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An integrated approach to evaluate dolomite in the Eocene Chorgali Formation, Khair-e-Murat Range, Pakistan: Implications for reservoir geology

Muhammad Awais*[1, 2], Muhammad Hanif[2], Muhammad Ishaq[2] and Irfan U. Jan[2]
1Department of Geology, University of Swabi, Swabi, Khyber Pakhtunkhwa, Pakistan
2National Centre of Excellence in Geology, University of Peshawar, Khyber Pakhtunkhwa
**Corresponding author's email: awais.geo89@gmail.com*
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Abstract

An integrated approach has been deployed to investigate dolomite of the Eocene Chorgali Formation exposed in the Khair-e-Murat Range, Potwar Plateau, Pakistan. Two typical genetic dolomite groups are identified and interpreted based on X-rays Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), chemical alizarin red staining and petrographic studies. The first group is represented by early-diagenetic alizarin-red-unstained dolomites. They are associated with evaporite(s) (gypsum) and characterized by stoichiometric composition of 50.28 mole % CaCO3 and degree of order is 0.682. The second group includes fine crystalline, alizarin-red-unstained relatively early late or late diagenetic dolomite crystals not associated with evaporite(s). It is represented by nearly stoichiometric composition of 48.76 mole % CaCO3 and degree of order varies from 0.58 to 0.9747. The dolomite associated with evaporite (gypsum) is interpreted to be precipitated in arid peritidal (sabkha) environment while the other dolomite not associated with evaporite is reflecting dolomitization in open diagenetic system (mixed marine-meteoric environment). Within the Chorgali Formation, the presence of dolomite is enhancing the reservoir capability making it prospective for hydrocarbon exploration. The photomicrographs based estimated porosity values are 2.0 % and 1.0% for dolomite associated with evaporite(s) and dolomite-not-associated with evaporite(s) respectively, however, qualitative permeability seems to be relatively higher in dolomite associated with evaporite(s).

Keywords: Chorgali Formation, Dolomite, Scanning electron microscopy, Energy dispersive x-ray spectroscopy, X-ray diffraction, Chemical staining, Khair-e-Murat Range.

1. Introduction

The Potwar Plateau and Salt Range are positioned in foreland region of the northwestern Himalayan Fold-and-Thrust Belt (Jaume and Lillie, 1988). According to Lillie et al. (1987), the Potwar Plateau rocks exemplify thin-skinned compressional deformation and the cover sequence is deformed on the Salt Range Formation basal decollement. The Potwar Plateau and Salt Range stratigraphic succession consists of four main groups from bottom to top i.e. Basement complex, Salt Range Formation, Platform and molasses successions (Khan et al., 1986). The present area of investigation belongs to Platform section and is a part of Khair-e-Murat Range, Northern Potwar Deformed Zone (NPDZ), Potwar Plateau (Fig. 1).

The Eocene carbonate rocks (i.e. Nammal Formation, Sakesar Limestone, Chorgali Formation and Margalla Hill Limestone) are exposed in Potwar Plateau and Salt Range (Kazmi and Abbasi, 2008). The term Chorgali Formation is suggested by Jurgan and Abbas (1991) for 80-90 m lower thin to thick bedded dolomitic rock unit on the basis of its detailed investigation at the type locality. The Chorgali Formation lower and upper contacts are conformable with the Margalla Hill Limestone and the Kuldana Formation respectively (Kazmi and Abbasi, 2008). According to Jurgan and Abbas (1991), the Chorgali Formation is interpreted to be deposited in intertidal-supratidal depositional settings during the Early Eocene Sea regression. Ghazi et al. (2014) carried out research on microfacies and depositional setting of the early Eocene Chorgali Formation in the Salt Range. The interpreted microfacies include bioclastic wackestone, bioclastic mudstone, bioclastic packstone and bioclastic grainstone reflecting inner shelf settings for the Chorgali Formation (Ghazi et al., 2014).

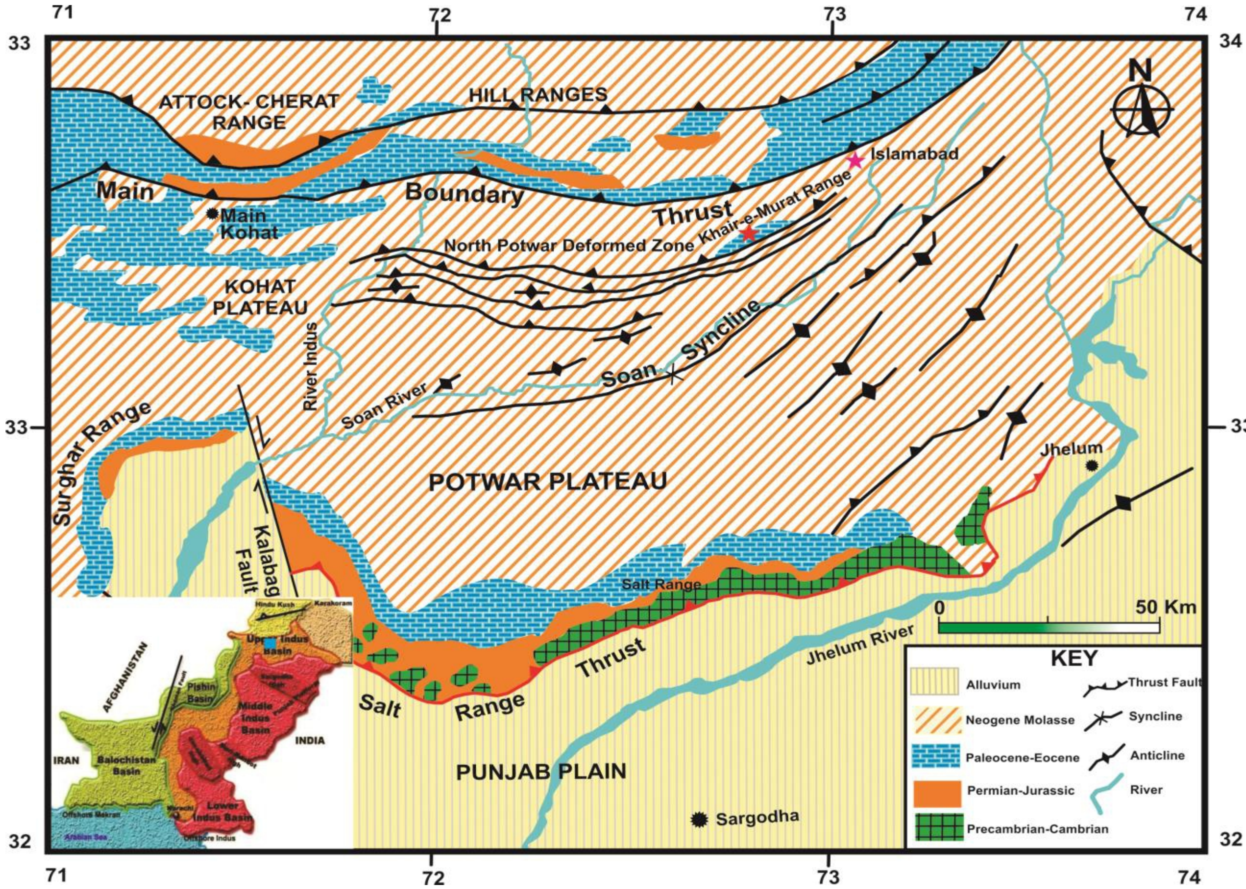

Fig. 1. Tectonic division of Kohat-Potwar plateaus (from Kazmi and Rana, 1982; Khan et al., 1986). Khair-e-Murat Range is marked by red star. In the lower left corner, Pakistan map with blue box showing the study area.

The Chorgali Formation, at the type section, is comprised of limestone, shale and dolomite (Jurgan and Abbas, 1991). The dolomite mineral is a bi-carbonate of Ca and Mg with a range of chemical variations and lattice structures (Warren, 2000). The dolomite has weak X-Ray Diffraction (XRD) response representing varying degrees of cation disorder (Hardie, 1987). In sedimentary rocks, the dolomites are usually non-stoichiometric ($Ca_{0.5}Mg_{0.5}CO_3$), however, Ca^{2+} and Mg^{2+} can vary from $Ca_{58}Mg_{42}$ to $Ca_{48}Mg_{52}$ (Tucker and Wright, 1990). According to Jones et al. (2001), the percentage (%) of Ca in sedimentary dolomite varies from 48 % to 62.5 %.

The dolomite stoichiometry in combination with texture and association with evaporites can aid in interpretation of the dolomite origin (Morrow, 1978, 1982a, b). There are two types of dolomites i.e. dolomite mixed with evaporite and dolomite not associated with evaporite (Morrow, 1978, 1982a, b). According to Lumsden and Chimahusky (1980) and Morrow (1978, 1982a, b), both types of dolomites i.e., the one which is mixed with evaporites and the one not related with evaporites, are generally early diagenetic, near-surface in origin. Furthermore, according to Haldar and Tišljar (2014), mixed marine-meteoric dolomitization can occur in early diagenetic or transitional stage varying from early to late diagenetic stage and even in late diagenetic stage. The Chorgali Formation depositional cycle is similar to modern Abu Dhabi sabkha complex (Mujtaba, 2001). According to Wenk et al. (1983), both ordered and less ordered dolomites in the modern coastal Abu Dhabi sabkha are present due to varying temperature and fluid chemistry in response to environmental parameters. The present research has taken into consideration integrated approaches such as petrographic studies, chemical alizarin red staining, XRD, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) to identify and evaluate dolomite in the Chorgali Formation exposed in the Khair-e-Murat Range.

2. Stratigraphy

The stratigraphy of study area consists of Eocene and Miocene successions. The Eocene succession include Chorgali and Kuldana formations while the Miocene succession includes Murree and Kamlial formations in ascending stratigraphic order respectively (Fig. 2). In the Gali Jagir Village (a part of Khair-e-Murat Range), the Chorgali Formation contains limestone, dolomite having algal laminations, shale and marls (Fig. 3). The Formation has lower faulted and upper conformable contact(s) with the Kuldana Formation (Awais et al., 2014; Awais, 2015).

3. Materials and methods

A geological field work was conducted in the Gali Jagir Village, Khair-e-Murat Range, Pakistan. A total of 14 carbonate rock samples were collected from the carbonate (limestone and dolostone) intervals. Lumsden equation is used to determine percent CaCO3 in dolomite: NCaCO3 = md + b, where NCaCO3 indicates percent CaCO3 in dolomite; m = 333.33; d is observed d104 value and b = -911.99; provided the samples should not contain more than 20 % quartz. The degree of order of dolomite crystal lattice is calculated using ratio between intensities of 015 and 110 peaks (Füchtbauer and Goldschmidt, 1965).

The XRD, SEM and EDS analyses and chemical staining were deployed due to difficulty in identification of certain minerals (especially dolomite) under the petrographic studies. Such techniques are extremely useful to reveal the carbonate rocks original mineralogy. XRD graphs were deciphered using XRD mineral databases of Standard X-ray diffraction powder patterns (Swanson, 1966; Kanen, 1997). The detailed depositional/diagenetic features and composition is studied using SEM and EDS. The EDS charts are interpreted using SEM Petrology atlas (Welton, 2003). The chemical staining (alizarin-red) in combination with petrographical studies are utilized to identify and interpret dolomite. The alizarin red solution was prepared using the methodology devised by Evamy (1963) and Dickson (1965). ImageJ and Inkscape softwares have been utilized for preparing and processing photomicrographs for estimating porosity.

4. Results

The biologically and chemically developed carbonate mineral(s) may be calcite, aragonite and dolomite during the deposition time. Over a period of time, the carbonate mineral(s) are most often modified to diagenetic carbonate mineral(s) e.g., aragonite is altered to calcite and calcite may be converted to dolomite or converted to low Mg calcite during the course of diagenesis and stabilization (Flügel, 2010). Consequently, it is fundamental to work out carbonate rocks original mineralogy.

In present study, two among the three dolomite categories of Morrow (1978) and Lumsden and Chimahusky (1980) are reported. These are identified on the basis of texture, stoichiometry and whether linked with evaporites or not (Figs. 3-6). According to Morrow (1978) and Lumsden and Chimahusky (1980), the fine crystalline dolomites mixed with evaporites are almost stoichiometric (51 - 52% CaC03) while finely crystalline dolomites not related with evaporites are usually Ca-rich (54 - 56% CaC03).

4.1. XRD analysis

The XRD analysis of the Chorgali Formation shows that it is dominated by calcite and dolomite but it also consists of aragonite, gypsum, atacamite, brianroulstonite, kaolinite, quartz and siderite (Fig. 4). The calcite and dolomite are dominant in the lower portion of the formation, infact they are commonly found throughout the formation while the other minerals are present in the upper part of formation. The major peaks of calcite, dolomite and other minerals, as revealed by XRD, are shown for different samples in Figure 4. Based on XRD data, two dolomite groups are noticed in the Chorgali Formation. The first dolomite group is associated with evaporite having stoichiometric composition of 50.28 mole % CaCO3 and degree of order is 0.682. It consists of dolomite, gypsum, calcite and aragonite (Fig. 4c). The second dolomite group is not associated with evaporite and consists of dolomite, calcite, aragonite, siderite, quartz, kaolinite, atacamite and brianroulstonite (Fig. 4a, b, d and e). It has stoichiometric composition of 48.76 mole % $CaCO_3$ and degree of order varies from 0.58 to 0.9747. The first group dolomite has comparatively lower degree of order than the second group dolomite.

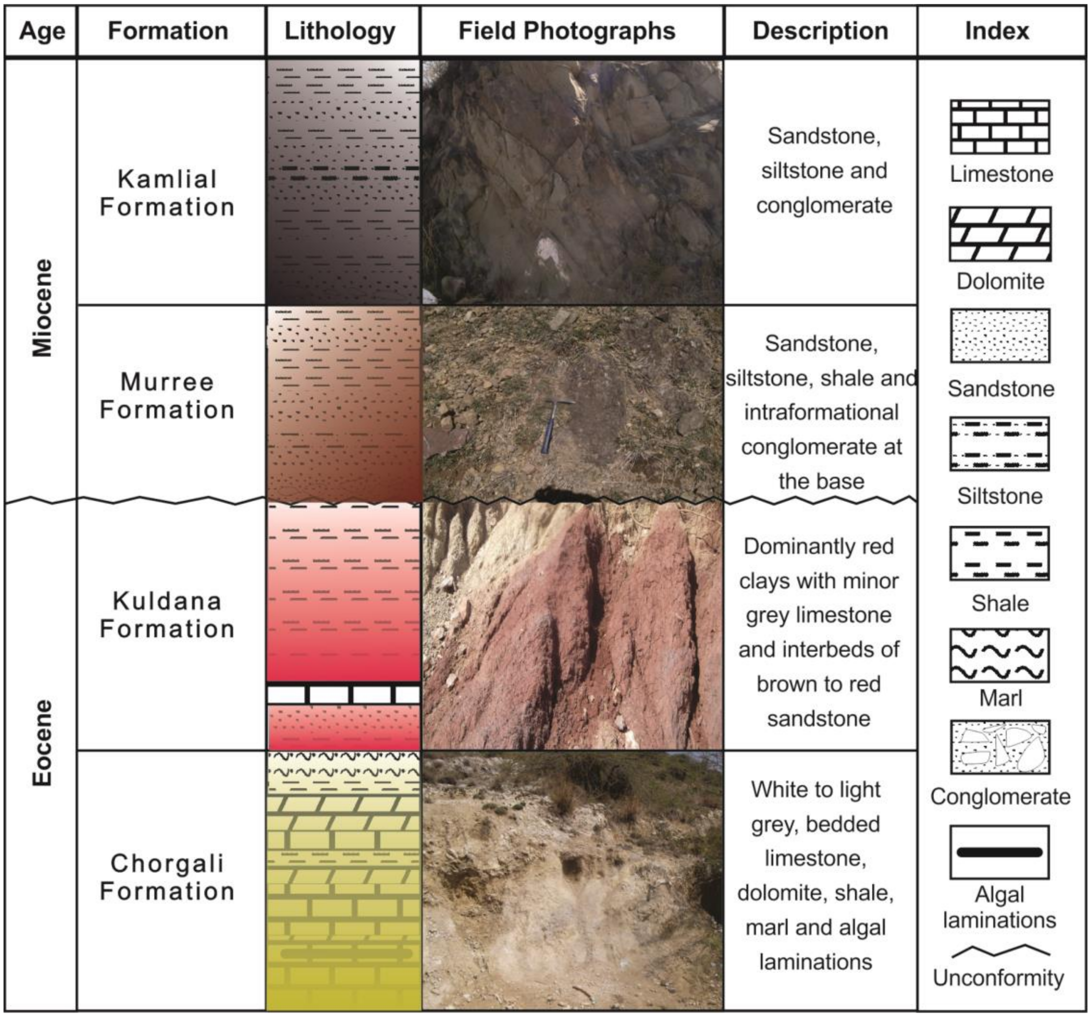

Fig. 2. Stratigraphy of the study area. The lithological description is adopted from Kazmi and Abbasi (2008).

Fig. 2. Outcrop photograph of the Chorgali Formation with marked zones of dolomite without and in-association with evaporite(s).

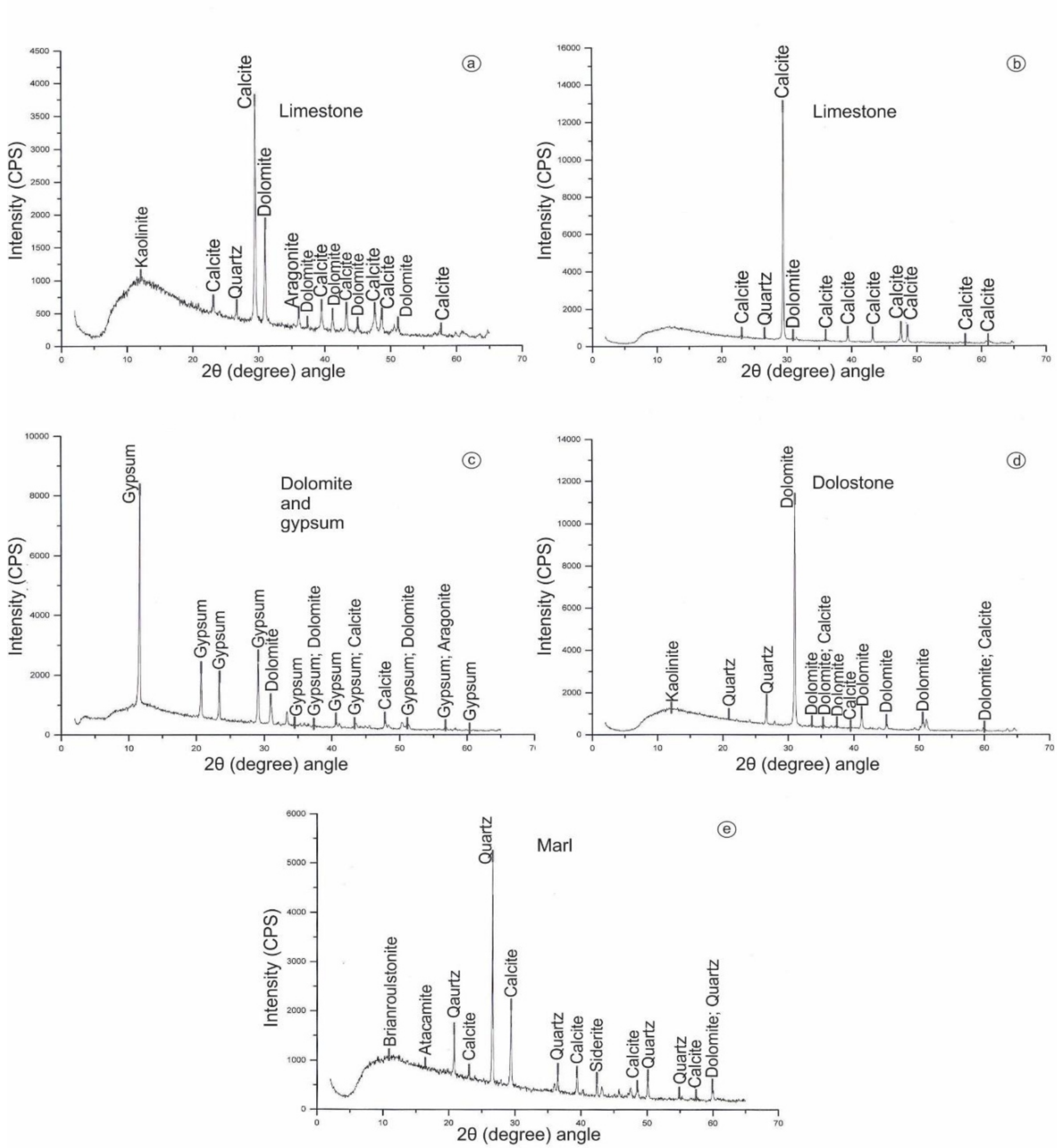

Fig. 4. XRD graphs of different samples of the Chorgali Formation: (a) and (b) Limestone, (c) dolomite and gypsum, (d) dolostone, and (e) marl.

4.2. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

The SEM and EDS analyses were conducted to study the rock under high magnification and to disclose detailed configuration and composition of respective samples. SEM provides actual three-dimensional grain relationships and details of the intergranular pore structures with high magnification (Welton, 2003). The EDS analysis involves identifying elements present in the sample by comparing each peak to the element list (Severin, 2004).

The key mineral composition of several sample(s) consists of calcite, dolomite, gypsum and quartz (Figs. 5a-5i). Dolomite associated with evaporite and dolomite not associated with evaporite are shown in Figures 5e-5f and 5g-5h respectively. The former group consists of gypsum, dolomite and calcite while the latter group includes dolomite, calcite, siderite, quartz and kaolinite (Fig. 5e-5l).

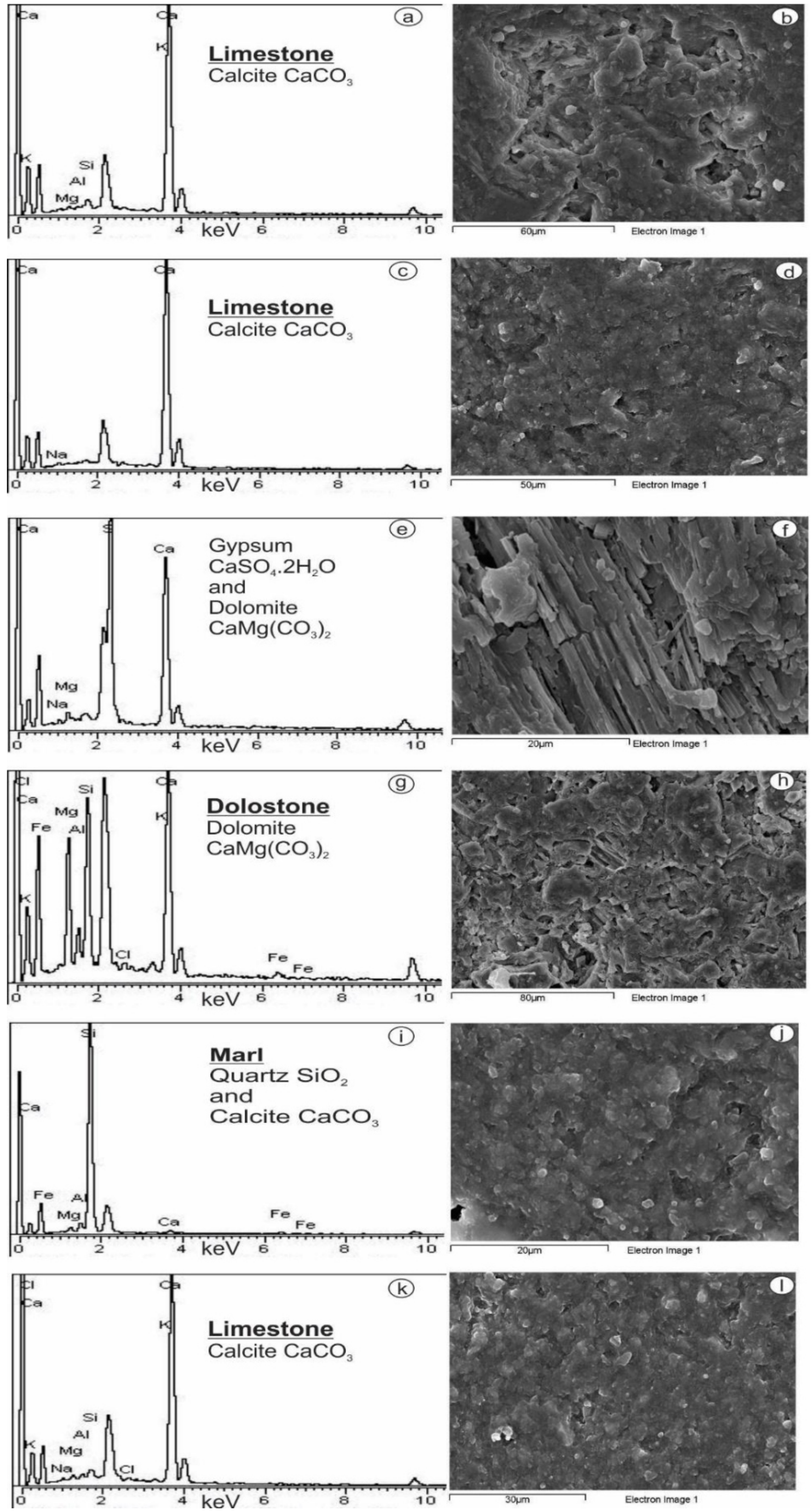

Fig. 5. EDS Spectrum and SEM photomicrographs showing the composition and structure of different samples: (a) and (b) EDS and SEM of calcite; (c) and (d) EDS and SEM of calcite; (e) and (f) EDS and SEM of dolomite and gypsum; (g) and (h) EDS and SEM of dolomite; (i) and (j) EDS and SEM of quartz and calcite; (k) and (l) EDS and SEM of calcite.

4.3. *Alizarin red staining*

The alizarin red staining technique is used to differentiate calcite from dolomite. The desired thin sections were placed for approximately 1 minute in the beaker containing the alizarin red solution. By doing so, the calcite stained red while dolomite remained unstained. The red stained calcite and colorless unstained dolomite is identified during petrographic studies under the polarizing microscope with the help of this staining technique (Figs. 6a-6d).

5. Discussion

5.1. Origin of dolomite and dolomitization model(s)

The dolomite associated with evaporites (early diagenetic dolomite) is interpreted to be formed in arid peritidal (sabkha) environment due to dolomitizing solutions with high Mg/Ca ratio in response to precipitation of gypsum, anhydrite and aragonite. The increase in Mg2+ will result in near stoichiometric dolomite (Kaczmarek and Sibley, 2011). The dolomite-not-associated with evaporite (relatively early late or late diagenetic dolomite) is indicating dolomitization in open diagenetic system (mixed marine-meteoric conditions) where the solution is reasonably oversaturated and undersaturated with respect to dolomite and calcite respectively (Tucker and Wright, 1990). According to Morrow (1978) and Lumsden and Chimahusky (1980) such dolomite groups are commonly early diagenetic, near-surface in origin. The reason of these associations is considered to be Mg/Ca ratio and salinity of dolomitizing solutions, with a climatic influence essential for dolomites of groups 2 and 3 of Morrow (1978) and Lumsden and Chimahusky (1980). The group 2 includes finely crystalline dolomites not related with evaporites and are commonly Ca-rich (54-56% CaC03). However, group 3 contains fine crystalline dolomites mixed with evaporites and are almost stoichiometric having 51-52% CaC03 (Morrow, 1978; Lumsden and Chimahusky, 1980). Where there is an evaporite association (group 3), demonstrating an arid climate, then pore fluids are likely to contain high Mg/Ca ratio from precipitation of gypsum, anhydrite and aragonite. It is envisaged that the abundance of Mg2+ ions in the fluids would lead to near-stoichiometric

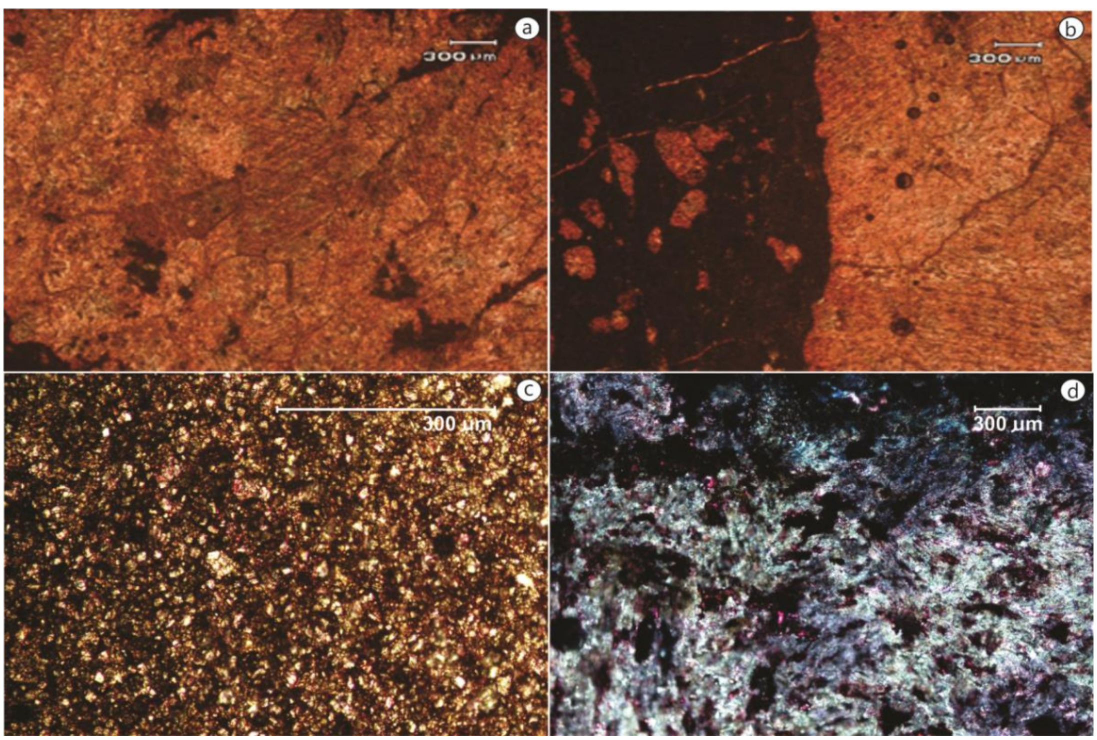

Fig. 6. Photomicrographs of alizarin red stained thin sections: (a) and (b) red stained calcite (light colored calcite crystal and dark colored calcitic micrite), (c) red stained micrite and unstained dolomite not associated with evaporite, and (d) unstained dolomite associated with gypsum and stained calcite

dolomite. The group 2 calcian dolomites are thought to have formed from solutions with lower Mg/Ca ratio, such as found in mixing zones, which are more active during humid climatic conditions (Morrow, 1978; Lumsden and Chimahusky, 1980).

Each model of dolomitization takes into consideration the source(s) of Mg2+ and pumping mechanism of Mg2+ rich fluids through the carbonate sediments (Tucker and Wright, 1990). In case of Chorgali Formation of the present area, the potential source of Mg2+ ions, in the dolomite associated with evaporites, is the diagenesis of the organic matter i.e. decomposing algal mats, which involved sulphate reduction leading to the alkaline fluids favorable for precipitation of dolomite (Tucker and Wright, 1990; Fig. 7). The source of Mg2+ ions in the dolomite-not-associated with evaporites can be the sea water and vigorous groundwater flow drives the dolomitization fluids through the limestone (Tucker and Wright, 1990; Fig. 8). It is suggested that the Mg2+ rich fluids are pumped via the limestone to the dolomitization site by the porosity-permeability network within the carbonates.

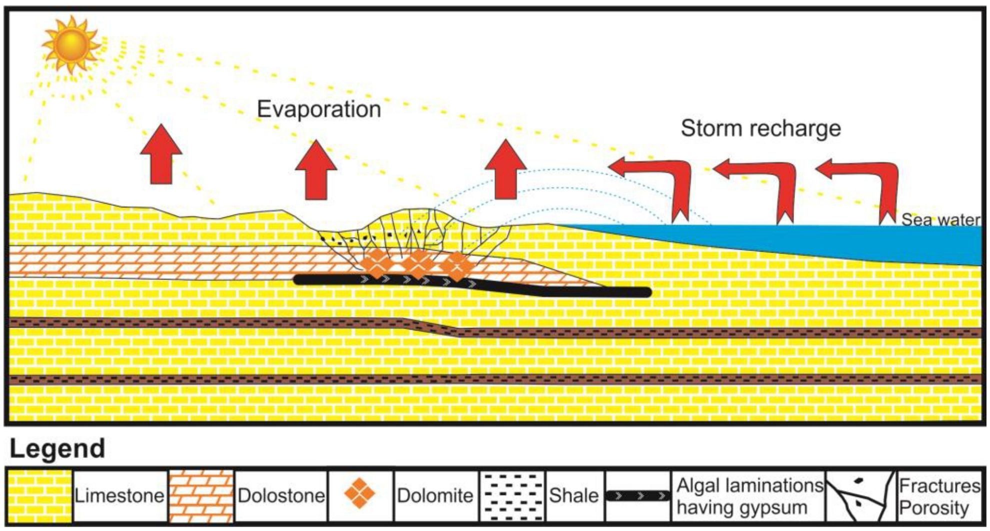

Fig. 7. Proposed dolomitization model for dolomite associated with evaporites.

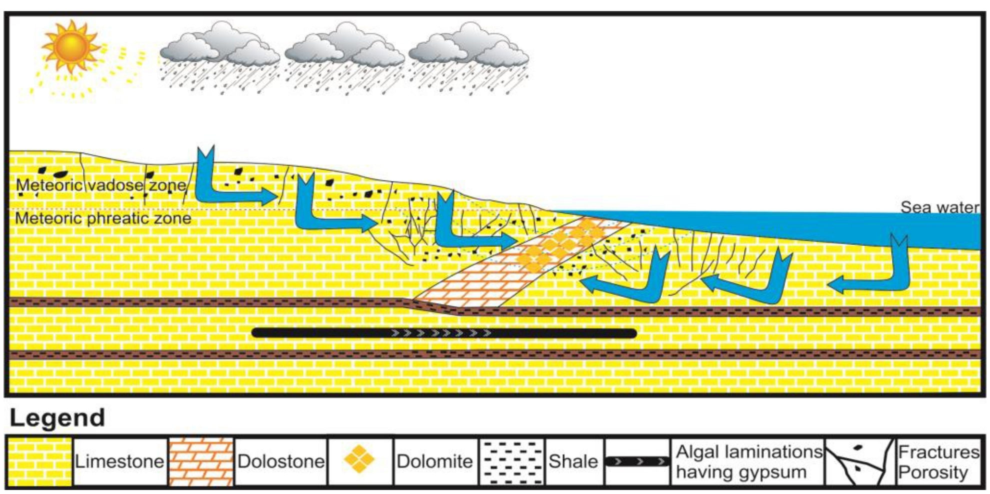

Fig. 8. Proposed dolomitization model for dolomite-not-associated with evaporites.

5.2. Implications for reservoir geology

Dolomitization can lead to the formation of porosity (i.e. intercrystalline porosity) and can improve the reservoir attribute. It is significant for accumulation of hydrocarbons as alteration of calcite to dolomite rises the porosity by 13 % (Chilingar and Terry, 1964). According to Sun (1995), most dolomite reservoirs are formed by early-diagenetic processes in combination with evaporites and these dolomites have been altered by post-depositional diagenetic phenomena such as karstification, fracturing and burial corrosion. These diagenetic processes improve reservoir quality in otherwise poor reservoirs. On the contrary, in non-evaporitic dolomites, karstification and fracturing provide fluid migration routes for the indigenous formation of dolomite reservoirs along fractures or unconformities (Sun, 1995). Within the Chorgali Formation, in the lower part the early dolomites are associated with evaporites (gypsum) and this rock is also fractured while the late dolomites, present above the former dolomites, are not associated with evaporites, however, it is also fractured but it might be due to tectonic deformation in the study area. The porosity has been estimated, using the photomicrographs of both the dolomite types, and it is concluded that dolomite associated with evaporites consists of 2.0 % porosity while dolomite-not-associated with evaporites consists of 01 % porosity (Figs. 9 and 10). However, qualitative permeability seems to be relatively higher in dolomite associated with evaporites as compared to the dolomite-not-associated with evaporites (Fig. 10).

Within the Chorgali Formation, gypsum (evaporite) and shale are potential seal/cap rocks for the reservoir lithologies i.e. limestone and dolostone thereby forming potential reservoir-seal couples at different intervals. Such reservoir-seal couples leads to the development of reservoir compartments within the formation. Similarly, the Chorgali Formation is overlain by the clays of Kuldana Formation which might serve as potential regional seal for the reservoir lithologies of the Chorgali Formation.

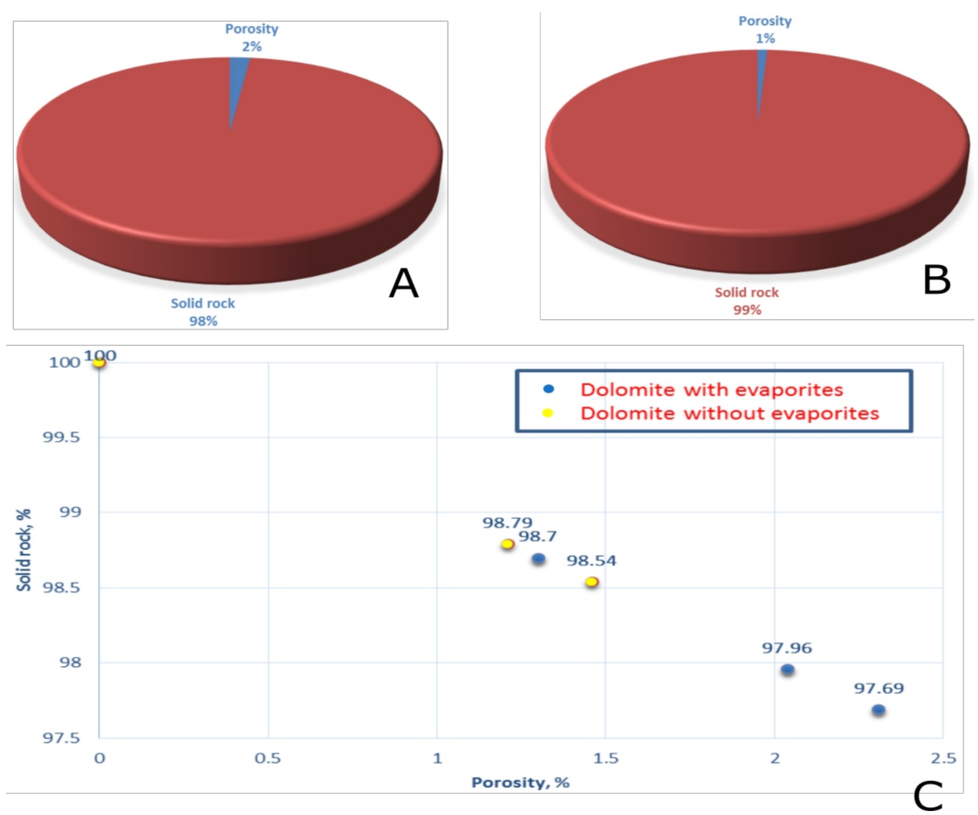

Fig. 9. Diagrammatic illustrations showing porosity in the Chorgali Formation: (A) and (B) Pie charts showing average porosity of dolomitic rock containing and lacking evaporites, (C) A graph showing solid rock volume versus porosity of dolomitic rock containing and lacking evaporites.

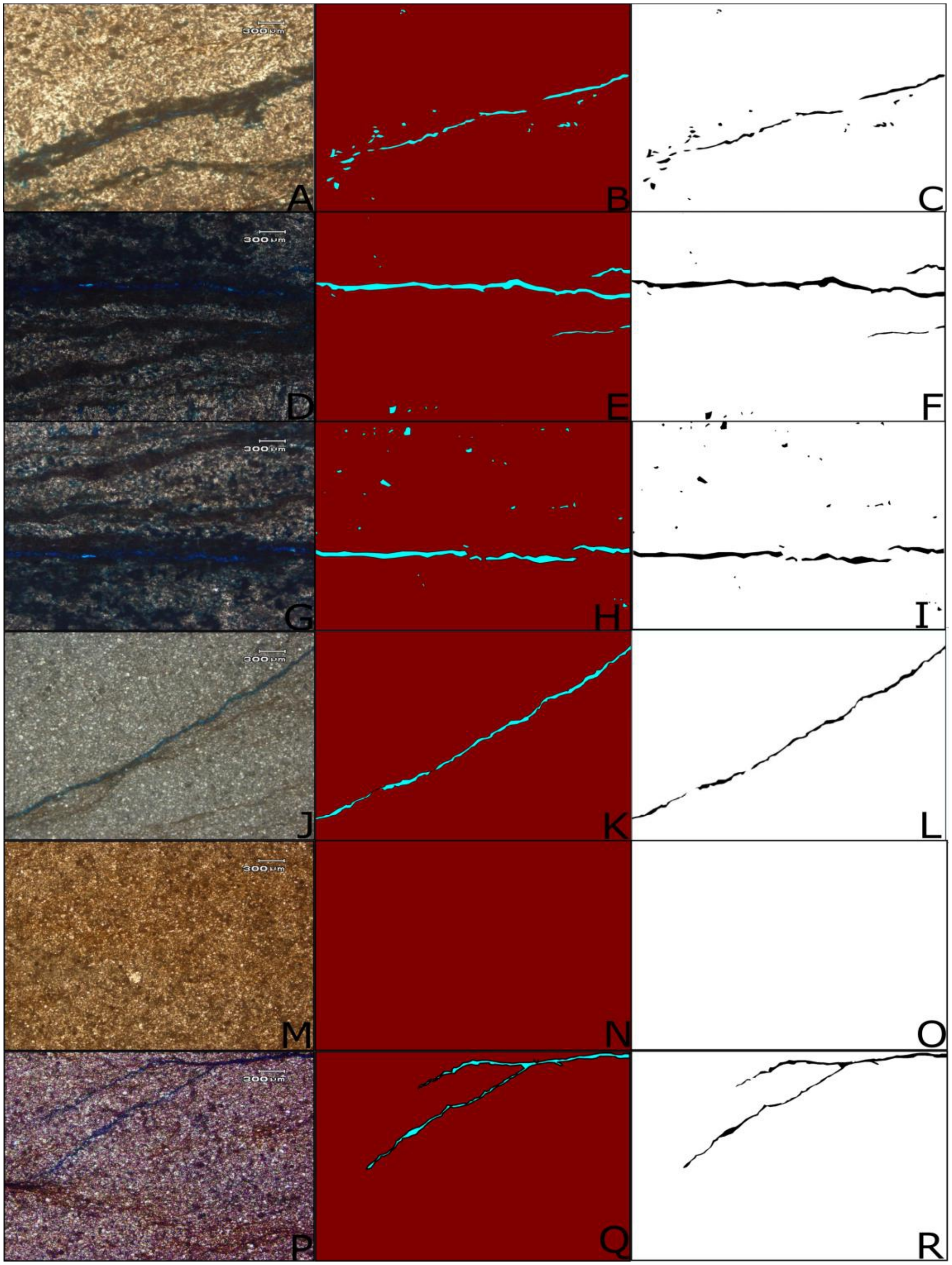

Fig. 10. Diagrammatic illustrations showing porosity in the Chorgali Formation: (A), (D) and (G) Photomicrographs of dolomite associated with evaporites; (B), (E) and (H) Sketches of Figs. 10A, 10D and 10G; (C), (F) and (I) Processed Figs. 10B, 10E and 10H in ImageJ software; (J), (M) and (P) Photomicrographs of dolomite-not-associated with evaporites; (K), (N) and (Q) Sketches of Figs. 10J, 10M and 10P; (L), (O) and (R) Processed Figs. 10K, 10N and 10Q in ImageJ software. In Figs. 10C, 10F, 10I, 10L, 10O and 10R, black spots marks porosity and white background is solid rock.

6. Conclusions

Two typical genetic dolomite groups are identified and interpreted based on XRD, SEM, EDS, chemical alizarin red staining and petrographic studies. One group is associated with evaporites and other is not associated with evaporites. Evaporites associated dolomite (early diagenetic dolomite) is characterized by stoichiometric composition of 50.28 mole % CaCO3 and degree of order is 0.682. The dolomite group not associated with evaporites (relatively early late or late diagenetic dolomite) is characterized by nearly stoichiometric composition of 48.76 mole % CaCO3 and degree of order varies from 0.58 to 0.9747. The former dolomite group is interpreted to be formed in arid peritidal (sabkha) environment due to dolomitizing solutions with high Mg/Ca ratio. The latter dolomite group is indicating dolomitization in open diagenetic system (mixed marine-meteoric environment) where the solution is reasonably oversaturated and undersaturated with respect to dolomite and calcite respectively. XRD, SEM and EDS interpreted the presence of calcite, dolomite, gypsum, aragonite, halite, quartz, kaolinite, muscovite, biotite, glauconite, brianroulstonite, atacamite, pyroaurite and siderite. Alizarin red staining discriminates stained red calcite from unstained dolomite. Dolomite can act as a good reservoir while gypsum as a seal and also can create reservoir compartments in the Chorgali Formation. The porosity values calculated using photomicrographs are 2.0 % and 1.0% for dolomite associated with evaporite(s) and dolomite-not-associated with evaporite(s) respectively, however, qualitative permeability seems to be relatively higher in dolomite associated with evaporite(s).

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Authors' Contribution

Muhammad Awais, proposed the main concept and involved in all stages of research paper preparation. Muhammad Hanif, also initiated and supported the main idea and assisted in interpretation of different analyses and improving the overall quality of the research paper. Muhammad Ishaq, involved in collection of data in the field; assisted in some laboratory analysis especially Scanning Electron Microscopy (SEM) and reviewed the manuscript. Irfan U. Jan, was also involved in collection of data in the field.

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