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Petrochemistry of Bhuban Formation rocks in and around Aizawl City, Mizoram, India

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Abstract

The area in and around Aizawl City is dominated by Middle and Upper Bhuban rock formations. Geologically and petrologically the area has not been so far explored therefore the present study was initiated. The study area is composed of sandstone and shale belonging to Middle and Upper Bhuban formation and lies in between 92°60' E longitude and 23°58' N latitude. Rock samples collected from different sections in the study area were analyzed to study the mineralogical compositions of the rocks and determination of the multi-elemental distribution using high precision X - ray fluorescence analysis. The study shows that the area is dominated by different rock units such as sandstone, shale, siltstone and shaly sandstones belonging to middle and upper Bhuban formation. Petrological studies reveal that sandstone is greywacke exhibiting argillaceous matrix mainly siliceous, ferruginous and calcareous (due to presence of fossils) and rock fragments. The oxide and silica weight percentage observed from the geochemical analysis indicate Na_2O, K_2O and MgO have the maximum variation in the study area. The trace elements Sc, Co, Ni, Cu, Zn, Ga, Pb, Th, Rb, U, Sr, Y, Zr, Nb, Ba, Cr, V in parts per million (ppm) show a different variation in sandstone, shale and siltstone. Ba is having maximum value >500 ppm followed by Zr in sandstone whereas Cr is maximum in shale. Prominent feature is a persistently higher amount of uranium (~4 ppm) in the rocks of Middle Bhuban rocks in contrast to the average abundance in sandstone i.e. 2 ppm.

Key words: Geochemistry; petrography; Bhuban Formation; Greywacke.

Introduction

The importance of geological and geochemical studies of the rocks exposed in and around Aizawl city, Mizoram is now being felt. An unpublished Geological Survey of India (G.S.I.) report in 1981-82 seems to be the only document where work has been approached from geological and geomorphological mapping in parts of northern Mizoram. During the mapping of rock around Aizawl, samples were also collected for further studies in the laboratory. The rock samples are to be sliced and grinded till they become

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transparent and good enough to be studied under petrographic microscope. The minerals which are in fact forming the rocks give relevant information to be identified on the basis of their diagnostic optical properties. The systematic description of textural relationship within the rocks and optical properties of minerals constituting petrography.

The geology of the area around Aizawl city is dominated by sandstone, shale, siltstone and shaly sandstones belonging to Middle and Upper Bhuban Formation, exhibits mixed appearance in all respects *viz.* colour, bedding plane, thickness of the beds, texture *etc.* In view of the fact that geology and geochemistry of Bhuban Formation rocks still need attention and very meager work so far has been done on these approaches.[1] Therefore, the present work has been undertaken to carry out petrochemistry of sandstone, shale, siltstone belonging to Middle Bhuban Formation. Petrochemistry deals with the chemistry of bulk rock composition comprising oxide percentages, rare earth elements (REE) and trace elements in parts per million (ppm).

The aim of the present study is to assess mineralogical and textural details of the Middle Bhuban Formation rocks along with a penetration into their chemical composition. The chemical composition includes major, minor and trace element analyses of sandstone, shales and silty shale exposed in the area around Aizawl city. Further, an attempt is been made to explain the process of weathering. The location map of the study area is shown in Figure 1.

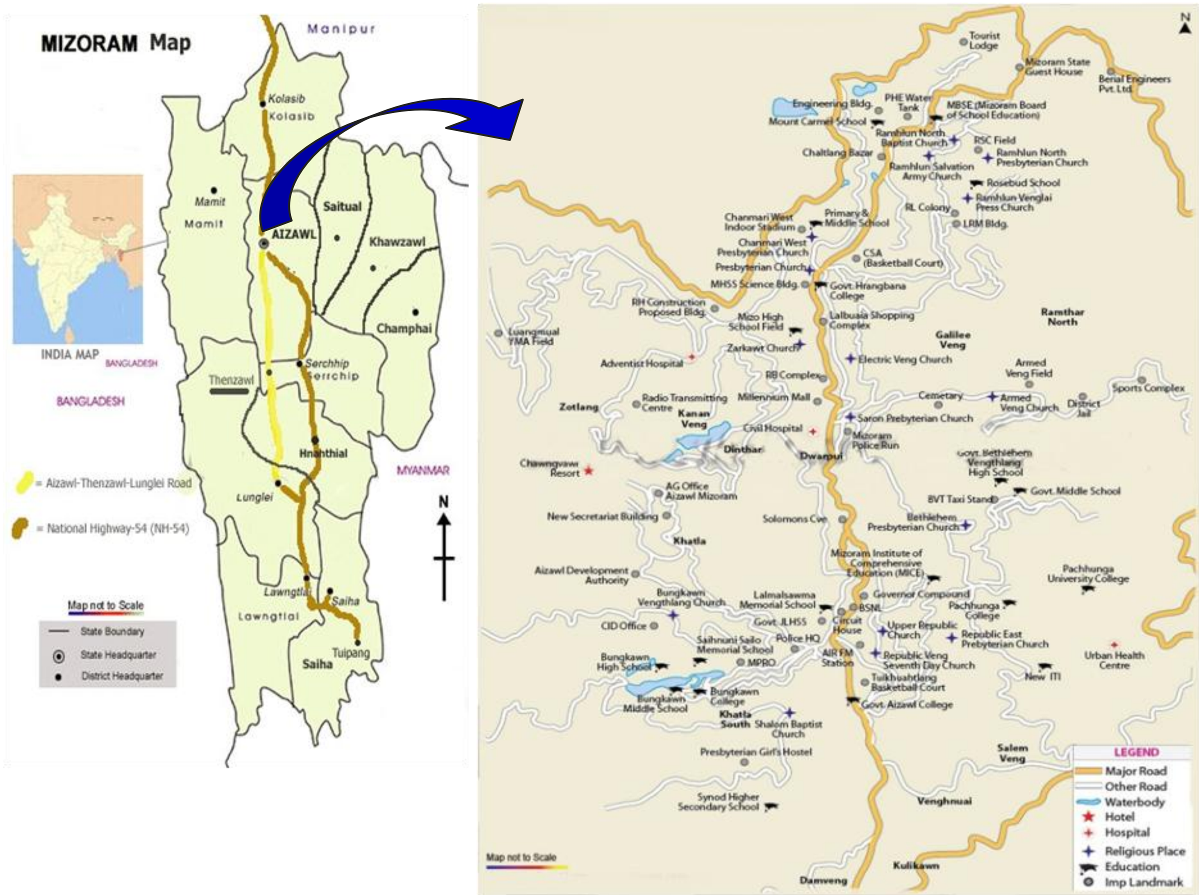

Figure 1. Location map of the study area.

Materials and Methods

Field study

Field work was carried out in various parts of Aizawl *viz.* along Chanmari-Chaltlang road cutting section, Vaivakawn-Chawnpui Veng, Treasury Square-College Veng, and Company Peng-Bawngkawn. Readings were taken in each sector, strike of the bed, dip amount, and dip direction of the rocks exposed along the road using Brunton compass. Samples were collected and prepared for the ideal section and analysis of major oxides from the field.

Microscopy

Among the collected samples, representative samples were sent to Gauhati University for the preparation of the thin sections. These thin sections were studied under Petrological Microscope. The texture and mineralogical compositions of the rocks were presented in the photomicrographs plates.

X-ray fluorescence analysis (XRF)

X-ray fluorescence analysis was one of the first multi-element instrumental techniques to be adopted widely for routine geochemical analysis. The technique is capable of determining to high precision not only the major elements but also a wide range of geochemical important trace elements. The technique also benefits from simple sample preparation requirements, major elements being routinely determined on powders that have fused with a suitable flux and cast as glass disks, trace elements being determined on compressed powder pellets. The analysis was performed at the Geochemical Laboratory of Wadia Institute of Himalayan Geology, Dehradun.

Results

Field work

***Company Peng-Bawngkawn Section*:** It is road section lies North-Western part of study area. This area exposes rocks of upper part of Middle Bhuban formation of Surma Group. The area characterized by alternate succession of argillites and arenite. The area comprises of different rock beds such as shale, siltstone and sandstone. The shales are thickly bedded relatively more compact, smooth and of gray colour. Thin bands of crumpled grey Shale have also been observed at places. In some rocks, the sandstone beds are very thick while in other thinly bedded. The sandstones are grey coloured, medium to coarse grained and some of them are also of brown colour. While in other part of the section, persistently grey colour sandstones are observed. Fossils are also observed throughout the study area.

***Republic Veng-College Veng Section*:** It is the road section which is running in the middle-eastern part of the area. This portion exposes rocks of middle Bhuban formation of Surma group. The area falls under the latitude of N23° 93’ 330” and longitude E 092° 93’ 330”. The area comprises rock types such as sandstone, shale and siltstone. The sandstones beds are very thick medium to coarse grained and are usually grey in colour and brown sandstones are also observed.

***Chanmari-Chaltlang Section*:** The area falls in the latitude of N 23° 44’ 93”, longitude E 092° 43’ 180”. In Chanmari-Chaltlang section, sandstones is more or less consistent with respect to this composition. They are grey coloured hard and compact in nature. Joint plane are also noticed but they are not closely spaced. The important change within the section is in the appearance of rocks all along road side. The repeated occurrence of sandstone, shale and mudstone is being noticed as we climb the hill named Chaltlang, through Chandmari-Chaltlang road. Sandstones which is occurring in proximity of shale and mudstone are relatively more argillaceous.[2]

***Chawnpui Veng-Vaivakawn Section*:** The section falls in the latitude of 23° 44’ 018” N and longitude 092°42’ 441” E, which is the western side of Aizawl city. The area comprises different types of rocks such as shale, sandstone and siltstone. Sandstone are thickly bedded and are mostly grey in colour, and in some parts, they are brown in colour. The sandstones are medium to coarse grained whereas the shale beds are thin and brittle and are mostly grey in colour.

Petrography

The representative samples are observed under the microscope. Microscopic studies are unable to provide substantial amount of contribution to the present study of slope instability. The rocks of the study area are belonging to the Middle Bhuban Formation, which is dominated by shale, mudstone and siltstone along with the sandstone. In most of the thin sections, it is found to be difficult to study the mineralogy and texture of sandstones simply because of the fact that presence of shale and other fine grained rocks are overshadowing the sandstones. Further, shale and other fine grained rocks are too fine to be studied under petrological microscope. Moreover, sandstones themselves are also fine grained, and having argillaceous matrix. Sometimes, siliceous, ferruginous and calcareous (due to presence of fossils) sandstones are also present.

The thin section study of the sandstone show, that the rock contains mainly angular to sub-angular fragments of quartz which show uniform extinction (Plates B-F). Muscovite is also noticed. The intercalating feature in one of the section is that there is perfect euhedral crystal of quartz, having uniform extinction but mostly in Middle Bhuban, sandstones are exhibiting rugged and corroded quartz. This irregular boundary of quartz grains are mainly because of the exaggerated weathering effects. These crystals do not show any detrital grains in the core. The matrix is mainly siliceous, calcareous and faintly argillaceous. The modal composition of the section shows that the sandstone is greywacke. The rock fragments are also noticed in Plates E & F. The modal composition of sandstone in one of the area immediately north to the study area.

The sandstone-shale intercalation is presented in Plate C, in which fine grained layer rich in argillaceous material can be visualized with a band of rock rich in quartz grain. These quartz grains are also elongated and shown to be flown in one direction probably with the argillaceous matrix. Shale-sandstone and shale-siltstone rocks of Middle Bhuban are too fine grained to be studied under microscope. One of the rocks is presented at Plate D. Fossils are also common in these rocks and can be seen under microscope also such as Plate H. Muscovite is also noticed in shale-sandstone alternation Plate I &J.

The sandstones in the upper part of Middle Bhuban contain more of the rock fragments Plate E & F. These grains look like quart but even under microscope it is difficult to distinguish between a cryptocrystalline quartz grain or rock fragment. In neighboring area sandstones are reported as greywacke.

Geochemical analyses

The chemical analysis of major and minor element has been performed on XRF. The oxide percentages and presented in the Table 1&2. The Trace elements in parts per million were also determined and presented in Table 1&2. The weight percentages of Major/Minor elements are presented in Table 3.

Discussions

The oxide weight percentages are plotted with silica percentage to observe the variation of oxides in all rocks of study area (Fig. 2A). In the plot, it evident that CaO and MnO are not affected at all, while Na_2O, K_2O and MgO show maximum variation. These oxides are mainly incorporating during the weathering processes where clay minerals are forming at the expense of feldspars. Rb/Sr ratio has been plotted for all rocks in Fig. 2B. In Sandstones Sr is more as compared to Rb, while vice versa is the case in shales.

Na_2O vs K_2O plot exhibits a tendency of increasing K_2O as compared to Na_2O (Fig. 2C). This trend is again inactive of active weathering processes which are active throughout the study area. The formation of muscovite during the digenetic formation of shale can also explain such trend. Same trend has also been observed when sandstones are shown separately (Fig. 3A)

The variation of Fe_2O_3 + MgO Vs Na_2O + K_2O (Fig. 3B) in sandstone exhibits an overall increasing trend due to formation of clay minerals illite and montimorillonite and same trend is also found when plotted for all rocks (Fig. 4A).

Fe_2O_3 + MgO Vs TiO_2 again shows the overall increasing trends when plotted for sandstone (Fig. 4B) and also when visualized for all rocks in the study area (Fig. 4C). This trend can be explained by the presence of sphene.

Further when behavior of (Fe_2O_3 + MgO) is compared with Al_2O_3/SiO_2 in Fig. 5A & B, it is evident that rocks of Middle Bhuban as a whole and Sandstone as a separate unit behave in a similar pattern *i.e.* gradual increasing trend. The increasing trend signifies that alumina is increasing with respect to silica as total iron and magnesia increases. It is in agreement with the observed fact that silica minerals are converting into sheet structure represented by clay minerals and a small amount of muscovite during the diagenetic processes.

The trace elements in parts per million (ppm) are also plotted to study their individual variation in sandstone, shale and siltstones of the study area (Fig. 5C, 6A, 6B & C). In Fig. 5C, it is observed that Ni is showing maximum variation with highest peak of ~70 ppm in shales. Cu follows similar trend and is maximum in shales. Co and Sc are fluctuating but less prominently. They are higher in shale and grey sandstone while low in brown sandstone and siltstone.

Prominent important information is exhibited in Fig. 6A, i.e. a persistently higher amount of (~4 ppm) uranium in the rocks of Middle Bhuban rocks in the study area.[3-5] Further, it was relatively low in shales as compared to sandstones. Thorium also follows a similar trend, but values are more as compared to uranium. Again Pb and Ga are also having higher values where uranium and thorium are higher.

Zn has been observed to be most fluctuating having highest value ~ 250 ppm in shales. sandstones are relatively less sensitive to Zn Variation. Rb and Sr are having sympathetic relation with a higher value of Rb.

Nb and V are constantly maintaining low amount with least variation, while Zr, Ba and Cr are observed to most sensitive to the composition variation in shale and sandstones (Fig. 6). Shale is relatively poorer in all three as compared to sandstones. Ba is having maximum value ~>500 ppm followed by Zr, whereas Cr is maximum in shale.

Diagenetic reaction are those that transform unconsolidated sediments deposited at the earth's surface- sand, mud, carbonate and organic matter- into coherent lithified rock of sandstone, shale, limestone and coal, respectively, as they are buried. The concentration can start early, as is evident in beach rock, rock formed at beaches from cementation of quartz grains by precipitation of calcium carbonate. In the early stage of diagenesis, the cements are typically aragonite or M-calcite, whereas silica cements are common in late (deeper) diagenesis. During diagenesis there is an overall general reduction of porosity and breakdown of any organic material present. Generally, sandstone retains a greater porosity with depth than shale or limestone.[6] Because of their greater solubility in water relative to alumino-silicate phases; limestone can recrystallize to massive units with low porosity but can also develop a secondary porosity due to later fracturing and dissolution. Typically, during diagenesis pores are filled with water, and it is through this water that the diagenetic reaction occurs. This water is present because it is:

1. Trapped at the time of deposition of sediments
2. Derived from fluid transport through the sediments due to a fluid pressure gradient; and/or
3. Produced by mineral dehydration reactions mainly in clays, during diagenesis.

Formation waters typically increase in salin-

Table 1. Chemical analysis of Lower and Middle Bhuban rocks major and minor oxides (in percentage).

Oxides in % tage.	**M/31 3**	**M/37 1A**	**M/42 2A**	**M/47 4A**	**M/62 4B**
Rock Type	**Sandstone**	**Silty Sandstone**	**Brown Sandstone**	**Shale**	**Shale**
Locality	**Chand-Chalt**	**Chawnpui**	**Chawnpui**	**Chawnpui**	**Company**
SiO_2	68.35	64.32	72.56	71.83	59.46
TiO_2	0.69	0.68	0.67	0.61	0.81
Al_2O_3	15.38	16.76	13.72	13.54	20.30
Fe_2O_3	5.65	6.38	3.84	4.62	6.07
FeO	-	-	-	-	-
CaO	0.33	0.31	0.21	0.45	0.27
MgO	1.54	2.00	1.23	1.79	1.98
MnO	0.038	0.152	0.033	0.088	0.039
Na_2O	1.54	1.22	1.15	1.91	1.05
K_2O	2.48	3.10	2.18	2.26	3.66
P_2O_5	0.105	0.100	0.098	0.101	0.103
Total	96.08	95.03	95.69	97.21	93.75
LOI %	4.59	5.1	3.44	3.81	6.27

Trace elements (in ppm)

Element (in ppm)	**M/31 3**	**M/37 1A**	**M/42 2A**	**M/47 4A**	**M/62 4B**
Sc	12	12	8	7	14
Co	14	19	8	15	18
Ni	37	48	32	41	72
Cu	25	29	19	23	38
Zn	80	100	254	74	113
Ga	18.2	20.5	13.4	13.6	27.8
Pb	18.1	27.1	29.8	17.8	29.7
Th	15.8	14.6	14.0	9.8	21.5
Rb	108.3	139.3	78.8	91.3	180.7
U	3.5	3.6	3.5	1.9	2.9
Sr	79	84	65	96	95
Y	34.1	**32.7**	**35.3**	21.9	38.9
Zr	238	212	413	178	230
Nb	15.7	13.9	12.2	11.1	17.3
Ba	373	527	343	337	352
Cr	103	249	197	188	223
V	89	133	87	87	90

Table 2. Chemical analysis of Lower and Middle Bhuban rocks major and minor oxides (in percentage).

Oxides in %	M/64 5 B	M/69 3C	M/28 1	M/53 1B	M/60 3B
Rock Type	**Sandy Shale**	**Silty Shale**	**Silty Shale**	**Gr. Sst.**	**Br. Sst.**
Locality	**Company peng**	**College Veng**	**Chand-chalt**	**Company peng**	**Company peng**
SiO_2	66.02	75.62	74.45	69.14	84.15
TiO_2	0.65	0.70	0.66	0.70	0.58
Al_2O_3	13.57	11.77	13.10	15.23	7.89
Fe_2O_3	4.54	4.79	4.64	5.62	3.33
FeO	-	-	-	-	-
CaO	4.42	0.29	0.38	0.38	0.22
MgO	1.61	0.99	1.56	1.86	0.75
MnO	0.224	0.077	0.033	0.039	0.030
Na_2O	1.46	1.62	1.83	1.54	1.58
K_2O	2.61	2.08	2.09	2.90	1.46
P_2O_5	0.104	0.096	0.106	0.088	0.079
Total	95.21	98.03	98.87	97.50	100.07
LOI %	7.18	4.01	3.47	4.4	2.85
Trace elements (in ppm)					
Element (in ppm)	**M/64 5 B**	**M/69 3C**	**M/28 1**	**M/53 1B**	**M/60 3B**
Sc	11	6	8	10	5
Co	13	13	11	15	9
Ni	33	37	41	51	26
Cu	22	23	23	26	17
Zn	69	66	68	85	46
Ga	14.8	14.6	14.9	19.3	9.2
Pb	19.4	18.3	23.2	25.2	11.5
Th	14.0	16.2	12.7	16.0	11.8
Rb	99.2	91.7	87.8	124.1	62.0
U	2.0	2.2	2.3	4.3	2.9
Sr	109	72	72	85	54
Y	30.1	**32.5**	30.2	30.1	27.5
Zr	255	361	293	238	326
Nb	13.6	15.8	14.2	14.7	12.8
Ba	369	309	409	313	306
Cr	239	247	483	262	254
V	101	68	97	79	77

Table 3. Chemical analysis of Lower and Middle Bhuban rocks major & minor elements (in percentage).

Elements in %	M/31	M/37	M/42	M/47	M/62	M/64	M/69	M/28	M/53	M/60
	3	1A	2A	4A	4B	5 B	3C	1	1B	3B
Rock Type	Sand-stone	Silty Sand-stone	Brown Sand-stone	Shale	Shale	Sandy Shale	Silty Shale	Silty Shale	Gr. Sst.	Br. Sst.
Locality	Chand-Chalt	Chawn-pui	Chawn-pui	Chawn-pui	Com-pany	Compa-ny peng	College Veng	Chand-chalt	Compa-ny peng	Compa-ny peng
Si	31.95363	30.0696	33.9218	33.58053	27.79755	30.86435	35.35235	34.80538	32.32295	39.34013
Ti	0.413655	0.40766	0.401665	0.365695	0.485595	0.389675	0.41965	0.39567	0.41965	0.34771
Al	0.365217	0.359924	0.354631	0.322873	0.428733	7.182601	6.229861	6.93383	8.061239	4.176177
Ca	0.235851	0.221557	0.150087	0.321615	0.192969	3.157206	0.207147	0.271434	0.271434	0.157146
Mg	0.928774	1.2062	0.741813	1.079549	1.194138	0.97083	0.59697	0.94068	1.12158	0.45225
Mn	0.024012	0.096049	0.020853	0.055607	0.024644	0.173488	0.059637	0.025559	0.030206	0.023235
Na	1.142526	0.905118	0.853185	1.417029	0.778995	1.083174	1.201878	1.357677	1.142526	1.172202
K	2.058896	2.57362	1.809836	1.876252	3.038532	2.166561	1.726608	1.734909	2.40729	1.211946
P	0.045822	0.04364	0.042767	0.044076	0.044949	0.045396	0.041904	0.046269	0.038412	0.034484

ity (to values greater than that of seawater) at depth in sedimentary basins. This increased salinity occurs because of dissolution of evaporite minerals in shales and salt layers. Also, charged clay mineral surfaces act to retain salts while allowing water molecules to escape upward. This then increases the salinity of the residual water. In general, relative to seawater, K in formation waters is lower and Ca higher because of reactions with minerals during burial.

Consider a marine mud. When it is deposited it can have a porosity of up to 80%. Two possibilities exist depending on the extent and makeup of its organic matter:

(1) Organic matter reacts with oxygenated seawater so seawater in the pores and above the sediment- water interface becomes anoxic, or

(2) Organic matter in the mud is completely oxidized by diffusion of oxygen from the overlying water mass, and formation water remains oxidized.[7]

In this latter case, organic matter is oxidized to produce CH_4 and /or CO_2, which is incorporated into the pore water. Reactions of clays with K^+ reduces the potassium concentration in the pore water and increases the illite content at the expense of other minerals in the clay assemblage. Bioturbation can cause many physical changes in the flocculated clay fabric accumulating at the seawater-sediment interface. Just below the first few centimeters of clay, the SO_4^{2-} from seawater in the pore fluid is reduced with the aid of bacteria and H_2S by the reaction

$$2H^+ + 2CH_2O \textit{ (Organic matter)} + \rightarrow 2CO_2 + H_2S + 2H_2O \quad (1)$$

This reaction can continue to a number of meters depths, but the limited organic matter is usually exhausted in an organic free mud. In anoxic waters the reaction can start in the water column above the top clay layer. In this case the reaction is typically limited by the amount of seawater derived SO_4^{2-} available and the mud can become organic rich. [8]

The H_2S produced in normal marine environments by reaction above, escapes into the overlying seawater or becomes oxidized in the local oxidizing environment to elemental S by a reaction as follows:

$$1H_2S + O_2 \rightarrow 2S + 2H_2O \quad (2)$$

Alternatively, in anoxic waters it reacts with the Fe^{2+} that is present in solution from the clays and precipitates amorphous $FeS*nH_2O$ as given by following reaction:

$$Fe^{2+} + H_2S + n\ H_2O \rightarrow FeS*nH_2O + 2H^+ \quad (3)$$

The S produced by reaction (2) and the $FeS*nH_2O$ produced by reaction (3) typically react during early diagenesis to produce pyrite, FeS_2. Fermentation of the organic matter also proceeds during early diagenesis down to a depth of about 1 km.

Much of the interstitial pore water is muddy sediments is expelled during compaction, but sediments at 1 km depth can contain approximately 30% H_2O, much of this is in interlayer of clays and absorbed to clay surfaces. The composition of typical shale in terms of Al, Si and alkali + earth elements, giving its concentration of illite + chlorite + Si phases. Clays and silicate phases (*e.g.,* quartz) dominate shales, but carbonate phases (calcite and dolomite) are often also present. Total organic matter in most shale is less than 1%, however, organic-rich shales, called black shales, can have greater than 15% total organic carbon.

Conclusions

In normal marine environments, organic matter is oxidized by bacteria to CO_2 in the water column or at the sediment-water interface; seawater sulphate trapped in the sediments is reduced to H_2S, which typically escapes upward. In anoxic marine environments, however, organic matter can accumulate with seawater sulphate being reduced to amorphous Fes $*nH_2O$. This transformed during diagenesis to pyrite.

During diagenesis of clay material, any calcite present is generally lost during an early stage by dissolution in under saturated pore solutions and removal by fluid advection during sediment compaction. Smectite- group minerals in the clay fraction are transformed to illite. With later diagenesis when the temperature reaches 300°C, illite is transformed to sericite. Further alteration at high temperatures to muscovite is generally considered a metamorphic reaction. At the present time the sedimentary marine carbonate is about two thirds, aragonite and one third Mg-calcite, with calcite dominant during clay deposition. Dolomite appears to form during diagenesis by solutions that have a higher Mg/Ca ratio than present seawater.

The present study opens several avenues to for further research in the area around Aizawl. Every rock unit except grey sandstone is more or less dominated by shale and shale is too fine grained to be studied under microscope. Research in order to explore mineralogical composition is already in progress through infra-red spectroscopy and X-ray diffraction. The probability of economic mineral deposits in the study area could also not be denied, rather some indications are favoring for presence of uranium in these rocks on the same line as it has been reported from Meghalaya and also from Potwar, Pakistan (in Siwaliks).

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