The Nucleus **51**, No. 2 (2014) 215-221

The Nucleus

A Quarterly Scientific Journal of Pakistan Atomic Energy Commission

NCLEAM, ISSN 0029-5698

CLAY MINERALOGY OF LITHOFACIES OF NORTHLAND ALLOCHTHON ROCKS, NORTH ISLAND, NEW ZEALAND

*N. AADIL

Department of Geological Engineering, University of Engineering and Technology, Lahore, Pakistan

(Received March 31, 2014 and accepted in revised form May 12, 2014)

Northland Allochthon, a bathyal depth sediments, comprises an originally fining-upwards passive margin wedge which accumulated adjacent to northeastern New Zealand between mid-Cretaceous and latest Oligocene. The Northland Allochthon is overlain by Miocene arc and arc-basin deposits. This paper provides clay mineralogy and its transformation of different lithofacies of the Northland Allochthon rocks of North Island, New Zealand to understand the processes of precipitation during deposition and diagenesis of these rocks and possible later effects associated with obduction and re-burial of these rocks. The clay mineral sequence observed in the study area is from smectite to illite through illite/smectite interstratified mixed-layered clays. X-Ray diffractometry and Scanning Electron Microscopy of mixed-layer illite/smectite (I/S) clay from sandstone and shale shows a progressive increase in illite layers with increasing age.

Keywords: Northland Allochthon, Clay mineralogy, X-Ray diffractometer, Scanning electron microscopy

1. Introduction

Clay minerals are useful tools for studying provenance, paleoclimatic conditions in the source area and give information about the burial history of sediments [1].

Clay minerals are hydrous aluminum sheet silicates with variable proportions of other cations such as Na, K, Ca, Mg and Fe [2]. Clay minerals are the main constituents of mudstone and related argillaceous sediments which together constitute about 75% of sedimentary deposits and occur in significant amount in another 20% of sediments. The use of clay minerals and mixed layer clays has been recognised in low grade metamorphic sequence. Illite/Smectite, Illite/Chlorite, Chlorite/Smectite and dickite and zeolite are the most useful indicator minerals for diagenetic and inchimetamorphic grade [3].

Clay minerals change in form and composition in response to increasing temperature and pressure, thus making them very useful as mineral geothermometers in both hydrothermally altered and low grade metamorphic rocks. The transformation from smectite to either illite or chlorite depends upon temperature and on the structure of the smectite. Dioctahedral smectites transform through illite/smectite structures to illite [4-6], whereas the less common trisoctahedral smectites transform through chlorite/smectite structures to chlorite [7]. The transformation of smectite to illite with increasing temperature or depth of burial, through a series of progressively more ordered illite/smectite inter-layers was studied [8].

The aim of this paper is to summarise the clay mineralogy of different lithofacies from the Northland Allochthon Rocks. It will give a general picture of the distribution of clay minerals which will help in understanding the processes of precipitation during deposition and diagenesis of these rocks and possible later effects associated with obduction and re-burial of these rocks.

2. Northland Allochthon

The Northland Allochthon is present both NE and SW of a structural high located between the Three Kings Island and Mt. Camel (Figure 1) in northern North Island of New Zealand. This is a thick widespread displaced allochthon rock unit contains rocks of Late Cretaceous to Early Miocene age [9]. The Northland Allochthon is estimated to have a present day volume of 32000 km^3 in an area of 26000 km^3. The volume of allochthon eroded from onshore Northland can only be guessed and the volume from the Three Kings Island-Mt. Camel Terrance is not yet known. 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. It overlies the autochthonous, paleogene non-marine to marine transgressive sediments. It is unconformably overlain by the Waitemata and correlative groups of Upper Oligocene-Lower Miocene age.

* Corresponding author : naadil@yahoo.com.au

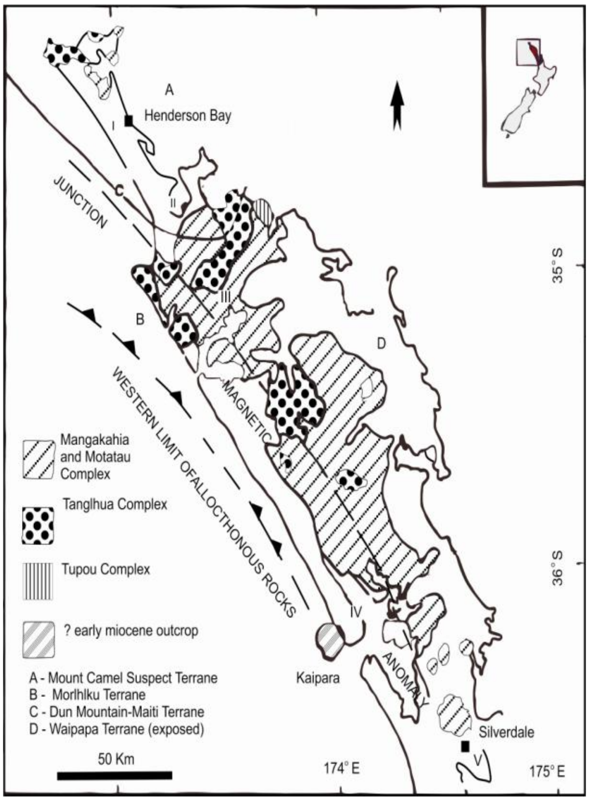

Figure 1. Outcrop distribution of the Northland Allochthon rocks and inferred basement terrane in Northland, New Zealand.

Northland Allochthon includes rocks as old as Early Cretaceous and as young as earliest Miocene. Because of poor exposure and complicated structure, these are grouped into four complexes [10] such as Tupou, Mangakahia, Motatau and Tangihua Complexes. These complexes are present in a series of highly deformed nappes with broken formation and melange [11, 12].

3. Methodology

Sample preparation for clay mineralogy begins with the gentle hand grinding of the samples and their subsequent dispersion in distilled water. Clay particles were separated after fractionation and then mounted by pipetting on a glass slide and then drying at room temperature to provide an oriented sample mount.

Using X-ray powder diffraction techniques, these fractionated and oriented clay sample mounts were used to identify the clay minerals. Samples were run in untreated form and then were progressively glycolate and heated to 250°C and 550°C to differentiate the different clay minerals. Glycolation serves to discriminate the swelling from the non-swelling clays which may be present either as a discrete component or as a part of mixed layer. Heating causes the clay minerals to collapse and by this we can differentiate between the kaolinite and chlorite because kaolinite collapses on heating (95-100%).

The clay samples were scanned with a Phillips X-Ray diffractometer having the copper target (CuK radiation = 1.3418°A) using the following parameters ; 40 Kv, 20 mA; range 2° to 32°2θ for clay samples and 2° to 65°2θ for bulk samples; chart speed 3 cm/min and the scanning speed 2 cm/min. XRD patterns are processed and printed out using Sietronics/Fein Marquart Computer software (i.e. SIE Ray 112 and micro PDSM) which is interfaced with XRD machine.

4. Scanning Electron Microscopy (SEM)

SEM was used to examine the fabric and to aid in determining the sample composition. Freshly fractured sample chips of about 4 mm size were wrapped in tissue paper and placed in an air tight jar with some silica gel for 48-hours. After drying, the samples were mounted in groups of four in a circular pattern on a 2 cm diameter brass sample stubs using fingernail polish as the mounting medium. Samples were then evacuated and coated with gold in a rotary shadower and stored in the desiccators prior to analysis. Mineral identification was made by comparing the electron micrographs to those displayed in other works [13, 14] and by examining the electron micrographs in the light of XRD results.

Table 1. The distribution of clay minerals from different lithofacies of the Northland Allochthon, North Island, New Zealand. Age is given in accordance with New Zealand geological time scale. Lw for Waitakian; Ab-Lw-Bortonian-Waitakian; Dm-Lwh-Mangaorapan–Whangaroan; Dm-?Lmh-Mangaorapan to probably Whangaroan; Mt-Dm-Teurian to Mangaoapan; Rm-Rt-Arowhanan; ?Cn-?Mh– Probably Ngaterian-probably Haumurian; Cn-Rm- Ngaterian-Mangaotanean; and ?Cm– Probably Motuan. Further, Sm, I/Sm, Ch/Sm, I/Ch, I, Ch, K, Qtz, Pl, Kf and Calc indicate Smectite, Illite/ Smectite, Chlorite/ Smectite, Illite/ Chlorite, Illite, Chlorite, Kaolinite, Quartz, Plagioclase, Potash Feldspar and Calcite.

Sample	Unit	Lithology	Age	Sm	I/Sm	Ch/Sm	I/Ch	I	Ch	K	Qtz	Pl	Kf	Calc
AU46154	Puriri m.st.	m.st.	Lw	##	#	?		-						-
AU46155		m.st.		##	#									-
AU46157		m.st.		##	#			#		-?	##	#		#
AU46159	Mahurangi L.st	l.st.	Ab-Lw	##	#			#			##	##		##
AU46I56		l.st.		#	#			#	*		##	#		#
AU46161		l.st.		-	#			*?	*	-	#	#		#
AU46162	Omahutu S.st.	s.st.	Dm-Lwh	#	-			*		-?	##			-
AU46163		s.st.		#	-			*		-	##	#		-
AU46164	Taipa m.st.	m.st.	Dm-?Lmh	##	#	-		#			##			
AU46165		s.st.		#	#	-				*	##	-		-
AU46171	Whangai Fm	s.st.	Mh-Dt	-	-			#			##	#		#
AU46172	Awapoko s.st.	m.st.	Rm-Rt		#		#	#	#	*?	##	#	-?	-
AU46173		s.st.		-	#		#	#	#		##	#		##
AU46176		s.st.					##	#		-	##	#		-
AU46177		m.st.					#	##	#	*	##	#		
AU46178		s.st.		*?	#				*		##	#		-
AU46179		s.st.	?Cn-?Mh	#	#			#	*?	#	##	#		-
AU46180		s.st.		#	#		*?			-	#	#		-
AU46184		m.st.		#	-		*	#	#	*?	##	#	*	
AU46185		s.st.		#	#					-	##	#	#	-
AU46186		m.st.		#	#			#		-	##	-		-
AU46213	Matukaraka Facies	s.st.	Cn-Rm	#	-	*?		#	#	#	##	#		#
AU46211		s.st.		-?	-	-	#	#	-		#	-	*	*?
AU46214		s.st.		*?	*?		#	##	#	-	##	#		#
AU46209		conc.		*?	*?		*?		#	-	##	-	-	-
AU46210		conc.		-	-				-?	-	##	#	-	-
AU46187		s.st.		#	-		#		#	-	##	#	-	#
AU46I88		s.st		#	#		#	#	#		##	#		
AU46189		s.st		-	*?			#	-	*?	##			#
AU46190		m.st.		-	##	*?		#	*	*?	##			-
AU46191		s.st		-	##			#		-	##	#		-
AU46193		s.st		-	-			#		-	##	#		-
AU46194		s.st		*?	-		#	#	#	-	##	#		-
AU46195		m.st.			-		*	#	#	*?	##		-	-
AU46196		s.st			-		-	#	#		##	#	-	*
AU46197		m.st.		#	-	*?		#	-	#	##	#		-
AU46199		s.st		#	#			#	-	*	##	#		
AU46200		s.st		-	-		#	##	##	-	##	#		-
AU46201		s.st		#	#			#		##	##	#		-
AU46202	Tokerau Clastics	m.st.	? Cm					##	#		##	#		
AU46203		s.st					#	#	#	-	##	#		
AU46204		s.st			-?	*?	#	#	#	#	##	#		
AU46205		s.st			?		-	#	#	#	##	#		-
AU46206		m.st.					-	##	*?	##	##	-		
AU46207		s.st			*?		#	##	#		##	#		
AU46208		s.st					#	##	#		##	##		-

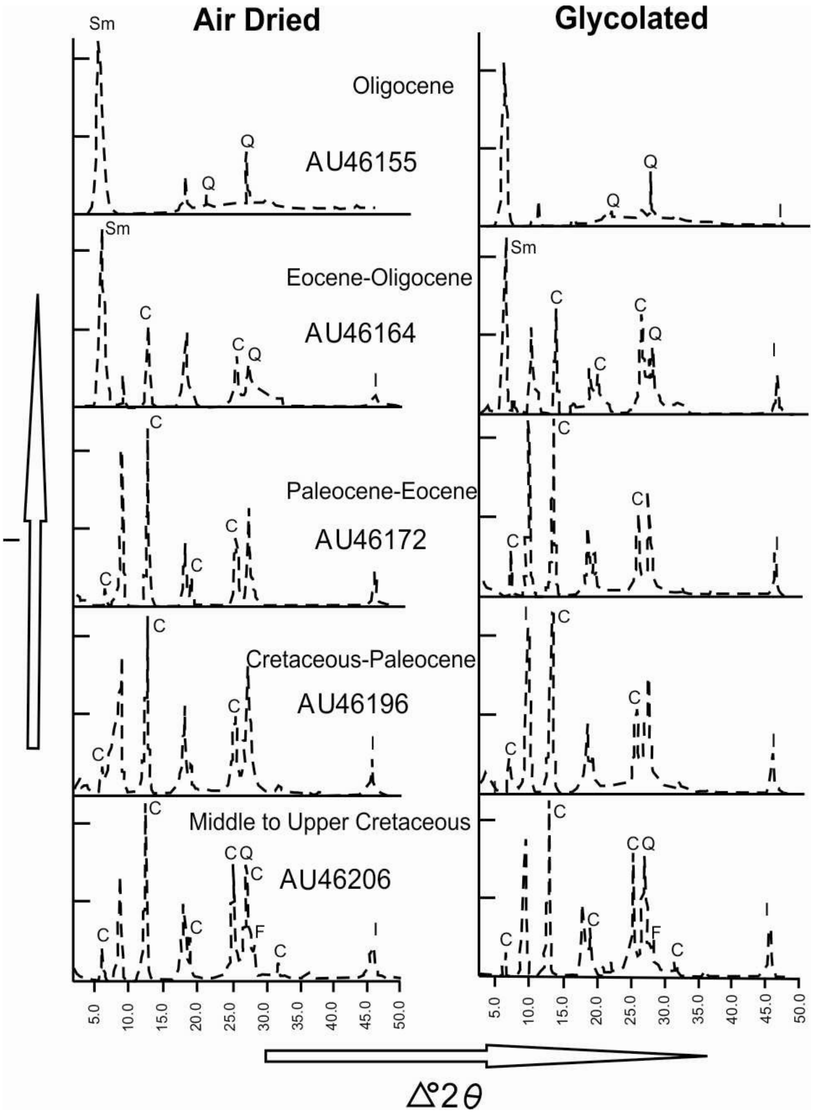

Figure 2. Major clay minerals and interstratified layer clays are identified by X-ray diffraction (XRD) scans.

5. Results

Smectite, Illite, Chlorite kaolinite and mixed layered clays (illite/smectite, chlorite/smectite) with rare halloysite, vermiculite and illite/vermiculite mixed layer, were identified in this study. The distribution of clay minerals from different lithofacies of the Northland Allochthon is shown in Table 1. Major clay minerals and interstratified layer clays are identified by X-ray diffraction (XRD) scans (Figure 2).

Smectite usually forms at a temperature below 100°C. Scanning electron microscope (SEM) micrographs show smectite of well developed, webby morphology (Plate A) from Taipa mudstone. XRD data show the (001) spacing of air dried samples ranging from 14°A to 15°A, but on treatment with ethylene glycol this expands to 16°A to 17°A. The first order basal spacing increase of approximately 2°A indicates that it is Ca-smectite.

Illite/smectite mixed layer clays occur in almost all samples. The interlayer occupancy of illite component increases regularly with increasing age of the formation. Illite/smectite seems to be the representative clay minerals from the alteration of plagioclase and mafic minerals. Illite/smectite and illite, most commonly form from volcanic glass in the groundmass and less commonly directly from plagioclase. They seem to cover a temperature range of 90°C - 220°C. The illite proportions less than 85% in the intercalated layers of illite/smectite structure, is shown by slightly crenulated to flaky crystals shown in Figure 3 (Plate B).

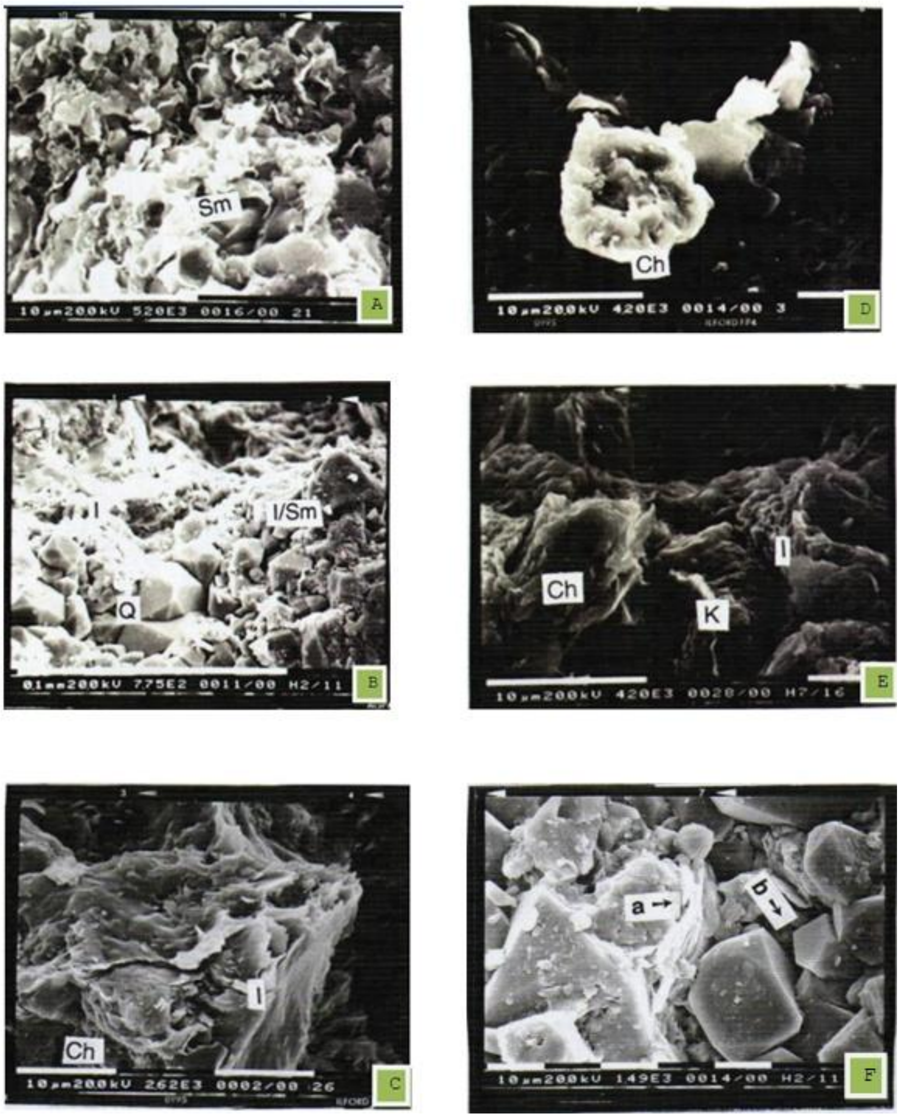

Figure 3. Plates: Scanning electron microscope (SEM) micrographs show smectite of well developed, webby morphology (Plate A), Illite/smectite mixed layer is shown by slightly crenulated to flaky crystals (Plate B), illite coatings (Plate C), fan shaped crystals Chlorite (Plate D), book shaped Kaolinite (Plate E) and Clinoptilolite - Zeolite (Plate F).

Illite appears at temperatures above 150°C. It is mostly shown in samples of Cretaceous age as represented by illite coatings (Plate C). Expansion of the basal layer of illite / smectite mixed layer clays decreases with increasing temperature. The basal d-spacing of air dried clays decreases while that of the glycolated samples increase with increasing geological age.

Chlorite commonly forms at a temperature from 90°C to 200°C. It occurs as an alteration product of glass, pumice, hornblende and biotite. SEM micrographs of chlorite show plate- or fan shaped crystals and 1-2µm in diameter (Plate D). Locally chlorites have about 5% to 10% smectite layers in their structures, forming true chlorite/smectite mixed layer clays (Table 1).

Kaolinite appears almost in all samples. It is distinguished from chlorite by the presence of peak position at 3.58°A. SEM micrographs of kaolinite are book shaped (Plate E) which indicates their authigenic origin.

The greatest differences in the clay minerals of <2 m fraction are to be found when comparing the younger sediments with older ones, within which the mineral assemblage is varied. Smectite content is abundant in younger sediment as compared to older and gradually diminishes downward stratigraphically. Detrital mica is the major mineral in almost all samples. Chlorite is generally scarcer with a fairly uniform content throughout the samples. The most notable difference occurs in the distribution of I/S and kaolinite. Kaolinite diminishes downwards stratigraphically but is found in almost all samples. The highest kaolinite content was found in Oligocene-Miocene rocks.

6. Discussion and Conclusions

The abundance of highly smectite I/S observed may suggest that there was an appreciable amount of disseminated volcanic glass. The alteration of volcanic glass to smectite and zeolite minerals is by a solution/reprecipitation mechanism. The general diagenetic sequence for rhyolitic tuff is initial hydration of the glass, formation of smectite rims and precipitation of zeolite minerals. The formation of smectite results in the uptake and release of cations and increase in the pH. The increase in pH can then promote the precipitation of zeolite minerals. The alteration of the volcanic glass to smectite appears to alter more rapidly than smectite to illite transformation because smectite to illite transformation occurs over a larger depth and temperature. This is consistent with the faster rate of transformation observed for glass to smectite than smectite to illite in the hydrothermal experiments [14].

Some of the clay minerals are probably detrital because most samples contain discrete mica minerals in the coarser clay size fraction (Table 1). However, the pyroclastic deposits typically include variable amount of quartz, feldspar and mica grains associated with the volcanic glass.

The increase in percent illite layers with geological age and temperature observed in this study is similar to the increase observed in the the U.S. Gulf Coast region [15]. Initial illitization of smectite coincide the quartz transformation and the increase in the percent illite layers in I/S occurs in quartz rocks. The decrease in the activity of silica should favour the alteration K-feldspar and smectite to illite, kaolinite and chlorite [16].

The mineral association observed in the Northland Allochthon rocks, I/S, illite, kaolinite, chlorite and quartz suggest that the availability of K^{+1} is limited during illitization of smectite. A limited source of K^{+1} is supported by the low abundance of K^{+}-feldspar in the samples from the studied area. It is unlikely that the kaolinite from the Northland Allochthon area is detrital in origin because of the lack of a suitable source area. Authigenic kaolinite occurs in large amount from samples of Cretaceous age and was proposed to form from the alteration of volcanic glass, smectite and plagioclase feldspar.

6.1 Zeolite Minerals

Zeolite is rare in the rocks and occurs only in minor to trace amounts. Clinoptilolite and mordenite are the predominant zeolite minerals in addition to some analcime. The controls on the diagenesis of zeolite minerals are complex and include the initial composition and grain size of the glass, temperature and pore water chemistry [17]. Clinoptilolite is more common in the rocks from Mangakahia complex rocks of Cretaceous age (Plate F).

On the basis of above discussion, following conclusions can be made from this study:

1. A significant amount of the I/S in the northland allochthon basins appears to be derived from the alteration of the volcanic material disseminated in the rocks. The alteration of volcanic glass to smectite appears to be rapid.
2. The percent illite layers in the I/S increases from 30% to 80% that correspond to a present day temperature of 100 - 200°C. The dominance of plagioclase over K-feldspar, the presence of diagenetic kaolinite and the anomalously high fixed ammonium content of the I/S suggest that K availability limits the amount of illitization and results in the transformation of smectite to kaolinite, chlorite.
3. Zeolite minerals are common in minor to trace amounts in many of the rocks studied. Analcime and mordenite were primarily identified in the quartz rocks. Formation of zeolites may be limited because the pH is buffered by the precipitation of dolomite.
4. Mineralogic constituents of different lithofacies from Northland Allochthon rocks are dominently detrital quartz, albite, illite, chlorite, kaolinite and smectite. The clay minerals occur both as distinct species and randomly interstrstified minerals. Mineralogy and chemistry are consistant with derivation from Waipapa source rocks, basement now exposed in the area.
5. Smectite may be converted to chlorite through chlorite/smectite mixed layers. Corrensite is a 1:1 regular chlorite/smectite or chlorite/vermiculite mixed layers with a low angle 28°A diffraction peak. Regular and irregular chlorite/smectite mixed layers occurred throughout zeolite facies sequence of North Range Group of Southland [18]. Corrensite indicates a temperature range of 90°-100°C during normal conditions of diagenesis [19]
6. Disappearance of Kaolinite upon burial is also dependant on compositional factors but unlike smectite shows very minor variation. Mineral transformation may have been affected by chemical composition of source materials and the pore water.

References

[1] E. Abdullayev, E.W. Ehrmann, C. Khalifazade and E. Huseynov (ANAS). Distribution of Clay Mineral Assemblages in Lower Pliocene Sediments, Western Flank of the South Caspian Sea. 74 EAGE Conference & Exhibition incorporating SPE EUROPEC 2012, Copenhagen, Denmark (2012) 4-7.

[2] R.E. White. Introduction to the Principles and Practice of Soil Science, Blackwell Scientific Publ. Inc. (1987).

[3] C. Yang and R. Hesse, Clay Minerals **26** (1991) 211.

[4] B. Velde, Mineralogical Magzine **49** (1985) 387.

[5] C. Buhmann. Clays and Clay Minerals **40** (1992) 53..

[6] H. Lindgreen, Clays and Clay Minerals **39**, No.1 (1991) 54.

[7] H.K. Chang, F.T. McKenzie and J. Schoonmaker, Clays and Cay Minerals **34** (1986) 407.

[8] R.M. Pollastro, Clays and Clay Minerals **33** (1985) 265.

[9] P.F. Ballance and K.B. Sporli, Journal of Royal Society of New Zealand **9** (1979) 259.

[10] F.J. Brook, M.J. Isaac and B.W. Hayward. Geology of Autochthonous and Allochthonous Sequence of Between Kaitaia and Whangaroa, Northern New Zealand. N.Z. Geolgical Survey Record (1988).

[11] F. J. Brook. Sheets N1 and N2 - North Cape. Geological Maps of New Zealand, Department of Scientific and Industrial Research, Wellington **1**, No. 63 (1989) 360.

[12] M.J. Isaac and P.L. Grieve, RSNZ Bulletin **26** (1989) 95.

[13] A. Steiner, Clays and Clay Minerals **16** (1968) 193.

[14] J.S. Compton. Clays and Clay Minerals **39**, No. 5 (1991) 449.

[15] E. Perry and J. Hower, Clays and Clay Minerals **18** (1970) 165.

[16] D.D. Eberl and J. Hower, Geological Society of American Bulletin **87** (1976) 326.

[17] A. Iijima. Geological Occurrences of Zeolite in Marine Environments, In Natural Zeolites Occurrence, Properties Use, L.B. Sand and F.A. Mumpton (eds.) Pergamon Press, New York (1978) pp. 175-198.

[18] H.J. Kisch. J. of Metamorphic Geology **9** (1991) 665.

[19] A. Iijima, M. Uttada and R.F. Gould, Am. Chem. Soc. (1971) 342.