



Geochemical study on Upper Bhuban shale in Aizawl district of Mizoram, India: an implication of chemical weathering, geochemical classification, tectonic setting and provenance

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ABSTRACT

Shales from the Upper Bhuban formation in the Muthi, Aizawl district, was analysed for major, trace and rare earth elements. These elements are competent alternative for determining lithological composition, geochemical classification, provenance and tectonic setting of the basin. It shows high content of SiO_2 varies from 62.85 wt% to 73.22 wt% and a small variation in Al_2O_3 (14.22–19.61 wt%). The average of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio vary from 0.15 to 0.22 with the average value of 0.18 which are close to the upper limit of the clay mineral range indicated that the illite is the dominant clay mineral in these shales. The value of chemical index alteration in the Muthi shale is high (75.10 to 81.77) indicating high intensity of chemical weathering in the source areas. The Muthi shales are classified as litharenite. Th/Sc, Th/Co, Th/Cr, Cr/Th, and La/Sc ratios of shales from this study are compared with those of sediments derived from felsic and basic rocks (fine fraction) as well as to upper continental crust (UCC) and PAAS values. This comparison suggested that these ratios are within the range of felsic rocks. Furthermore, it shows slightly LREE enriched and flat HREE patterns with negative Eu anomalies 0.65 (average). The $(\text{Gd}/\text{Yb})_N$ ratio 2.47 (average) of Muthi shale is higher than 2 which suggested that these shales were derived from the large HREE depleted source rocks.

Key words: Chemical Index Alteration; geochemical classification; provenance; tectonic setting; Upper Bhuban shale in Aizawl District.

INTRODUCTION

No systematic geochemical work has been carried out in the Upper Bhuban shales in Ai-

zawl district of Mizoram. This is the first and newly reported from this area. It is in this background that a detail study on the geochemical signatures of shale in the Upper Bhuban unit of Bhuban Formation exposed at Muthi Village in the Aizawl district of Mizoram has been selected. However, geochemical studied reveal that intense chemical weathering and active con-

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tinental margin for the sandstone of the Upper Bhuban unit of the Muthi section in Mizoram.¹¹

Geochemical data have been widely used as an indication of provenance of sedimentary formations, tectonic and climatic conditions in which they were deposited. Thus, the geochemical composition is a guide to the source rocks in the provenance and the tectonic setting of the depositional basin.^{2-4,15}

Many recent studies have shown a close relationship between geochemical compositions of sedimentary rocks and their provenance characteristics, tectonic environment and palaeoweathering conditions have been observed by many workers. Alteration of minerals due to chemical weathering mainly depends on the intensity and the duration of weathering. The dominant proc-

ess during weathering of the upper crust is the degradation of feldspar and formation of clay minerals. The degradation of feldspar, which is very sensitive to chemical weathering, increases the mobility of many elements through clays.^{5,12,16} During weathering, calcium, sodium and potassium are removed from feldspar.¹³ Thus, the abundance of easily removable elements serves as an index of chemical weathering.

Location and geology of the study area

Muthi village (23° 46' 20" N & 92° 45' 50" E, in the Survey of India Topo Sheet No. 84A/13), is located nearly 15 km northeast of Aizawl city in Mizoram (Fig. 1). Mizoram geologically is a

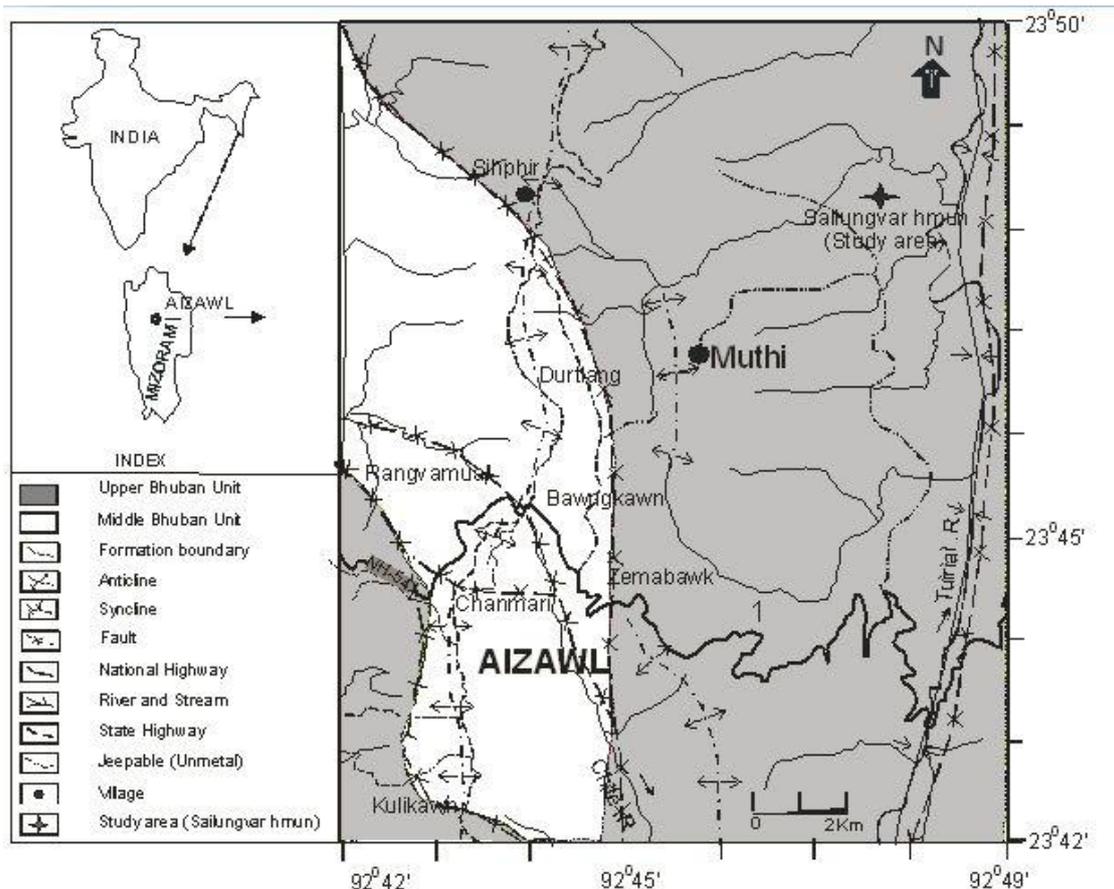


Figure 1. Location map of the study area, Muthi, Aizawl district.

part of Tripura–Mizoram depositional basin and it has been considered as the southern extension of Surma Valley. The entire sedimentary column of the area is a repetitive succession of arenaceous and argillaceous rocks. This succession form N-E trending longitudinally plunging anticlines and synclines affected by numerous faults and thrusts. The generally N-S trending beds dip at 20° to 50° either eastward or westward. The exposed sequences comprise sandstones, siltstones, and shales, mudstones with pockets of shell limestones, calcareous sandstones and intraformational conglomerates.^{8,9}

The sediments in Mizoram have been grouped under the Surma Group and the Tipam Group. The Surma Group is divided into the lower Bhuban Formation and the upper Bokabil Formation. The Bhuban Formation is further subdivided into the Lower, Middle and Upper Bhuban units with conformable contacts. The rock succession in the vicinity of Muthi village constitutes a part of the Upper Bhuban unit of the Bhuban Formation, Surma Group (Lower to Middle Miocene). This unit is represented by a repetitive succession of shales, shell limestone, siltstones, sandstones and their admixture in various proportions and constitutes an eastern limb of the Aizawl anticline. The shales are grey to dark grey and brownish in colour, thinly laminated, crumpled and are splintery in nature. Samples from the exposed shale were collected for geochemical study.

MATERIALS AND METHODS

Samples were collected from the outcrop sections. The collected samples were washed thoroughly in distilled water to remove contamination. Representative rock samples were powdered and processed for their analyses for major oxide, trace element and rare earth element. Major oxides were analyzed by X-ray fluorescence (XRF) Philips PW 2440 microprocessor controlled. Pressed pellets were prepared by using collapsible aluminium cups. These cups are filled with boric acid and about 1 g of the finely powdered rock sample is put on the top of the

boric acid and pressed under a hydraulic press at 20 tons pressure. The samples were ready for analysis of major oxides. Trace elements and rare earth elements were measured on inductively coupled plasma-mass spectrometry (ICP-MS) Perkin Elmer SCIEX Model ELAN[®] DRC 11 (Toronto, Canada) instrument. 0.05 g were digested with 4 ml HNO₃ and 1 ml of HClO₄ for 24 hours in a tightly closed Teflon vessel on a hot plate at temperature <200°C, and then digested with a mixture of 4ml of HF and 1 ml of HClO₄. Later, the solution was evaporated to dryness, and extracted with 10 ml of 1% HNO₃. The digested samples were ready for determination of trace elements and rare earth elements. The analytical work of XRF and ICP-MS has done at National Geophysical Research Institute (NGRI), Hyderabad, India.

RESULTS

Major elements

The result of major oxides and some of the elemental ratios are given in Table 1. The shale in the Muthi show high content of SiO₂ varies from 62.85 to 73.22 wt% the shales show a small variation in Al₂O₃ (14.22-19.61 wt%). The Al₂O₃/TiO₂ ratio ranges from 18.05 to 21.91 with average value of 19.63.

Trace elements

The results of trace elements and elemental ratios in the Muthi shales are presented in Table 2. Trace elements of the shales in the Muthi were normalized using Post Archean American Shale (PAAS) values¹⁶ and are plotted in a multi element diagram presented in Fig. 2. Ni, V, Sr, Cr, Co, Rb, Zr show a depletion in PAAS normalized patterns of trace elements whereas Hf, Pb, Th, U contents are enriched with respect to those of PAAS.

The shales are enriched in Sr (49.37 to 143.82 ppm), the enrichment of Sr may be due to the association of calcite minerals. The conce-

Table 1. Concentration of major oxides (in wt %) and some of the elemental ratios in the Muthi Shales.

	MK-R-9	MK-R-10	MK-R-12	MK-R-13	MT-BLR-2	MT-BLR-3	MT-BLR-17	MT-BLR-18	MT-BLR-19	MT-BLR-20
SiO ₂	65.52	64.98	73.22	66.43	69.13	67.79	65.71	70.95	62.85	67.98
TiO ₂	0.79	0.84	0.76	0.93	0.84	0.83	0.98	0.82	1.03	0.87
Al ₂ O ₃	17.31	17.91	14.22	17.65	16.41	16.24	17.69	16.33	19.61	16.75
Fe ₂ O ₃	6.63	7.12	4.75	6.89	6.54	6.49	7.53	6.37	9.12	7.53
CaO	1.07	0.48	0.6	0.65	0.79	0.87	0.86	0.46	0.57	0.63
MgO	2.58	2.41	1.67	2.24	0.75	2.26	1.26	0.48	1.08	0.64
MnO	0.08	0.05	0.16	0.06	0.07	0.07	0.08	0.09	0.07	0.16
Na ₂ O	0.88	0.91	1.05	0.87	0.91	0.92	0.73	0.67	0.63	0.90
K ₂ O	3.79	3.95	2.44	2.93	2.93	2.90	3.16	2.51	3.47	2.83
P ₂ O ₅	0.09	0.11	0.11	0.15	0.14	0.14	0.10	0.12	0.13	0.13
Sum	98.72	98.77	98.97	98.81	98.51	98.51	98.10	98.8	98.56	98.42
CIA	75.1	77.03	77.66	79.86	77.99	77.59	78.83	81.77	80.76	79.34
K ₂ O/Al ₂ O ₃	0.22	0.22	0.17	0.17	0.18	0.18	0.18	0.15	0.18	0.17
Al ₂ O ₃ /TiO ₂	21.91	21.32	18.71	18.98	19.54	19.57	18.05	19.91	19.04	19.25

CIA = Chemical index alteration

tration of Barium varies from 299.31 to 714.49 ppm. Barium enrichment in sedimentary rocks can be considered as an indicator of detrital flux. The shales were deposited in shallow marine environment and hence may be enriched by Barium.

Rare earth elements

The concentration of rare earth elements are given in Table 3. It is observed that \sum REE content show a large variation (145.48 to 03.48 ppm). The chondrite-normalized REE of Muthi shales is shown in Fig. 3 and the shales shows LREE enriched and flat HREE pattern with negative Eu anomaly.

The elemental ratios of REE in the Muthi shales are shown in Table 3. It is also observed that the Muthi shales show less fractionation of REE ($La/Yb = 6.78$ to 14.48) than the PAAS [$(La/Yb)_{PAAS} = 9.5$, Taylor and McLennan, 1985] except in the three samples (MK-R-9, MT-BLR-2, MT-BLR-17).

DISCUSSION

Geochemical classification of the Muthi shales

Many Researchers have proposed the geochemical classification diagrams for terrigenous sedimentary rocks using major elements. Using the geochemical classification diagram of Herron¹⁰ the Muthi shales are classified as litharenite. This diagram is shown in Fig. 4.

Palaeoweathering

The influence of weathering on sedimentary rocks can be calculated by using chemical index of alteration (CIA) Nesbitt and Young.¹³ The CIA values which indicate the degree of weathering of source rocks and are determined by the equation:-

$$CIA = \frac{[Al_2O_3 (Al_2O_3 + CaO sil. + Na_2O + K_2O)] \times 100}{[Al_2O_3 (Al_2O_3 + CaO sil. + Na_2O + K_2O)] \times 100}$$

The value of CIA is shown in Table 2. Hence

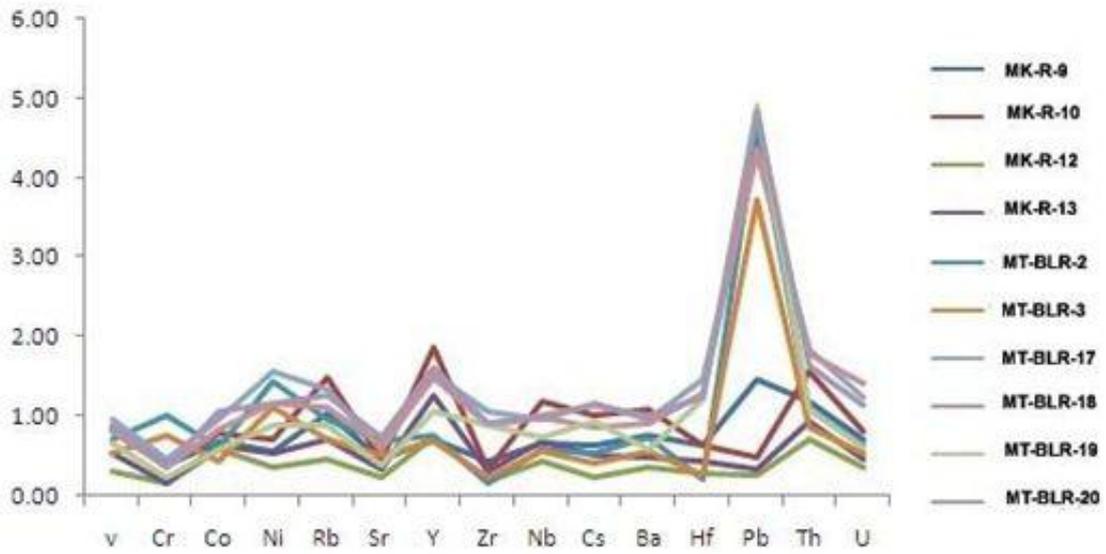


Figure 2. Multi-element of trace elements in shale.

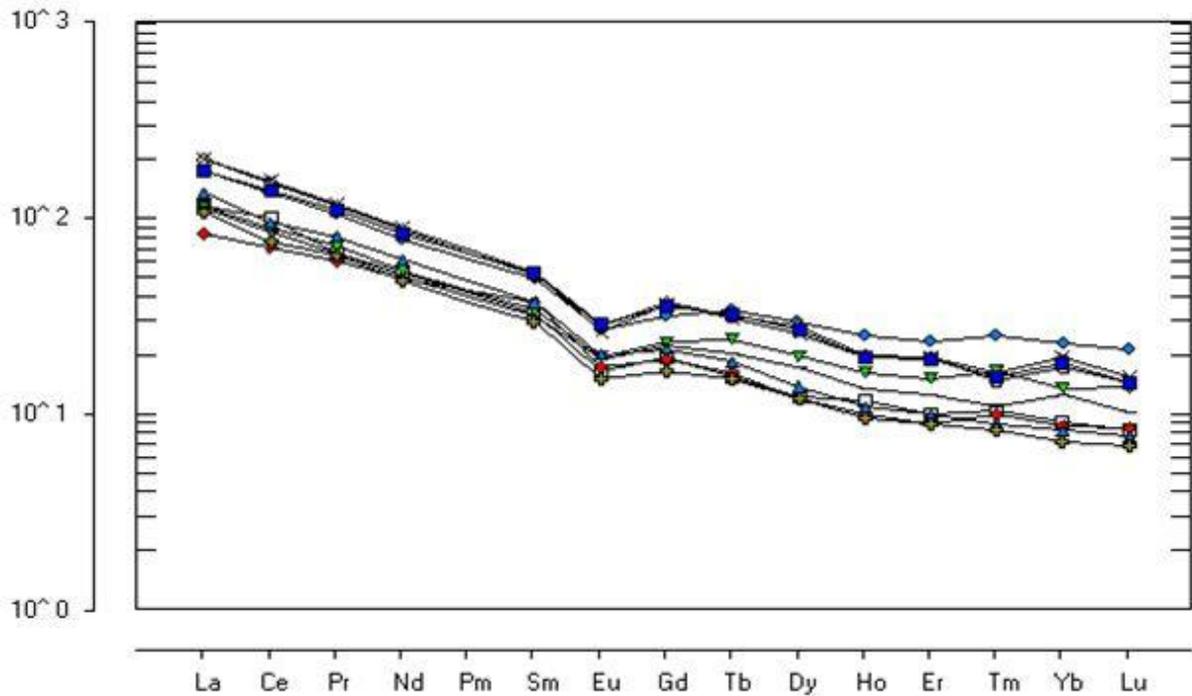


Figure 3. The concentration of REE in the Muthi shales normalized by COND-Boynton 1984.

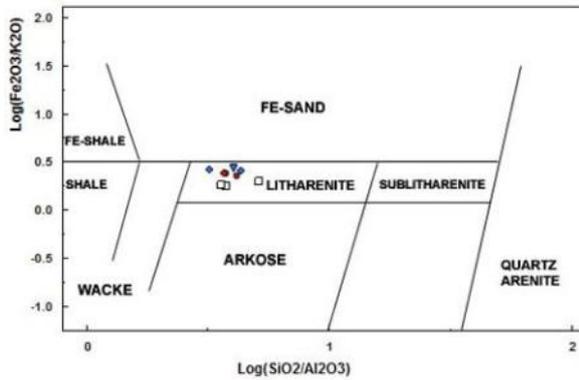


Figure 4. Plot for geochemical classification of Upper Bhuvan shale in Muthi after Herron, (1988).

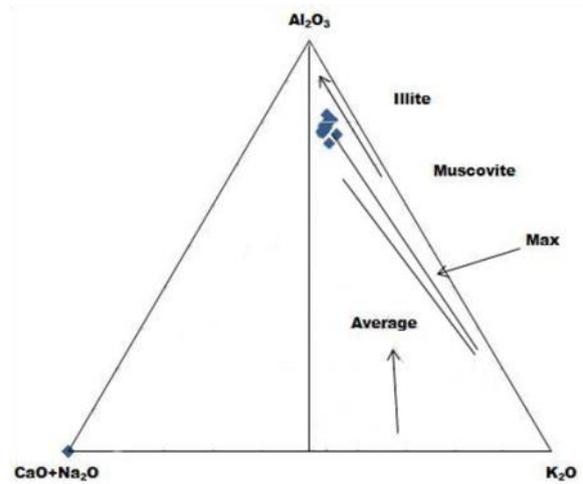


Figure 5. The CaO+ Na₂O-Al₂O₃-K₂O diagram of Nesbitt and Young (1984, 1989) showing the weathering trend for maximum and average. Plot for Muthi shales samples where mole fraction Al₂O₃, CaO (silicate fraction only), Na₂O and K₂O. Most shale samples plot around the field of average shale illite, suggesting a maximum weathering history for the provenance.

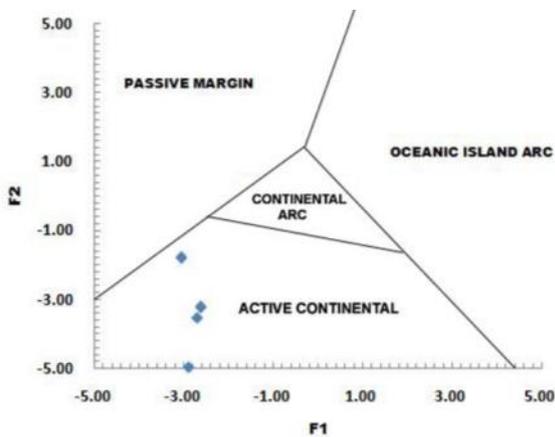


Figure 6. Diagram for discrimination function analysis of Muthi shales after Bhatia (1983). The different tectonic fields are Oceanic Island Arc, Continental Island Arc, Active Continental Margin and Passive Margin.

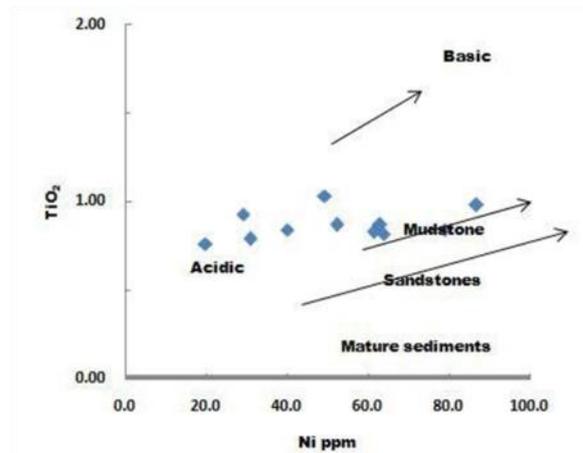


Figure 7. TiO₂ versus Ni bivariate plot for shale samples from the Muthi shales (fields after Floyd et al., 1989).

Table 2. Concentration of trace elements (in ppm) and some of the elemental ratios in the Muthi Shales.

Analyte	MK-R-9	MK-R-10	MK-R-12	MK-R-13	MT-BLR-2	MT-BLR-3	MT-BLR-17	MT-BLR-18	MT-BLR-19	MT-BLR-20
Sc	15.525	17.978	6.056	10.081	16.85	13.08	22.05	19.08	15.95	20.88
V	121.737	130.823	48.337	80.867	105.90	78.92	145.27	119.21	101.58	133.00
Cr	42.077	47.788	18.677	17.381	112.31	83.77	50.92	38.48	26.40	38.39
Co	15.622	18.535	13.319	14.434	13.76	9.84	22.35	18.77	13.80	24.34
Ni	30.639	39.765	19.657	28.949	78.63	61.12	86.66	63.69	49.13	62.77
Cu	26.64	39.047	12.655	22.862	70.09	31.81	47.76	56.94	25.96	58.37
Zn	103.84	31.22	10.25	21.9	101.19	53.71	76.42	72.39	46.11	64.04
Ga	19.12	27.82	9.17	14.86	21.20	16.04	31.25	24.68	21.17	28.48
Rb	165.93	241.40	74.33	111.53	152.93	110.76	213.41	174.81	143.01	199.79
Sr	89.793	95.031	49.371	68.424	136.21	97.52	115.81	126.65	75.65	143.82
Y	19.47	50.55	19.68	33.83	20.77	17.92	41.35	39.91	28.95	43.23
Zr	91.658	72.854	39.922	62.507	33.58	46.63	225.23	181.86	186.70	188.43
Nb	12.784	22.783	8.089	12.713	10.97	10.53	18.34	18.51	14.04	19.19
Cs	9.39	15.369	3.768	7.416	8.17	5.87	17.36	12.59	14.12	17.00
Ba	489.20	714.49	229.31	320.18	480.92	359.13	625.80	589.03	385.33	652.30
Hf	3.21	3.22	1.43	2.1	1.02	1.28	7.40	6.41	6.06	6.11
Ta	24.53	1.644	0.537	0.825	0.77	0.80	0.06	1.37	0.95	1.33
Pb	29.39	10.18	5.54	6.47	92.35	74.58	86.61	86.81	97.86	96.40
Th	17.31	22.99	10.30	13.63	15.94	12.49	26.81	25.87	16.06	23.98
U	2.19	2.57	1.11	1.43	1.99	1.63	3.84	4.37	1.88	3.46
La/Sc	2.36	3.08	4.37	3.60	2.51	2.62	2.84	3.29	2.22	2.67
Th/Sc	1.12	1.28	1.70	1.35	0.95	0.96	1.22	1.36	1.01	1.15
La/Th	2.11	2.41	2.57	2.66	2.66	2.74	2.34	2.42	2.21	2.32
Cr/Ni	1.37	1.20	0.95	0.60	1.43	1.37	0.59	0.60	0.54	0.61
Cr/Th	2.43	2.08	1.81	1.27	7.05	6.71	1.90	1.49	1.64	1.60
Th/Co	1.11	1.24	0.77	0.94	1.16	1.27	1.20	1.38	1.16	0.99
U/Th	0.13	0.11	0.11	0.11	0.13	0.13	0.14	0.17	0.12	0.14
V/Cr	2.89	2.74	2.59	4.65	0.94	0.94	2.85	3.10	3.85	3.46
Ni/Co	1.96	2.15	1.48	2.01	5.71	6.21	3.88	3.39	3.56	2.58
Cu/Zn	0.26	1.25	1.23	1.04	0.69	0.59	0.63	0.79	0.56	0.91

Table 3. Concentration of rare earth element (in ppm) and some of the elemental ratios in the Muthi Shales.

Analyte	MK-R-9	MK-R-10	MK-R-12	MK-R-13	MT-BLR-2	MT-BLR-3	MT-BLR-17	MT-BLR-18	MT-BLR-19	MT-BLR-20
La	36.57	55.38	26.44	36.28	42.35	34.28	62.73	62.68	35.44	55.73
Ce	81.79	111.09	58.10	73.82	78.46	62.82	125.43	128.04	69.95	113.52
Pr	8.29	13.13	7.48	8.98	9.99	7.98	14.39	14.72	8.21	13.57
Nd	32.46	48.11	29.84	33.29	37.59	29.50	53.42	54.51	30.86	50.87
Sm	6.49	9.68	7.38	6.72	7.43	5.84	10.14	10.54	6.30	10.39
Eu	1.23	2.01	1.30	1.48	1.51	1.14	2.12	1.99	1.42	2.16
Gd	5.13	8.47	5.07	6.14	5.72	4.42	9.77	9.66	5.93	9.31
Tb	0.75	1.65	0.78	1.18	0.89	0.74	1.55	1.50	1.00	1.56
Dy	4.03	9.63	3.97	6.54	4.55	3.93	9.21	8.52	5.69	8.82
Ho	0.86	1.84	0.73	1.21	0.80	0.69	1.48	1.43	0.98	1.42
Er	2.15	5.00	1.92	3.28	2.14	1.92	4.16	4.22	2.70	4.06
Tm	0.35	0.83	0.33	0.55	0.30	0.27	0.49	0.54	0.37	0.52
Yb	1.95	4.95	1.87	2.89	1.77	1.57	3.74	4.21	2.70	3.88
Lu	0.28	0.70	0.28	0.45	0.26	0.23	0.47	0.51	0.34	0.47
ΣREE	182.30	272.48	145.48	182.80	193.75	155.34	299.10	303.08	171.88	276.27
LREE	165.60	237.39	129.24	159.09	175.82	140.42	266.11	270.49	150.75	244.08
HREE	16.71	35.09	16.25	23.71	17.93	14.92	32.99	32.60	21.13	32.20
LREE/HREE	9.91	6.77	7.95	6.71	9.81	9.41	8.07	8.30	7.14	7.58
Eu/Eu*	0.63	0.66	0.61	0.69	0.68	0.66	0.64	0.59	0.70	0.66
(La/Yb) _N	11.36	6.78	8.59	7.60	14.48	13.26	10.18	9.02	7.96	8.71
La/Sm	5.64	5.72	3.58	5.40	5.70	5.87	6.19	5.95	5.63	5.37
(Gd/Yb) _N	2.63	1.71	2.72	2.12	3.23	2.82	2.61	2.29	2.20	2.40

LREE = Light rare earth element, HREE = Heavy rare earth element

the value of CIA in the Muthi shale is high (75.10 to 81.77).

In the ternary diagram CaO+ Na₂O-Al₂O₃-K₂O all the samples fall in maximum weathering process and illite may be the most probably clay mineral. The diagram is depicted in Fig. 5.

Tectonic setting

In the tectonic discrimination diagram after Bhatia and Crook,^{2,3} most of the Muthi shale

falls into active continental margin (ACM) Fig. 6.

Provenance

The geochemical signatures of clastic sediments have been used to find out the provenance characteristics.^{1,5-6,16} Al₂O₃/TiO₂ ratios of most clastic rocks are essentially used to infer the source rock compositions, because the Al₂O₃/TiO₂ ratio increases from 3 to 8 for mafic

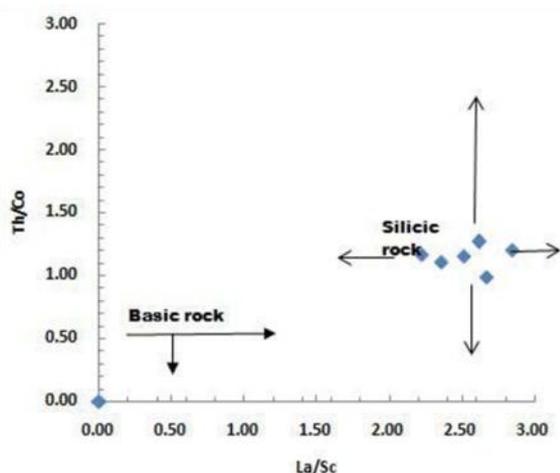


Figure 8. Th/Co versus La/Sc diagram for shale samples from the Muthi shales after Cullers, 2002.

igneous rocks, from 8 to 21 for intermediate rocks, and from 21 to 70 for felsic igneous rocks. It is observed that the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio in the Upper Bhuban shale of Muthi ranges from 18.05 to 21.91 with average value of 19.63. Titanium is mainly concentrated in phyllosilicates and is relatively immobile compared to other elements during various sedimentary processes and may strongly represent the source rocks. The content of TiO_2 in the Muthi splintery shales is low (0.76 to 1.03 wt%) with the average value of 0.87 which suggests evolved of felsic material in the source rocks. The average of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio varies from 0.15 to 0.22 with the average value of 0.18. In most of the samples in the upper Bhuban shale, the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios are close to the upper limit of the clay mineral range, indicated that the illite is the dominant clay mineral in these shales. This interpretation is supported by $\text{CaO} + \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{K}_2\text{O}$.

The concentration of P_2O_5 ranges from 0.09 to 0.15 wt% with average value of 0.12. Most of the samples in the upper Bhuban shale of Muthi have low content of P_2O_5 which is varies from 0.09 to 0.15 wt% with the average value of 0.12. The depletion of P_2O_5 may be explained by the lesser amount of accessory phases such as apatite and monazite.

Thus, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of this study suggests that intermediate to felsic granitoid rocks must be the probable source rocks for the shales in the upper Bhuban shale of Muthi. This interpretation is further supported by the TiO_2 vs. Ni bivariate plot Fig. 7⁷ and Th/Co vs La/Sc after Cullers 2002 in Fig. 8 which also indicate that these shales were mainly derived from felsic source rocks.

The abundance of Cr and Ni in siliclastic sediments are considered as a useful indicator in provenance studies. The content of Chromium varies from 17.38 to 112.31 ppm with average value of 47.61 and Ni concentrations ranges from 19.65 to 86.66 ppm and the average value is 52.10. The Cr/Ni ratios are low (~ 0.54 – 1.43) in splintery shales of upper Bhuban unit of Bhuban formation in Aizawl District. However, the Th/Cr ratio is (~ 0.14 – 0.67) with average value of 0.5 which is higher than in PAAS (Th/Cr = 0.13).¹⁶ The elemental ratios of the trace elements such as La/Sc, Th/Sc, Th/Co, and Th/Cr are significantly different in felsic and basic rocks and may allow constraints on the average provenance composition.

Th/Sc, Th/Co, Th/Cr, Cr/Th, and La/Sc ratios of shales from this study are compared with those of sediments derived from felsic and basic rocks (fine fraction) as well as to Upper Continental Crust (UCC) and Post Archean American Shale (PAAS) values. This comparison also suggests that these ratios are within the range of felsic rocks. In addition, the La/Th and Th/Sc ratios are fairly constant in sedimentary rocks (2.4 and 0.9, respectively). The La/Th and Th/Sc ratios of the shales in the present study are more or less close to PAAS,¹⁶ which suggest a felsic nature of the source rocks. Furthermore, the Th/Co vs. La/Sc plot also suggests that the Muthi shales were derived from felsic source rocks.

The Muthi shales show high LREE/HREE ratios (6.77 to 9.91) and negative europium anomaly (avg. 0.65), which suggest that these sedimentary rocks were mainly derived from the felsic source rocks. The $(\text{Gd}/\text{Yb})_N$ ratio varies from 1.71 to 3.23 with average value 2.47 of

Muthi shale is higher than 2, which suggest that these shales were derived from the large HREE depleted source rocks. The $(Gd/Yb)_N$ ratio also document the nature of source rocks and the composition of the continental crust.¹⁶

CONCLUSION

The high average values of chemical index alteration reveal high intensity of chemical weathering in the source area. Geochemically, the Upper Bhuban shale in Muthi is classified as litharenite. Tectonic discrimination diagrams indicated that an active continental margin. The chemical composition of K_2O , Al_2O_3 , Na_2O and CaO indicated that the most dominant clay mineral in the Upper Bhuban shale is illite. Furthermore, the LREE/HREE with negative europium and $(Gd/Yb)_N$ reveal that the shale were derived from highly depleted felsic rocks and the source rock of the sediment was intermediate to felsic granitoid rocks.

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