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Geochemistry of Shales of Barail group Occurring in and around Mandardisa, North Cachar Hills, Assam; India: Its Implications

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Abstract

Geochemical studies of shale samples from Barail Group occurring in and around Mandardisa, North Cachar hills, Assam have been carried out The major, minor and trace elements present in the shale samples show significant results in determining provenance and source rock composition, tectonic setting, palaeoweathering, chemical maturity and palaeoclimate. The different bivariate plots suggest their derivation from felsic source rock of granitic dominated upper continental crust. In the CaO-K2O-Na2O ternary plot of the shale samples fall in active continental margin. The CIA values indicate moderate to high degree of chemical weathering. The shales of the studied area show increasing chemical maturity under humid climatic condition.

Keywords: Geochemistry, Shales, Mandardisa, North Cachar Hills, Assam.

Introduction

Shales are considered to represent the average crustal composition and the provenance in a much better way than sandstones (McCulloch and Wasserburg, 1978), because of the homogeneous nature and post-depositional low permeability. Geochemistries of shales are best suited for provenance studies. Major and trace element geochemistry of shales has been proved useful in provenance and palaeoenvironment studies of many sedimentary basins (eg., Cullers, 2000; Bhat and Ghosh, 2001; Lee, 2002; Hofmann et. al., 2003). Immobile elements such as Al, Ti and Zr are particularly helpful for estimating the nature of source rock (Taylor and McLennan, 1985).

Tectonic setting of sedimentary basins is based on relative variation of major elements within shales (Roser and Korsch, 1986; Zhang et. al., 1998; and many others). Major element analysis is equally applicable in understanding paleoweathering and paleotectonic setting (Taylor and McLennan, 1985; Hayashi et. al., 1997; Nesbitt, 2003). Hence many studies have used the major, minor and trace elements geochemistry as a tool to characterize source rock weathering, provenance and tectonic setting from the terrigenous sediments of India (Das, et. al., 2006; Dey et. al., 2009; Nagarajan et. al., 2007; Ranjan and Banerjee, 2009)

The relative distribution of the immobile elements that differ in concentration in felsic and basic rocks, has been used to infer the relative contribution of felsic and basic sources in shales from different tectonic environments (Wronkijewicz and Condie, 1989). It has been observed that the ration of Ti and Al can effectively be used as an index of provenance, since they behave as immobile phases because of their low solubility and similar behaviour during weathering (McLennan et. al., 1979).

Geology of the Area

The Tertiary sedimentary rocks are well exposed in and around Mandardisa of North Cachar Hills, Assam. The area is covered by the survey of India toposheet no. 83G/2 and lies between the longitude 93°05/- 93°10/E and latitude 25°40/- 25°45/N. (Fig.1)

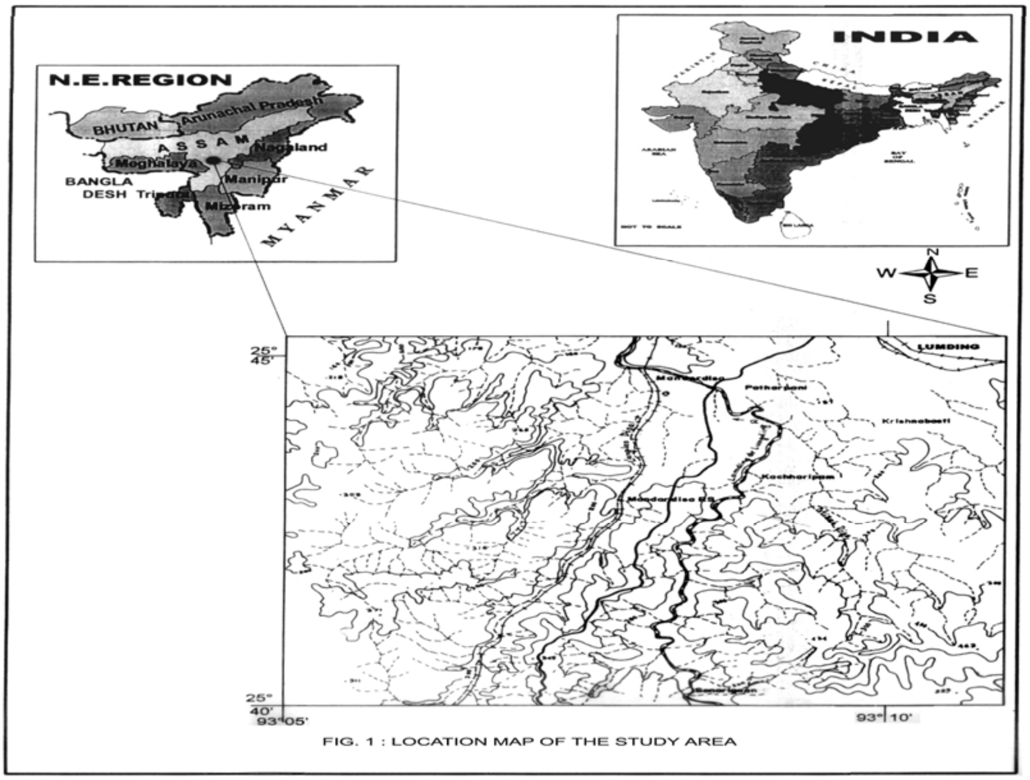
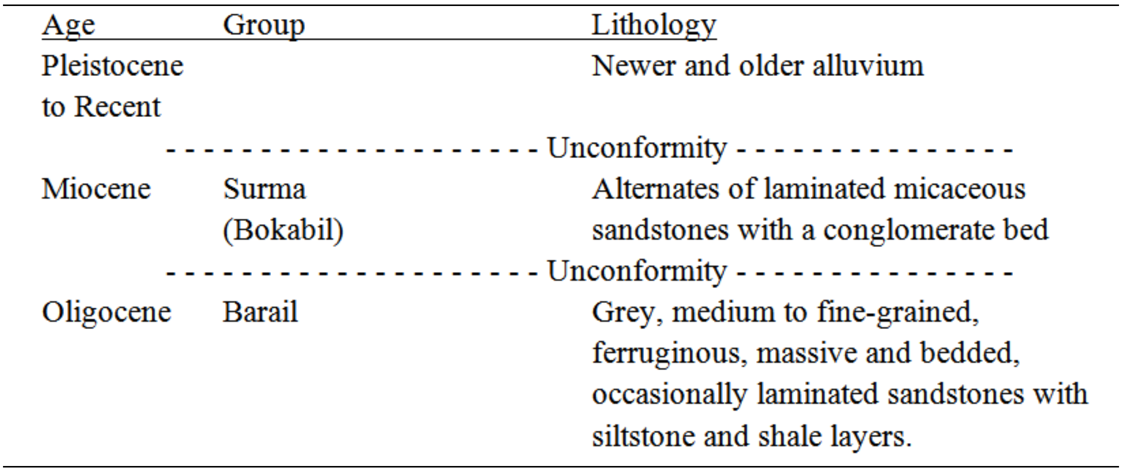


Figure 1: location map of the study area.

The sedimentary rocks exposed in the area dominantly composed of sandstones with siltstone and shale which represent the Barail Group of rocks. As the area is geologically virgin, no detail lithology of the rocks is found elsewhere. However, after field observations, the following stratigraphic succession has been made along with salient lithological characters.

Stratigraphic succession of the study area (Table - 1)



Age	Group	Lithology
Pleistocene to Recent		Newer and older alluvium
- - - - - - - - - - - - - - - - - - - -	Unconformity	- - - - - - - - - - - - - - -
Miocene	Surma (Bokabil)	Alternates of laminated micaceous sandstones with a conglomerate bed
- - - - - - - - - - - - - - - - - - - -	Unconformity	- - - - - - - - - - - - - - -
Oligocene	Barail	Grey, medium to fine-grained, ferruginous, massive and bedded, occasionally laminated sandstones with siltstone and shale layers.

Geochemical Analysis

Geochemical analysis of shales from Barail Group mainly includes major and minor element oxides and trace elements.

Analytical Note

16 representative shale samples were analysed for major, minor and trace elements. The shale samples were analysed in the department of Instrumentation and USIC by XRFS method. The major, minor elements (oxides) and trace elements have been studied for chemical analysis.

Major and minor elements oxides

The percentage of major and minor element oxides of shale samples of studied area includes SiO2, Al2O3, Fe2O3, Na2O, K2O, Cao, MgO, TiO2, MnO and P2O5. These are shown in Table 1. These oxides are used for determination of source rock composition, tectonic setting, palaeoweathering environment, chemical maturity and palaeoclimate.

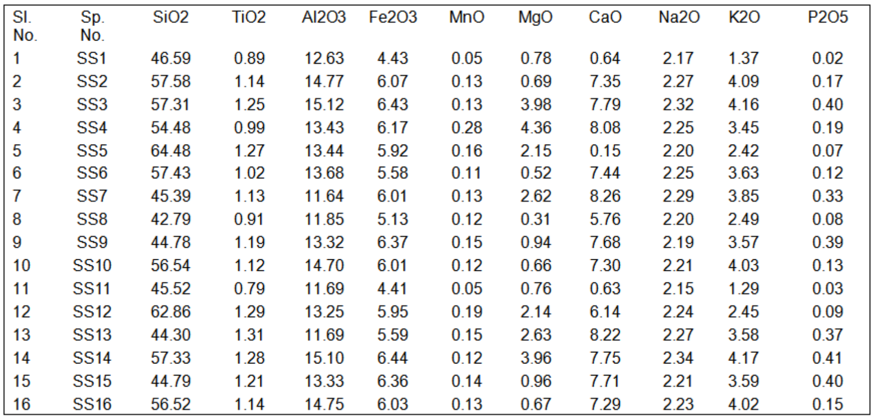
Trace elements

The trace element concentrations in sediments result from the influence of provenance, weathering, diagenesis etc. Trace elements are important for various applications. Certain trace elements because of their relatively low mobility have been used to distinguish depositional environment, source rock composition and tectonic setting. The different trace elements present in shale samples are shown in Table 2.

Immobile trace elements of Cr, Ni, V and Sc concentration suggest the felsic source rock. The presence of V and Cr indicates an oxic depositional condition (Jones and Manning, 1994). The sufficient amount of Co, Cr, Ni and Zn in the shales suggests that these elements were derived from ferromagnesian minerals of metamorphic rocks (Raghuwanshi, 2007).

The overall trace elements present in the shale samples of studied area indicate unstable tectonic setting.

Table 2: XRFS Chemical analysis data of major and minor element oxides. (All values in wt%)



Sl. No.	Sp. No.	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5
1	SS1	46.59	0.89	12.63	4.43	0.05	0.78	0.64	2.17	1.37	0.02
2	SS2	57.58	1.14	14.77	6.07	0.13	0.69	7.35	2.27	4.09	0.17
3	SS3	57.31	1.25	15.12	6.43	0.13	3.98	7.79	2.32	4.16	0.40
4	SS4	54.48	0.99	13.43	6.17	0.28	4.36	8.08	2.25	3.45	0.19
5	SS5	64.48	1.27	13.44	5.92	0.16	2.15	0.15	2.20	2.42	0.07
6	SS6	57.43	1.02	13.68	5.58	0.11	0.52	7.44	2.25	3.63	0.12
7	SS7	45.39	1.13	11.64	6.01	0.13	2.62	8.26	2.29	3.85	0.33
8	SS8	42.79	0.91	11.85	5.13	0.12	0.31	5.76	2.20	2.49	0.08
9	SS9	44.78	1.19	13.32	6.37	0.15	0.94	7.68	2.19	3.57	0.39
10	SS10	56.54	1.12	14.70	6.01	0.12	0.66	7.30	2.21	4.03	0.13
11	SS11	45.52	0.79	11.69	4.41	0.05	0.76	0.63	2.15	1.29	0.03
12	SS12	62.86	1.29	13.25	5.95	0.19	2.14	6.14	2.24	2.45	0.09
13	SS13	44.30	1.31	11.69	5.59	0.15	2.63	8.22	2.27	3.58	0.37
14	SS14	57.33	1.28	15.10	6.44	0.12	3.96	7.75	2.34	4.17	0.41
15	SS15	44.79	1.21	13.33	6.36	0.14	0.96	7.71	2.21	3.59	0.40
16	SS16	56.52	1.14	14.75	6.03	0.13	0.67	7.29	2.23	4.02	0.15

Provenance and Source Rock Composition

This type of bivariate plots between Al2O3/TiO2 and Al2O3 is used widely provenance indicator for many sedimentary terrains (McLennan et. al., 1979; Schieber, 1992). Most of the plots suggest granite (felsic) source rock for the shales. (Fig 2).

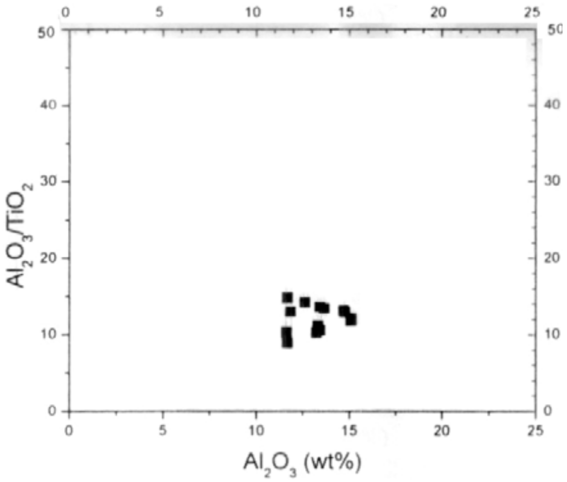


Figure 2: Al2O3/TiO2 vs Al2O3 plot (After Schieber, 1992)

The bivariate plots between Al2O3 and TiO2 for the shales indicates the source into two categories based on relative contribution of granitic and basaltic provenance.

Moreover, Zr is one of the most immobile phases amongst the trace elements and it is considered as useful tracer for source rock composition (Hayashi et. al, 1997). Since both Zr and Ti behave as immobile phases in the weathering profile, transportation and deposition. Hence, ratio of the two elements can be used for a valuable indicator of the source rock. (Hayashi et. al, 1997) Therefore, abundance of these two elements faithfully reflect the composition of the source rocks. Zirconium content of the Barail shale samples from 146 to 267 ppm, which is similar to the average value for granite.

The bivariate plot of Al2O3 vs TiO2 (After McLennan et. al, 1979) indicates the acidic and basic igneous source rocks (Fig.3) and the TiO2 versus Zr plot (Fig.4) represents predominantly felsic source rock for Barail shales.

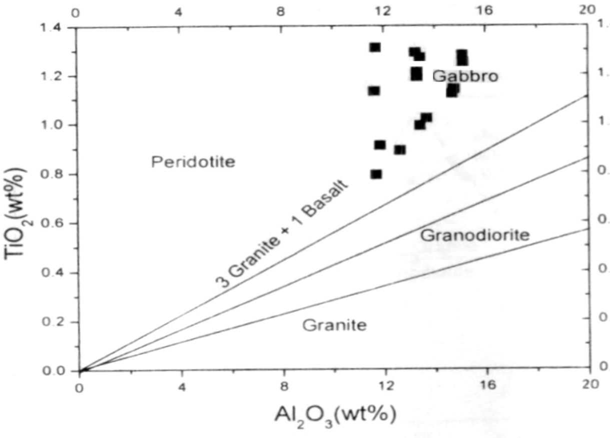


Figure 3: Al2O3 vs TiO2 bivariate plot (After McLennan et. al, 1979)

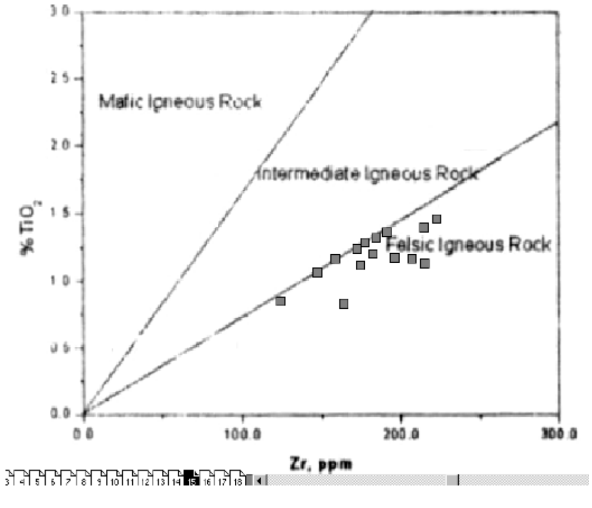


Figure 4: TiO2 vs Zr plot for the Barail shales. (After Hayashi et. al., 1997)

Tectonic Setting

The K2O vs Na2 (Crook, 1974), K2O/Na2O vs SiO2 plot (Roser and Korch, 1986) and CaO-K2O-Na2O ternary plot (Bhatia, 1983) may be used to determine the tectonic setting of shales.

The K2O/Na2O ratio varies distinctly for different tectonic environments with respect to the SiO2 content. Roser and Korch (1986) demonstrated three different tectonic setting of sedimentary basins i.e., passive margin or intracratonic, active continental margin and oceanic island arc margin, based on a bivariate plot between SiO2 and K2O/Na2O. The method has been applied to shale samples for the depositional basin of the area.. The study suggests tectonically active setting for the basin. (Active continental margin) (Fig.5)

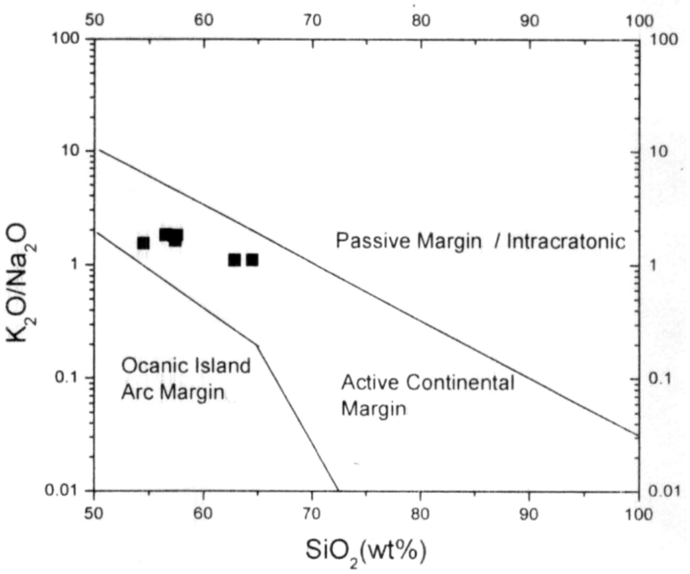


Figure 5: Tectonic discrimination diagram (Roser and Korsch, 1986)

The K2O vs Na2O plots of Barail shales fall in quartz rich field of Crook (1974) (Fig.6). McLennan et. al (1993) also observed same result from this type of study and suggested the derivation fo shales from a granite dominated upper continental crust.

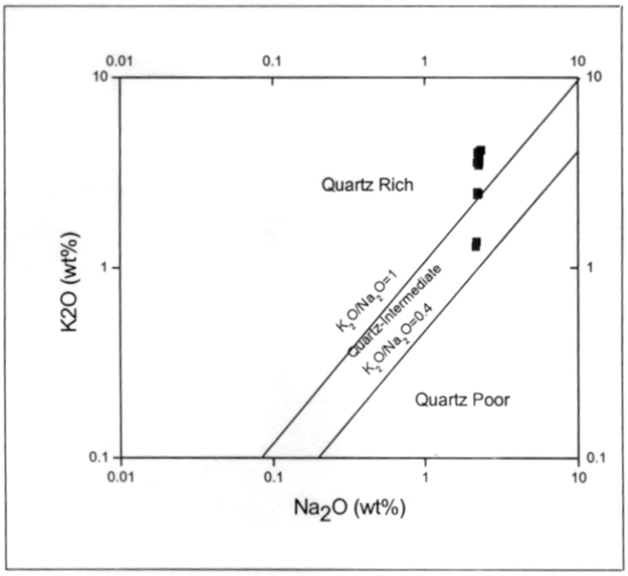


Figure 6: K2O - Na2O diagram (After Crook, 1974)

Palaeoweathering Environment

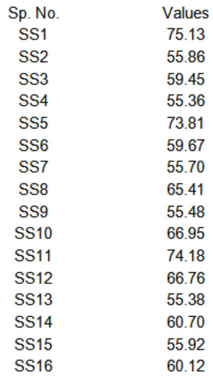
The rate of chemical weathering of source rocks and the erosion rate of weathering profiles are controlled by climate as well as source rock composition and tectonics. An useful way to interpret the Palaeoweathering of the rock is chemical index of alteration (CIA) = (Al2O3/ Al2O3+CaO+Na2O+K2O)x100 (Nesbitt and Young, 1982).

CIA values range from almost 50 in case of fresh rocks to 100 for weathered rocks. CIA values thus increase with increasing weathering intensity. CIA values for shales vary between 65 and 75 (Taylor and McLennan, 1985; Young and Nesbitt, 1988). The range of values suggests moderate to high degree of chemical weathering in the source area. The present CIA values of shale samples are shown in Table-3.

Table 3: Trace element (All values in ppm)

Sl. No.	Sample No.	Lab. No.	Ba	Co	Cr	Cu	Ga	Ni	Pb	Rb	Sc	Ti	U	V	Y	Zn	Zr
1	SS1	2562	772	<	10	<	2	<	39	35	18	75	3	145	17	894	146
2	SS2	2563	1030	<	20	<	6	<	28	106	<	35	3	80	26	424	155
3	SS3	2654	520	<	43	<	5	<	39	99	<	39	3	155	26	472	169
4	SS4	2655	966	<	17	<	4	<	25	84	<	37	3	70	26	454	192
5	SS5	2656	829	<	19	<	3	<	26	53	9	14	4	88	18	197	267
6	SS6	2657	1043	<	38	<	6	<	32	100	<	36	4	134	25	450	163
7	SS7	2658	808	<	44	<	5	<	38	92	<	40	4	155	25	476	164
8	SS8	2659	894	<	36	<	5	<	29	87	<	36	5	121	23	428	148
9	SS9	2660	759	<	29	<	5	<	34	75	<	50	3	152	25	444	165
10	SS10	2661	864	<	24	<	2	<	26	61	9	35	4	150	26	890	234
11	SS11	2662	935	<	28	<	4	<	28	53	11	31	2	155	26	426	323
12	SS12	2663	759	<	29	<	5	<	34	36	<	50	3	85	22	402	252
13	SS13	2664	1006	<	23	<	5	<	28	65	<	35	3	163	24	444	157
14	SS14	2665	1050	<	31	<	6	<	27	75	13	39	2	159	27	484	264
15	SS15	2666	1045	<	78	<	6	<	40	75	<	51	3	105	25	624	206

Table 4: Showing CIA values of shale-samples



Sp. No.	Values
SS1	75.13
SS2	55.86
SS3	59.45
SS4	55.36
SS5	73.81
SS6	59.67
SS7	55.70
SS8	65.41
SS9	55.48
SS10	66.95
SS11	74.18
SS12	66.76
SS13	55.38
SS14	60.70
SS15	55.92
SS16	60.12

Weathering can be evaluated by plotting the CIA values in A-CN-K where A stands for Al2O2, CN stands for CaO+Na2O and K stands for K2O. The solid line represents the predicted weathering path for the samples of granitic composition. (Fig.7) Moderate to high weathering of the source rock is shown by the CIA values. The weathering conditions is thus a reflection of tectonic instability of the basin and relatively humid climatic condition. A-CN-K plot interpretation is also supported by TiO2/Al2O3 ratio that indicates granitic (Felsic composition) of the source rock.

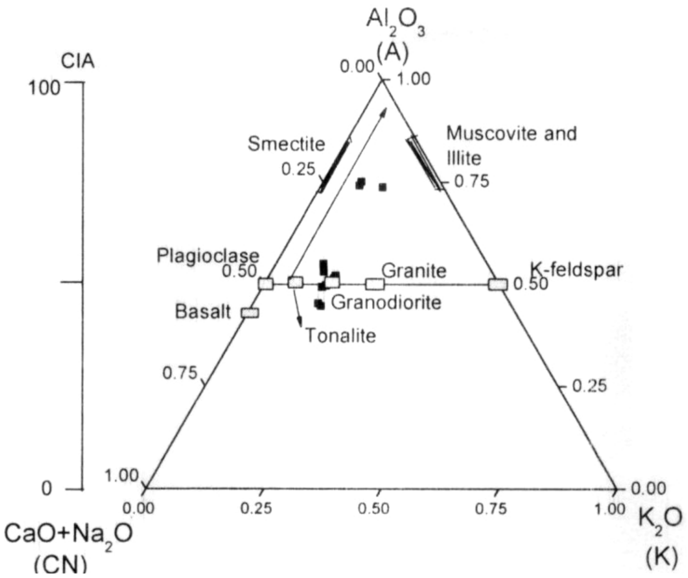


Figure 7: A-CN-K plot (After Nesbitt, 2003)

The diagnotic plot of Na vs Mg concentration of shale fall in the field of a marine to shallow marine depositional environment (Nicholson, 1992). (Fig.8)

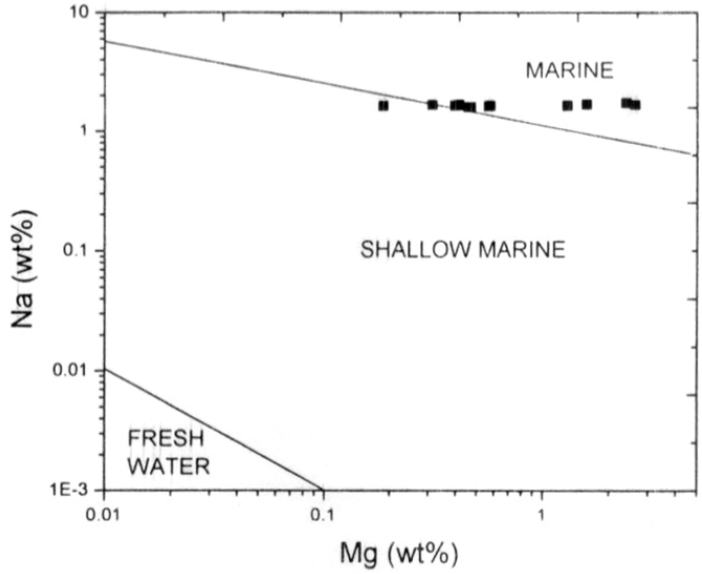


Figure 8: Mg vs Na diagnostic plot (After Nicholson, 1992)

The Al-Si discrimination diagram of the shale (Choi and Hariya, 1992) decipher the hydrogenous origin. (Fig.9)

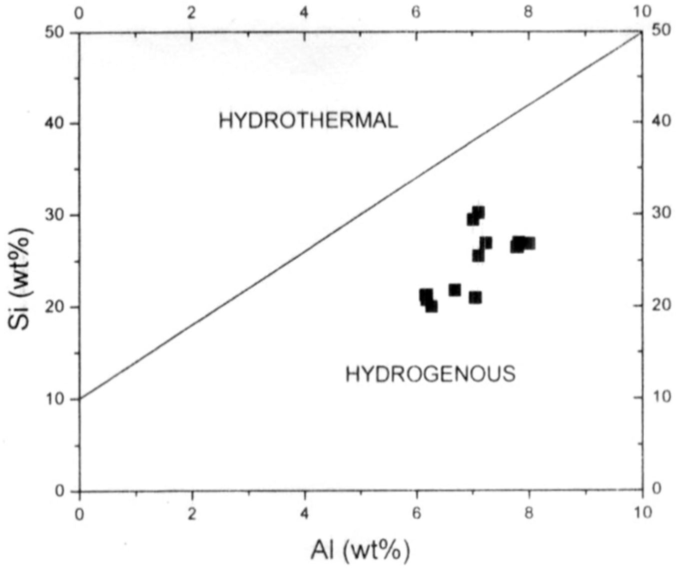


Figure 9: Al-Si discrimination diagram (After Choi and Hariya, 1992)

Chemical Maturity and Palaeoclimate

Chemical Maturity Index (CMI) of clastic sediments can be expressed as SiO2% and SiO2/Al2O3 ratio defining chemical maturity (Pettijhon et. al., 1972).

The shales show comparatively higher SiO2/Al2O3 ratio. The plot of SiO2 against Al2O3+K2O+Na2O against SiO2 in the Suttner and Dutta (1986) binary diagram (Fig.10) suggest increasing chemical maturity.

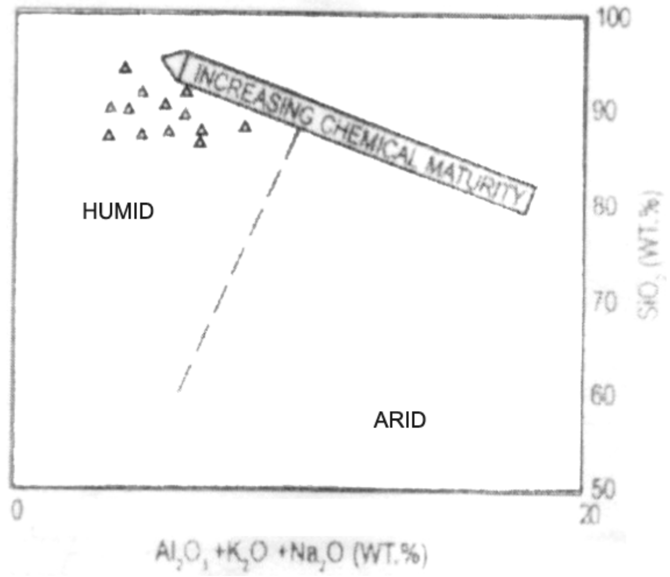


Figure 10: Scatter Plot of Al2O3 + K2O + Na2O vs SiO2 (After Suttner and Dutta, 1986)

Major elemental data provides useful information regarding the climatic conditions which prevailed during the deposition of sedimentary rocks (Suttner and Dutta, 1986). The bivariate plots of Al2O3+K2O+Na2O against SiO2 differentiate the climate conditions under which the sediments were deposited (Fig.10).

The plots of Al2O3+K2O+Na2O against SiO2 in the Suttner and Dutta (1986) binary diagram suggest mostly humid climatic condition.

Conclusions

The major, minor and trace-elements of the shale samples of the Barail Group show significant results in determining provenance and source rock composition, tectonic setting, palaeoweathering environment, chemical maturity and palaeoclimate.

1. The bivariate plots of Al2O3/TiO2 and Al2O3 suggest granite (felsic) source rock for the shales. The bivariate plots between Al2O3 and TiO3 for the shales indicate the source into two categories based on relative contribution of granitic and basaltic provenance. The TiO2 vs Zr plot represents felsic source rock for the shales.
2. For tectonic setting of shales, K2O vs Na2O plots of Barail shales fall in quartz rich field of Crook. K2O/Na2O ratio of these shales suggest their derivation from a granitic dominated upper continental crust.
3. CIA values for shales vary from 65 to 75. The values suggest moderate to high

degree of chemical weathering in the source area. A-CN-K plot suggests granitic composition of the source rock.

4. The diagnostic plot of Na vs Mg concentration of shales falls in the field of marine to shallow marine depositional environment and Al-Si discrimination diagram deciphers the hydrogenous origin of the shale.
5. The shales show increasing chemical maturity under humid climatic condition.

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References

[1] Bhat, M.I. and Ghosh, S.K. (2001): Geochemistry of the 2.51 Ga old Rampur Group pelites, western Himalayas: implications for their provenance and weathering. Precambrian Research vol.108, pp.1-16.

[2] Bhatia, M.R. (1983): Plate tectonics and geochemical composition of sandstones. Jour. Geol., vol.91, pp.611-627.

[3] Bhatia, M.R. and Crook, K.A.W. (1986): Trace element characteristics of greywackes and tectonic setting discrimination of sedimentary basins: Contributions to mineralogy and petrology vol.92, pp.181-193.

[4] Choi, J.H. and Hariya, Y. (1992): Geochemistry and Depositional Environment of Mn Oxide deposits in the Tokoro Belt, Northeastern Hokkaido, Japan, "Economic Geology", vol.87, pp.1265-1274.

[5] Crook, K.A.W. (1974): Lithogenesic and geotectonics: the significance of compositional variations flysch arenites (greywakes). In: Dott, R.H. and Shaver, R.H. (Eds.), Modern and Ancient Geosynclinal Sedimentation. Soc. Econ. Paleo. Min. Spl. Publ., vol.19, pp.304-310.

[6] Cullers, R.L. (2000): The geochemistry of shales, siltstones and sandstones of Pennsylvanian-Permian age, Colorado, USA: implications for provenance and metamorphic studies. Lithos vol.51, pp.181-203.

[7] Das, B.K.; Al-Mikhlafi, A.S. and Kaur, P. (2006): Geochemistry of Mansar lake sediments, Jammu, India: Implication for source-area weathering, provenance, and tectonic setting. Jour. Asian Earth Sci., vol.26(6), pp.649-668.

[8] Dayal, A.M. (2003): Strontium isotopic systematics of Meso proterozoic Lower Vindhyan shales: Implication for provenance. Geochimica Cosmochimica Acta 67, Supplementary vol.1, A76p.

[9] Dey, S.; Rai, A.K. and Chaki, A. (2009): Palaeoweathering, composition and tectonics of provenance of the Proterozoic intracratonic Kaladgi-Badami basin, Karnataka, southern India: Evidence from sandstone petrography and geochemistry. Jour. Asian Earth Sci, vol.34, pp.703-715.

[10] Hayashi, K.; Fujisawa, H.; Holland, H.D. and Ohmoto, H. (1997): Geochemistry of -1.9 Ga sedimentary rocks from northeastern Labrador, Canada. Geochimica Cosmochimica Acta vol.61, pp.4115-4137.

[11] Hofmann, A.; Bolhar, R.; Dirks, P. and Jelsma, H. (2003): The Geochemistry of Archean shales derived from a mafic volcanic sequence, Belingwe greenstone belt, Zimbabwe: Provovenance, source area unroofing and submarine versus subaerial weathering. Geochimica Cosmochimica Acta vol.67, pp.421-440.

[12] Jones, B. and Manning A.C. (1994): Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstone. Chem. Geol, vol.III, pp.111-129.

[13] Lee, Y. II. (2002): Provenance derived from the geochemistry of the Palaeozoic-early Mesozoic mudrocks of the Pyeongan Supergroup, Korea. Sedimentary Geology vol.149, pp.219-235.

[14] McCulloch, M.T. and Wasserburg, G.J. (1978): Sm-Nd and Rb-Sr chronology of continental crust formation. Science vol.200, pp.1003-1011.

[15] McLennan, S.M.; Fryer, B.J. and Young, G.M. (1979): The geochemistry of the carbonate rich Espanola Formation (Huronian) with emphasis on the rate earth elements. Canadian Journal of Earth Science vol.16, pp.230-239.

[16] McLennan, S.M.; Hemming, S.; Mcdaniel, D.K. and Hanson, G.N. (1993): Geochemical approaches to sedimentation, provenance and tectonics. In: Johnsson, M.J. and Basu, A. (Eds.), Processes controlling the composition of clastics sediments. Geol. Soc. Amer. Spec., paper No. vol.284, pp.21-40.

[17] Nagarajan, R.; Armstrong-Altrin, J.S.; Nagendra, R.; Madhavaraju, J and Mouttle, J. (2007a) Petrography and geochemistry of terrigenous sedimentary rocks in the Neoproterozoic Rabanpalli Formation, Bhima Basin, southern India: Implications for paleoweathering condition, provenance, and source rock composition. Jour. Geol. Soc. India, vol.70(2), pp.297-312.

[18] Nesbitt, H.W. (2003): Petrogenesis of siliciclastic sediments and sedimentary rocks. In: Lenz, D.R. (ed.), Geochemistry of Sediments and Sedimentary Rocks. Geological Association Canada, Newfoundland, Geotext 4, 39-51.

[19] Nesbitt, H.W. and Young, G.M. (1982): Early Proterozoic climates and plate motions inferred from major elements of lutites. Nature, vol.299, pp.715-717.

[20] Nicholson, K. (1992): Contrasting mineralogical-geochemical signatures of Manganese oxides Genesis to Metallogenesis ‘Economic Geology’ vol.87, pp.1253-1264.

[21] Pettijhon, F.J,; Potter, P.E.; Siever, R. (1972): Sand and Sandstones, New York, Springer-Verlag 352p.

[22] Raghuwanshi, R.S. (2007): Petrographic and geochemical characteristics of the Kanar Sandstone Formation. NE of Barwah, Khargene District, Madhy Pradesh Jour. Geol. Soc. Ind. vol.69(6), pp.1298-1304.

[23] Ranjan, N. and Banerjee, D.M. (2009): Central Himalayan crystallines as the primary source for the sandstone-mudstone suites of the Siwalik Group: New geochemical Evidence, Gondwana Res., vol.16, pp.687-696.

[24] Raza, M.; Casshyap, S.M. and Khan, A. (2002) Geochemistry of Mesoproterozoic Lower Vindhyan Shales from Chittaugarh, Southern Rajasthan and its Bearing on source rock composition, palaeoweathering conditions and tectono-sedimentary environment. Jour. Geol. Soc. India vol.60, pp.505-518.

[25] Roser, B.P. and Korch, R.J. (1986): Determination of tectonic settings of sandstone-mudstone suits using SiO2 content and K2O/Na2O ratio. Jour. of Geol. vol.94, pp.635-650.

[26] Sambasiva, Rao V.V.; Sreenivas, B.; Balaram, V.; Govil, P.K. and Srinivasan, R. (1999): The nature of the Archean upper crust as revealed by the geochemistry of the Proterozoic shales of the Kaladgi basin, Karnataka, South India. Precambrian Research vol.98, pp.53-65.

[27] Schieber, J. (1992): A combined petrographical-geochemical provenance study of the Newland Formation, Mid-Proterozoic of Montana. Geol. Magazine vol.129, pp.223-237.

[28] Suttner, L.J and Dutta, P.K. (1986): Alluvial sandstones composition and palaeoclimate framework mineralogy, Jour. Sed. Petrol, vol.56, pp.329-345.

[29] Taylor, S.R. and McLennan, S.M. (1985): The Continental crust: its composition and evolution L an examination of the geochemical record preserved in sedimentary rocks using inductively coupled plasma source spectrometry. Chem. Geology vol.33, pp.141-153.

[30] Wronkjewiz, D.J. and Condie, K.C. (1989): Geochemistry and provenance of sediments from the Pongola supergroup, South Africa. Geochimica-Cosmochimica Aeta vol.53, pp.1534-1549.

[31] Young, G.M. and Nesbitt, H.W. (1998): Processes controlling the distribution of Ti and Al in weathering profiles, siliciclastic sediments and sedimentary rocks. Jour. of Sed. Petrol. vol.68, pp.448-455.

[32] Zhang, L.; Sun, M.; Wang, S. and Yu, X (1998): The composition of shales from the Odos basin. China: effects of source weathering and diagenesis. Sedimentary Geology vol.116, pp.129-141.