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Petrographic and Geochemical Characteristics of Dolomites in Devonian Shogram Formation, Karakorum Ranges, North Pakistan

NAME OF THE AUTHORS WITH AFFILIATIONS

1. Maryam Saleem
   i. Department of Earth sciences, Quaid e Azam University, Pakistan
   ii. Department of Earth & Environmental Sciences, Bahria University, Islamabad, Pakistan
   Email: maryamsaleem17@gmail.com

2. Faisal Rehman
   Department of Earth sciences, Quaid e Azam University, Pakistan
   Email: faisalrehman_ar@yahoo.com

3. *Abbas Ali Naseem
   Department of Earth sciences, Quaid e Azam University, Pakistan
   Email: abbasaliqau@gmail.com

4. Emadullah Khan
   Department of Geology, Abdul Wali Khan University, Mardan, Pakistan
   Email: emadgeo@awkum.edu.pk

5. Syed Wasim Sajjad
   Department of Earth sciences, Quaid e Azam University, Pakistan
   Email: geowaseem777@yahoo.com

6. Zubair Ahmad
   Department of Earth sciences, Quaid e Azam University, Pakistan
   Email: zubiamds@gmail.com

*CORRESPONDING AUTHOR
Name: Abbas Ali Naseem
Email ID: abbasaliqau@gmail.com
Contact: +923339019719
Petrographic and Geochemical Characteristics of Dolomites in Devonian Shogram Formation, Karakorum Ranges, North Pakistan
Maryam Saleem1,2, Faisal Rehman1, Abbas A. Naseem1,*, Emadullah Khan3, Syed Wasim Sajjad1, Zubair Ahmed1

1 Department of Earth Sciences, Quaid-e-Azam University Islamabad, Pakistan
2 Department of Earth & Environmental Sciences, Bahria University, Islamabad, Pakistan
3 Department of Geology, Abdul Wali Khan University, Mardan, Pakistan
* Correspondence: abbasaliqau@gmail.com; Tel.: +923339019719

Abstract: Excellent outcrops of Devonian carbonate rocks are present in Karakorum ranges of north Pakistan that are highly dolomitized. The Devonian Shogram Formation comprises of both matrix and cement dolomite. The petrographic studies revealed the texture of matrix dolomite as fine-grained anhedral dolomite (D1), medium grained subhedral to anhedral dolomite (D2), medium grained euhedral dolomite (D3), and coarse-grained anhedral dolomite (D4). The saddle cement dolomite phase of hydrothermal origin precipitated in vugs and fractures. The origin of various dolomitization phases are interpreted based on petrographic associations, elemental and stable isotopes signatures of each phase. First two phases of dolomitization are affiliated with the compaction flow of overlying shales based on evidence of low Fe and Mn content and isotopically light signatures of δ18O. The increase in burial resulted in third phase of dolomite showing signatures of redox conditions and high depleted δ18O as compared to the original marine signatures. The final phases of matrix dolomite and saddle dolomite cement are associated with tectonic activity in Karakorum region which brought up the deep source Mg rich fluids along the Reshun Fault.

Keywords: Burial; Devonian; hydrothermal; Karakorum; Reshun fault

Introduction
Dolomite is a carbonate mineral that forms by the process of dolomitization of limestone1. Economic base-metal deposits and hydrocarbons reservoirs formed by hot fluid circulations
are commonly associated with dolomite. About 80% of North America and 50% of world’s carbonate reservoirs occur within dolomite. The dolomitization process destroys partially or completely the original texture of precursor limestone. In recent years hydrothermal dolomite got a great attention. The hydrothermal dolomite demonstrates high temperature of formation and is used to evaluate the burial depth. During earlier time dolomites were classify based on their texture diversity which was later on followed by a modified classification system and presents a new classification based on crystal boundary and crystal size distribution. Crystal boundaries will be either planar or non-planar. Planar crystals have many face junctions while non-planner is considered by crystal boundaries with curved, serrated, lobate or irregular face junctions. Planar dolomite resulted due to faceted crystals growth of early-stage diagenesis while non-planar dolomite formed due to non-faceted growth of crystals. Dolomites characterised by planar crystal boundaries must develop at a growth temperature below 50°C while dolomites having non-planar crystal boundaries show an elevated temperature above 50°C. In general, the crystalline shape mineral is the function of growth kinetics, while the crystal order and size depend on its growth and nucleation.

**Tectonic setting**

The study area is a part of Karakoram ranges (Figure 1a), which is tectonically evolved during Pliocene uplift as product of Indian-Asian continental collision. The Karakoram block located at the south of the Eurasian plate, northward it is surrounded by the Pamir fault, and its southern portion is thrust over the Kohistan Island Arc. Toward east and west, it is bounded by Karakoram and Sarobi faults respectively. From south to north, the Karakoram block is divided into three main tectonic units i.e., the Southern Metamorphic Belt, the Karakoram Batholith, and the North Karakoram Terrain. The Southern metamorphic belt undergone pre-collisional and post-collisional metamorphic events which is evident by the presence of interlayered kyanite or sillimanite-grade pelites, garnet+clinopyroxene...
amphibolites, and dolomitic beds. The Karakoram batholith located in the central part of the Karakoram terrane which encompasses pre-collision, Andean-type subduction-related granites and post-collisional crustal melt monzogranites and leucogranites. The North Karakoram Terrain is a belt of sedimentary sequence of Permian to Cretaceous age and comprises of thick and poly-phase stack of thrust sheets. The regional thrust fault of Karakoram block includes Reshun, Upper Hunza and Chaprusan thrust faults while Ayun, Naz Bar and Shishi Faults contribute the small scale thrust fault system. The present research is the first detailed study in Chitral which is a part of the westward continuation of northern sedimentary belt of the Karakoram block (Figure 1a). In Chitral, it is a limited and narrow belt of Devonian to Triassic rock sequence which is illustrated in a simplified stratigraphic column (Figure 1b).

**Methodology**

Field work was carried out in the dolomitized hills and sampled for laboratory studies. 151 samples were collected which were cut into slabs followed by thin section preparation. Petrographic examinations on thin sections were performed using conventional microscopy at Department of Earth Sciences Quaid-e-Azam University Islamabad, Pakistan. The thin sections were previously stained with Alizarin Red-S and potassium ferricyanide to differentiate calcite from dolomite and ferroan carbonate from non-ferroan carbonate. For determination of major and trace element composition inductively coupled plasma - optical emission spectrometry (ICP-OES) technique was performed on 41 samples at Pakistan Institute of Nuclear Sciences and Technology (PINSTECH). 18 samples were selected from different dolomite for stable oxygen and carbon isotopic study which were analysed at Isotope Application Division, PINSTECH, Islamabad. All δ¹³C and δ¹⁸O values are conveyed in per mill (‰) relative to Vienna Pee Dee Belemnite (V-PDB).

**Field observations**
The studied outcrop of Parpish section comprises of an alternating thick and thin bedded light grey colour dolomite (Figure 2a,b). The weathered surface of dolomites shows light grey colour while fresh surface is dark grey in colour (Figure 2c). The remarkable and diagnostic feature of dolomite i.e., Chop-board weathering was also observed (Figure 2d). Field observation revealed presence of vugs and fractures which were filled by various cementing agents like saddle dolomite, calcite and pyrite minerals. The vugs are mostly irregular in shape with variable size which is cemented by the late-stage coarse crystalline saddle dolomite SD (Figure 2f). At some places, the occluded vugs are separated from one another by the thin to thick veneer of host dolomite (Figure 2g). The SD also encloses various pores and veins (Figure 2h). Several slicken lines are also observed which were filled by the calcite cements (Figure 2i). Low angle stylolite passing through the dolomite rock body which is infilled through rusty yellow colour pyrites (Figure 2j and 2k).

**Petrography**

In petrography, two different dolomite phases were recognised including matrix dolomite phase and cementing dolomite phase. The dolomites display interlocked, euhedral, subhedral to anhedral crystal rhombic morphology where the intercrystalline porosity is diminished. Using classification, four replacive matrix dolomite phases were distinguished which includes: i) fine grained anhedral dolomite (D1), ii) medium grained subhedral to anhedral dolomite (D2), (iii) medium grained euhedral dolomite (D3), iv) coarse grained anhedral dolomite (D4).

D1 exhibits nonplanar anhedral crystal rhombs having a crystal size ranging from 20 to 40μm (Figure 3a). The dolomite D1 obscured the original texture of the precursor limestone (Figure 3a). The crystal size of dolomite D2 ranging from 80 to 230μm having nonplanar subhedral to anhedral rhombic crystal morphology (Figure 3b). A sharp contact between D1 and D2 is also observed (Figure 3c) where at some places dolomite D2 crosscut earlier phase dolomite D1
(Figure 3d). The third phase is dolomite D3 with a crystal size of 200-300 μm and shows a sharp contact with dolomite D1 and crosscut D1 dolomite (Figure 3e and 3f). The anhedral and coarsely crystalline dolomite D4 is the last phase of dolomitization. The D4 crystal size ranging from 200 to 620μm (Figure 3g) which crosscut the earlier formed fine grain dolomite D1 (Figure 3h). The SD represents the cementing phase of dolomitization which is coarse grained with a size range from 400μm to 1mm (Figure 3i). SD also occurs in a contact with D1 and D2 dolomite (Figure 3j). Fracture and pore filling calcite cementation is also observed (Figure 3k). Stylolite also occurred which crosscut the earlier formed dolomite (Figure 3l).

Geochemistry

Inductively coupled plasma – optical emission spectroscopy (ICP-OES)

The recognition of major and trace element in dolomite provide valuable information about the diagenetic process, dolomite origin, diagenetic solution and dolomitization mechanism\textsuperscript{13,14}. To determine the chemical composition of dolomites, ICP-OES analyses were carried out as shown in Figure 4. The D1 dolomite comprises of 4027 to 5972 ppm of Fe, 372 to 479 ppm of Mn, 131 to 188 ppm of Sr, and 231 to 195 ppm of Na. The D2 dolomite has 6402 to 8957 ppm of Fe, 372 to 492 ppm of Mn, 76 to 131 ppm of Sr, and 115 to 169 ppm of Na. The D3 dolomite has the concentration of 8189 to 9979 ppm of Fe, 376 to 548 ppm of Mn, 71 to 105 ppm of Sr, and 84 to 135 ppm of Na. The D4 has concentration 9580 to 10564 of Fe, 425 to 584 ppm of Mn, 78 to 120 ppm of Sr and 43 to 101 ppm of Na.

Oxygen and Carbon Isotope Analysis

Representative samples were selected for δ\textsuperscript{18}O and δ\textsuperscript{13}C isotopes analysis based on the identified phases of dolomite from the petrographic results. The correlation of δ\textsuperscript{18}O and δ\textsuperscript{13}C values is carried out with the original Devonian seawater signatures. The known oxygen isotope signatures of Devonian seawater for host limestone prior to interaction with magnesium-rich fluid ranging from −3.8 to 4.2 %\textsubscript{o} V-PDB and that of carbon ranges from 0 to
1.9% V-PDB, while the Devonian marine dolomite δ¹³C ranges from 0.5 to 2.5% V-PDB and that of δ¹⁸O ranges from -2.5 to -0.5% V-PDB. The oxygen and carbon composition of various diagenetic phases of the Shogram Formation dolomite are given in (Figure 6). These different diagenetic phases show a wide range of isotopic signatures. Dolomite D1 shows δ¹⁸O signatures ranging from -6.72 to -6.1% V-PDB and δ¹³C signature ranges from 1.2 to 1.9% V-PDB.

The dolomite D2 shows depleted isotopic signatures as compared to dolomite D1 (Figure 5). The δ¹⁸O values of dolomite D3 is highly depleted that is ranging between -9.1 to -8.8% V-PDB, while the δ¹³C values ranges from 0.9 to 1.4% V-PDB. In addition matrix dolomite D4 shows highly depleted isotopes signatures and their δ¹⁸O and δ¹³C values ranges from -11.5 to -10.4% V-PDB and 1.2 to 1.6% V-PDB respectively. Furthermore, the saddle dolomite SD exhibit highest depleted δ¹⁸O values ranging from -14.1 to -12.4% V-PDB, whereas δ¹³C values are with in the range of original marine signatures that is 0.51 to 1.4% V-PDB.

Discussion

The study area had experienced various stages of deformation. During Late Permian to Early Triassic rifting of Karakorum block from Gondwanaland followed by the compressional tectonism of Late Cretaceous age due to Kohistan-Karakorum collision resulted into widespread plutonism. Four stages of deformation occur in Karakorum block after Kohistan-Karakorum collision. The Paleocene to Eocene deformations are related to granitic magmatic intrusions, metamorphism and crustal thickening followed by Indian-Eurasian collision in Eocene. The southward motion along Main Karakorum Thrust (MKT) was active since the closure of Indus Suture and up to Miocene and after. Dextral motion is also observed along MKT, in association with reverse faulting.

In the study area, the Reshun Fault thrust over the Devonian Shogram Formation over the Cretaceous Reshun Formation (Figure 2a). A detailed paragenetic sequence has been
established based on field observations, petrographic studies, and geochemical analysis of the studied outcrop of the Shogram Formation which revealed a multistage diagenetic evolution (Figure 6). These multistage dolomitization events in Devonian Shogram Formation are discussed as below. The dolomite D1 has partially inherited the original nature of limestone where peloidal structure of host limestone is replaced (Figure 3c). Dolomite D2 exhibits coarser crystal rhomb but show similarity in texture to dolomite D1. Coarsening in dolomite crystal size occur due to factors like precipitation rate increased temperature and overgrowth of later stage dolomite on existent cores of earlier dolomite. Dolomite type D3 shows cloudy centres and clear rims (Figure 3f). The cloudy centre often indicates post-depositional replacive dolomitization. D3 will be either formed from direct replacement of carbonate or through recrystallization of early dolomite types D1 and D2. Dolomite type D4 shows undulose extinction and distorted crystal lattice which indicate crystal growth at high temperatures (>60 °C) during deep burial settings. The occurrence of cementing phase saddle dolomite (SD) reveals the deepest diagenetic settings for their formation during progressive burial which follows replacive matrix phases and occluded the brittle fracturing. Calcite cementation (Figure 3k) occurs after the activation and reactivation of faults at different times which caused intense fracturing in dolomite. The diagenetic process in dolomite is controlled by the dolomitizing fluids which can be traced through different elemental concentration like sodium, strontium, manganese, and iron. Previous studies show that during carbonate diagenesis the Mn concentration increases and the Sr decreases. The studied dolomites phases show significant amount of Mn content (Figure 4a) and low concentration of Sr (Figure 4b), which are comparable to those dolomite precipitated from marine waters. Sr contents of >300 ppm, have been predicted for dolomite forming from normal marine seawater. This is significantly more Sr than that contained in Devonian Shogram Formation.
The Sr concentrations exhibit inverse relation with crystal size and show a significant decrease of Sr concentrations with increasing crystal size\textsuperscript{25}. Unlike Sr, the Fe and Mn concentration shows reducing state environment for diagenetic and dolomitizing fluids. Dolomite types D3 and D4 shows higher concentration of Fe and Mn as compared to D1 and D2 which suggests their formation under reducing conditions during burial diagenesis\textsuperscript{26}. The distribution of Fe and Mn in solution is strictly controlled by redox conditions as well as their concentrations in precursor limestone and precipitation rate\textsuperscript{13}.

Stable isotope analyses of dolomites show a pronounced shift of δ\textsuperscript{18}O values from the original Devonian marine signatures of calcite and dolomite (Figure 5). The non-depleted δ\textsuperscript{18}O signatures reveal their formation in the surface environment of evaporitic condition\textsuperscript{27}. Stable isotope values reveal a wide range of δ\textsuperscript{18}O values mainly between –11.98 and –5.153‰ V-PDB, which is reliable with multiphase diagenetic history\textsuperscript{28,29}. Dolomite D1 represents first phase of replacive dolomite phase and showing less depleted δ\textsuperscript{18}O signatures from D2 which suggest a relatively low temperature for their formation as compared to D2. Furthermore, dolomite D3 δ\textsuperscript{18}O signatures are more depleted in reference to D1 and D2 and suggest their formation from buffering of host limestone at higher temperature from preceding dolomite phases. The measured δ\textsuperscript{18}O values shows a further depletion from original marine Devonian signature and a most pronounced shift is observed in the fourth phase of dolomite D4 (Figure 5). Dolomite D4 formed at much higher temperature then the early diagenetic dolomite phases. Early diagenetic dolomite phases reveal heavier δ\textsuperscript{18}O values and are formed at lower temperature as compared to later diagenetic dolomites with lighter δ\textsuperscript{18}O values\textsuperscript{30}. Similarly, vugs and veins filling cementing phase saddle dolomite (SD) show high depletion of δ\textsuperscript{18}O values (Figure 5). The more pronounced negative shift of oxygen isotopic trend of saddle dolomite SD (–14.53 to –11.98‰ V-PDB) suggest high temperature fluid from a greater depth than the replacive dolomitizing fluids. This late-stage saddle dolomite (SD) indicates
higher temperatures\textsuperscript{31}. All the observed diagenetic phases show deviation toward negative oxygen-isotope signatures, and increased temperature is the likely source of depleted $\delta^{18}$O values.

**Mechanism of dolomitization**

As discussed earlier that Devonian Shogram Formation has undergone various episodes of deformation and plutonism. Based on stratigraphic and structural setting, field observations, petrographic studies, and geochemical analysis, burial dolomitization model is suggested for the studied outcrop of the Shogram Formation (Figure 7). In general, burial dolomitization models are essentially hydrological models which differ in terms of the nature of the drives and direction of fluid flow\textsuperscript{32}. The development of non-planar crystal textures more than about 60°C and the presence of saddle dolomite suggest temperature of formation more than about 80°C. The initial phase of dolomitization (D1 and D2) resulted from the compactional dewatering of the overlying Sarikol Shales where the fractures acted as a conduit to the underlying Shogram Formation which caused the initial dolomitization which is supported by the low content Fe and Mn and less depleted $\delta^{18}$O values. Increasing burial resulted in the formation of D3 dolomite which is evident by more redox conditions at depth and high depleted values of $\delta^{18}$O. Finally, the activation of regional Reshun fault provided pathways for Mg-rich dolomitizing fluids from the deeper source resulting in the formation of D4 and saddle dolomite (SD) as evident by more depleted values of $\delta^{18}$O values and the presence of certain hydrothermal minerals i.e., willemite and merwinite. Aside from hydrothermal mineral other high temperature minerals include kutnohorite and bustamit found in association with D4\textsuperscript{33}. The source of Mg rich hydrothermal fluid in D4 could be widespread igneous intrusion in Karakorum region during collisional or post collisional times.

**Conclusion**
The Devonian Shogram Formation in North-western Karakorum was studied in detail through field observations, petrographic studies, and geochemical analysis. In the petrographic studies, four replacive matrix dolomite types along with cementing saddle dolomite phase were recognised. The influences of diagenetic and hydrothermal fluids were traced through Fe and Mn concentration. All dolomite phases show high content of Fe and Mn but are very high in dolomite D3 and D4 which suggests an environment of reducing conditions. While the variation of Sr concentration in different dolomite phases suggest multistage diagenetic process. Dolomite D1 has lowest while D4 has higher Sr content, indicating later diagenetic environment for D4 as compared to D1. The oxygen carbon isotope signature suggesting that all the studied dolomites have their generation in variable temperature conditions. The measured δ¹⁸O V-PDB values of fine-grained dolomite are heavier than those of dolomite D2, D3 and D4. This less depleted δ¹⁸O values of D1 suggesting lower formation temperature. Whereas dolomite D3 and D4 have more depleted δ¹⁸O isotope values, indicating multiphase dolomitization and high temperature origin. Furthermore, saddle dolomites cement (SD) exhibits highly depleted δ¹⁸O values and indicate very high temperature. Conceptual dolomitization model suggest three phases of dolomitization events. Initially, replacive dolomites (D1 and D2) are formed by the compactional dewatering of overlying shale to cause dolomitization in shallow burial conditions, which is supported by petrographic and geochemical data. It is followed by deep burial conditions which resulted in formation of dolomite (D3), evident by more depleted δ¹⁸O values and enhanced Fe and Mn content. Moreover dolomites (D4 and SD) are related with the activation of NE - SW Reshun fault, which provided pathways for the Mg rich hydrothermal fluids, supported by highly depleted δ¹⁸O values, high Fe and Mn content and presence of high temperature hydrothermal minerals along with dolomite (D4) which is evident from the fact of the recrystallization and formation of coarse crystals in dolomite (D4) The coarsening crystal size in association with increase in
burial conditions, lower concentration of Na, Sr, higher amount of Mn, Fe content and the depleted oxygen isotope values indicate that replacive dolomite of Shogram Formation are recrystallized by diagenetic solutions at increased temperature during burial. Possible source of hydrothermal fluids in later stages could be magmatic or deep-seated hydrothermal fluids which circulated along the faults.

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References


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Figure Legends:

Figure 1. (a) Geological Map of the Chitral area where the study area is marked by yellow box (b) Stratigraphic column of the study area.

Figure 2. Representative field photographs of Shogram Formation, Parpish Section. (a) and (b) outcrop view comprising of alternating thick and thin bedded dolomite. (c) dark grey colour dolomite on fresh surface. (d) Chop-board weathering (e) light grey (l), (g) and dark grey (d), (k), colour dolomite. (f) and (g) vugs occluded by cementing phase saddle dolomite (SD). (h) occurrence of saddle dolomite (SD) in veins and vugs. (i) slicken lines filled with calcite. (j) and (k) low angle stylolite (ST) passing through dolomite.

Figure 3. Microscopic examinations of different dolomite phases. (a) fine grained anhedral dolomite D1. (b) medium grained subhedral to anhedral dolomite (D2). (c) and (d) sharp contact between D1 and D2. (e) sharp contact between medium grained euhedral dolomite D3 and dolomite D1. (f) medium grained euhedral dolomite D3. (g) coarse grained anhedral dolomite (D4). (h) Dolomite D1 crosscut early phase dolomite D1. (i) coarse crystalline cementing phase saddle dolomite (SD). (j) dolomite D1 with dolomite D2 and cementing phase saddle dolomite SD. (k) occurrence of calcite cementation (CC), saddle dolomite (SD) in a contact with fine grained anhedral dolomite D1. (l) late-stage stylolite (St) which crosscut the early phase dolomite.

Figure 4. Cross plots major and trace element concentration. (a) Enrichment of Fe and Mn showing increase in reduction state in dolomites compared to sea water values. (b) Concentration of Sr and Fe in different dolomites. The content of Sr is decreasing compared to sea water values. (c) Concentration of Na and Fe in different dolomite phases.

Figure 5. Oxygen and carbon isotope signatures of various dolomite phases compared to middle Devonian marine limestone and dolomite in blue box.

Figure 6. Various digenetic events of dolomite and calcite phases in relationship with time.
Figure 7. Dolomitization model for Devonian Shogram Formation where the dolomitization occurred in two stages.
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