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Prediction of Paleoclimate of Eocene Salt, Kohat Basin, Khyber Pakhtunkhwa, Pakistan

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Fluid inclusion analysis is a significant tool to evaluate the paleoclimate reconstruction of ancient evaporite precipitation. The current study is a significant research to evaluate the ancient climate of Eocene salt. The thin sections petrography, XRD, SEM, Laser raman spectroscopy, and Microthermometric analysis have been used to evaluate the prediction of paleoclimate of Eocene salt. Two sections were measured and samples were collected for thin sections analysis. Under thin section, halite is mainly cubic shape euhedral form and also consists of other minerals like gypsum, anhydrite, polyhalite, sylvite, and dolomite. Geochemical data obtained from XRD, indicates the presence of Na and Cl as major ions, with subordinate Ca, SO₄, Mg, etc. Laser raman spectroscopy analysis reveals that water and CO₂ fluids are trapped within the inclusions. Generally, fluid inclusion analysis and geochemistry are useful tools to evaluate the origin and paleoclimate of Eocene Salt. Geochemical data shows that the Eocene salt is not a product of marine water but it also consists of meteoric and surface water. Low concentration of Br⁻ and presence of SO₄ shows that halite is precipitated from SO₄ type water. Homogenization temperature (Th) ranges from 14°C to 43°C. Microthermometric data shows that fluids were entrapped during and after salt precipitation. Histogram of fluid inclusions also shows that primary and secondary inclusions have discontinuous behavior that shows inclusions were not trapped at the same time of deposition. Some are formed at the time of precipitation and some are formed after precipitation. The presence of impurities like Fe, Mg, Ca, and other ions within the halite show that halite was exposed to the atmosphere by tectonic activities and meteoric water/surface water percolates through fractures and is trapped as inclusion along with the micro fractures. So the Th variation indicates that fluid was trapped at various seasons. Low temperature show inclusions were trapped in winter/spring seasons and high temperatures

indicates inclusions were trapped in the summer season. The maximum homogenization temperature of fluid inclusions in halite is 43°C which is closed to the maximum climatological temperature of the present summer. The result shows that Eocene salt has been deposited in hot, arid, and dry conditions during Eocene time. The alternating period of desalination and evaporation is responsible for the formation of soluble halite.

Introduction

The prediction of paleoclimate and paleo-environment of lacustrine sedimentary recodes is a significant field in the study of ancient global variation (Zhang et al., 1999). Brackish (Saline) lakes that are acting as salt precipitation basins are the key aspects of research into paleo-environment, paleoclimates, and future global changes (Hu et al., 1997). Quantitative paleo-climatic evidence has been indirectly attained from geochemical and biological methods, including palynological assemblages (Lu et al., 2011) organic biomarkers (Cranwell, 1985; Song et al., 2013; Hofmann et al., 1998; Zhang, 2010; Chen et al., 2014), and hydrogen isotopes (Yao et al., 1996; Mc Carroll and Loader, 2004; Jouzel et al., 2007). However, it is hard to obtain precise paleo-temperature data from evaporites sediments in a salt basin using these methods. Theoretically, fluid inclusions are excellent geo-thermometers (Meng et al., 2011). Homogenization temperatures (Th) attained from primary liquid (single-phase) fluid inclusions in Eocene Salt through the so-called cooling nucleation method can replicate paleo-brine temperatures during salt periods (Roberts and Spencer, 1995; Lowenstein et al., 1998; Liu and Ni, 2005). Moreover, the paleo-brine temperature is usually close to the environmental paleo-temperature in shallow lake water (Meng et al., 2011).

Fluid inclusions are the points when a rock crystal develops within the sight of a fluid stage, approximately a portion of the fluid might be confined by way of imperfections in the developing rock crystal towards system fluid inclusions (Benison and Goldstein, 1999). The confined fluid possibly will be liquid, gas, or supercritical fluid, as well as the alignment of the confined fluid may contain uncontaminated water,

seawaters of different salinity, gas or gas behavior fluids, and silicate, sulfide or carbonate melts, between others (Bodnar and Samson, 2003). Fluid inclusion studies are frequently employed to sedimentary rocks, especially rock salt as paleothermometers, climate indicators, and basal variation in chemistry and salinity measures (Meng et al., 2015).

Salt deposits play a significant role in providing particular records of ancient climatic conditions in arid regions. Overall the precipitation of salt has been studied by petrographic thin section analysis. Syndepositional (Primary) and post-depositional (Secondary) halite crystals have been differentiated by thin section analysis (Roedder, 1984; Goldstein and Reynolds, 1994; Roberts and Spencer, 1995). The primary fluid inclusions have been studied along the growth planes of the salt. These fluid inclusions consisting residual of brines that has been formed by the precipitation of salt so that's why it can provide geochemical records of the past. Fluid inclusion analysis reveals the paleo climatic surface temperature (Robert and Spencer, 1995). To predict the paleo climatic condition of fluid inclusion analysis is an intricate method, variation is done by differential forces.

The present study was undertaken to carry out the prediction of paleoclimate of Eocene Salt by fluid inclusions analysis, Kohat Basin, Khyber Pakhtunkhwa (KP), Pakistan. The current study is aimed to achieve the following goals; 1) to interpret the primary and secondary fluid inclusions, 2) to interpret the chemistry of salt, 3) to predict the paleoclimate of Eocene Salt.

Regional Geology

Geologically Pakistan lies on two plates comprising Eurasian Plate and Indian Plate. Province Punjab and Sindh province deceptions proceeding the western edge of the Indian Plate. While the Khyber Pakh-

tunkhwa and Baluchistan deceptions in the Eurasian Plate which mostly includes the Iranian Plate and a certain portion of Central Asia and the Middle East. The Indus Suture demarcates the northern margin of the Indian Plate with the Asian plate. Whereas the Indian and Karakoram plates are separated by Kohistan Island arc that is generated by intra-oceanic subduction of neo-thethy and then collided with Karakorum block (Ullah et al., 2020a, b). Indus suture zone with afghan block consisting of mafic and ultramafic rocks (Ullah et al., 2020a, b). The studied basin is located to the north side of the Bannu and Lakki Marwat districts and south of Kohat district along the main Indus Highway between Karachi and Peshawar, generally it is situated 123 km away from the capital city of Peshawar (Fig. 1) (lat. $33^{\circ}09'54''\text{N}$ and long. $70^{\circ}59'53''\text{E}$).

The studied Karak area is a part of Kohat Basin that is located in the western part of the Himalayan Foreland Folds and Thrust Belt, 40 miles (70 km) varied on the north and south sides. Kohat-basin is bounded by Main Boundary Thrust (MBT), and Surghar Range in north and south respectively. The Kalabagh Strike-Slip Fault (KSSF) separates Surghar Range from the Salt Range (Khan et al., 1986; Lillie et al., 1987; Jaume and Lillie, 1988) (Fig. 1) (lat. $33^{\circ}09'54''\text{N}$ and long. $70^{\circ}59'53''\text{E}$). The eastern part of the Kohat-basin touches the River Indus which separate it from the Potwar-Plateau, whereas, the Kurram Fault occur towards the west which compares highly distorted Mesozoic rocks of Samana, Darsamand, Thal, and North Waziristan Agency by the Eocene to Miocene deposits of the Kohat-basin (Khan et al., 1986). Towards the south, the Bannu basin demarcates unreformed sediments from the southern boundary of the basin (Fig. 2a). The MBT in the Kohat-basin carries Mesozoic and younger strata above the molasse sediments of the Siwalik Group. The study area (Karak and adjoining area) constitute the southern part of the Kohat-basin which mainly consists of rocks of the Siwalik Group. It is bounded by the Karak Thrust trendy in the north and the Banghar Syncline pres-

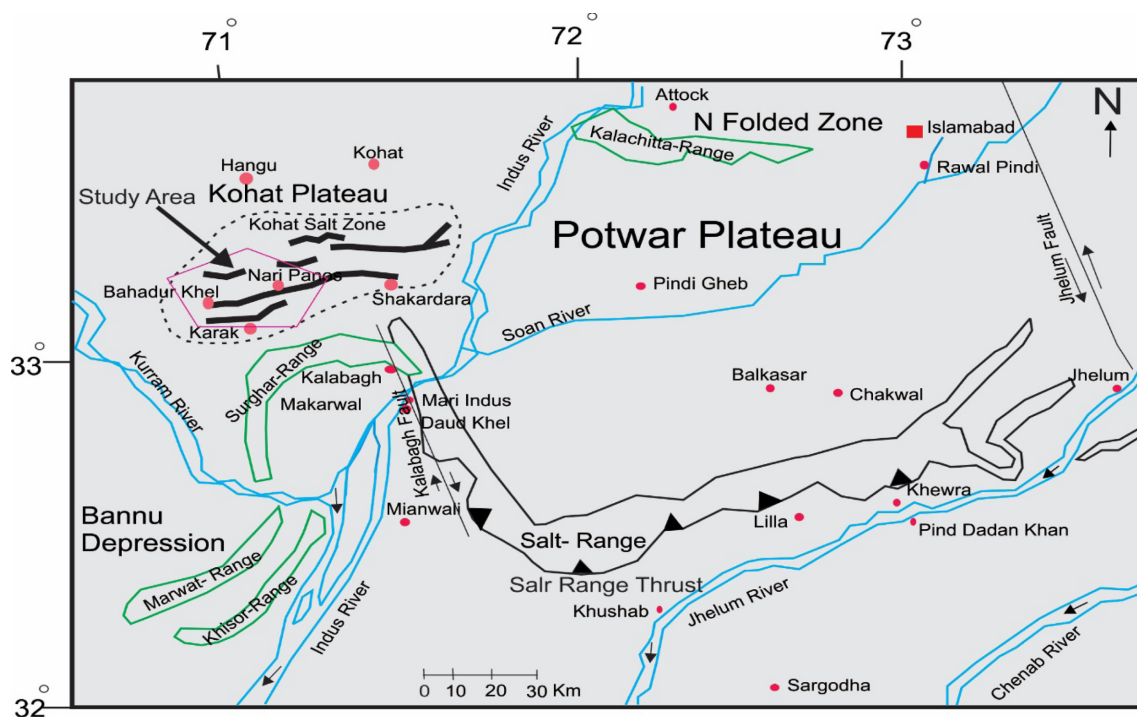


Figure 1. Geographical location map with a tectonic element of the study area.

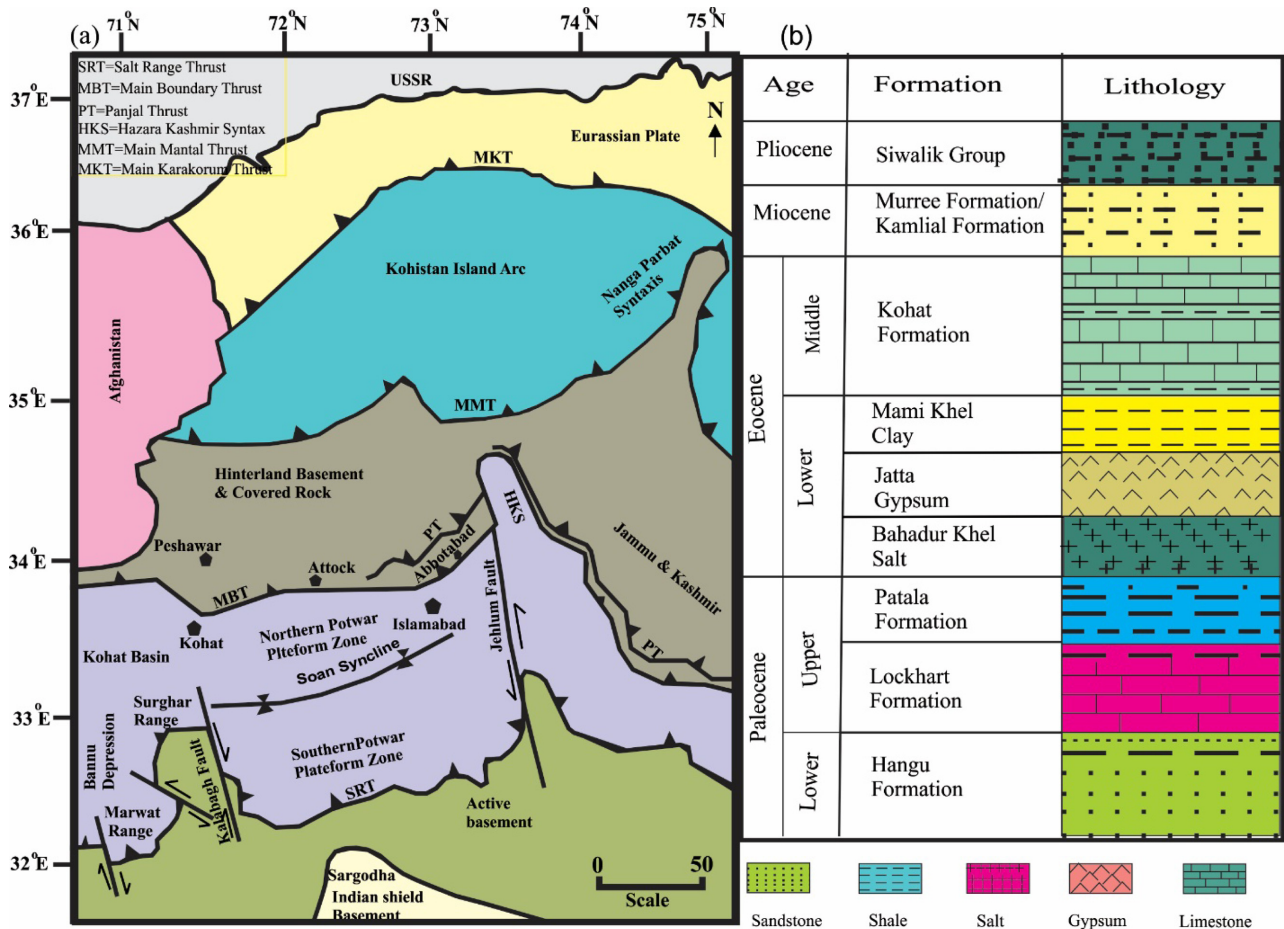


Figure 2. (a) Tectonics elements of Northern Pakistan (modified by Chaudhry and Ghazanfar, 1994) Phanerozoic age, (b) Stratigraphic column of the study area, Karak, KP, NOT KPK, Pakistan.

ent in the south. The Kohat area comprises duplex structures, Pop-ups, broad syncline, and anticline labeled evaporite record high-definition high-volume translations near Eocene evaporites (Khan et al., 1986) refers to the nature of the Kalabagh Strike slip-Fault.

Eocene stratigraphy in Kohat, comprising carbonate and evaporites, represents a limited marine area (Meissner et al., 1974; Pivnik and Wells, 1996). A molasse layer in the Kohat area formed by the Miocene to Pliocene clastic pledges, divided by the Early and Middle Miocene Rawalpindi Group. The Bahadar Khel Salt, Jatta Gypsum, Sheikhan Formation, Kuldana Formation and Kohat Formation of the Eocene age are well preserved (Fig. 2b). The oldest formation that has been exposed in the study area is Hangu Formation and consists of sandstone with shale intercalation. Lockhart Limestone overlies the Hangu Formation, which is well preserved and mainly consists of gray to medium gray limestone, with some shell beds. Its basic component consists of dark gray to light blue and flaggy fossiliferous limestone. Overlaying the Lockhart Limestone the Patala Formation consisting of shale and marl with limestone and sandstone as well as a small amount of coal in some areas. Shale is pale green, selenite bearing, carbonaceous, and calcareous marcasite nodules with mixed limestone. After Paleocene, the Eocene succession is well exposed in the study area. Bahadar Khel Salt (Eocene) comprises of salt that is white with black stringers in places, it also consists of bedded to massive clear salt crystals and dark color bituminous with fetid odor with slightly

pyritic in places, with lower contact with Patala Formation and upper contact with Jatta Gypsum. Jatta Gypsum is mainly white to green in color, with massive beds. The slight separation of the reddish-purple and green clay occurs at different intervals. Kohat Formation consists of limestone mixed with shale. Its lower contact with Jatta Gypsum and upper contact with Kuldana Formation. Kuldana Formation comprises of gypsiferous shale, with interbedded limestone and minor sandstone. The Kuldana Formation Upper contact with Miocene rocks (Murree/Kamlial Formation). The Murree Formation is mainly comprises of purple and dark red clay and purple grey and greenish-grey sandstone with the minor count of conglomerates. The Kamlial Formation comprises of a reddish-gray and black sandstone that are medium to massive bedded with and green and purple shale with yellow conglomerates. Its lower contact with Murree Formation and upper contact with Siwalik Group (Chinji and Nagri Formations). The Chinji Formation consists of sandstone that is moderate to medium-grained with low clay and conglomerates. Whereas Dhok Pathan Formation consists of sandstone and mud.

Methodology

Different instrumental and laboratory techniques have been used to predict the paleoclimate of the Eocene Salt. The first step is to collect

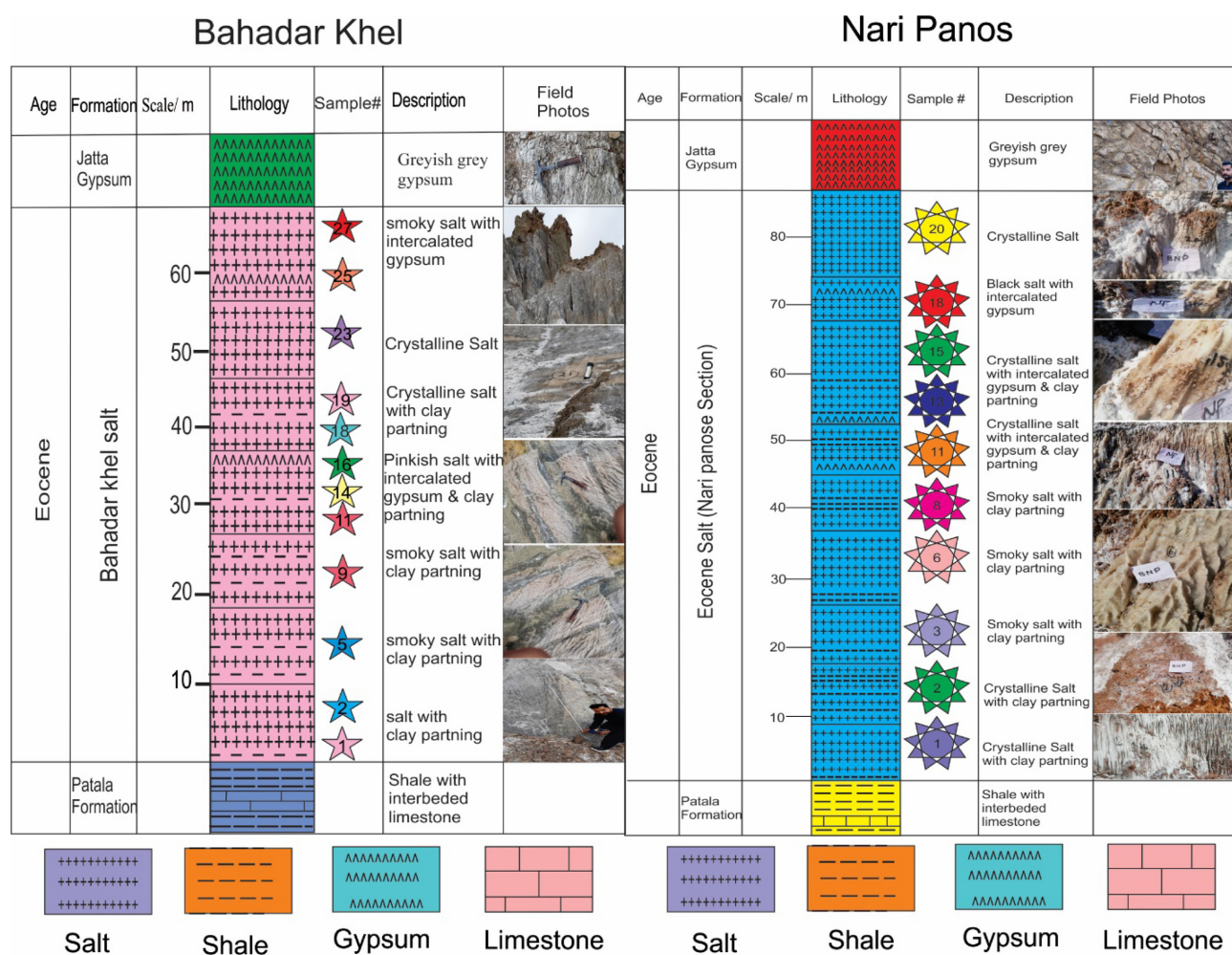


Figure 3. Lithology of the Eocene Salt (Bahadur Khel Salt) of Bahadur Khel area and Naripnose area, Kohat plateau, KP, Pakistan.

the samples from the outcrop. The information preserved in chemical sedimentary rocks, particularly Bahadur Khel Salt was observed and recorded in the two geological sections (Fig. 3a, b). The fieldwork activities were consisting of exploration of the area, section measurements, outcrop observation, and data (sample) collection. The samples were collected from the Bahadur Khel and Naripnose area KP, Pakistan (Fig. 3a, b). The salt beds are approximately 70 m thick in Bahadur Khel area, while 85 m thick in the Naripnose area.

Fifty (25 from each section) thin sections were prepared with the help of a super-saturated salt solution and glycol with high heat conductivity as grinding fluids and polishing solution can contaminate the salt samples. As well as anhydrous ethanol as a fluid medium throughout the preparation methods (grinding fluid, cooling fluid for cutting blades, wetting agent for polishing, and cleaning fluid to clean the samples by ultrasonic cleaner). The micro photographed were taken by an attached digital camera (Optical-B9) by using a compound microscope (Lambomed, CXR3) under achromatic objectivity of $\times 4$, $\times 10$, and $\times 40$ magnification at the Department of Earth Sciences, University of Sargodha.

Scanning Electron Microscopy created images of samples by scanning the surface with a focused beam of the electron. The electrons interconnect with atoms in samples creating numerous signals that comprise information about sample's surface features and composi-

tion. Ten samples were selected for elemental analysis, several points have been selected under SEM to study the chemical properties of a specimen, an analytical technique EDS (energy dispersive spectroscopy) has been used. SEM JEOL, JSM 5910, Japan, with EDS, Oxford, INCA 200, and the UK have been conducted at CRL (Central Resource Laboratory), University of Peshawar. X-rays diffraction is a significant non-destructive technique for crystalline material. It provides evidence on crystal structure, preferred crystal texture, phase, and other structural constraints like strain, grain size, crystal defects, and crystal property. Eight samples were selected for XRD analysis. The selected samples were arranged according to the standard methods (Tucker, 1988) and were exposed to XRD examination at the XRD Laboratory (Central Resource Laboratory, University of Peshawar).

Laser raman micro spectroscopy is used in place of a standard raman spectrometer. A raman micro spectrometer comprises a particularly designed raman spectrometer combined with an optical microscope. This allows the experiment to obtain raman spectra of microscopic samples. For laser raman spectroscopy, six samples has been selected and arrange them according to the standard methods and exposed them to laser raman spectroscopy analysis (Ramboss raman spectroscopy Argon laser 514 nm) at COMSATS University Islamabad.

Salt thin sections were stored in a freezer for ten to fifteen days to permit vapor bubbles to nucleate or large adequate to be visible. Then

transported with ice pads from the freezer to the lab for the microthermometric fluid inclusion heating/freezing stage. Homogenization temperatures were measured using a USGS microthermometry system and a Linkham THMSG 600 system. The homogenization temperature (Th) has been recorded that represents the minimum formation temperature of the host mineral by microthermometry analysis. For fluid inclusion analysis, six samples has been selected and arrange them according to the standard methods, and were exposed to fluid inclusion analysis at UPC (China University of Petroleum East China).

Results

Types of Bahadar Khel Salt

In the studied area, Bahadar Khel Salt consists of five (5) types i.e. i) pink salt, ii) black salt, iii) white salt, iv) smoky salt, and v) crystalline salt (Fig. 4). **Pink salt:** This rock Salt has been mined from Punjab (Precambrian Salt Range Formation) as well as from KPK (Eocene Bahadar Khel Salt) of Pakistan. This type of salt is given a pinkish tint due to the trace minerals, basically, it is used as a food additive to replace refined table salt. It is also used for cooking purposes. Mainly it comprises 96% to 99% of sodium chloride (NaCl) with subordinate trace minerals like calcium, chromium, iron, zinc, sulfate, and magnesium ($\leq 1\%$) (Abrar et al., 2017) as well as consisting of impurities (Clays, etc.) (Fig. 4a). **Smoky salt:** It is a pungent salt. It is used to enhance the inherent flavor of food, also imparting a smoky paste. It is commonly found in the Naripanoose area as well as in the Bahadar Khel area (Fig. 4b). **Black salt:** This type of salt is a kiln-fired rock salt with sulphurous, pungent smell. The pungent smell is due to the sulphurous content (Fig. 4c). The raw black salt has been derived

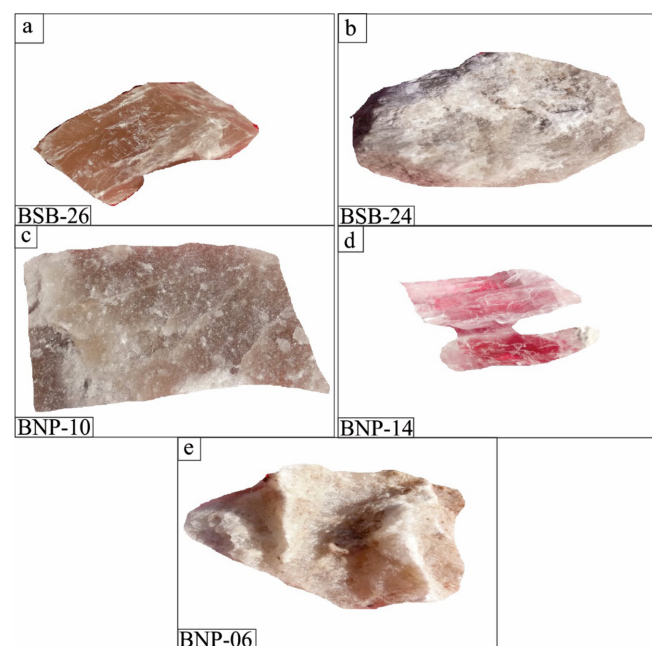


Figure 4. Various lithofacies with different characteristics i.e. (a) Pink Salt, (b) Smoky Salt, (c) Black Salt, (d) Crystalline Salt, and (e) White Salt; BNP-Bahadar Khel Salt Naripanoose; BSB-Bahadar Khel Salt Bahadar Khel area, KP, Pakistan.

from the Himalayas, Salt Range, and Kohat Plateau.

Crystalline salt: It has been mined from Punjab (Precambrian Salt Range Formation) as well as from KP (Eocene Bahadar Khel Salt) of Pakistan. Crystalline Salt is chemically similar to table salt. This precious type of salt is found in various colors from off-white to transparent and has 96% to 99% of sodium chloride with some impurities (Abrar et al., 2017). **White salt:** This type of salt is also known as table/regular salt (Fig. 4e). Refined white salt mostly comprises sodium chloride along with anti-caking agents to prevent clumping. It has been mined from Punjab (Precambrian Salt Range Formation) as well as from KP (Eocene Bahadar Khel Salt) of Pakistan.

Types of Fluid Inclusions

Primary fluid inclusion

Fluid inclusions are a small volume of paleo fluids confined in minerals that deliver essential information about geological events, from the high temperature at greater depth towards low temperature near the earth's surface (Randive et al., 2014). These inclusions are trapped as liquid, gases, and crystals that are trapped in a single phase are as a heterogeneous mixture of multiphase (multi-phase) in a single cavity. Generally, the composition of trapped fluid inclusions constitutes include CO_2 , H_2O , Fe, Cl, Br, S, Na, K, Ca, and Mg.

Primary Fluid Inclusions have a cubic to a rectangular shape. Their size ranges from a few microns to 700 μm (Bukowski et al., 2020). At some slides, numerous two-phase (Liquid and Gas) inclusions were trapped (Fig. 5). The gas phase consists mainly of water vapor. Primary fluid inclusions are mostly trapped along the growth zone and crystal phases, are tend to occur solitary or isolated. Primary inclusions are very good indicators of the condition of crystallization of host minerals.

Secondary fluid inclusion

Secondary inclusions represented two-phase (Gas and liquid) and three-phase (Gas, Liquid, and Solid) types. Secondary fluid inclusions are generally formed at the early diagenetic stage (Bukowski et al., 2020). Secondary inclusions were placed between chevron and transparent bands, and their size exceeded $200\mu\text{m}^2$ and the pressure in primary and secondary inclusions were closed to atmospheric pressure. Whereas, secondary single-phase (Liquid), two-phase (Gas and Liquid), and multiphase inclusions were found in recrystallized transparent halite (Fig. 5). Whereas multiphase inclusions had more than one isotropic mineral.

Secondary fluid inclusions are confined along with the fractures that are formed after the formation of host minerals and caught due to the healing of fractures. The occurrence of secondary inclusions in halite shows that liquid fluid was generally trapped after the halite deposition, suggesting that the liquid mechanism could have been episodic. Generally in salt secondary inclusions size ranges from 5 μm to 8 μm in their longest dimension.

Fluid Inclusions Evaluation

Several methods have been used to evaluate the analysis of fluid

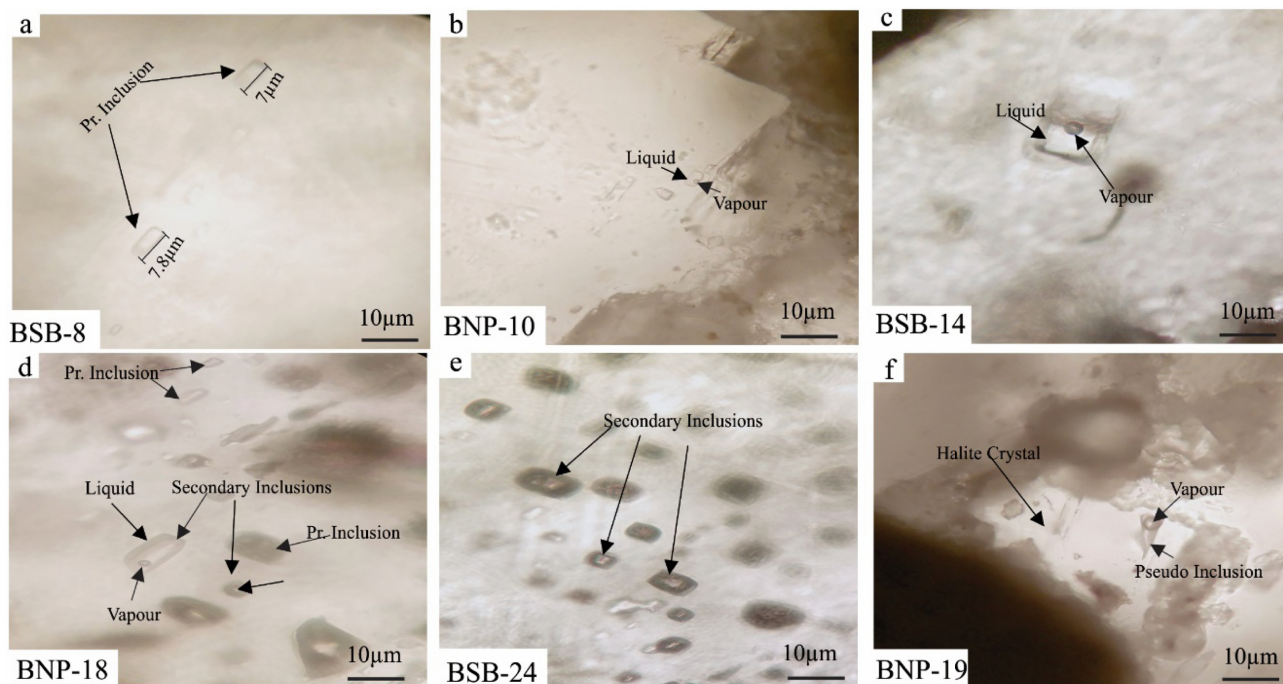


Figure 5. Thin section showing the primary and secondary fluid inclusions with liquid, and gaseous state of Bahadur Khel area and Naripnose area, KP, Pakistan.

inclusions. Based on all these approaches, the prediction of paleoclimates of Bahadur Khel Salt (Eocene) has been evaluated. Techniques that are used to evaluate the prediction of paleoenvironment are.

Thin section petrography

A petrographic study provides significant information about the population of fluid inclusions, such as the number of inclusions, their chronology, and type concerning the geological event. Halite is the dominant mineral that has been observed under thin sections with other subordinate minerals. Well preserves cubic shape halite minerals have been observed under thin sections (Fig. 6). At a few places it occurs as distorted form, most of the distortion is due to tectonics and dissolution phenomenon. Other subordinate minerals are anhydrite, gypsum, and minor dolomite (Fig. 6, 7) (Table 1).

Chemical composition evaluation (by XRD)

The chemical composition of the studied halite consisting of Na^+ and Cl^- are major ions, subsequently Ca^{2+} , K^+ , and SO_4^{2-} as well as it consisting of Si, S, C, Al, and O as trace amounts. Primary inclusion (Single Phase) is representative of the brine from which they have been precipitated (Lowenstein et al., 2003; Brennan et al., 2004). Sodium (Na^+) content ranges from 26.54% to 42.90%, potassium (K^+) content ranges 0.031% to 3.4%, calcium content (Ca^{2+}) ranges from 0.04% to 1.59%, magnesium (Mg^{2+}) ranges from 1.32% to 1.45%, aluminum (Al^{3+}) ranges up to 0.25%, sulphate (SO_4^{2-}) ranges from 2.05% to 25.5%, silica (Si) content ranges up to 0.50%, sulphur (S) ranges from 0.47% to 1.11% and oxygen (O^+) ranges from 3.24% to 3.95%, (Table 2, 3). The studied result indicates that there is a positive correlation between Mg^{2+} and K^+ . The Ca^{2+} content changes are reliable with the K^+ con-

tent except for the Ca^{2+} content that indicates a wide range of difference with the low content of K^+ and the relation between K^+ and Na^+ are not clear.

The diffraction patterns confirmed halite as the major component. With one exception, the samples did not comprise any other minerals except halite. The halite peaks (Fig. 7) were repeatedly recognized in the patterns of microcrystalline deposits that may be formed by evaporation of the gypsum deposits. It has been broadly understood that halite is macroscopically mono mineralic; however, the evaporation of gypsum contents results in the crystallization of halite.

The hypothetical salt shows that the percentage of halite in samples ranges between 94% to 97% and other salts range from 1% to 3%. Based on trace elements data it has been observed that it is present in a low concentration less than the permissible limits. Generally the identified minerals by XRD in salts derived from the outcrop or halite (NaCl), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and magnesium sulphate hydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), sylvite (KCl), and sodium chlorate (NaClO_3). More abundant minerals consisting of NaCl are present in the rock at the first stage, and other minerals were precipitated/ developed at a later stage. Halite has been identified by XRD analysis because the halite solubility decreases due to CO_2 addition (Duan and Li, 2008). Minor constituents like calcite, ferro dolomite, ankerite, anhydrite minerals and Mg, Ca, O, K, Si, and Al ions (from XRD, ED's data) indicate that rock exposed to the atmosphere and contacted with meteoric water. XRD analysis indicates that halite is a predominant mineral with subordinate minerals including calcite (CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$], quartz (SiO_2), and fluorite (CaF_2).

Scanning Electron Microscope (SEM) analysis

The SEM analysis indicates the irregular crystalline structures of

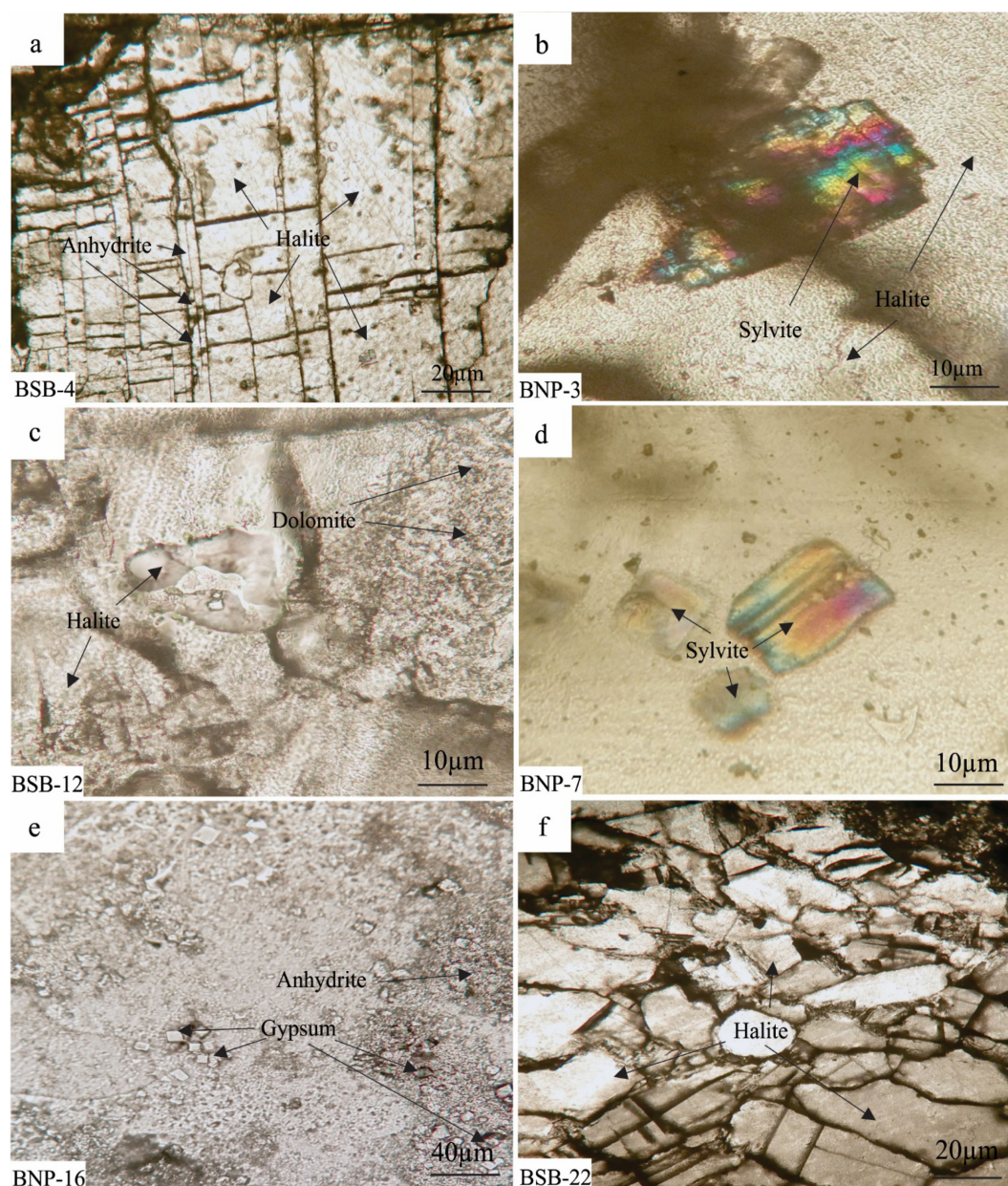


Figure 6. Showing the evaporite minerals; halite, gypsum, anhydrite, and sylvite in the studied samples of KP, Pakistan.

Table 1. Showing the mineral percentage within the studied area, KP, Pakistan

Serial No.	Sample No	Gypsum %	Dolomite %	Anhydrite %	Halite %
1	BSB-2	1	1	1	97
2	BSB-5	1	2	1	96
3	BSB-9	2	2	2	94
4	BSB-11	2	-	1	97
5	BSB-15	1	2	2	95
6	BSB-18	1	2	2	95
7	BNP-3	3	-	-	97
8	BNP-7	2	1	2	95
9	BNP-10	2	2	2	94
10	BNP-18	1	1	2	96
11	BNP-23	-	2	1	97
12	BNP-26	1	2	1	96

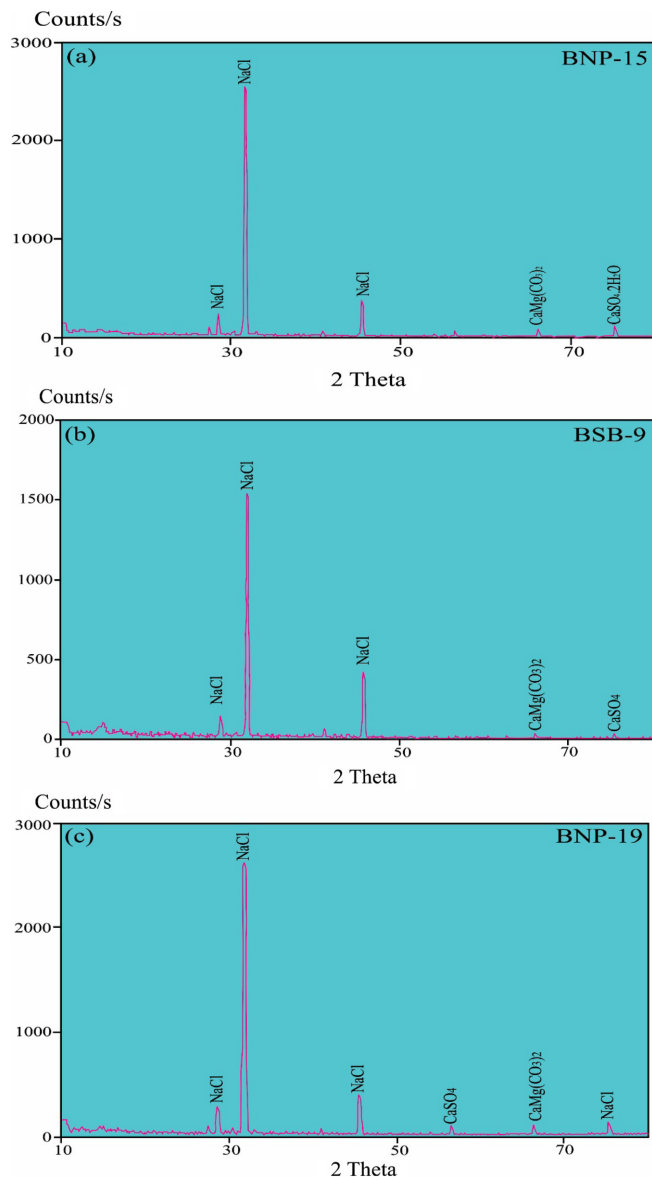


Figure 7. Showing the X-Ray Diffraction analysis of Bahadur Khel Salt; showing the halite, gypsum, anhydrite, and dolomite minerals.

the rock salt. Salt crystals were quadrilateral, prismatic and cubic shape at the microscopic level as well as it consisting of gypsum, sylvite, polyhalite, and dolomite (Fig. 9). The energy dispersive spectroscopy (EDS) on the SEM technique permits the identification of the definite element along with the relative proportions in terms of atomic concentration. Elemental composition was characterized by EDS. The atomic concentration of oxygen (O) 4.08% to 9.85%, sodium (Na) 27.22% to 30.04 % and chlorine (Cl) % respectively (Table 2 to 5). The presence of sodium (Na) and chlorine (Cl) indicating the natural halite and the presence of subordinate oxygen (O₂) indicates that other oxide minerals like iron (Fe) and calcium (Ca) might be present in rock salt. The presence of Ca, S, O shows the occurrence of calcium sulphate anhydrite (CaSO₄) or gypsum (CaSO₄·2H₂O). Moreover, some other elements silica, magnesium, and calcium may be associated with presence of aluminosilicates and other sulphate like magnesium sulphate (MgSO₄·7H₂O) and hexahydrate (MgSO₄·6H₂O). The presence of sulphate and

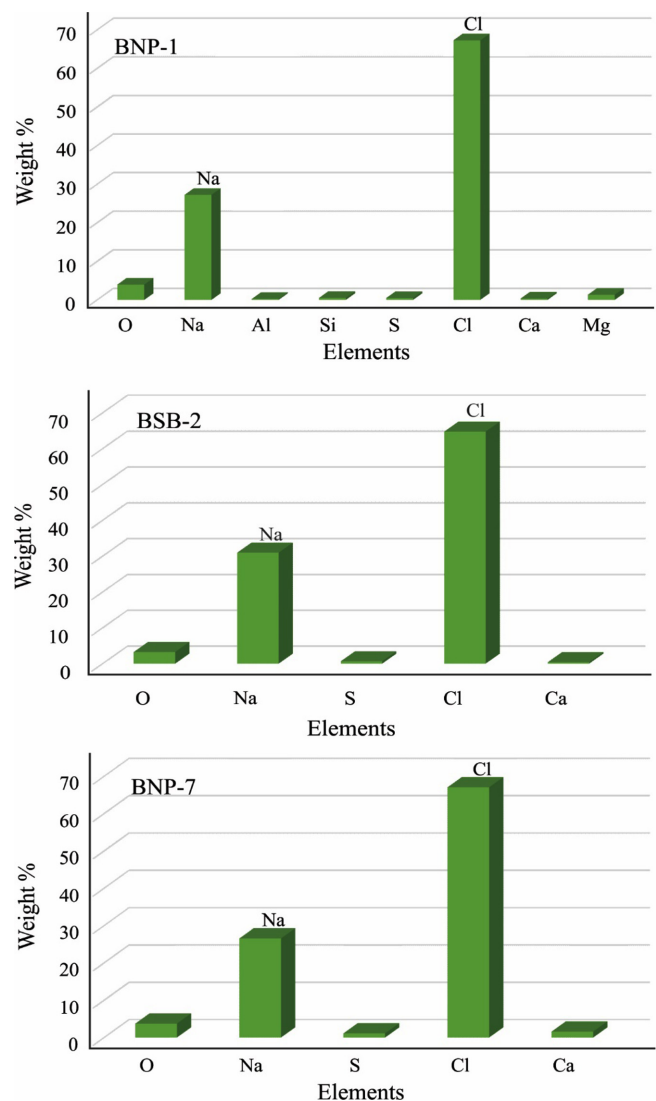


Figure 8. Microphotograph shows that the elements and weight % and showing the Na and Cl are the major elements.

nitrate that are present in the studied salts indicates that the atmospheric acid gases (SO_x NO_x) can be reacting with the carbonates to give rise to secondary air-borne particulate matters of salts that can grow to larger sizes depending on the different atmospheric condition. Temperature, pressure, and relative humidity play a significant role in this reaction.

Laser Raman Micro-Spectroscopy (LRM)

Raman spectroscopy is a famous technique to investigate the intricate fluid inclusions (Loppnow et al., 2004). Primary inclusion results in laser raman micro-spectrometer start mostly 0-3000 wavenumber/cm or raman shift/cm and intensity ranges 9000 to 60000 counts/sec (Fig. 10) and intensity curve behavior is also steep then broad and gentle in most of the samples. It is interpreted that secondary fluid inclusions are associated with tectonic activity. As well as fracturing in halite crystals leads to providing the fluid migration pathway. The highest concentrations of gases were noticed in halite-anhydrite breccia which confirms the tectonic origin of these rocks. Whereas in sec-

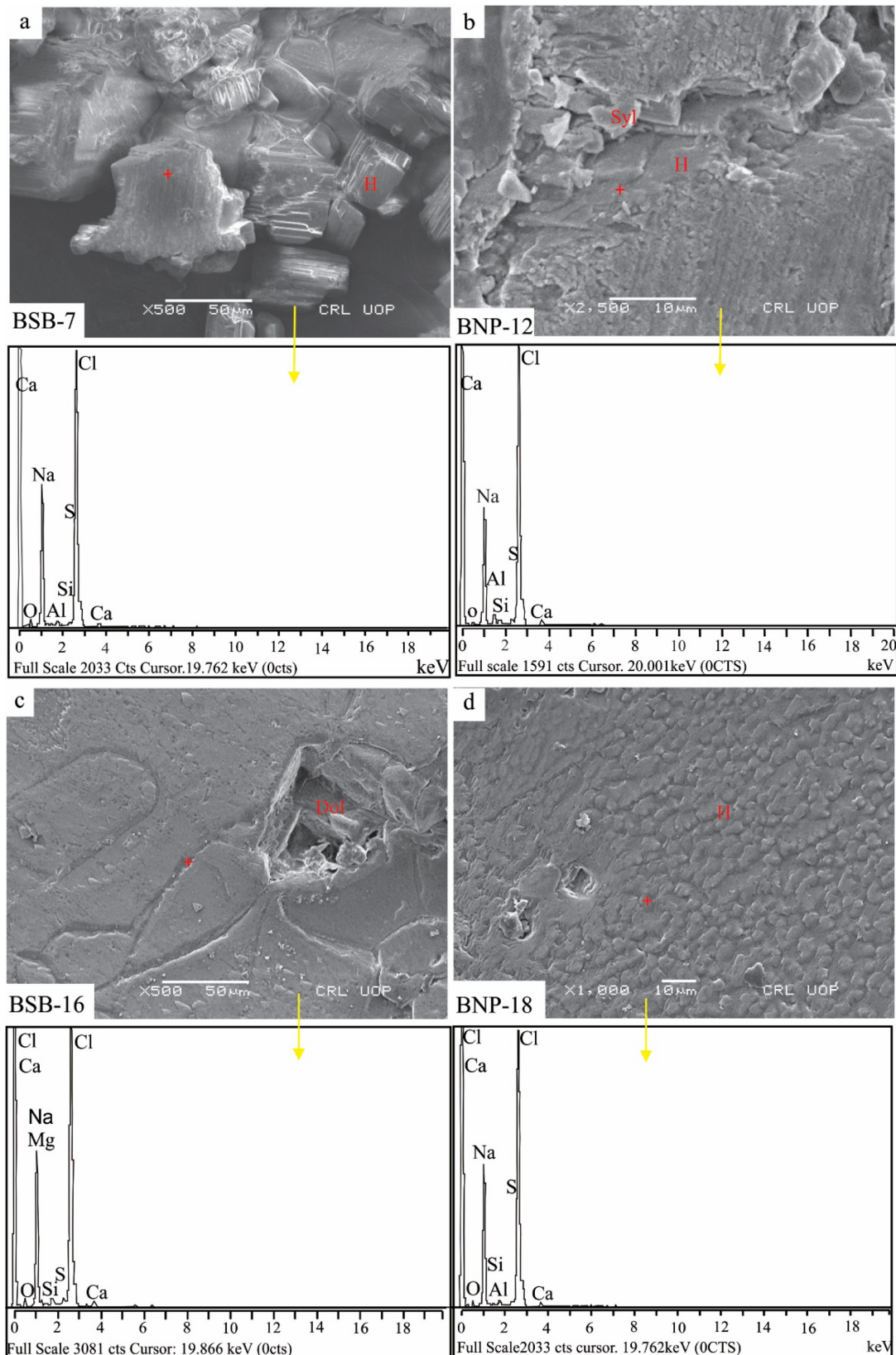


Figure 9. SEM microphotographs showing the type of salt that has been confirmed by EDX that showing the major constituent as NaCl, CaCl_2 with subordinate silica and dolomite.

ondary fluid inclusion samples the laser raman micro spectrometer shows the wavenumber\cm ranges from 0 to 3000 wavenumber\cm

and intensity range 9000 to ≤ 60000 counts/sec (Fig. 10) and intensity curve behavior is also steep then after getting peak and then gentle

Table 2. Showing the chemical composition of BSB-1, Bahadar Khel area, Karak, KP, Pakistan

Element	Weight %	Atomic %
O, K	3.24	5.94
Na, K	30.97	39.55
S, K	0.65	0.59
Cl, K	64.75	53.62
Ca, K	0.40	0.29
Total	100	100

Table 3. Showing the chemical composition of BNP-4, Nari Panose area, Karak, KP, Pakistan

Element	Weight %	Atomic %
O, K	3.95	7.32
Na, K	27.22	35.04
Al, K	0.25	0.27
Si, K	0.50	0.53
S, K	0.47	0.43
Cl, K	67.27	56.16
Ca, K	0.34	0.25
Mg, K	1.32	1.45
Total	100	100

Table 4. Showing the chemical composition BSB-2, Bahadar Khel area, Karak, KP, Pakistan

Element	Weight %	Atomic %
O, K	4.08	7.55
Na, K	25.76	33.19
Al, K	2.08	2.28
Si, K	0.52	0.54
S, K	0.94	0.86
Cl, K	65.50	54.73
Ca, K	1.14	0.85
Total	100	100

Table 5. Showing the chemical composition BNP-1, Nari Panose area, Karak, KP, Pakistan

Element	Weight %	Atomic %
O, K	9.85	16.95
Na, K	29.32	55.12
Mg, K	1.19	1.35
Si, K	1.19	1.17
S, K	1.27	1.09
Cl, K	56.06	43.55
Ca, K	1.12	0.77
Total	100	100

behavior in most of the samples.

The extending vibration of water displays an extensive and high band with a broad peak at about 1500–2250 cm^{-1} (a) whereas 1500–2500 cm^{-1} in (c) whereas in Figures 10(b) and (d) show the sharp peaks

that is 1900 cm^{-1} to 2600 cm^{-1} and from 1700 cm^{-1} to 2500 cm^{-1} respectively and the sharp peaks representing the presence of water. The fluid phase would be saturated with halite (NaCl) due to the host mineral being salt (halite), and according to the laser raman results, the band shape of water shows high salinity (Mernagh and Wilde, 1989). Most of the primary inclusion shows the high intensity as compared to secondary inclusion suggesting the high saturated and high concentrated fluid. At some places, it was found that the intense bands are symmetrical and some are asymmetrical (Fig. 10). Raman spectra with broad bands belong to the vibration of absorbed water (Kompan and Malyshkil, 2018). Some spectra indicate weak broadband. The product of secondary alteration is similar to the natural halite inclusions in halite after a short period in the atmosphere.

Microthermometry analysis

The measured homogenization temperature (T_h) of fluid inclusions assemblages ranges from 14°C to 43°C (Fig. 11, Table 6). The majority ranges from 15°C to 20°C in the Bahadar Khel area and 15°C to 30°C in the Naripanose zone. Generally, T_h values are used to interpret the paleotemperature of the surface brines during salt precipitation. The maximum temperature ($T_{h\text{ max}}$) of fluid inclusions in salts was found to match the maximum temperature of surface brines during the salt precipitation. Fluid inclusions size ranges from 0.1 μm to 8 μm and most are liquid single and double phase inclusions (Fig. 5). Microthermometric measurements were focused on all liquid single-phase inclusions in halite. Almost 40 fluid inclusions were measured for T_h values. Normally the microthermometric data were evaluated by plotting the T_h against the frequency of fluid inclusions (Fig. 11). Results show that the T_h of all liquid single-phase fluid inclusions are independent of sample depth and fluid inclusions size and suggested that there was a minimum effect of burial diagenesis and little stretching or collapsing of the inclusions walls after the entrapment. Calculated temperature coincides with the previous paleo-latitude that indicates that the basin has a regional arid climate during the Eocene age. Whereas the minimum homogenization temperature from studied samples shows the minimum temperature of the surface brines in the winter season during the salt precipitation.

Fluid inclusions are trapped during the growth of the normal crystal. High sodic composition enhances the crystal growth, as the temperature increases the composition of fluid has been changed and particles other than evaporites deposited on the crystal surface, may lead to trapping of primary inclusions on the growth surface (Voigt and Brantley, 1991). One characteristic that has been used in the past to specify a primary origin is the shape of the inclusions. Therefore, negative-crystal-shaped inclusions (a specific kind of inclusion consisting of foreign material is trapped within the host crystal) have been construed to be primary, irrespective of their location and/or distribution within the crystal.

Discussion

Homogenization Temperature (T_h)

The presence of gas or vapor within the fluid inclusions generally

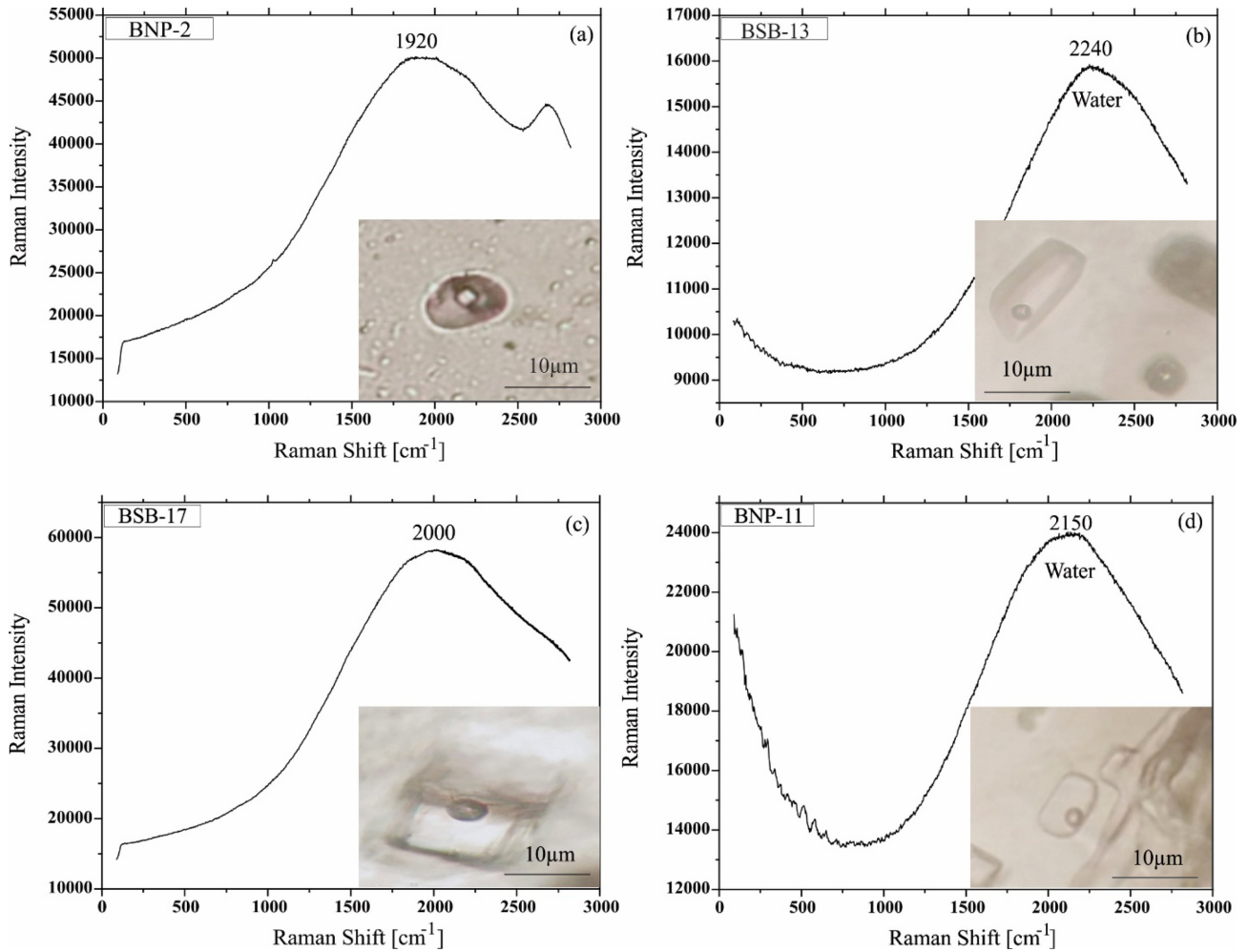


Figure 10. Raman spectroscopy analysis of fluid inclusion analysis between Raman intensity and Raman shift/wavenumber/cm.

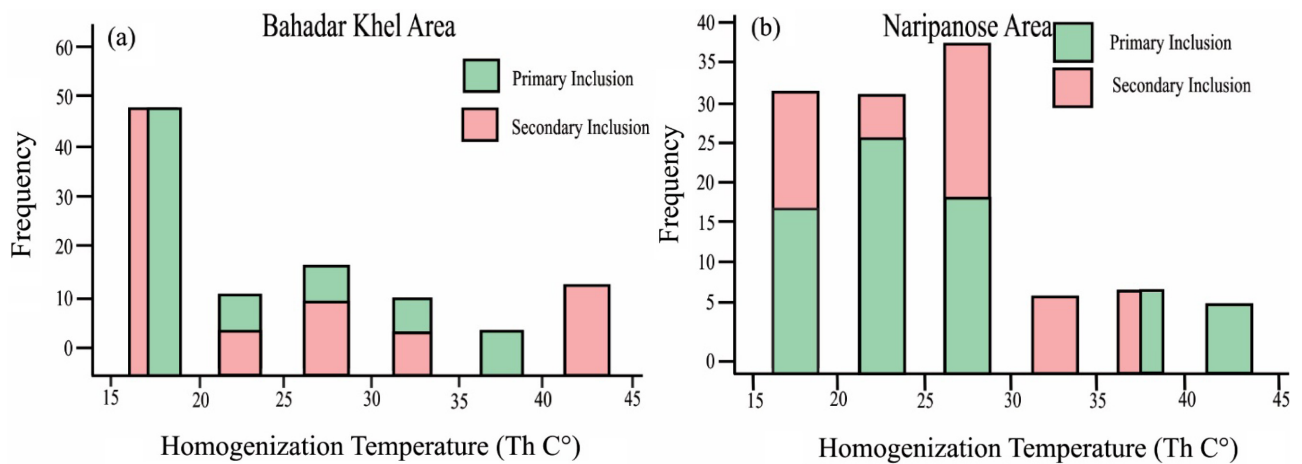


Figure 11. Histogram showing the primary and secondary fluid inclusion homogenization temperature.

leads to showing high homogenization temperature (Th) (Lowenstein et al., 1998). Homogenization temperature of fluid inclusions from the studied sample record the brine surface temperature during the salt deposition or surface air temperature in a shallow environment and mostly precipitation has been formed during May to August (Zambito and Benison, 2013). Salt precipitation is usually higher during the daytime (at noon) and in the summer season (Benison and Goldstein,

1999). The formation of salt replicates not only temperature but also depends upon the humidity and wind velocity (Robert and Spencer, 1995). Homogenization temperature concentrated from 14°C to 43°C represents the water surface condition. Representation of the maximum homogenization temperature from fluid inclusions may be equal to the highest brine temperature through halite crystallization.

Homogenization temperature also depicts the seasonal temperature

Table 6. Showing the homogenization temperature of primary and secondary fluid inclusions with their maximum and minimum homogenization temperature; Th-Homogenization temperature

Sr.no	Sample no.	Inclusion type	Homogenization Temperature (Th °C)					Th Max °C	Th Min °C
1	BSB-5	I-Inclusion	18	35	17	18	16	35	16
		II-Inclusion	18	22	26	29	43	43	18
2	BSB-12	I-Inclusion	20	24	26	28	34	34	20
		II-Inclusion	17	18	21	32	19	32	17
3	BSB-18	I-Inclusion	17	20	27	40	16	40	16
		II-Inclusion	20	16	42	18	14	42	14
4	BNP-7	I-Inclusion	18	29	16	16	24	29	16
		II-Inclusion	26	28	30	34	24	34	24
5	BNP-13	I-Inclusion	26	41	16	22	20	41	20
		II-Inclusion	16	18	22	24	28	28	16
6	BNP-21	I-Inclusion	22	24	36	24	26	36	22
		II-Inclusion	24	16	40	26	26	40	16

and Th values from single-phase fluids inclusions formed in April and May are moderate during the growth of halite crystal (Robert and Spencer, 1995; Hu et al., 2016; Warren, 2016). Measured daily variations in brine temperature, with low-temperature indication early morning and high temperature indicate the afternoon time. Most of the halite generally formed at the air-brine interphase and grew at noontime. During that time temperature changes from 10°C to 12°C in the summer season. Generally, most of the fluid inclusions Th fall within the temperatures range that was measured during the growth of salt. Homogenization temperature of primary and secondary inclusions are not continuous (Fig. 11), so it indicates that halite didn't precipitate over the entire range of brine temperature that has been measured. Consequently, the absence of homogenization temperature in the low ranges of observed brine temperature generally indicates the absence of salt precipitation. The range of the fluid inclusions Th is a significant characteristic of the data because it delivers the record of the brine temperature during the salt crystallization. Salt crystallize more rapidly due to high temperatures and high evaporation rate that correlate with humidity, wind velocity, and temperature. Fluids inclusion formation depends upon the crystallization rate, impurities, turbidity, and development of the fractures at the surface of the salt (Robert and Spencer, 1995). In a perennial lake system, halite precipitation is expected to develop during the driest and hottest month of the year, so that the annual maximum temperature should be revealed in the fluid inclusions Th values.

Secondary fluids inclusion can easily be distinguished from primary inclusion because secondary inclusions are in irregular shape one phase inclusion along the curved shape healed microfractures that crosscut halite crystal boundaries (Robert and Spencer, 1995; Meng et al., 2011) (Fig. 5e). The inclusions with the highest temperature indicate that it has been formed in the afternoon when air and water were at their warmest condition whereas the lowest homogenization temperature indicates that the salt/halite formed in the evening (Robert and Spencer, 1995). Whereas studied data didn't explain the comprehensive record of the total range of day and night variation because inclusions may not have been trapped during the cooler part of the diurnal cycle.

Implication of Paleoclimates

Major halite deposits in Pakistan are situated at the Salt Range (Punjab) and Kohat Basin (KP) (Hussain et al., 2019, 2020, 2021). Salt Range Formation of Precambrian age is the oldest and major halite deposit in Pakistan. Whereas the youngest halite deposits of Eocene age are present in the northwestern Kohat Basin (KB) and the main deposits are present in the central part of the basin. The research area is highly fractured and faulted, the Khurram Thrust covering the northern and western part of the study area. XRD data shows that the Bahadar Khel Salt has a low bromine Br⁻ concentration as compared to other basins that show the presence of non-marine water or recycling or dissolution of the ancient marine salts (Shouakar-Stash, 2008; Han et al., 2019). Overall the geology demonstrated that Bahadar Khel Salt in KB has a marine origin (Pivnik and wells, 1996) that has been precipitated from the ancient Tethys (Hussain and Zhan, 2018). Whereas the low concentration of Br⁻ can be elucidated by several inputs of non-marine water. Generally, the Bahadar Khel Salt has been deposited by saline and meteoric water and at some places by the recrystallization of ancient halite.

The decreasing of bromine content with continuous recycling processes describes the common and multiple dissolutions and precipitation processes (Eggenkanp et al., 2019b; Han et al., 2019) that depict the depositional basin was separated from the marine environment that allows the multiple precipitation/dissolution. That represents the salt having various origins (Holland, 1984). Under the wet condition, dissolution of pre-existing deposits of salt is the main cause of Cl, whereas in dry spell conditions a limited quantity of Cl is in the basin. These high values indicate a sudden high depth lake and are a significant amount of water entering into the basin (Holland, 1984; Warren, 2016).

At the end of the Early Eocene short time regression takes place within the Kohat Basin that is evidenced by evaporitic deposits like Jatta Gypsum with gypsiferous shale and halite. During the Middle Eocene major transgression has been occurred covering the Kohat Basin due to the Mami Khel Clay that overlies Chorgali Formation that was deposited in the coastal or tidal saline water environment during the transgression process (Paracha, 2004; Hussain et al., 2021). Whereas

the deposition of the Kohat Formation shows transitional marine condition (Paracha, 2004) that developed a foredeep basin between the Asian and Indian Plate after that it has been converted into a confined evaporitic basin that is followed by a terrestrial foreland basin and an open marine basin. Whereas during the Pliocene to Pleistocene time that basin is terrestrial foreland basin (Pivnik and Han, 1996). All these tectonic units have been controlled by regional tectonics including the rise of NW Indian Craton between the Eocene and Oligocene span that creates the evaporitic basin (Hussain et al., 2021).

Halite has been deposited in the marine environment and after deposition halite has been moved to the earth's surface due to tectonic activity. So the presence of Mg, Fe, Ca, and other ions within the inclusion suggested that Eocene halite exposed to the surface of the earth and meteoric/surface water with Mg, Fe, and Ca has been moved along the fracture and trapped in inclusion. Secondly break in homogenization temperature (Fig. 11) also indicates that inclusions are not trapped at a single time that trapped in episodic time intervals.

Origin of Eocene Salt

Quantitative paleotemperature data can provide information about the ancient time climatical condition. The maximum homogenization temperature (T_h max) of fluids inclusions in salt is 43°C within the study area. That indicates the hot and arid climatical condition in Kohat Basin at Eocene time. The final product of the lake evolution is a saline lake that is a key aspect of research for interpreting the paleoclimates, global changes and paleoenvironment (Fan et al., 2014). Sometimes the lake environment/conditions changed into brackish water, at that particular condition thin and dispersive gypsum was also deposited. The strong uplift by tectonic activity has resulted in the formation of depressions. Primary halite is normally formed at the air-water interface and chevron crystal is formed at the floor of the salt lakes (Lowenstein and Hardie, 1985). Primary fluid inclusions in halite have been trapped during the crystal growth and have a square shape.

Maximum homogenization temperature of fluid inclusions characterizes the highest air temperature during the halite precipitation. That is based on surface air temperature and homogenization temperature that is obtained from the halite fluids inclusions. The value of homogenization temperature that is attained from the halite fluid inclusions indicates that the hot and arid climate during Eocene is a necessary condition for potash formation (Liu et al., 2016; Xiao et al., 2017). Overall the climatical condition of Kohat Basin is cooled and dry in winter and hot and arid in summer seasons. So it has different temperatures throughout the year, that's why the homogenization temperature also varies from 14°C to 43°C, which indicates the various ranges of temperatures throughout the year during the halite precipitation. The record of the homogenization temperature of fluid inclusions within the halite mineral is a significant tool for studying the consequence of climatical change on halite precipitation (Xiao et al., 2017).

Normally after precipitation of polyhalite, water brines become so concentrated and pure halite was precipitated during the short intervals of time brines were hyper-concentrated and the rock salt containing the polyhalite has been deposited. After dilution of the highly saturated brines for the alteration of lower salinity brines halite that contains

anhydrite starts to precipitate. Generally, polyhalite has been developed due to the dissolution of magnesium and salt due to the release of water during dehydration of gypsum (Xiao et al., 2017). The pink and orange color of the salt is due to the presence of Fe^{2+} oxide or oxyhydro-oxide that shows the existence of oxygenated water and salt was crystallized near the surface of the water column. Whereas the maroon color is due to the brine rich in iron and calcium migrated from the shallow depth and mixed with magnesium and oxygenated potassium fluid (Zhao et al., 2020). After that they mixed with fluid rich in Ca^{2+} and SO_4^{2-} it can lead to the development of polyhalite followed by the formation of gypsum. Dissolution, recrystallization, and dilution can cause a decrease in Br⁻ contents. The inflow of the brines rich in K^+ and polyhalite start to precipitate, the Br⁻ concentration is considerably decreased (Peryt et al., 2005). A high concentration of K^+ ions and low content of Br⁻ is due to the mixing of K-rich and Mg-rich brines with less saline fluids. Whereas the mixing of chemical fluid containing the high concentration of Ca^{2+} and SO_4^{2-} that can reduce the amount of Br⁻.

Generally, Eocene salt was deposited in dissected part of the basin, the shallow water provides the rapid evaporation condition that produced the Mg^{2+} and K^+ ions. Whereas the presence of gypsum was deposited within the small salt sags when a high concentration of SO_4^{2-} and Ca^{2+} were present due to freshwater replacement and combined with abundant content of brines, which can cause produce the traces of sylvite with protogenetic halite and gypsum (Fig. 12c). These solutions (dilute brine) have experienced strong concentration and evaporation. While the minor impact from freshwater; the Mg^{2+} and K^+ becomes highly concentrated again and precipitated downwards. The Mg^{2+} , and K^+ reacted with gypsum and halite crystal to generate the polyhalite (Fig. 12d). The Eocene salt is mostly white to orange-pink whereas polyhalite generally developed simultaneously with maroon colored halite indicating oxidizing environment. Overall the paleoclimates were characterized by the recurrent variation of the humid and dry climate. The ancient marginal land and paleo-uplift provide the terrestrial water with SO_4^{2-} and Ca^{2+} into the protogenetic brine and play a significant role to develop the polyhalite (Fig. 12d).

Overall the study area comprises dissected salt lakes that are surrounded by high concentrated gypsum at the time of deposition of the salt whereas the shallow water provides environments for the quick evaporation and concentration of brines, so that the Mg^{2+} and K^+ were concentrated. Whereas arid and hot climates maybe not be lasted a long time so the concentration of brines in lakes was continually intermittent by the moist climate that can bring them some freshwater from the periphery of salt lakes. Generally, the ancient land and paleo uplift can provide a large amount of terrestrial water as well as the channel or streams transport the high concentration of Ca^{2+} and SO_4^{2-} into the lake brines. It can provide a suitable condition for the formation of halite and gypsum, conversely the frequent alteration of the arid, hot, and moist climatical condition can affect the precipitation of evaporites. The dilution generally occurs when the brines in the lakes become concentrated at the stage of sylvite formation so the overall Eocene Bahadar Khel Salt was deposited at the hot, dry, and moist climatical condition in a lacustrine basin. Fluid inclusions homogenization overall temperatures indicate inclusion were trapped throughout the year.

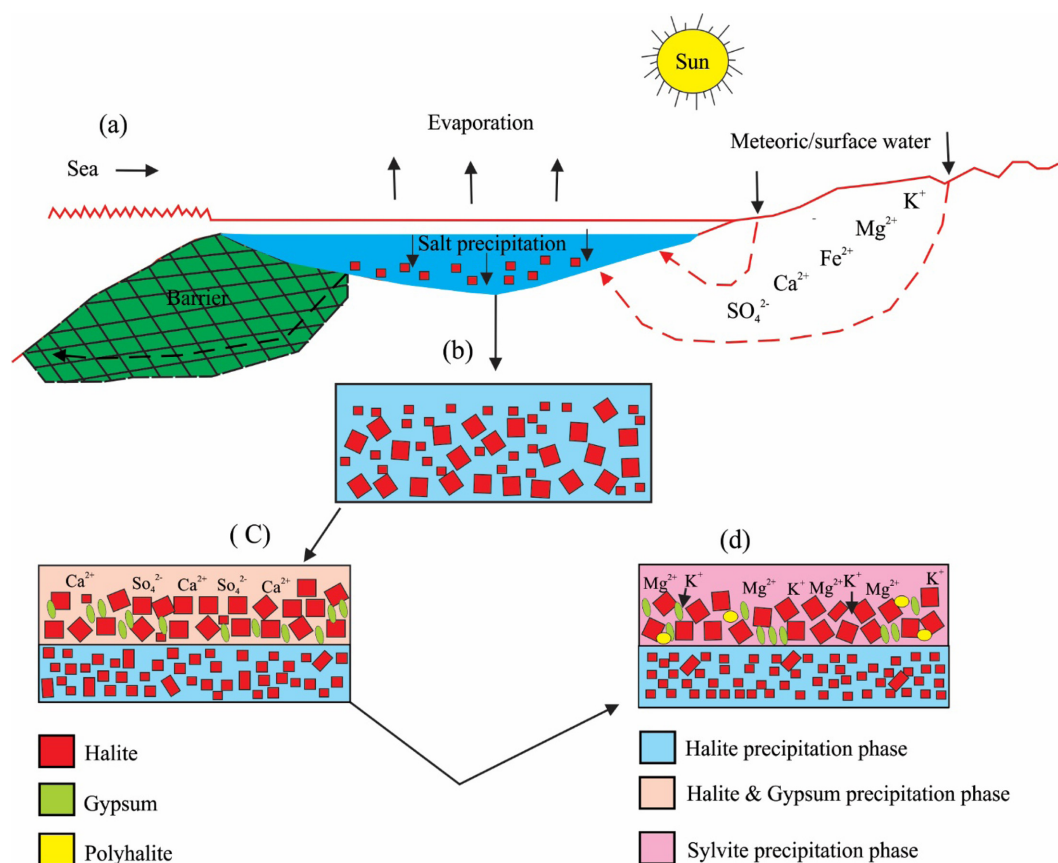


Figure 12. Schematic model of evaporite deposition; (a) lake environment with salt precipitation as well as meteoric and surface water desalinate the lake water; (b) precipitation of halite phase; (c) precipitation of gypsum with halite; (d) precipitation of sylvite and polyhalite formation.

Conclusion

Bahadar Khel Salt of Eocene is well exposed in Kohat Basin including Bahadar Khel, Karak, Jatta Ismael Khel, and Naripanoose area. Generally, its thickness varies in both areas i.e. 70 to 85 m in Bahadar Khel and Naripanoose area respectively. Two sections have been measured from Naripanoose and Bahadar Khel from the continuous interval. Lithologs have been constructed based on scale and variation in composition. The petrographic thin section indicates that Eocene salt consists of halite as a dominant mineral with subordinate gypsum, anhydrite, sylvite, polyhalite, and dolomite as subordinate minerals. The presence of impurities indicates that Eocene salt is not deposited in a uniform environment. It has been formed in a fluctuating environment. At the end of the Early Eocene, there was a wide but short time regression occurred within Kohat Basin, and high evaporation starts that causes to deposit the gypsiferous shale and salt (Bahadar Khel Salt).

Mineralogy and geochemistry of rock, as well as fluid inclusions, are useful tools to evaluate the origin and paleoclimate of Eocene salt. It is suggested that the source of Bahadar Khel Salt is not uniform, showing the variation in environment i.e. restricted environment and meteoric/surface water. Low Br^- is evidence of non-marine water, the presence of SO_4^{2-} associated with Ca^{2+} also shows that halite precipitated from SO_4^{2-} type water. Limited primary fluid inclusion also shows

unstable regional paleoclimate prevailed at various stages of Bahadar Khel Salt precipitation. At the early stage, it was shallow seawater existed that favored the formation of evaporite basin and then this basin changed into terrestrial foreland basin and then open marine and at last acting as a terrestrial foreland basin. All these events were controlled by active tectonic events.

Microthermometry of fluid inclusion represents the homogenization temperature (T_h) of fluid inclusion trapped during precipitation. T_h value ranges from 14°C to 43°C . This T_h variation shows that fluid inclusions were not trapped within a single climatical condition or at a constant/same time. It has been concluded based on fluid inclusions analysis, that Bahadar Khel Salt was deposited throughout the large time at summer the water-air interface temperature is high with high T_h values, low T_h indicates that halite deposited during winter and spring season. Overall the Bahadar Khel Salt was deposited in an arid and hot environment.

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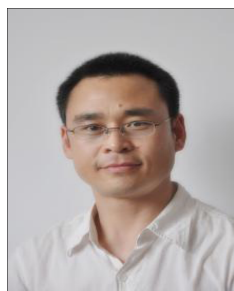
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