



Mineralogical and Geochemical investigations of Celestite and Gypsum from GanjoTakkara area, Hyderabad, Sindh, Pakistan

A. H. MARKHAND⁺⁺, M. H. AGHEEM, S. A. SHAIKH, Q. D. KHOKHAR, A. G. SAHIT, M. A. JAMALI

Centre for Pure and Applied Geology, University of Sindh, Jamshoro, Pakistan

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Abstract: The mineralogical and geochemical studies on the celestite and gypsum deposits at the GanjoTakkara area of Hyderabad, Sindh, Pakistan in the stratigraphic horizons of Meting Shale and Laki Limestone belonging to the Laki Formation of the Eocene (Ypresian) age are conducted to decipher their mode of formation. A total of 07 samples were collected during fieldworks and were later on processed for the major element concentration using XRF and for the mineral compositions using the XRD techniques. The Gypsum varieties found in the study area are the Fibrous and the Rose Gypsum. The Celestite in the study area is massive and a bit fibrous. The studies revealed that the solution/sea water from which the Celestite and Gypsum are formed through evaporation and as anhydrite experienced the extreme arid conditions at the time of the formation of these deposits. The mineral assemblages determined through the XRD are of three types: (a) Gypsum, Quartz low, Calcite (b) Calcite, Ankerite, Gypsum, and (c) Ankerite, Dolomite, Calcite. In these assemblages the enrichment of Quartz low is probably not the syngenetic. Meanwhile, the presence of Ankerite supports the idea of prevalence of extreme arid climate because it bears Fe⁺⁺ (Bivalent Iron) which is indicative of anoxic conditions.

Keywords: Celestite, Gypsum, Geochemistry, Mineralogy, GanjoTakkara, Pakistan.

1. INTRODUCTION

The celestite (SrSO₄) belongs to the sulfate group of minerals and is commonly found in the sedimentary rocks such as dolomite, dolomitic limestone, and limestone often in association with gypsum and other evaporites. The dissolution of buried biogenic carbonates and precipitation of inorganic calcite are the vital sources of release of strontium leading to the deposits of celestite (Baker *et al.*, 1987). Besides this, the celestite may also be formed as a result of the hydrothermal solution associated recrystallization of carbonates along the fault planes. The gypsum, named as hydrated calcium sulfate (CaSO₄.2H₂O) is a common sulfate mineral formed by the evaporation, it is also termed as the first of the mineral salts to precipitate from sea water during evaporation (Ochsenius, 1888). The gypsum deposits are usually found in the strata such as clay, shale, limestone, dolomite, and sandstone. Osborne (1941) proposed the occurrence of gypsum as an alteration product of anhydrite. Bundy (1956) in a study of gypsum-anhydrite deposits suggests that in most evaporite deposits, gypsum was precipitated first and was later converted into anhydrite.

The studies of Khan (1973) on the celestite deposits of Pakistan hold the status of the pioneering studies besides this the studies of Malkani (2010, 2011, 2012)

and Malkani *et al.*, (2016) are the major studies available reporting the occurrence and to some extent reserve estimate of the deposits at various locations of the country i.e., DeraBugti, Kohlu, Musa Khel, DaudKhel, and ThanoBula Khan. The celestite at the above areas occur as veins and nodules in the Eocene age strata (Drug, Kirthar, Ghazij, and Laki formations). The studies on gypsum deposits of Pakistan include those of Ahmad *et al.*, (1996); Alizai *et al.*, (2000); Malkani (2011); Khan (1982); Heron (1955); Kazmi and Abbas (2001); Hussain and Karim (1993); and Malkani (2013). These studies report and describe the gypsum deposits in the areas of Azad Kashmir, Hazara, Karak, Dera Ismail Khan, Dera Ghazi Khan, Chagai, Lasbella, Johi, Khairpur Nathan Shah, GanjoTakkara, Thar desert, and ThanoBula Khan in the strata ranging in age from Precambrian to Miocene.

Both the celestite and gypsum have various industrial uses including cement, ceramic, paint, and medicine chiefly and both are considered amongst the mineral wealth for any country. The present study is undertaken to have an insight on the mineral and major oxide composition of celestite and gypsum, eventually leading to the understanding of the conditions that prevailed at the GanjoTakkara area at the time of formation of the said deposits.

⁺⁺Corresponding author: Akhtar Hussain Markhand markhand.akhtar@usindh.edu.pk

2. MATERIALS AND METHODS

The fieldworks for sample collection and other field features were carried at GanjoTakkar area near Hyderabad city. The study area lies in the survey of Pakistan toposheet No: 40 C/7 which is the part of Hunting Survey Corporations Geologic map No: 40 C-G (**Fig.1**). A total of 07 samples were collected, the details of samples are given in (**Table 1**). The samples were labelled with the prefix of GT that stands for GanjoTakkar followed by the number of sample.

Table 1. The coordinates and description of samples from Ganjo Takkar area.

Sample No.	Latitude and Longitude	Description
GT-01	25° 11' 42" N 68° 22' 28" E	The fibrous gypsum found in the partly sandy and partly shelly limestone
GT-02	25° 11' 42" N 68° 22' 27" E	The Rose variety of Gypsum embedded in the shelly limestone bed
GT-03	25° 11' 42" N 68° 22' 27" E	Shelly limestone
GT-04	25° 11' 42" N 68° 22' 27" E	Shale
GT-05	25° 11' 41" N 68° 22' 26" E	Celestite
GT-06	25° 11' 38" N 68° 22' 29" E	Sandy limestone
GT-07	25° 11' 26" N 68° 22' 23" E	Celestite

Table 2. Major Oxide concentrations (weight percentage) in the samples from the study area.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	LOI	Total
GT-01	22.08	1.872	9.92	13.36	16.56	1.16	0.2736	0.272	0.952	0.0692	13.44	20	99.9588
GT-02	21.92	1.248	8.08	11.6	19.28	1.32	0.1784	0.4456	1.144	0.0976	14.72	20	100.03
GT-03	10.57	0.777	5.341	6.818	42.77	2.03	0.3381	0.5656	0.2625	BDL	0.5565	30	100.02
GT-04	30.45	2.226	15.12	14	3.612	1.778	0.3276	0.3108	0.987	0.0721	1.127	30	100.01
GT-05	13	0.772	5.37	3.77	6.49	1.25	BDL	0.415	0.71	0.0884	68.1	0	99.96
GT-06	6.12	0.252	2.844	12.3	29.94	7.32	0.3978	0.1224	0.1488	0.0463	0.4884	40	99.97
GT-07	28.4	1.34	10.6	9.59	10.9	1.84	0.109	0.681	1.47	0.123	35	0	100.05

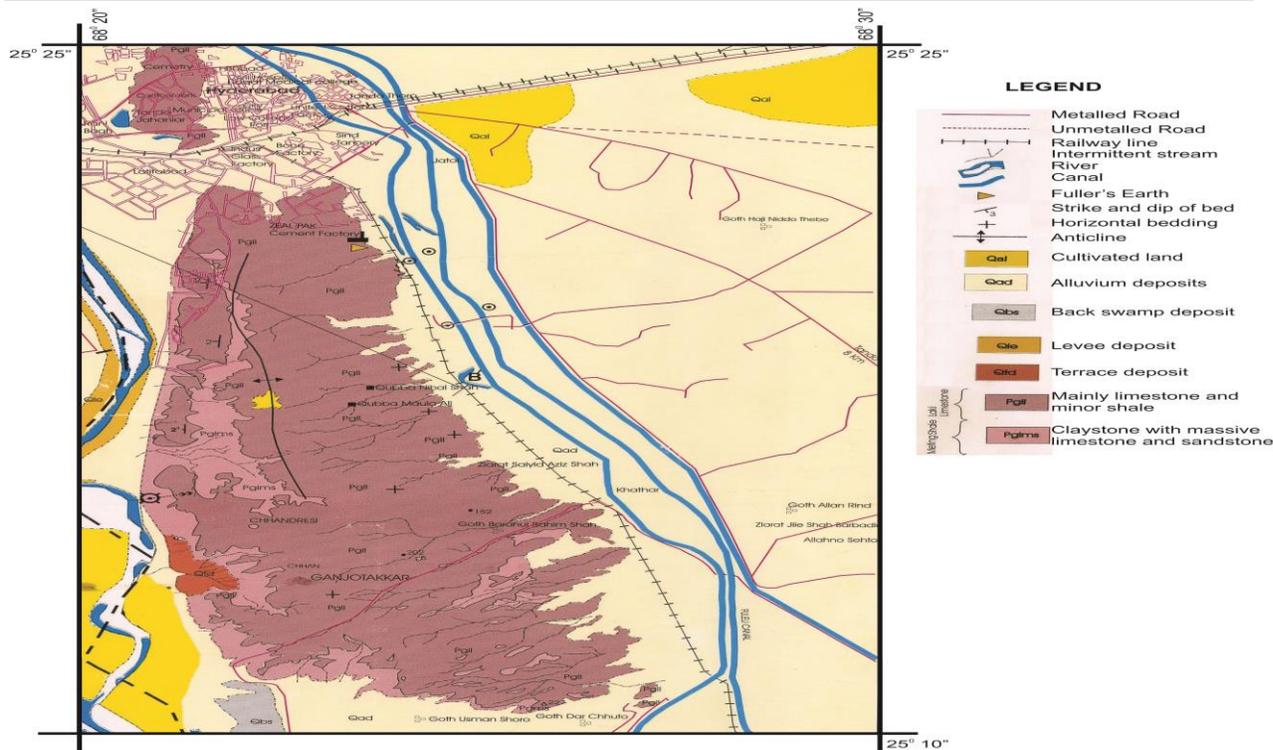


Fig. 1. Geological map of Ganjo Takkar area (modified and reproduced after Ahsan *et al.*, 2006).

The samples were processed for the measurement of major oxides concentration using Geomajor method on the S4 Pioneer WD X-ray Fluorescence Spectrometer and for the mineral composition using the X-ray Diffraction techniques at the laboratories of the Centre for Pure and Applied Geology of the University of Sindh, Jamshoro. The analytical procedures given in Agheem *et al.*, (2020) and Jan *et al.*, (2017) were adopted.

3. RESULTS

The geochemical results acquired through XRF technique in the form of major oxides are presented in

(Table 2). The various discrimination diagrams are prepared for the acquired results (weight percentage) such as; bivariate plots of SiO₂ versus Al₂O₃, SiO₂ versus K₂O, SiO₂ versus TiO₂, SiO₂ versus MnO, SiO₂ versus P₂O₅ and SiO₂ versus MgO (Fig. 2). A paleoclimatic diagram based on the SiO₂ versus Al₂O₃+K₂O+Na₂O (Fig. 3) is also prepared.

The mineralogical results acquired through XRD technique are presented the form of diffractograms (Figs. 4, 5, 6, and 7). The varieties of celestite and gypsum observed and collected during the fieldwork are shown in (Fig. 8).

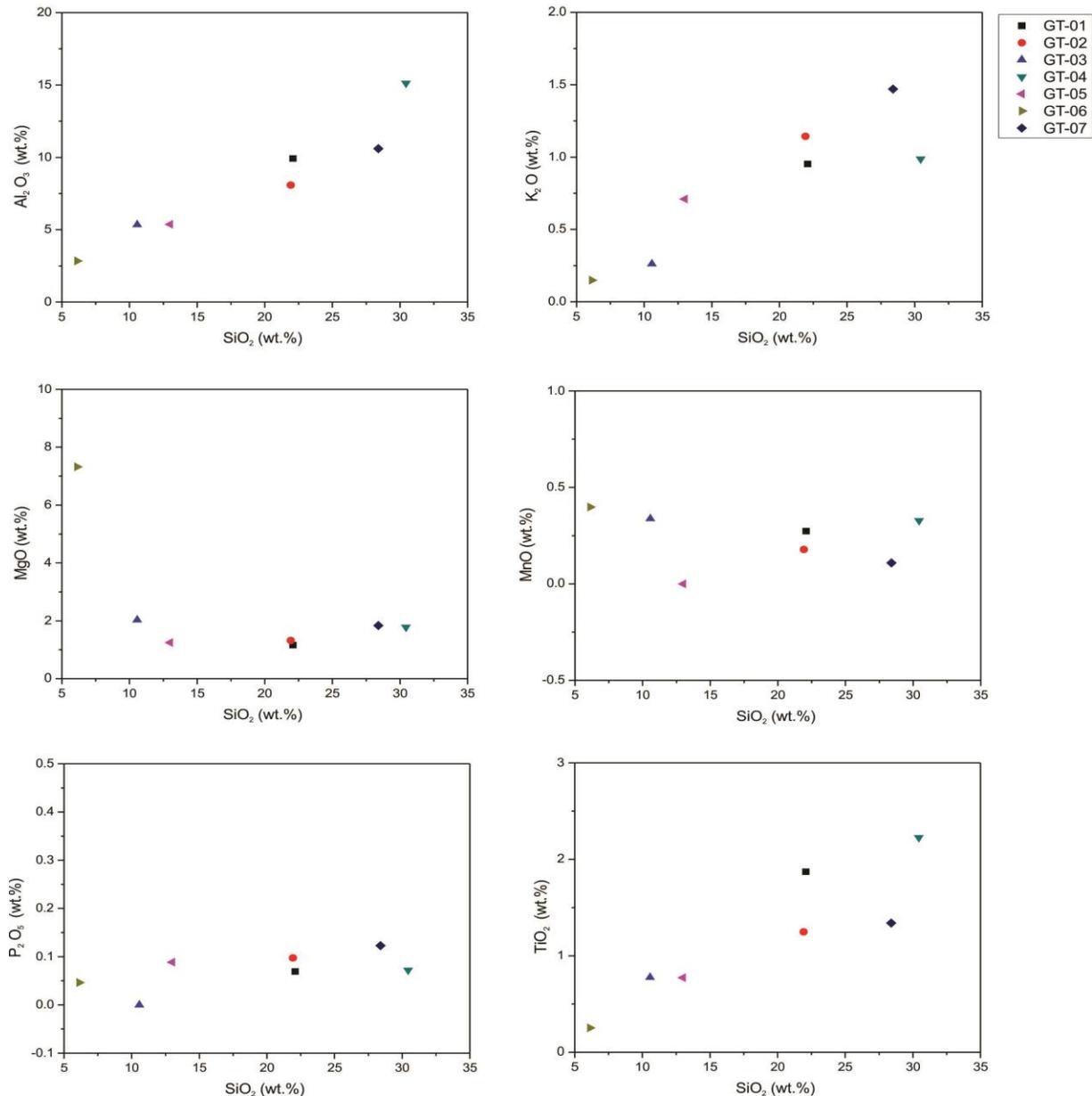


Fig. 2. SiO₂ versus other major oxides bivariate plot of the studied samples (after Harker, 1909).

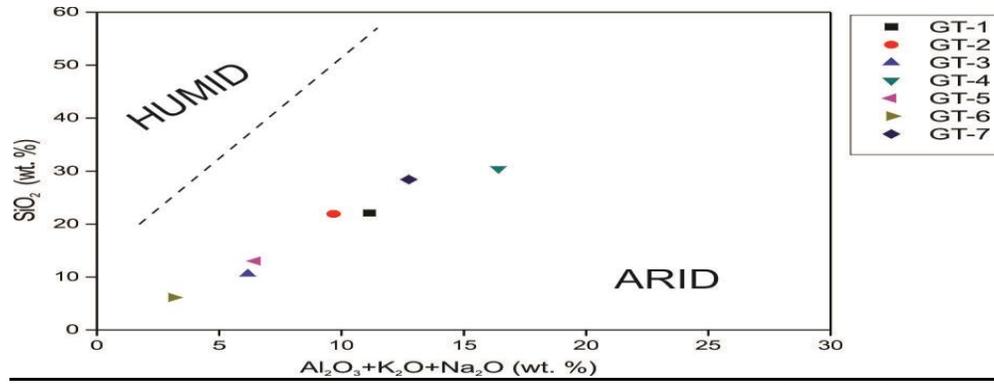


Fig. 3. Paleoclimatic plot of the studied samples (after Suttner and Dutta, 1986).

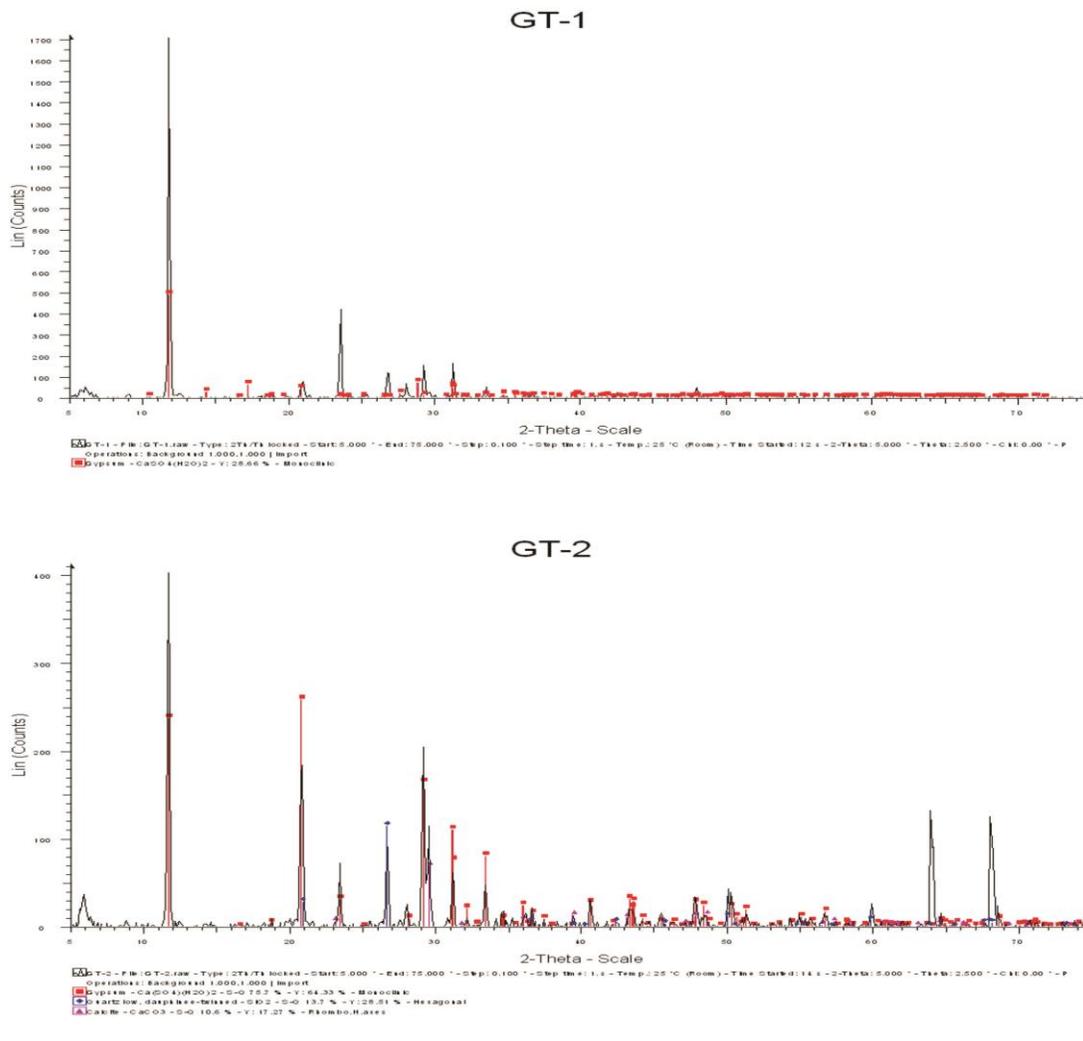


Fig. 4. X-ray Diffractograms of the gypsum samples from the study area.

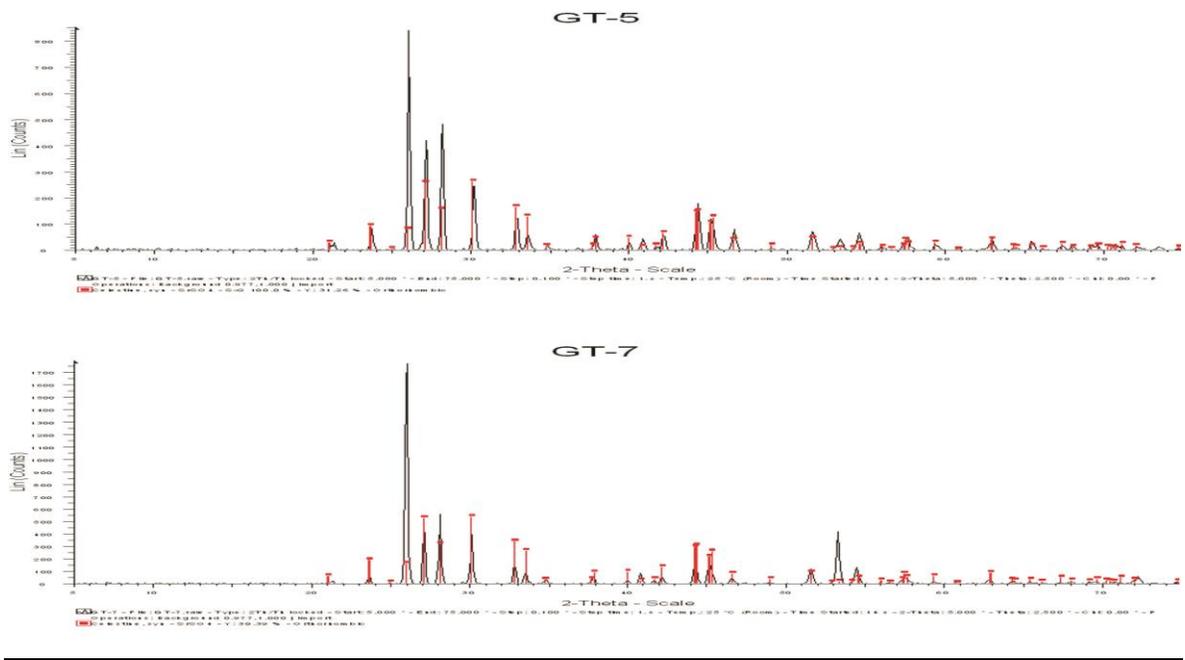


Fig. 5. X-ray Diffractograms of the celestite samples from the study area.

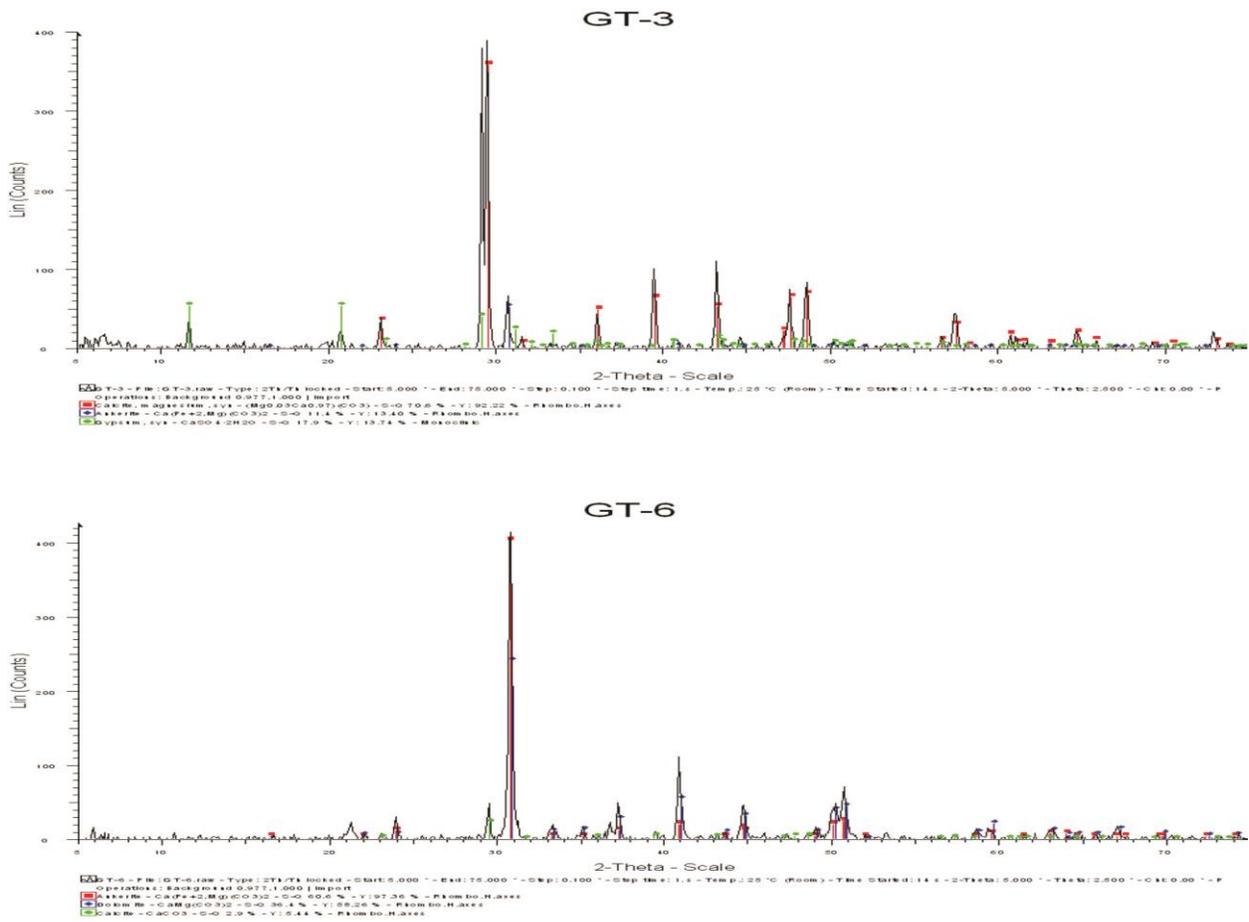


Fig. 6. X-ray Diffractograms of the limestone samples from the study area.

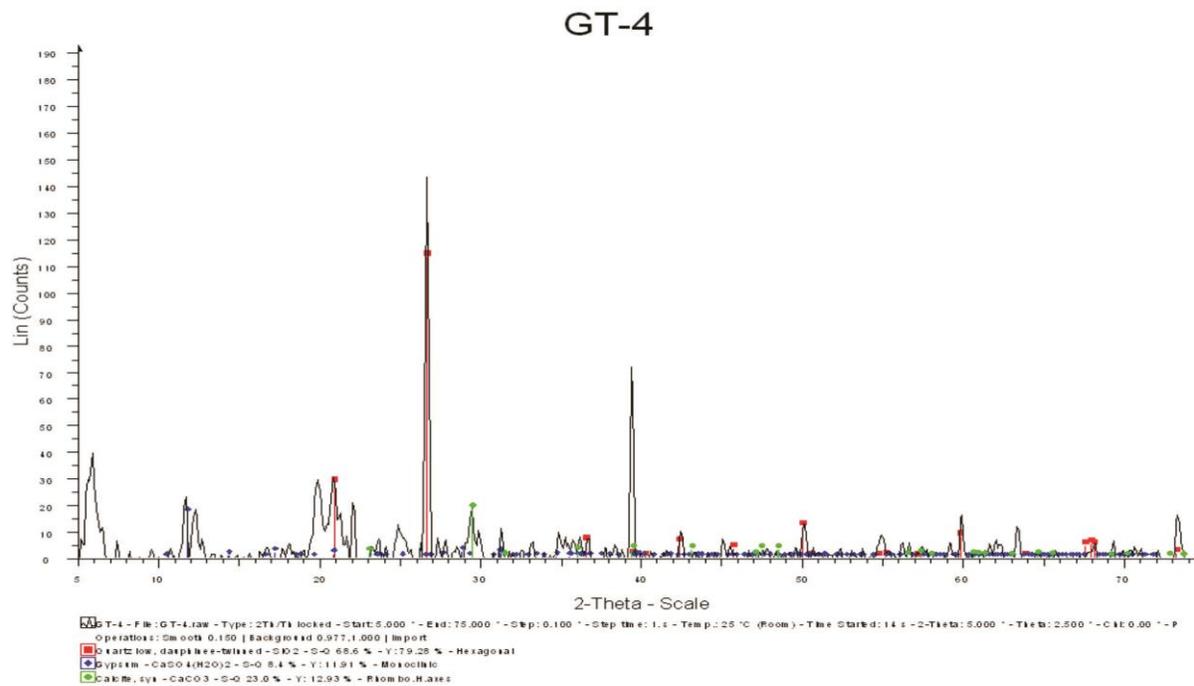


Fig. 7. X-ray Diffractogram of the shale sample from the study area.

Celestite



Gypsum



Fig. 8. Photographs of the Celestite and Gypsum Samples from the study area.

4. **DISCUSSION**

The acquired results when plotted against the Harker's bivariate plots of the SiO_2 versus (v/s) other major oxides displayed gradual increase in the concentration of Al_2O_3 (wt. %) with respect to increasing SiO_2 (wt. %) concentration in the studied samples. In the (Fig. 2), the SiO_2 v/s K_2O plot reveals a classic style of increasing pattern in SiO_2 content with respect to K_2O content in all the samples. In the SiO_2 v/s TiO_2 plot it is interesting to observe that the sample GT-02 and sample GT-01 shuffle to each other's positions as compared to SiO_2 versus K_2O , the sample GT-07 and sample GT-04 also show same trend. The SiO_2 v/s MnO content plot shows that the MnO content remains low in all the samples (ranging from 0.109 to 0.3978 wt. %) except for sample GT-05 in which the MnO is not detected probably because of concentration Below Detection Limit (BDL). Meanwhile, the SiO_2 v/s P_2O_5 plot shows the decreased P_2O_5 content (ranging from 0.04638 to 0.123 wt. %) in all the samples except for the sample GT-03 in which the P_2O_5 content is not detected because of concentration below detection limit. The SiO_2 v/s MgO plot display decreased concentration of MgO with respect to increasing SiO_2 , except for one sample (GT-06) where the MgO value of 7.32 is observed. The Paleoclimatic determination plot using the major oxides data proposed by Suttner and Datta (1986) is used in present study. The major oxide results acquired in present study when plotted against the Paleoclimate diagram; the studied samples fall in the region of Arid climate which supports the phenomenal understanding of the deposits categorised as the evaporites (Fig. 3).

The diffractogram of sample GT-01 (Fig. 4) reflects the clear peaks of Gypsum showing the purity of gypsum that there is no any other mineral constituent present in it. Therefore, it is a pure gypsum without other inclusions. The diffractogram of sample GT-02 (Fig. 4) displays the mineral peaks of Gypsum, Quartz and Calcite with the semi quantitative values of 75.75, 13.7% and 10.6%, for each respectively. Though, the megascopic study supports that it is a pure variety of gypsum but the present XRD data show its inhomogeneity. The significant presence of quartz and calcite supports the notion that at the time of formation of gypsum, the prevailed solution was also enriched in the calcium and silicon. Moreover, it is also possible that the carbonate solution was there and the silica was present as a detrital constituent. Along with x-ray diffractogram, the major element geochemical data also support the above finding. Along with calcium and sulphur contents; the silicon is also present up to 21.92 wt % (Table 2) and hence favours the presence of quartz. In addition to above three minerals, there is also possibility of a few more minor constituents because

some very minute peaks are not evaluated; however, the major oxide data show that aluminium and iron are present and there is possibility that minute clays may be associated with this type of gypsum. The diffractogram of sample GT-03 (Fig. 6) show the peaks of calcite, ankerite, and gypsum with the semi quantitative values of 70.6%, 11.4%, and 17.9% for each respectively. As this sample is the limestone and was collected to check its mineral constituents along with whole rock geochemistry for the sake of comparison that the genesis of gypsum and celestite is primary or secondary in origin. The present XRD data show that along with calcite and ankerite; the gypsum is present up to 17.9%. It is very significant proportion to say that during the chemical weathering of such limestone; the secondary hydrothermal solutions enriched in calcium and sulphur may have been generated and in the result the formation of both gypsum and celestite have taken place. Not only the XRD data but whole rock major oxides also favours it. As far as, the presence of calcite and ankerite are concerned, it is probable that either both of these are present within this limestone or only calcite is there. However, a peak at 30.5 two-theta along with the concentration of MgO (2.03%) and Fe_2O_3 (6.81) there are chances for the presence of ankerite or dolomite. The sample GT-04 (Fig. 7) contains the mineral peaks for Quartz low, Gypsum and Calcite in the diffractogram with the semi quantitative values of 68.6%, 8.4%, and 23%, respectively. Some of the veins, variable in size were also observed in the shale unit of the Laki Formation. Like the earlier limestone sample; a shale sample was also collected to check the genesis of evaporites. The above XRD analysis shows that along with quartz and calcite; the gypsum is also present in it. So far, this may be of dual nature origin such as the primary as well as secondary. The XRD pattern of GT-04 also show that a few peaks are there but not evaluated along with above three minerals. These peaks are in between 5-35 two-theta. In this range normally the clay minerals are present. A small peak at 12 two theta represents the kaolinite along with illite etc., at 6 two-theta. Along with XRD data, the major oxides also support the above findings where SiO_2 , Al_2O_3 , Fe_2O_3 and CaO are the main constituents along with SO_3 .The higher percentage of Al_2O_3 also favors the presence of clays as mentioned above.

The sample GT-05 (Fig. 5) displays the celestite peaks with semi quantitative values of 100% suggesting the sample being the pure celestite in the diffractogram. However, the percentage of SiO_2 , Al_2O_3 , Fe_2O_3 suggests that the celestite is atleast not pure in terms of its chemical composition. The significant percentages of above oxides are either present as inclusions within the celestite at atomic level or qualify for other minerals. There are more chances for the occurrence of quartz in

it because it is very much clear from the XRD pattern that both quartz and celestite have a common strong peak at 26.5 two-theta. As a hand specimen, the GT-06 is a sandy limestone but the XRD analysis does not support it. The diffractogram of sample GT-06 (Fig. 6) display the mineral peaks of Ankerite, Dolomite, and Calcite with the semi quantitative values of 60.6%, 36.4%, and 2.9% respectively. There is no any peak of quartz, so far, at least it is not of siliceous nature. Moreover, the semi-quantitative analysis shows that the ankerite and dolomite are the major constituents rather than calcite. Therefore, this sample is dolomite/dolostone instead of limestone. As far as the presence of ankerite and dolomite are concerned, as stated above, either both or any one of them is present because on the basis of XRD data, it is difficult to distinguish between them having same XRD pattern/crystal system. However, the concentration of Fe_2O_3 favors the ankerite because the Fe^{2+} is the major cation of crystal structure of ankerite while it is usually not present in dolomite structure but again confusion exists due the occurrence of ferro-dolomite. The presence of small amount of silica and aluminium indicates the clays that are represented by few small peaks from 5-35 two-theta in the XRD pattern. On the basis of XRD analysis the sample GT-07 (Fig. 5) is also plotted as pure celestite in the diffractogram.

5. CONCLUSIONS

The deposits of Celestite and the Gypsum are present in the stratigraphic horizons of Meting Shale and Laki Limestone belonging to the Laki Formation. The Gypsum varieties found in the study area are the Fibrous variety (sample GT-01) and the Rose Gypsum (sample GT-02). The Celestite found is massive and a bit fibrous.

The Geochemical character (determined through major oxide investigations using XRF) reflects that the solution/sea water from which the Celestite and Gypsum are formed through evaporation and as anhydrite experienced the extreme arid conditions at the time of the formation of these deposits.

The sea water (solution) in the study area during the deposition of studied samples had the lesser proportion of MnO , P_2O_5 , and MgO as compared to the other major oxide concentrations, this could lead to the discourse of the provenance area on the basis of finding similar concentrations trend (if studies conducted).

The Celestite deposits in the study area could be the result of the strontium rich solutions interacting with the calcite. As well as it could have been formed as the deposition of Gypsum at first and was later converted into anhydrite under extreme arid conditions.

The mineral assemblages determined through the XRD are of three types: (a) Gypsum, Quartz low, Calcite (b) Calcite, Ankerite, Gypsum, and (d) Ankerite, Dolomite, Calcite. In these assemblages the enrichment of Quartz low is probably not the syngenetic. Meanwhile, the presence of Ankerite supports the idea of prevalence of extreme arid climate because it bears Fe^{++} (Bivalent Iron) which is indicative of anoxic conditions.

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