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The Palaeo-Salinities of the Despositional Waters During the Deposition of "Kussak Formation" of Cambrian age, Exposed at Salt Range, Punjab, Pakistan

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Abstract: The elemental sulphur was investigated in 128 samples collected from Kussak Formation exposed at Salt Range, Punjab, Pakistan. The sulphur was analysed in Carbon-Sulphur analyzer to know the local and regional variations of sulphur in the Kussak Formation. It varies from 0.01% to 0.96% in the Formation. The sulphur gradually increases from the eastern Salt Range to the central Salt Range and again decreases towards the western Salt Range. The increase of sulphur towards the central part indicates comparatively more saline conditions within the central Salt Range. The salinity of depositional waters probably decreased again towards west. It is most likely that the quantity of sulphur from east to west represents a general gradual increase in the depth of depositional basin towards central Salt Range. The decrease of sulphur towards west indicates some local highlands, responsible for a local decrease in the salinity of the marine waters.

Keywords: sulphu analysed the Kussak Formation. Salt Range.

1. INTRODUCTION

The Kussak Formation of Cambrian age is exposed in the eastern and central Salt Range **(Fig. 1).** In the Salt Range, the Kussak formation disconformably overlies by Khewra Sandstone, and conformably overlain by the Jutana dolomite. The Cambrian succession exposed in the Salt Range is as follows.

AGE	FORMATION
Cambrian	Baghanwala Formation
	Jutana Dolomite
	Kussak Formation
	Khewra Sandstone
Pre- Cambrian	Salt Range Formation

In the west the Kussak Formation was mostly eroded away with the exception of one section exposed at Khan Zaman Nala. The Permian conglomerates of the Tobra Formation cut the Cambrian rocks deeper towards west and eroded most of the Kussak Formation (Lillie *et al.,* 1987)

The Kussak Formation consists of inter-bedded silty to sandy shales, argillaceous, calcareous sandstones and sandy argillaceous limestones. The thickness of the formation varies from place to place. The sandstones are generally glauconitic, oolitic and display greenish to brown colour. The limestones are thinly bedded, argillaceous and sandy. The shales are massive to thinly bedded. Received 12th August 2012 and Revised 11th September 2012 Representative samples were collected from Ludwa, Kussak Fort, Khewra Gorge, Nila Wahan, Kallar Wahan, Katha Roadside and Khan Zaman Nala, representing the stratigraphical variations from the base to the top. **(Fig. 1)** provides the location map of the area and sampling

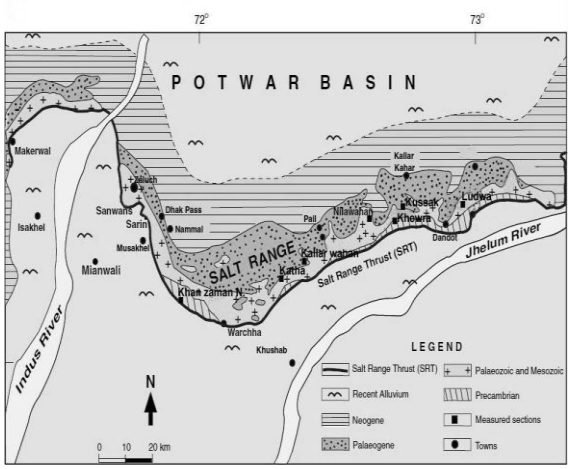

Fig. 1. Map showing the location of seven sections of Cambrian succession in the Salt Range, Pak. (Modified from Ghazi *et al.,* 2012)

sites. The formation is 68m thick at Ludwah, 52m thick at Kussak Fort, 65m thick at Khewra Gorge, 54m thick at NilaWahan, 15m thick at Kallar Wahan, 12.19m to 15.7m at Katha and 41m thick at Khan Zaman Nala (Baqri, 1992). The Kussak Formation disconformably overlies the Khewra Sandstone of the Cambrian age and is conformably overlain by the Jutana Dolomite of the Cambrian age (Shah, 1977).

The Sulphur was analyzed in all 128 collected samples to understand the Palaeo-salinities of the depositional waters. The elements generally found with the sulphate ions are interesting idicators to find the proximal and distal ends of a depositional basin and have been used successfully to locate the salinities of the

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palaeo basins by different workers (e.g., Berner and Raiswell, 1983, 1984; Morse and Berner, 1995; Hasegawa *et al.,* 2010).

The sulphur may occur in various forms such as the monosulfide sulfur, disulfide sulfur, elemental sulfur, inorganic sulfate and organically bound sulfur (Robert, 1964; Cynthia *et al.,* 1993). Along with other forms of sulphur, the elemental sulphur is being used as a geochemical indicator for the palaeo-salinities of the depositional waters. Hence it is used here for the palaeo-salinities of the Kussak Formation. The main focus of the present study is on the presence of elemental sulphur to determine the palaeo-salinities of the area, because along with other geochemical indicators; the elemental and isotopic sulphur are the good indicators for the past depositional environments (Kaplan *et al.,* 1963; Hasegawa *et al.,* 2010).

Previous Work

The Kussak Formation was named due to its excellent exposure near the Kussak Fort in the Eastern Salt Range **(Fig. 1)**. Several workers studied the Kussak Formation with reference to its stratigraphic position in the Cambrian times (e.g., Shah, 1977). (Waagen 1895) studied the fossils of the Kussak Formation and reported the presence of bioturbations in it. (Gee 1935) provided the detailed description of the lithology and stratigraphic position of the formation. The Kussak Formation disconformably lies over the Khewra Formation of Cambrian age marked by a bed of conglomerates that separates it from the underlying Khewra Formation. The Formation is conformably overlain by the Jutana Dolomite. (Sahni 1947) also studied the microfossils of the area.Gosh and Bose (1950) studied the microfossils from the Kussak Formation and proved the presence of bioturbations. (Wadia 1957) provided the lithological and stratigraphical details ussak Formation of the Salt Range.

2. EXPERIMENTAL METHODS

For the determination of sulphur, the Carbon-Sulphur Analyzer, **LECO C-S 244** was used. In such Carbon-Sulphur analyzing instrument, a sample is ignited in a non-reacting metallic boat at 1200-1300^{o}C and a computer attached to the instrument directly gives the concentration of analyzed elements in the percentage (%).

3. DISCUSSION

Along with other geochemical parameters, the TS/TOC (total sulphur/ total organic carbon), C/S (carbon/sulphur ratio) are being used by various workers (e.g., Berner and Raiswell, 1983, 1984; Morse and Berner, 1995; Hasegawa *et al.,* 2010) for the determination of paleo-salinities or to distinguish between the fresh and marine depositional conditions. Though due to one or another reason, TOC or simply organic carbon is not determined in the studied samples but the percentage of elemental sulphur can be used here as a single parameter for the paleo-salinities of Kussak Formation. (Hasegawa *et al.,* 2010) reported that if the TS/TOC values are below 0.11 then these sediments were deposited under freshwater conditions and when TS/TOC ratio increases, it points towards marine conditions. This interpretation was also justified by the occasional occurrences of freshwater facies fossils by (Fujita 2003) and Matsukawa *et al.,* 2006) in the sediments of Tetori Group, Japan. Such types of studies were also carried out by (Raiswell and Berner 1986) by giving detailed account about the presence of organic carbon and sulphur. On the basis of C/S ratio, they distinguished the marine and fresh water sediments. In regard, majority of samples from Kussak Formation, especially at its eastern and western extremities have lower values of sulphur, hence lower salinities.

4. RESULTS

(Table 1, A-G**)** provides the percentage of sulphur at different sections of the Kussak Formation exposed at Ludwah Hills, Kussak Fort, NilaWahan, Kallar Wahan, Katha Roadside and Khan Zaman Nala, respectively. **(Table 2)** gives the mean values of quantitative analyses of sulphur from the above mentioned locations. Figure 2 provides the trends of variations of sulphur from east to west in different sections exposed in Salt Range. In the Central Salt Range; especially at the Kallar Wahan, the sulphur is as high as 0.29 % while the mean value is 0.19%. Like the eastern side, the concentration of sulphur gradually decreases towards west again, representing the decrease of sulphur ions. Although, the sulphur contents are relatively higher in the Central Salt Range but locally some of the samples (i.e., KU-KU-12, KH-KU-11) in the eastern Salt Range and samples such as (KNR/2-KU-6 and KZN-KU-5) in the western Salt Range have also higher values of Sulphur. Along with mean; the standard deviation, skewness and Kurtosis values are also calculated for the sulphur contents at different sample location.

The sulphur is added to the sediments as organic sulphur compounds along with other forms. The dissolved sulphate ions are dependent upon the presence or absence of dissolved oxygen for the diagenesis. The organic sulphur in the compounds simply oxidized to sulphates in aerobic conditions and is deposited as sulphates and suffers no changes during the diagenesis (Cynthia *et al.,* 1993). The sulphate reducing bacteria can reduce the sulphate ions to H_2S and HS^- ions in anaerobic conditions and may also be responsible for the addition of more sulphates from the organic matter. The dissolved sulphates may react with iron minerals to from iron sulphates. In sea water, with high SO_4^{2-} concentration, high H_2S formation in organic matter rich sediments is extremely common. The Kussak Formation displays bioturbations, algal fossils and oolites and therefore provides the evidence of marine organic matter (blue green algae and invertebrates) during its depositions.

Table 1. The Quantitative Analyses Of Sulphur In The Kussak Formation

A. Sulphur at Ludwah Hills

Sample code	% of Sulphur
LU-KU-4	0.00
LU-KU-5	0.31
LU-KU-5A	0.01
LU-KU-7	0.13
LU-KU-8	0.02
LU-KU-9	0.01
LU-KU-10	0.02
LU-KU-12	0.02
LU-KU-15	0.02
LU-KU-16	0.02
LU-KU-17	0.01
LU-KU-19	0.04
LU-KU-20	0.00
LU-KU-21	0.05
LU-KU-22	0.03
LU-KU-23	0.01
LU-KU-24	0.01
LU-KU-25	0.10
Mean	0.05
Std. Dev.	0.07
Skewness	3.06
Kurtosis	10.22

B. Sulphur at Kussak Fort

Sample code	% of Sulphur
KU-KU 1	0.01
KU-KU-2	0.03
KU-KU2A	0.01
KU-KU -3	0.04
KU-KU-4	0.07
KU-KU-6	0.07
KU-KU-7	0.01
KU-KU-9	0.01
KU-KU-11	0.02
KU-KU-12	0.19
KU-KU-13	0.03
KU-KU-14	0.00
KU-KU-15	0.02
KU-KU-16	0.02
KU-KU-17	0.00
KU-KU-18	0.06
KU-KU-19	0.08
KU-KU-22	0.81
KU-KU-23	0.04
KU-KU-24	0.06
KU-KU-25	0.02
KU-KU-26	0.05
Mean	0.08
Std. Dev.	0.17
Skewness	4.28
Kurtosis	19.09

C. Sulphur at Khewra Gorge

Sample code	% of Sulphur
KH-KU-1	0.14
KH-KU-2	0.22
KH-KU-2A	0.24
KH-KU-3	0.04
KH-KU-4	0.07
KH-KU-6	0.17
KH-KU-7	0.15
KH-KU-8	0.21
KH-KU-10	0.04
KH-KU-11	0.64
KH-KU-12A	0.19
KH-KU-12B	0.01
KH-KU-13	0.03
KH-KU-14	0.00
KH-KU-15	0.02
KH-KU-16	0.05
KH-KU-17A	0.00
KH-KU-17B	0.00
KH-KU-17C	0.00
KH-KU-18A	0.06
KH-KU-18B	0.04
KH-KU-19A	0.82
KH-KU-19B	0.05
KH-KU-19C	0.04
KH-KU-20	0.14
KH-KU-22A	0.08
KH-KU-22B	0.10
KH-KU-22C	0.07
KH-KU-23	0.04
KH-KU-24	0.06
KH-KU-25A	0.04
KH-KU-25B	0.02
Mean	0.12
Std. Dev.	0.17
Skewness	3.07
Kurtosis	10.07

D. Sulphur at Nila Wahan

Sample code	% of Sulphur
NWN-KU-2A	0.23
NWN-KU-2B	0.02
NWN-KU-5A	0.08
NWN-KU-5B	0.27
NWN-KU-5C	0.07
NWN-KU-7	0.04
NWN-KU-9	0.02
NWN-KU-10	0.96
NWN-KU-12	0.08
NWN-KU15	0.02
NWN-KU-17	0.00
NWN-KU-18	0.06
NWN-KU-20	0.14
NWN-KU-21	0.05
NWN-KU-23	0.06
NWN-KU-24	0.59
NWN-KU-29	0.01
NWN-KU-31	0.02
NWN-KU-34	0.04
NWN-KU-35	0.01
NWN-KU-36A	0.06
Mean	0.14
Std. Dev.	0.23
Skewness	2.88
Kurtosis	8.57

E. Sulphur at Kallar Wahan

Sample code	% of Sulphur
KNR-KU-1	0.25
KNR-KU-4	0.26
KNR-KU-7	0.29
KNR-KU-8	0.04
KNR-KU-9	0.12
KNR-KU10	0.05
KNR-KU11	0.02
KNR-KU12	0.63
KNR-KU13	0.06
Mean	0.19
Std. Dev.	0.20
Sewnwss	1.58
Kurtosis	2.73

F. Sulphur at Katha Roadside

Sample No	Sulphur (%)
KNR/2-KU-2	0.16
KNR/2-KU-4	0.07
KNR/2-KU-5	0.03
KNR/2-KU-6	0.38
KNR/2-KU-7	0.06
KNR/2-KU-13	0.03
KNR/2-KU-15	0.29
KNR/2-KU-16	0.13
Mean	0.15
Std. Dev.	0.13
Skewness	1.09
Kurtosis	0.01

G. Sulphur at Khan Zaman Nala

Sample code	% of Sulphur
KZN-KU-1	0.01
KZN-KU-5	0.14
KZN-KU-7	0.13
KZN-KU-8	0.03
KZN-KU-9	0.02
KZN-KU-10	0.08
KZN-KU-12	0.10
KZN-KU-13	0.03
KZN-KU-14	0.04
KZN-KU-15	0.00
KZN-KU-19	0.00
KZN-KU24A	0.01
KZN-KU-24B	0.08
KZN-KU-26	0.01
KZN-KU-27	0.01
KZN-KU-29A	0.01
KZN-KU-29B	0.07
Mean	0.05
Std. Dev.	0.05
Skewnwss	0.96
Kurtosis	-0.35

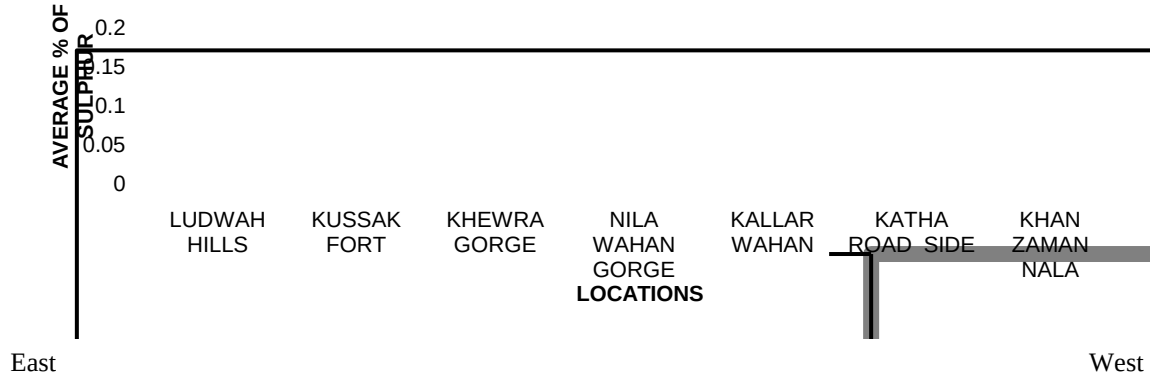

Fig. 2 Trends of Sulphur in the Kussak Formation (From East to West) exposed at Salt Range, Punjab, Pakistan.

Table 2: Average Quantitative analyses of Sulphur at different locations of Kussak Formation

Location	Average % of Sulphur
Ludwah Hills	0.05
Kussak Fort	0.08
Khewra Gorge	0.12
Nila Wahan Gorge	0.14
Kallar Wahan	0.19
Katha Road Side	0.15
Khan Zaman Nala	0.05
Mean	0.11

Provided the curves of sulphate core versus depth for H_2S containing sediments in the Gulf of California. He found that the H_2S was absent in top 20 centimeters. He concluded that there is a decrease with the time in sulphate reduction rate at the sediment water interface.

The sulphate ions generally increase from fresh water to continental marine environments (Berner and Raiswell, 1983, 1984; Morse and Berner, 1995; Hasegawa *et al.,* 2010). In the studied area, sulphur gradually increases from the eastern Salt Range to the central Salt Range and again decreases towards the western Salt Range. Therefore in the Kussak Formation, the salinity of the depositional waters increased from east to central Salt Range and again decreases towards west. It is more likely that the quality of sulphur from the east to west represents a gradual increase in the depth of depositional basin towards west with the exception of the local highs.

4. CONCLUSIONS

The quantitative analysis of sulphur determined in the rocks of the Kussak Formation is 0.05% at Ludwah Hills, 0.08% at Kussak Forte, 0.01%at Khewra Gorge, 0.14% at Nila Wahan, 0.19% at Kallar Wahan, 0.15% at Katha roadside and 0.05% at Khan Zaman Nala.

The mean value of sulphur in the Kussak Formation in the Salt Range is 0.11%

The Sulphur gradually increases from east to west and represents the salinities of the depositional waters. The salinities of depositional water were comparatively higher towards west during the deposition of Kussak Formation, with the exception of some local high areas, indicating shallow water conditions towards east comparatively deeper water conditions towards west.

The proximal end of the depositional basin during the deposition of Kussak Formation was towards east and distal end towards west.

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