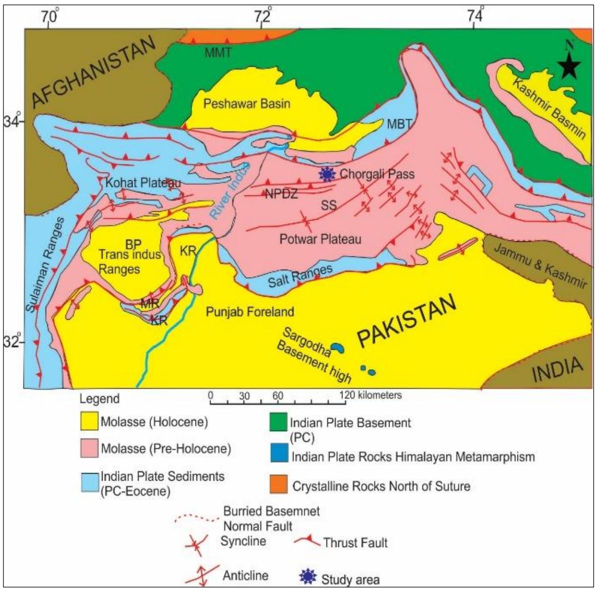

Figure 1. Geo-Tectonic map of Kohat-Potwar area showing the location of the study area (modified after Kazmi and Rana, 1982). Abbreviations used are; SS= Soan Syncline, NPDZ= North Potwar Deformed Zone, MBT= Main Boundary Thrust, MMT=Main Mantle Thrust, KR= Kishor Range, MR= Marwat Range, and BP= Bannu Promontory

2. GENERAL TECTONIC CONTEXT

The research site is being a portion of the Indian Plate. Previous work revealed that the Indian Plate has traveled 9000 kilometers during its tectonic evolution after detachment from its position in the Gondwana, its consecutive departure from other continents of Gondwana, its frequent disintegration, its movement in the north direction, and its sequential crash with KIA and with Asia (Chatterjee, 1992; Chatterjee and Scotese, 1999, 2010). Furthermore, the Indian Plate represents distinct and highly complex tectonic antiquities (Chatterjee et al., 2013). During its northward movements, the Indian plate experienced unexpected acceleration from Late Cretaceous to Early Eocene, about 20 cm/year, and then histrionically reduced to 5 cm/year during its collision with Eurasian Plate (McKenzie and Sclater, 1971; Patriat and Achache, 1984; Lee and Lawver, 1995). The crash (i.e., happened around 67±2 Ma) between the Indian Plate and Eurasian Plate is considered the intense tectonic incident of the Cenozoic and is responsible for the uplift of the Himalayan-Tibetan Plateau (Powell et al., 1988; Powell and Conaghan, 1973).

The study area lies in the area of the Northern Potwar Deformed Zone of the Indian Plate, where extensive complex structural and tectonic features are present (Figure 1; Jaswal et al., 1997). Multipart and tight folds, which are trending east-west and are overturned to the south at sheared by step-angle faults are present in the area (Baker, 1987). Furthermore, the studied area is highly tectonically disturbed with seven episodes of fracturing were identified showing the complex deformation past that is characteristic of a fold-and-thrust belt (Benchilla et al., 2002b). Main Boundary Thrust (MBT) lies in the north and Soan Syncline exists south of the area (Figure 1). Furthermore, the studied section can be accessed from all sides of the country by roads, approximately lies 55 km in the south-west of the main capital Islamabad and 190 km from Peshawar (Figure 1).

3. MATERIAL AND METHODS

Forty-one representative samples were taken from 150-meter-thick studied sites during field studies (Figure 1). Dolomite samples were separated by applying pre-microscopic methods (etching, staining, peeling, etc.,). Petrographic thin sections were prepared including alizarin red S and K-ferricyanide analysis and studied under a microscope for the identifications of various diagenetic phases. Thin sections preparation, Petrography, XRD analysis, and SEM studies were executed at Geoscience Advance Research Laboratories, Geological Survey of Pakistan Islamabad. Polarizing microscope (OPTIPHOT2-POL) with an attached camera (Moticam 2000) were used for the identification of diagenetic phases. A powdered sample of 2-5 grams was taken in a specified XRD sample holder and prepared for XRD analysis. The XRD analyses were carried out by Panalytical X'Pert Pro Diffractometer (XRD) at 45 kV and 40 mA with CuKα radiations scanning speed at 0.05°/s. The XRD patterns were identified by using X pert High Score Plus software. SEM Model JEOL JSM 6610LV with EDS (OXFORD X-MAX 20 mm2) is used in the present study. Moreover, during sample preparations, carbon coating is well applied all around the samples to avoid charging the samples under the SEM.

For measuring carbon and oxygen stable isotopic composition of various diagenetic phases micro sampled were obtained by using a dentist's micro-drill. Bulk rock analyses were carried out at PINSTECH (Pakistan Institute of Nuclear Science and Technology), Islamabad. During this process, the carbonate powders were reacted with 100% phosphoric acid (density >1Æ9; Wachter and Hayes, 1985) at 75°C in an online carbonate preparation line (Carbo-Kiel – single sample acid bath) connected to a Thermo Finnigan 252 mass-spectrometer (Thermo Electron Corp., Waltham, MA, USA). All values are reported in per million relatives to Vienna Pee Dee belemnite standard (V-PDB) by assigning a δ13C value of +1Æ95& and a δ18O value of)2Æ20& to National Bureau of Standards (NBS) 19. Oxygen isotopic compositions of dolomites were corrected using the fractionation factors given by Rosenbaum and Sheppard, (1986). Reproducibility based on a replicate analysis of laboratory standards is better than ±0Æ02& for δ13C and ±0Æ03& for δ18O.

4. FIELD OBSERVATIONS

In the studied section the Chorgali Formation is mainly comprised of two main units. The lower unit exhibits the presence of dolomite, dolomitic limestone, and shale, whereas the upper unit contains one thick bed of dark grey color limestone and a bed of nodular argillaceous limestone almost near the top. The shale is greenish-grey, red occasionally variegated, and calcareous. Some grit beds are also intercalated. Well preserved cyanobacterial mat, lamination, mud-cracks, and horizontal burrows have also been observed. Anhydrite nodules are also noted during field observations (Figure 2a-e).

Figure 2. Field observations of dolomites of Eocene Chorgali Formation, near Chorgali Pass; (a) General view of the dolomites of Eocene Chorgali Formation, near Chorgali Pass (b) Dolomite sample exhibiting well preserved cyanobacterial mat (c) Dolomite sample showing well-developed lamination, mud-cracks and horizontal burrows (d) Irregular laminations observed in dolomites (e) The presence of anhydrite nodules (white color) in dolomites of Chorgali Formation

5. PETROGRAPHIC STUDY

5.1. Fine crystalline dolomite (Df)

According to Sibley and Gregg, (1987) classification scheme, fine crystalline dolomites (Df) are 5-50 µm in size, planar-s, light grey to medium grey color dolomites and are mostly comprised of partially dolomitized fossiliferous micrite with sparse, randomly distributed, very fine-grained detrital quartz grains are present (Figure 3a). Bioclasts include sparse ostracod and some unidentified very small-sized fossil fragments. Fine to very finely crystalline dolomite crystals are common and randomly distributed in the micritic matrix. A few well-developed, medium-sized, dolomite rhombs are noticed with cloudy centers and comparatively clear rims. A few, fine sand-sized, intraclasts are also present. Randomly distributed dolomicritic intraclasts are common and represent disintegrated algal mats (Figure 3b). Although fabric destructive dolomitization has completely destroyed the original fabric information, a few intraclasts ghosts are present. Open micro molds and micro vugs are common and randomly distributed. Locally developed microfractures are noticed filled with anhydrite (Figure 3c). Anhydrite nodules show the phenomenon of chicken wire features, indicating growth by displacement. Very finely crystalline, well-developed, pyrite-looking crystals are locally common within the groundmass of dolomite and anhydrite laths (Figure 3d).

5.2. Medium crystalline dolomite (Dm)

Dm is 50-200µm, medium to dark grey, locally laminated dolomites. Dolomite crystals are medium crystalline, equigranular, and subhedral (Figure 3e;

Sibley and Gregg, 1987). Furthermore, intercrystalline spaces are filled with cryptocrystalline carbonate. Most of the dolomite crystals have light-brown cloudy centers with clear rims. Dolomitization has completely destroyed the fabric information of the precursor sediments.

5.3. Coarse crystalline dolomite (Dc)

These consist of 200µm -2 mm-sized, medium gray, coarse crystalline euhedral to subhedral dolomites that occur generally as infilling of fractures (Figure 3f-g; Sibley and Gregg, 1987). Dc is locally stylolites and fractures associated. Filled and partially open fractures and microfractures are locally common. Pyritization is also associated. Light gray dolomite (collapse breccia). Ghosts of intraclasts and fecal pellets are randomly scattered in a groundmass of finely crystalline dolomite. Dolomite crystals have mostly cloudy centers and clear rims. Intercrystalline and vuggy porosity are locally common. Some of the pores are partially filled with natural solid bitumen. Open microfractures and a few microstylolites are present.

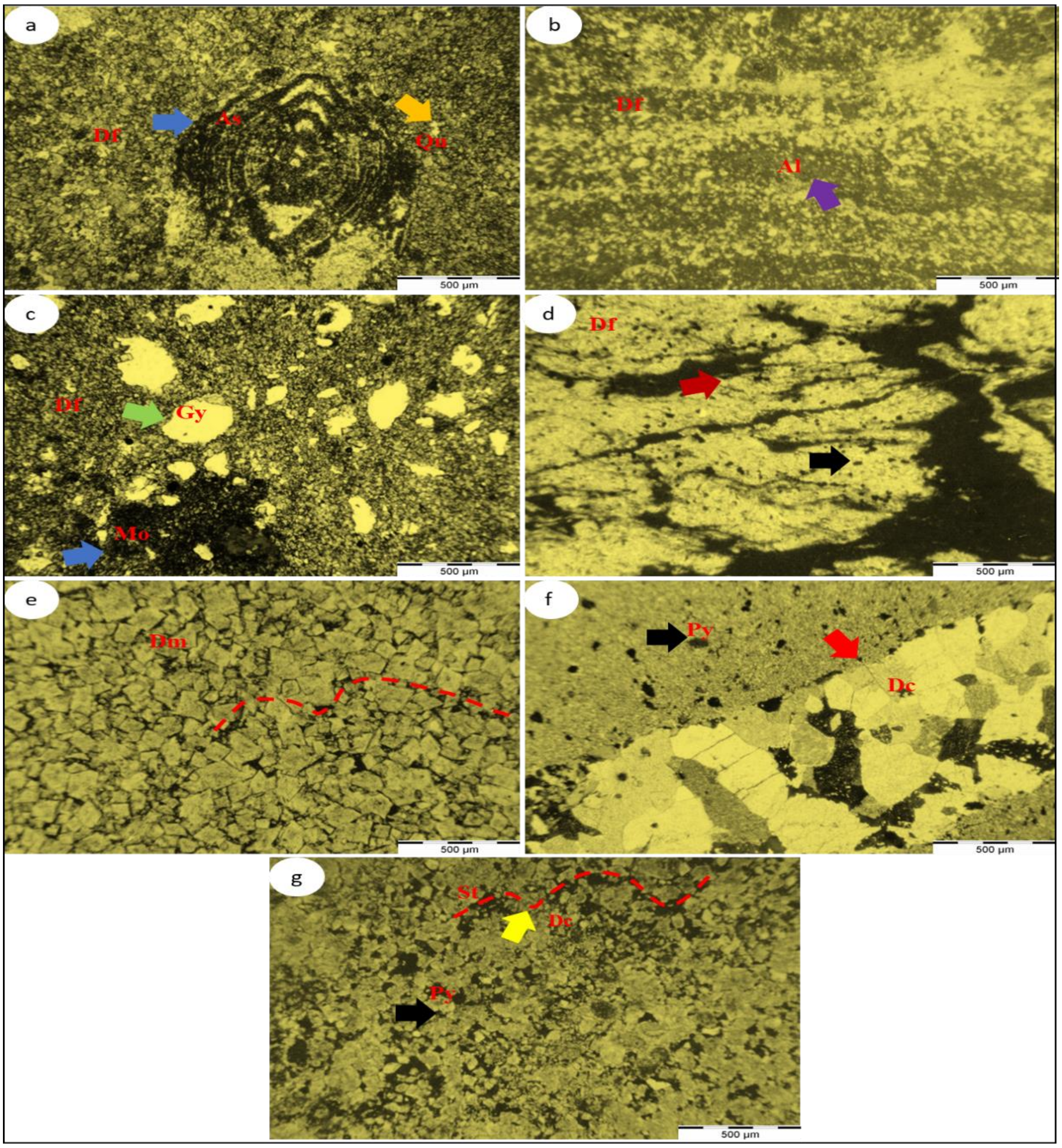

Figure 3. Petrographic characteristics of dolomites of Chorgali Formation; (a) Photomicrograph exhibiting fine crystalline dolomites (Df), the blue arrow shows the presence of dolomitized bioclast (i.e., Assilina) whereas blue arrow represents fine quartz grains (b) Fine crystalline dolomites (Df), purple arrow shows ghost of the algal mat (c) Fine crystalline dolomites (Df) with open molds as blue arrow and presence of gypsum anhydrite as green arrow (d) Fine crystalline dolomites (Df) with chicken wire features as brown arrow and pyrite existence as a black arrow (e) Photomicrograph exhibiting medium crystalline dolomite i.e., Dm with stylolite seems (f) Photomicrographs showing coarse crystalline dolomite (Dc) as a red arrow, pyrite represented by black arrow (g) Coarse crystalline dolomite (Dc) as a red arrow, pyrite represented by the black arrow, yellow arrow shows stylolite seems. Abbreviations; Df=fine crystalline dolomites, As=Bioclast (Assilina), Qu=Quartz, Al =Algal mat, Gy=Gypsum, Mo=Open mould, Dm=Medium crystalline dolomite, Py=Pyrite, Dc=Coarse crystalline dolomite, St=Stylolite

6. XRD ANALYSIS

XRD studies of representative samples were carried out. Df exhibited the presence of dolomite (40%), gypsum (27%), quartz (17%), and albite (16%) respectively (Figure 4a). In Dm and Dc, the existence of dolomite (100%) is observed (Figure 4b-c). Besides this, the mol % Ca Vs I(d105)/I (d110) plot showed that Df is low stochiometric low ordered dolomites, whereas Dm and Dc are near stochiometric ordered dolomites (Figure 5 and Table 1).

Table 1. XRD results of analyzed samples

Site	Stage	d_{104}	d_{015}	d_{110}	$I(d_{015})/I(d_{110})$	mol % Ca
Chorgali - pass	D. I	2.871	2.531	2.401	1.054	45.000
	D. I	2.869	2.531	2.402	1.054	44.334
	D. I	2.872	2.532	2.402	1.054	45.334
	D. I	2.870	2.530	2.401	1.054	44.667
	D. II	2.880	2.535	2.402	1.055	48.000
	D. III	2.881	2.536	2.402	1.056	48.334
	D. III	2.882	2.536	2.401	1.056	48.667

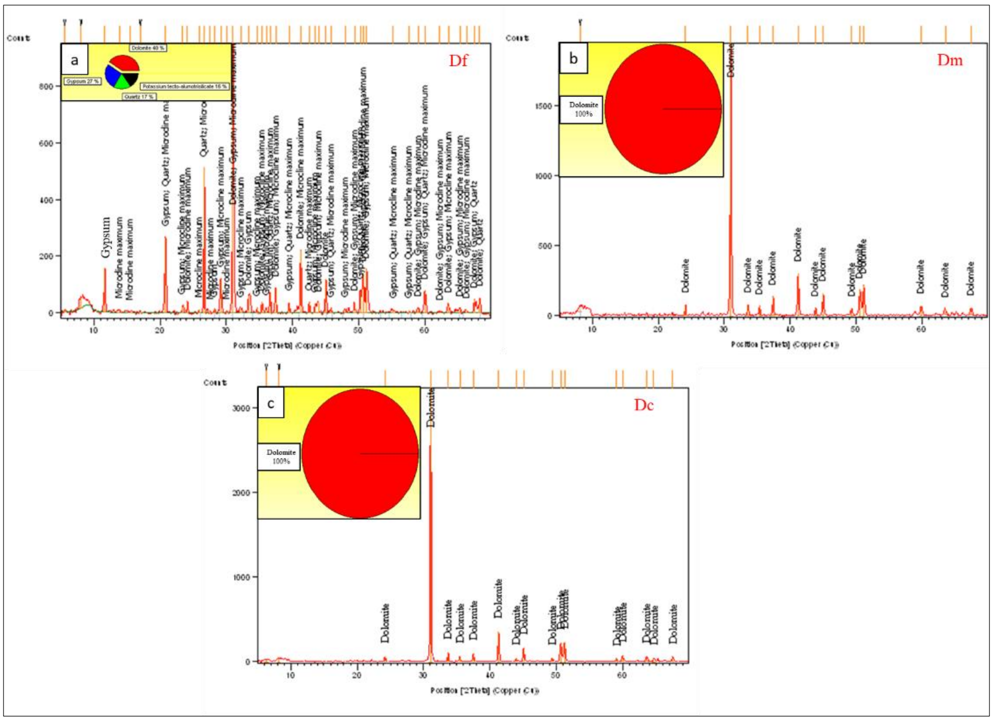

Figure 4. XRD results of the dolomites in Eocene Chorgali Formation; (a) XRD pattern showing mineralogical description with quantification of Df, (b) XRD pattern showing mineralogical description with quantification of Dm and, (c) XRD pattern showing mineralogical description with quantification of Dc. Abbreviations; Df=Fine crystalline dolomites, Dm= Medium crystalline dolomite, Dc= Coarse crystalline dolomite

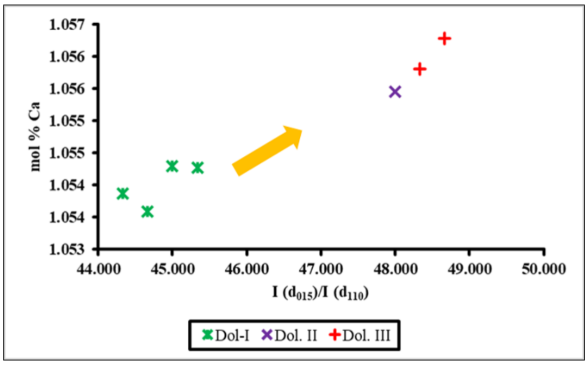

Figure 5. Mol % Ca vs I $(d_{015})/I(d_{110})$ plot of various phases of Eocene Chorgali dolomites

7. SEM-EDS ANALYSIS

In the SEM-EDS studies, Df showed the presence of Mg, Ca, O, Na, Si, and Fe concentrations (Figure 6a). The highest concentrations of Mg, Ca and O are observed in Dm and Dc respectively (Figure 6b-c).

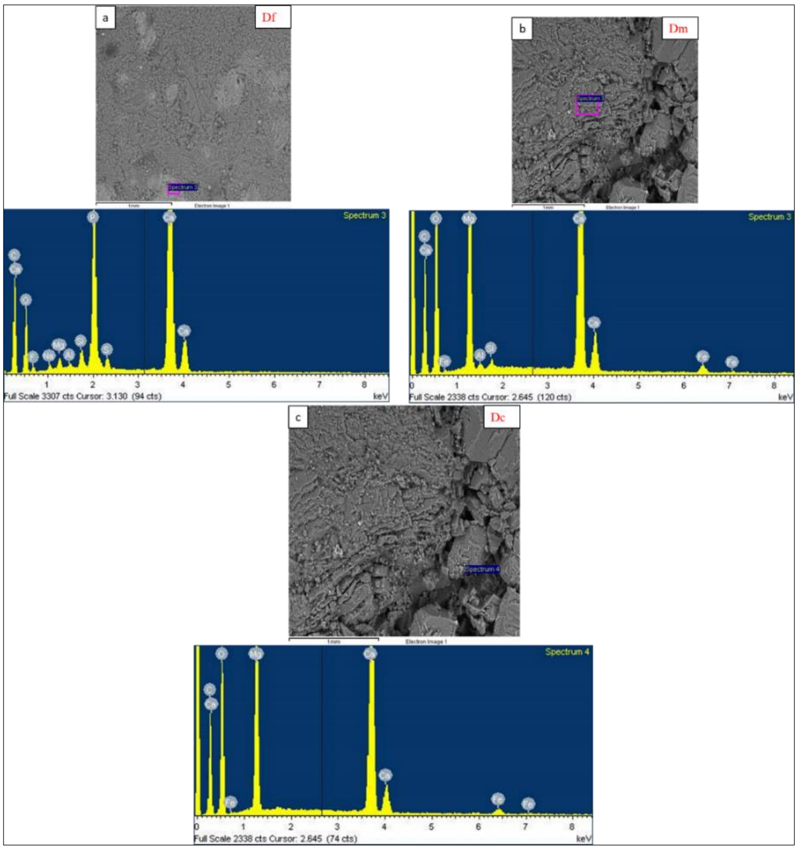

Figure 6. Scanning electron microscope (SEM) results of selected samples from identified dolomite phases; (a) detailed SEM results of Fine crystalline dolomites (Df), (b) SEM results of Medium crystalline dolomite (Dm) and, (c) SEM results of Coarse crystalline dolomite (Dc)

8. STABLE ISOTOPES ANALYSIS

Stable isotopes (δ18O and δ13C) values for Df are -5.95 to -396 and δ -0.85 to 2 respectively (Figure 7 and Table 2). In Dm δ13C and δ18O are -7.947 and -0.104 respectively, whereas Dc revealed δ18O (-9.227 to -8.302) and δ13C (-0.928 to 1.337) values (Figure 7 and Table 2).

Table 2. Isotopes results of analyzed samples

Section	Stage	$\delta^{18}O$	$\delta^{13}C$
Chorgali - Pass	Df	-3.96	-0.96
	Df	-5.95	-0.085
	Df	-3.96	2.96
	Df	-3.96	-0.96
	Dm	-7.947	-0.104
	Dc	-8.302	-0.928
	Dc	-9.227	1.337

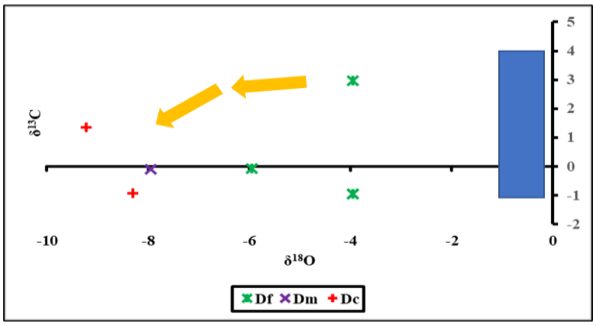

Figure 7. δ18O Vs δ13C plot of various phases of Eocene Chorgali dolomites. The blue rectangle represents the marine signatures of Eocene Limestone

9. Discussions

During field investigations, the presence of well-preserved cyanobacterial mat, lamination, mud-cracks, and horizontal burrows are observed along with the dolomites of the Chorgali Formation (Figure 2a-e). The presence of anhydrite nodules with chicken is also associated with these dolomites (Figure 2e). Cyanobacterial mat, lamination, mud-cracks, horizontal burrows, and gypsum/anhydrite nodules are typical features of inter-and supra-tidal settings and are found in dolomites formed in tropical and arid conditions (Gasparrini et al., 2003;

Warren 2000, 2006). In such arid conditions, increased rates of evaporation in lagoons produce denser and more saline waters (with respect to seawater), promoting dolomitization as Mg becomes highly concentrated in the brines and the kinetic constraints of dolomitization alleviated. Thus, hypersaline fluids, usually produced by high rates of evaporation, resulting in the precipitation of dolomites along with gypsum and anhydrite (Mckenzie, 1981). During petrographic examinations, fine crystalline dolomite (Df) exhibited small crystal size and planar intercrystalline boundaries with fabric retentive character are the possibilities of the dolomites formed in supratidal and intertidal realms in the early stage of diagenesis near-surface low-temperature conditions (Figure 3a-d; Saller, 1984; Gregg and Sibley, 1984; Land, 1985; Sibley and Gregg, 1987; Mitchell et al., 1987; Gregg and Shelton, 1990; Rahimi et al., 2016). According to Shah, (2009) the epeirogenesis experienced resultant emergence in various areas of Pakistan, and this caused unconformities of varying magnitude. These early-stage diagenetic processes can be possibly related to Middle-Late Eocene unconformities. The XRD studies showed the existence of dolomite, gypsum, quartz, and albite in Df (Figure 4). Based on XRD data Df is identified as low stochiometric low ordered dolomites (Figure 5). Furthermore, SEM analysis accredited low concentrations of Mg, Ca, O, Na, Si, and Fe in these dolomites (Figure 6). Stable isotopes (C & O) exhibited slightly depleted values for Df (Figure 7).

Based on field observation, microscopic examinations linked with XRD, SEM-EDS, and Isotopes analysis fabric retentive dolomites (Df) can be interpreted to be of early diagenetic origin. Furthermore, the similarity between Chorgali shallowing upward sequence and Persian Gulf sabkha sequence suggests that the formation of these early diagenetic Chorgali dolomites was similar to that of Holocene dolomite in the Persian Gulf; where the sediments are being dolomitized by evaporated seawater (Illing et al., 1965; Mckenzie, 1981; Patterson and Kinsman, 1982).

The microscopic examinations revealed that medium crystalline dolomites (Dm) are fabric destructive in character and with stylolite seems, which predominantly occupy the lower portion of the sequence (Figure 2e) and their formation possibly occurs at slighter depth after the formation of Df (Mountjoy et al., 1999; Duggan et al., 2001; Fabricius et al., 2007). The XRD results showed that it contains 100% mineral dolomite and is nearly stochiometric ordered dolomite (Figure 4a-c and Figure 5). Furthermore, SEM-EDS analysis identified strong concentration peaks of Mg in Dm (Figure 6). Stable Isotopes values (δ18O) of these dolomites are highly depleted than Df reflecting its formation in a higher temperature at depth (Figure 7).

The late diagenetic fracture and void filling dolomite cement (Dc) with curved surfaces and undulatory extinction under cross-polarized light probably formed as fluids moved along paths of increased permeability created by burrows, fractures, and stylolites (Figure 3f-g; Zenger, 1983; Amthor and Friedman, 1991). Petrographic characteristics combined with XRD data, SEM-EDS analysis, and stable isotopes results identified that these dolomites are formed at great depth with elevated temperature after the deposition of thick sedimentary cover above (Figure. 4-7; Guo et al., 2016; Feng et al., 2017). Pyritization marks the end of diagenesis (Figure 8).

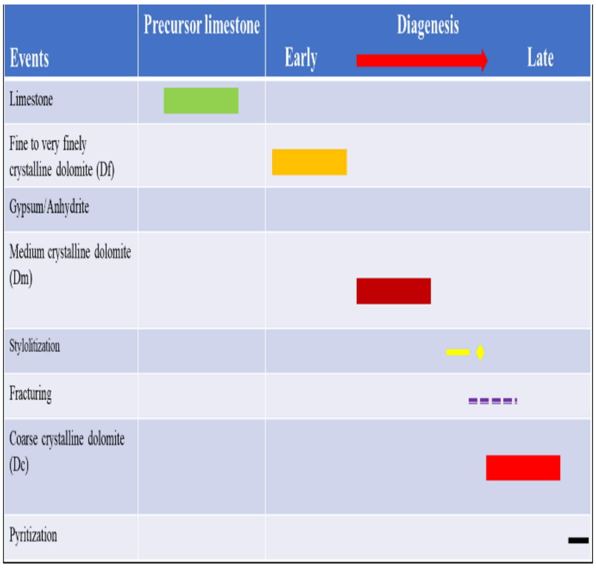

Figure 8. Paragenetic sequence of different types of the dolomite of Eocene Chorgali Formation

10. CONCLUSION

Based on detailed field observations and microscopic examinations along with XRD analysis, SEM results, and Isotopic data of representatives taken from the dolomites of the studied formation mentioned below conclusion can be made;

During field studies the presence of well-preserved cyanobacterial mat, lamination, mud-cracks, horizontal burrows, and anhydrite nodules with chicken wire structures were observed in the dolomites of Chorgali Formation

The petrographic studies observed relics of the pre-existing textures with the presence of gypsum flakes in Df. Moreover, Dm is destructive in character with the presence of stylolites, whereas Dc is fractures associated. Based on Petrographic characteristics three types of dolomites are identified which contain Df (fine crystalline dolomite), D. II (medium crystalline dolomite), and Dc (coarse crystalline dolomite).

XRD study revealed Df as non-stoichiometric low ordered dolomite, while Dm and Dc are stochiometric ordered dolomites.

SEM results showed a low concentration of Mg, Ca, O, Na, Si, and Fe in Df, and High concentrations of Mg, Ca, and O are observed in Dm and Dc.

Stable isotopes data exhibits slight depletion δ18O values for Df, whereas Dm and are highly depleted representing the elevated temperature at depth. Further, δ13C values of Df, Dm, and Dc lie in the marine signatures range.

The above studies revealed that fine crystalline dolomites (Df) are formed near-surface conditions during the early stage of diagenesis, whereas medium crystalline dolomite (Dm) and coarse crystalline dolomite (Dc) are formed at depth with elevated temperature.

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Author Contributions

Sajjad Khan: Conceptualization, Methodology, Software, Data curation, Writing-Original draft preparation. **Mehboob ur Rashid**: Visualization Supervision, Writing-Reviewing and Editing.

Conflicts of Interest

The authors declare no conflict of interest.

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