# PROVENANCE & TECTONIC SETTING OF NORTHLAND ALLOCHTHON ROCKS, NORTH ISLAND, NEW ZEALAND USING GEOCHEMICAL ANALYSIS

N. Aadil<sup>\*</sup>, S. Ismail<sup>\*</sup>, A. A. Bhatti<sup>\*\*</sup>, M.Z. Abu Bakar<sup>\*</sup>

<sup>1</sup>Department of Geological Engineering, UET, Lahore
<sup>2</sup>Department of Petroleum Engineering, UET, Lahore Corresponding E-mail: <a href="mailto:naadil@yahoo.com.au">naadil@yahoo.com.au</a>

**ABSTRACT:** The Northland Allochthon is a displaced rock unit in New Zealand. It overlies the autochthonous sediments of non-marine to marine transgressive sediments and unconformably overlain by the Waitemata and correlative groups of Upper Oligocene-Lower Miocene age. Lithologically, the allochthonous unit is mostly composed of sandstone, siltstone, greensand, siliceous mudstone, argillaceous micritic limestone, and rare coal measures, along with dispersed organic matter. In this paper, the provenance & tectonic setting of different lithofacies of Northland Allochthon rocks is inferred using geochemical analysis. Major and trace element composition of these lithofacies are analyzed by X-ray spectrometer using standard analytical techniques. The results indicate that SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are most abundant with dominance of quartz, feldspar and clay. The SiO<sub>2</sub> correlate negatively with all other oxides, however, Al<sub>2</sub>O<sub>3</sub> correlate positively. Variation of CaO, K<sub>2</sub>O and Na<sub>2</sub>O content appears to be independent of Al<sub>2</sub>O<sub>3</sub> content. This indicates that major element variation could result from processes other than simple dilution by Si2O2 and Al2O3. Trace elements exhibit a systematic relationship with Al<sub>2</sub>O<sub>3</sub> and its concentration increase as grain size and SiO<sub>2</sub> content decreases. K<sub>2</sub>O/Na<sub>2</sub>O vs SiO<sub>2</sub> discriminant plot indicates the tectonic setting of Northland Allochthon rocks, New Zealand belong to active continental margin. Immobility of elements is indicated by Zr and Yttrium concentration. Depletion of Al is indicated by the replacement of plagioclase and matrix by calcite tends to behave like Ti as suggested by a positive correlation between these elements

Key words: Northland Allochthon, Provenance, Tectonic Setting, Geochemical Analysis, X-Ray Spectrometer, Discriminant Diagram, Immobility of Elements.

### **INTRODUCTION**

In northern North Island of New Zealand, the Northland Allochthon, a thick widespread displaced rock unit is comprised of rocks of Late Cretaceous to Early Miocene (Kear and Waterhouse, 1977; Balance and Sporli, 1979). The Northland Allochthon is present both NE and SW of a structural high located between the Three Kings Island and Mt. Camel (Figure 1). It overlies the autochthonous, Paleogene non-marine to marine transgressive sediments (Hayward et al. 1989). It is unconformably overlain by the Waitemata and correlative groups of Upper Oligocene-Lower Miocene age. Lithologically, the allochthonous rocks are mostly composed of sandstone, siltstone, greensand, siliceous mudstone, argillaceous micritic limestone, and rare coal measures, along with dispersed organic matter.

Optical petrography is normally restricted to sandstones, so fine grained lithologies have not been widely used for determination of provenance and tectonic setting (Blatt et al. 1980) but such restriction does not apply to geochemical data. A number of studies have recognised characteristic  $K_2O/Na_2O$  ratios and  $SiO_2$ content of sandstones from contrasting tectonic setting (Crook, 1974; Schwab, 1975; Bhatia, 1983). Roser and Korsch (1986) used the illustrated effect of grains on modal and chemical composition and extended



Figure 1: Outcrop distribution of the Northland Allochthon rocks and inferred basement terrane in Northland, New Zealand.

 $K_2O/Na_2O-SiO_2$  classifications developed by Crook (1974) to include finer grained members of sedimentary units. They used a selection of analysis from ancient and modern terrane to define three first order tectonic categories based on SiO<sub>2</sub> content and  $K_2O/Na_2O$  ratio and used modern data to test them. They successfully distinguished the following tectonic settings of some of the major pre-Cenozoic terrane of New Zealand with this diagram.

In this paper, the provenance & tectonic setting of different lithofacies of Northland Allochthon rocks are inferred using geochemical analysis.

## METHODOLOGY

Chemical analyses of various sedimentary rocks were carried out to find out whether geochemical characteristics can be used to correlate the lithologies which have similar provenance. Twenty samples of different lithofacies from Northland Allochthon were analyzed for major and trace element composition by Xray spectrometer using standard analytical techniques (Norrish and Hutton, 1969). Major elements analyses were performed on glass fusion discs and trace elements analysis on boric acid baked pressed powder pellets. Results and method of preparation and analyses are given in Table I. Methods of preparation and analyses are detailed in Palmer (1990).

### **RESULTS AND DISCUSSION**

**Major Elements:** The results indicate that  $SiO_2$  and  $Al_2O_3$  are most abundant because of the dominance of quartz, feldspar and clay (Table I).  $SiO_2$  content ranges from 65.91 to 83.85 weight percent (wt%) and  $Al_2O_3$  content ranging from 11.63 to 16.49 wt%. Most of  $K_2O/Na_2O$  ratios range between 0.48 and 1.44 (Table I). Only one sample (AU9247) has  $K_2O/Na_2O$  ratio of 5.74 having very little of Na<sub>2</sub>O (0.31). The compositions are compatible with estimates of average shales and mudstone cited in Blatt, Middleton and Murray (1980). Slightly higher Na<sub>2</sub>O content in some sample (AU46165) has very little Na<sub>2</sub>O (0.33) as compared to  $K_2O$  (1.88) which may be because high concentration of muscovite.

The SiO<sub>2</sub> correlate negatively with all other oxides however, Al<sub>2</sub>O<sub>3</sub> correlate positively. Al<sub>2</sub>O<sub>3</sub> shows significant correlation with TiO<sub>2</sub>, total Fe and MgO indicating their association with clay. The molecular proportion of Na<sub>2</sub>O corresponding to albite content is in all samples very close to total Na<sub>2</sub>O content. This indicates that sodium is derived almost exclusively from albite with insignificant contribution from clay minerals. There is poor positive correlation of K<sub>2</sub>O with clayassociated elements. The main source of K is illite. Unsystematic distribution of  $K_2O$  is more likely introduced by the occurrence of minor but variable quantity of K-feldspar and muscovite. Occurrence of CaO is also erratic. It is partly clay associated (smectite) but mainly contributed by calcite fossil fragments. Four samples (AU9219; AU9245; AU9249 and AU9250) contain high percentage of CaO as compared to other samples. Biogenic carbonate and calcite cementation are contributors to calcium content of the sediment but both are additional to the terrigenous detritus except where there is calcite replacement of framework minerals. Samples having high  $P_2O_5$  indicate a biogenic input as compared to others.

Variation of CaO, K2O and Na2O content appears to be independent of Al<sub>2</sub>O<sub>3</sub> content, and may reflect small variations in feldspar composition. Chemical weathering of feldspar prior to deposition can result in the loss of CaO and Na<sub>2</sub>O into weathering solutions, and the retention of K<sub>2</sub>O in product clays (Sawyers, 1986). Variation in feldspar composition, the degree of chemical weathering in the source area and at the site of deposition, plus any post-depositional alteration may account for the scatter in abundance of these elements. Figure 3 gives a weathering trend on a (CaO+Na2O)-Al2O3-K2O triangular plot for different lithofacies of the Northland Allochthon in North Islanad, New Zealand. The trend follows the mixing line representing the removals of alkalies and Ca in solution during the breakdown of first plagioclase and potassium feldspar and ferromagnesium silicates. The deviation from these trends in the studied area is due to different diagenetic effects during deposition.

Major element variation could result from processes other than simple dilution by Si2O2 and Al2O3. A good relationship can e observed between MgO and Na2O with TiO2 (Figure 4). Cox (1985) has compiled all the available chemical data on the basement rocks of North Island and has attempted comparison of different facies.

**Trace elements:** Many trace elements exhibit a systematic relationship with  $Al_2O_3$  and grain size. In general  $Al_2O_3$  and trace element concentrations increase as grain size and SiO<sub>2</sub> content decreases. Several trace elements occur preferentially in ferromagnesian minerals. Elements with an affinity to Fe<sup>+3</sup> are Cr<sup>+3</sup>, V<sup>+3</sup> and Ga<sup>+3</sup> (Taylor, 1965). Cu<sup>+2</sup>, Ni<sup>+2</sup>, Sc<sup>+3</sup>, and Zn<sup>+2</sup> all readily replace Fe<sup>+2</sup> sites in mineral lattices. Elements with high valencies such as Nb<sup>+5</sup>, Th<sup>+4</sup>, U<sup>+4</sup> and Zr<sup>+4</sup> can occur in zirconium or substitute with Ti<sup>+4</sup> and accompany it into Fe<sup>+4</sup> sites (Taylor, 1965). Y<sup>+3</sup> is closet in size to Ca<sup>+2</sup> but, because of charge balance difficulties, enters ferromagnesian minerals rather than feldspars (Wager and Mitchell, 1951). Pb<sup>+2</sup> can occur in both micas and feldspars. Ba<sup>+2</sup> and Rb<sup>+</sup> are identical in size to K<sup>+</sup>, the

latter have similar chemical character as well. All these three elements with felsic affinities, preferentially entering feldspar rather than micas in the  $K^+$  site (Taylor, 1965). Lack of their correlation may be the result of

minor modal variations of feldspar composition or of differing mobility of these elements in weathering solutions.

 Table 1. Major (weight %) and trace (ppm) element geochemistry for twenty samples from Northland Allochthon lithofacies, Northland. LOI represents loss of volatiles on ignitions.

Major Elements											
Sample	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	
AU46135	67.31	0.93	15.61	6.48	0.09	1.96	1.82	3.21	2.47	0.13	
AU46165	83.85	0.3	6.31	5.81	0.01	1.11	0.25	0.33	1.88	0.14	
AU46166	75.69	0.46	12.49	3.61	0.06	1	2	2.95	1.63	0.12	
AU46171	87.97	0.27	6.91	1.92	0.01	0.9	0.21	0.79	1	0.01	
AU46173	72.14	0.57	15.45	4.18	0.06	1.35	0.52	3.09	2.54	0.07	
AU46187	65.91	0.81	18.77	5.91	0.12	1.82	0.58	2.44	3.53	0.13	
AU46189	69.27	0.53	12.42	3.99	0.19	1.29	8.14	2.01	1.98	0.11	
AU46190	80.39	0.5	11.63	3.03	0.01	0.77	0.16	1.79	2.06	0.07	
AU46197	77.53	0.5	11.87	2.96	0.04	0.96	0.82	2.54	2.39	0.09	
AU46200	73.73	0.55	14.43	4.02	0.07	1.19	0.93	2.57	2.43	0.07	
AU46203	67.62	0.73	16.49	5.24	0.09	2.31	1.5	3.88	2.36	0.25	
AU46204	68.03	0.76	16.71	5.5	0.08	0.91	1.29	4.2	2.28	0.22	
AU46205	70.64	0.63	15.77	3.4	0.05	1.33	0.88	4.78	2.29	0.2	
AU46208	69.28	0.6	16.48	4	0.05	1.67	1.3	3.75	2.63	0.18	
AU46210	76.88	0.41	12.99	2.18	0.04	0.49	1.27	3.04	2.67	0.02	
AU46211	72.91	0.5	14.93	3.1	0.05	0.96	1.56	3.18	2.71	0.08	
AU46212	68.85	0.74	16.64	3.97	0.08	1.66	1.39	3.82	2.65	0.2	

Trace Elements														
Sample	Ba	Sr	Zr	Nb	Y	Rb	Th	Pb	Zn	Cu	Ni	Cr	V	La
AU46135	554	243	307	13	21	73	7	13	80	19	24	69	122	23
AU46165	190	48	106	4	16	74	5	5	58	9	5	94	59	21
AU46166	74	55	9	1	5	3	1	2	10	4	25	3	25	4
AU46171	216	201	120	6	12	70	5	12	54	12	10	66	55	21
AU46173	522	135	186	9	19	86	7	21	96	15	21	36	95	24
AU46187	558	144	259	14	24	129	15	10	91	21	23	50	99	35
AU46189	405	87	128	6	14	54	5	8	47	13	19	44	70	23
AU46190	385	249	139	6	18	62	6	12	66	14	22	41	81	20
AU46197	508	182	210	7	16	71	8	18	62	20	18	51	68	27
AU46200	513	203	143	5	12	75	7	13	62	18	17	37	85	17
AU46203	488	312	176	8	26	75	10	19	84	24	20	54	111	27
AU46204	248	296	175	10	19	68	11	16	86	35	21	41	106	23
AU46205	407	287	194	10	17	59	9	13	78	21	18	39	87	28
AU46208	539	286	171	10	18	91	8	19	69	5	20	42	105	25
AU46210	571	310	120	6	8	74	5	15	33	0	10	37	44	10
AU46211	562	342	101	7	15	80	5	12	55	15	23	31	64	18
AU46212	531	298	258	11	24	90	11	20	77	22	23	45	103	33

The average Zr concentration of 140 ppm suggests the immobility of this element. Yttrium also seems to be immobile. The immobility of Y during low grade metamorphism has also been suggested by Lambart and Holland (1974) and Humphris and Thompson (1978). La<sup>+</sup> tend to be concentrated in fine grained sediments, being diluted by quartz in coarser material (Culler et al., 1979), and commonly resides in feldspars and accessory

minerals. This is an immobile element and is readily retained in clay minerals on the breakdown of feldspars and labile igneous minerals (Taylor and MacLennan, 1988).

**Provenance discrimination diagram:** Bhatia and Crook (1986) established the geochemical criteria which distinguish lithologies of different provenance using a

large sample of greywacke of known depositional setting. They found that the large ion lithophile and light rare earth elements, especially K, Rb, Pb, Th, U, Zr and Nb correlated positively with terrigenous components, such as mica, rutile, tourmaline and zircon and with the maturity index of a sedimentary rock, while ferromagnesian elements Fe, Ti, Mn, Se and V and small cations Na, Ca and Sr correlates positively with chemically unstable components such as volcanic lithic, epidote and feldspar.



Figure 2: La/Th diagram to discriminate the tectonic setting in the Northland Allochthon rocks, Northland, New Zealand.

Using elemental abundances to tectonic setting criteria by Bhatia and Crook (1986), an active continental margin is the most likely setting for most of the Northland Allochthon samples because of high abundance of aluminosilicates. The La/Th discriminant diagram (Figure 2; Bhatia and Crook, 1986) supports this. The very high TiO<sub>2</sub> contents may reflect derivation from a deeply weathered landmass; Ti is concentrated by weathering processes at greater than 2.5.

Geochemical analysis and provenance: Data of SiO<sub>2</sub> and K<sub>2</sub>O/Na<sub>2</sub>O (Table I) of sandstone and siltstone from different lithofacies of Northland Allochthon rocks mostly plot within the active continental margin field of Roser and Korsch (1986) except in two samples (AU46166 & AU46187), suggesting that the sediments were derived from a quartzofeldspathic continent or dissected magmatic arc and were deposited in an active convergent or transverse margin environment. K<sub>2</sub>O/Na<sub>2</sub>O values appear to be independent of grain size and thus plot as a horizontal trend on the diagram (Figure 3).

**Immobile elements:** Some elements like Ti, Zr, Y, Nb and Al are considered to be immobile during weathering, hydrothermal alteration and metamorphism (Cann, 1970; Pierce and Cann, 1971, 1973; Floyd and Winchester, 1978; Finflow-Bates and Stumpfli, 1981). Figure 4 are

 $TiO_2$ -Zr and  $Al_2O_3$ -Zr plots for the Northland Allochthon rocks and have been made to ascertain the elemental immobility of these elements. Few samples have very high silica content (sample AU9204, AU9206, AU9220 and AU9247, see Table I) or large precipitation of secondary minerals. Depletion of Al is indicated by the replacement of plagioclase and matrix by calcite tends to behave like Ti as suggested by a positive correlation between these elements.



Figure 3: K<sub>2</sub>O/Na<sub>2</sub>O vs SiO<sub>2</sub> discriminant plot showing the inferred plate tectonic setting of Northland Allochthon rocks, Northland, New Zealand (after Roser & Korsch, 1986).

### SUMMARY

Variation in major and trace elements concentration described above indicate that the transition from sandstone to siltstone is chemically gradational in the Northland Allochthon rocks. Many major and trace elements are enriched in fine grained samples reflecting the control on bulk chemistry by modal mineralogy. With decreasing grainsize, SiO<sub>2</sub> decreases as clastic quartz and feldspar become less dominant and ferromagnesium minerals in the fine fraction concentrate in many of the analyzed elements. Elements which show no systematic variations with SiO<sub>2</sub> or  $Al_2O_3$  content reflect minor compositional differences in common terrigenous components and/or external factors such as biogenic input or secondary alteration processes.

Low MnO content (0.01-0.09 wt%) in the samples except AU9219, AU9213, AU9245 suggest rapid deposition perhaps as radiolarian turbidite. High abundance of  $Fe_2O_3$  with  $Al_2O_3$  in some samples (AU9213, AU9239, AU9253) suggests that they may be detrital.



Figure 4: Plots showing mutual relationship of some "conventionally" immobile elements in the Northland Allochthon rocks, Northland, New Zealand.

#### REFERENCES

- Ballance, P.F. and K.B. Sporli: Northland Allochthon. Journal of Royal Society of New Zealand, 9: 259-275 (1979)
- Bhatia, M.R. and K.A.W. Crook: Trace elements characteristics of greywacke and tectonic setting determination of sedimentary basins. Contribution to Mineralogy & Petrology, 92: 181-192 (1986)
- Bhatia, M.R.: Plate tectonics and geochemical composition of sandstones. Journal of Geology, 91: 611-627 (1983).
- Blatt, H.; G. Middleton and R. Murray: Origin of Sedimentary Rocks. Englewood Cliffs, NJ. Prentice Hall, 782p. (1980)
- Cann, J.R.: Rb, Sr, Y, Zr, and Nb in some ocean-floor basaltic rocks. Earth & Planet. Science Letter, 10 (1970).
- Cox, M.E.: Geochemical examination of the active hydrothermal system at Ngawha, Northland, New Zealand: Hydrothermal model, element

distribution and geological setting. Ph.D. thesis, University of Auckland, New Zealand, (1985).

- Crook, K.A.W.: Lithogenesis and geotectonic: The significance of compositional variation in flysch arenites (greywacke). In R.H. Dott, Jr. and R.H. Shaver (eds.), Modern and Ancient Geosynclinal Sedimentation: Society of Econ. Paleon. Mineral. Sp. Public. 19: 304-310 (1974).
- Finflow-Bates, T. and E.F. Stumpfl: The behavior of so called immobile elements in hydrothermally altered rocks associated with volcanogenic submarine-exhalative ore deposits. Mineral Deposits, 16: 319-328 (1981).
- Floyd, P.A. and T.A. Winchester: Identification and discrimination of altered and metamorphosed volcanic rocks using immobile elements. Chemical Geology, 21: 291-306 (1978).
- Hayward, B.W.; F.J. Brook and M.J. Isaac: Cretaceous to middle tertiary stratigraphy, paleogeography and tectonic history of Northland Allochthon, New Zealand. Royal Society of New Zealand Bulletin, 26: 47-64 (1989).
- Humphris, S.E. and G. Thompson: Trace element mobility during hydrothermal alteration of oceanic basalts. Geochim. et Cosmochlm. Acta, 42: 127-136 (1978).
- Kear, D. and B.C. Waterhouse: Onerahi Chaos breccia: further thoughts (Notes). New Zealand Journal of Geology and Geophysics, 20: 205-209 (1977).
- Lambert, R.S.J. and J.C. Holland: Yttrium geochemistry applied to petrogenesis utilizing calcium-ytrium relationship in minerals and rocks. Geochim et Cosmochim. Acta, 38: 1393-1414 (1974)
- Norrish, K. and J.T. Hutton: An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. Geochim. et Cosmo. Acta, 33: 431-453 (1969).
- Palmer, P.M.: Provenance of Cretaceous accretionary wedge sediments: the Mangapokia Formation, Wairarapa, New Zealand. New Zealand Journal of Geology and Geophysics, 33: 125-135 (1990).
- Pearce, J.A. and J.R. Cann: Ophiolite origin investigated by discriminant analysis using Ti, Zr and Y. Earth and Planetary Science Letter, 12 (1971).
- Pearce, J.A. and J.R. Cann: Tectonic setting of basic volcanic rocks determined using trace element analysis. Earth and Planetary Science Letter, 19: 290-300 (1973).
- Roser, B.P. and R.J. Korsch: Determination of tectonic setting of sandstone mudstone suites using  $SiO_2$  content and  $K_2O/Na_2O$  ratio. Journal of Geology, 94: 635-650 (1986).
- Sawyer, E.W.: The influence of source rock type, chemical weathering and sorting on

geochemistry of clastic sediments from the Quetico Meta-sedimentary Belt, Superior Province, Canada. Chemical Geology, 55: 77-95 (1986).

- Schwab, F L.: Framework mineralogy and chemical composition of continental margin-type sandstones. Geology, 3: 487-490 (1975).
- Taylor, S.R.: The application of trace element data to problems in petrology. In Ahrens (ed.), Physics and Chemistry of the Earth, 135-201 (1965).
- Wager, L.R. and R.L. Mitchell: The distribution of trace elements during strong fluctuation of basic magma: A further study of the Skaergaard intrusion, Greenland. Geochem. et Cosmo. Acta, 1.1: 129-208 (1951)