Sedimentary Zeolite Deposits in New Zealand

Introduction:

Reviews of zeolite mineral resources in New Zealand were published in MacFarlan and Barry (1991), Thompson et al. (1995), and Christie et al. (2002). New Zealand occurrences of various zeolite minerals are listed in Railton and Watters (1990), and zeolites hosted in sedimentary rocks are found in three geological settings (see map):

1 Altered rhyolitic tuffs in lake beds of Quaternary age in the Taupo Volcanic Zone,
2 Marine tuffs and volcaniclastic sandstones of Miocene age in Northland and Auckland,
3 Weakly metamorphosed marine tuffs and volcaniclastic sandstones of Triassic-Jurassic age in Southland and southwest Auckland.

The only current mining of zeolite in New Zealand is from altered rhyolitic tuffs in lake sediments of Quaternary age in the Taupo Volcanic Zone (Brathwaite et al., 2006), although efforts have been made to market mordenite-rich tuff from the Paradise Quarry deposit in Northland (2 above). There is also some potential for production from zeolite deposits in Miocene marine tuffs in the Auckland region (2 above) and from Triassic-Jurassic marine tuffs in Southland and southwest Auckland (3 above).

Zeolites in rhyolitic tuffs in lake sediments of Quaternary age in the Taupo Volcanic Zone

Geology and Mineralogy:

Zeolite minerals are widespread as alteration minerals in tuffs and ignimbrites in the Taupo Volcanic Zone. Mordenite and clinoptilolite occur as alteration products of vitric-rich lacustrine tuffs and ignimbrites (Roberts, 1997; Brathwaite, 2002a, 2002b, 2003, 2006; Brathwaite et al., 2006). Mordenite, clinoptilolite, laumontite and wairakite occur as vein minerals in some active and extinct geothermal fields (Steiner, 1953, 1955, 1977; Henneberger and Browne, 1988; Simmons et al., 1992). Wairakite was first described from the Wairakei geothermal field by Steiner (1955).

Zeolites are most abundant in lacustrine tuffs of the Ngakuru Formation, a 100-300 m thick sequence of finely stratified siltstone, diatomite, sandstone, conglomerate and interbedded tuffs (Brathwaite, 2003; Brathwaite et al., 2006)*. The formation overlies Ohakuri Ignimbrite dated at 240 ka, and is overlain by the 64 ka Earthquake Flat Pyroclastics and younger alluvial sands and gravels. Individual zeolite deposits contain 30-80% mordenite ± clinoptilolite over a thickness of up to 45 m in thinly stratified tuff beds (Figs. 1 & 2).

Figure 1. Thinly bedded zeolitic vitric tuff sequence at Mangatete Road quarry, Ngakuru.

* Information on geological units mentioned in this article can be found in the New Zealand Stratigraphic Lexicon database at: http://data.gns.cri.nz/stratlex/index.jsp.

Figure 2. Thinly bedded zeolitic vitric tuff at Mangatete Road quarry, Ngakuru.

The tuffs are composed mainly of glass shards and pumice clasts, with minor volcanic plagioclase, quartz and biotite crystals. Glass shards in the tuffs are replaced by zeolite minerals, which from X-ray diffraction (XRD) analysis consist of the silica-rich zeolites mordenite and clinoptilolite. Scanning electron microscope (SEM) micrographs show that mordenite occurs as a mesh of acicular crystals replacing glass shards (Fig. 3a, b,c), and as thin fibres coating platy crystals of clinoptilolite (Fig. 2d). Both the mordenite and clinoptilolite are very fine grained (1-10 µm). The zeolites are accompanied by hydrothermal K-feldspar, opal C-T and smectite, along with relict volcanic quartz.

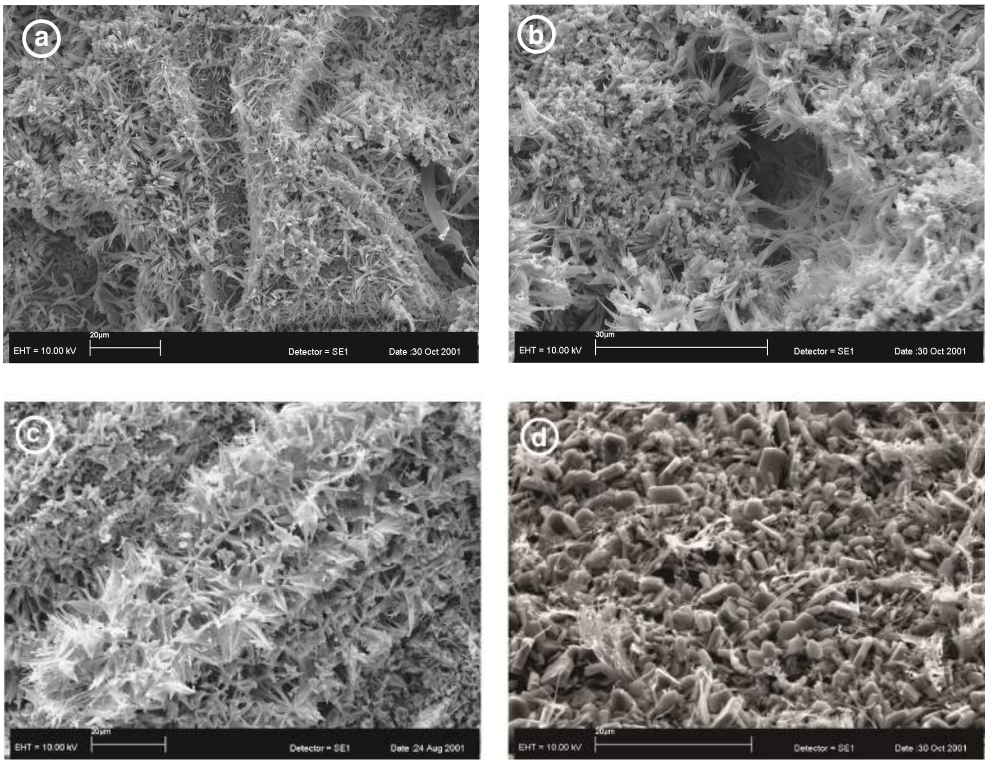

Figure 3. SEM images of zeolites from zeolitic tuffs at Ngakuru. (a) Acicular mordenite replacing matrix and molds of glass shards (curved). (b) Mesh of acicular mordenite crystals. (c) Aligned mesh of acicular mordenite crystals. (d) Tabular clinoptilolite crystals with minor fibrous mordenite.

Chemistry:

Semiquantitative analyses by SEM-EDS of mordenite and clinoptilolite show Si/Al ratios of 5.2-5.5 and 3.7-4.6 respectively as shown in the following Table (clinoptilolite and mordenite from Ngakuru) and in Brathwaite (2003).

Zeolite / Sample	**Clinoptilolite**[a]					**Mordenite**[b]	
	64958a	64958b	64960a	64961a	64961b	64957a	64957b
Si	28.80	29.39	29.59	29.39	29.84	40.38	40.62
Al	7.67	7.00	6.66	6.46	6.08	7.71	7.38
Fe^{3+}	0.74	0.43	0.11	0.14	0.23	0.03	0.12
Mg	0.29	0.27	0.25	0.29	0.29	0.27	0.36
Ca	0.79	1.08	1.10	1.22	1.01	1.08	1.56
Na	1.26	1.17	0.90	0.99	0.56	3.99	2.34
K	0.90	0.74	1.85	2.79	2.84	0.66	1.02
Si/Al	3.75	4.20	4.44	4.55	4.91	5.24	5.50
Ca/K	0.88	1.45	0.60	0.44	0.36	1.64	1.53
Ca/Na	0.63	0.92	1.23	1.23	1.80	0.27	0.67

[a] Nos. of ions based on 72 oxygens. [b] Nos. of ions based on 96 oxygens.

Representative XRF analyses of the zeolitic tuffs from Ngakuru (analysts Spectrachem Analytical) are given in the following Table and Brathwaite (2003).

Site / Sample	**Mangatete**				**Twist Road**				
	64956	64958	64960	64961	64982	64983	64984	64985	13-03
SiO_2 (%)	71.89	71.67	78.47	73.28	70.80	70.67	71.92	70.94	72.25
TiO_2	0.18	0.17	0.13	0.16	0.14	0.21	0.14	0.15	0.20
Al_2O_3	13.70	13.16	11.09	11.90	11.69	12.41	11.21	12.33	12.96
Fe_2O_3	1.61	1.19	1.39	0.83	1.17	1.41	1.07	0.87	0.98
MnO	0.03	0.02	0.06	0.04	0.01	0.02	0.01	0.01	0.01
MgO	0.31	0.39	0.37	0.34	0.17	0.18	0.16	0.16	0.70
CaO	1.25	1.82	1.16	1.81	2.01	2.05	1.93	1.87	1.25
Na_2O	2.29	2.15	0.46	0.73	1.19	1.63	1.17	1.16	1.91
K_2O	2.79	1.69	2.18	4.11	4.31	4.01	4.15	4.20	3.92
P_2O_5	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.02	0.02
Loi	5.62	7.35	4.34	6.22	8.31	7.09	7.93	7.91	5.67
Sum	99.68	99.61	99.67	99.43	99.81	99.69	99.72	99.62	99.82
Ba (ppm)	389	1232	765	1175	637	624	633	644	749
Rb	170	193	118	258	133	123	128	135	72
Sr	57	115	65	131	90	103	91	92	95
Y	35	26	26	24	42	38	40	42	42
Zr	206	195	151	190	149	177	149	172	192
Nb	11	9	7	10	12	11	11	10	9
Th	11	10	6	13	14	12	12	13	14
Ga	19	14	12	13	14	14	13	14	17
Zn	55	71	51	56	37	45	35	38	50
Cu	4	2	3	2	3	3	2	1	3
Cr	3	<1	2	2	6	7	15	8	2
Sc	10	11	9	10	<1	<1	<1	<1	13
U	2	3	1	2	3	4	2	2	3
La	31	35	28	26	29	33	37	34	39
Ce	68	62	43	40	50	56	58	57	72

The cation exchange capacity of representative mordenite-rich tuff samples from the Twist Road deposit is in the range of 102-122 cmol(+)/kg (equivalent to meq/100 g) (see Table).

Sample	Exchangeable[a]				CEC[b]	**Base saturation** (%)
	Ca^{2+}	**Mg^{2+}**	**K^{+}**	**Na^{+}**		
Z1/10/1-3	53.6	2.05	36.8	24.5	114	102
Z1/10/4-5	29.7	19.2	25.7	36.1	102	109
Z1/10/6-7	23.5	25.6	23.9	40.2	109	104
Z1/13/1-2	56.9	1.96	33.0	25.8	122.0	96
Z1/13/3-5	26.8	26.0	22.9	37.4	117.6	96
Z1/13/6-7	21.0	21.6	16.5	35.0	107.0	88

[a] Exchangeable base (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) values, expressed as (cmol(+)/kg), were determined by ammonium acetate extraction.
[b] CEC values, expressed as cmol(+)/kg, were determined by measuring colorimetrically the ammonium ions displaced from the exchange sites by leaching the sample with NaCl.
For details of these methods see:http://www.landcareresearch.co.nz/services/laboratories.

Physical properties:

Mordenite-rich tuff, Twist Road

Appearance (colour)	white cream
Bulk Density	0.7-1.0 g/cm^3
Thermal stability	450°C
Rock porosity	52-73%

Additional information:

Several of the zeolite deposits are overlain by phreatic hydrothermal eruption breccias and silica sinters, which have been C-14 dated at c. 32 to 8.5 ka (Brathwaite, 2003; Drake et al., 2014). The zeolite and associated sinter deposits appear to be localised at the intersections of lineaments orthogonal to NE-striking faults within a large graben structure (Drake et al., 2014).

Lower grade zeolite deposits occur near Ohakuri dam, where glass within the Ohakuri Ignimbrite is hydrothermally altered to mordenite, clinoptilolite, opal and smectite (Henneberger and Browne, 1988).

Figure 4. Thinly bedded zeolitic vitric tuff sequence at Twist Road quarry, Ngakuru.

Reserves and production: Blue Pacific Minerals Ltd quarries about 50,000 tonnes of zeolitic tuff annually, mainly from the Twist Road (Davies Farm) deposit (Fig. 4) near Ngakuru. Substantial tonnages of zeolite are present in this and nearby deposits, with an inferred resource in excess of 5 Mt in the Twist Road and Mangatete deposits. The Twist Road Quarry and the processing plant at nearby Tokoroa are currently (2015) being expanded to handle an annual production of 60,000 tonnes.

Main applications: Two of the deposits (Twist Road and Mangatete) near Ngakuru are being worked by Blue Pacific Minerals and uses include: 1) adsorbents for oil/chemical spills and animal wastes, 2) stockfeed additives, 3) water treatment and filters, 4) conditioners for sports turf and slow release fertilizer, and 5) cement/pozzalan applications (Nguyen and Tanner, 1998; Mowatt, 2000; Brathwaite et al., 2006; www.bluepacificminerals.co.nz). These uses are engendered by the high porosity (50-70%) and odour absorption, and cation exchange capacity (90-120 meq/100 g) of the zeolitic tuffs (Nguyen and Tanner, 1998; Brathwaite et al., 2006). Blue Pacific Minerals have recently developed a modified zeolite product (AQUAL-P), which scavenges phosphate from water and has wide applications in aquaculture and in the treatment of waste water and eutrophic lakes (e.g. Özkundakci et al., 2010).

Zeolites in marine volcaniclastic sediments of Miocene age in Northland and Auckland

The zeolite minerals analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite are variously present in the Miocene age Waitemata Group sedimentary rocks in the wider Auckland area, and in its correlatives in Northland, and at Fletcher Bay at the northern end of the Coromandel Peninsula (Fig. 1). They were formed by the alteration of volcanic glass in volcaniclastic beds during diagenesis (Sameshima, 1978; Davidson and Black, 1994).

At Whareana Bay, Tom Bowling Bay Formation contains 70-90% clinoptilolite in tuff beds. The clinoptilolite is a silica-poor (Si/Al^{+}Fe^{+3} = 3.85), high-K variety (Sameshina, 1978). A fine ash bed (2 m thick) at the top of a sequence of bedded tuffs at Whanghape Harbour contains about 60% mordenite (Maxwell, 1968). At Paradise limestone quarry near Whangarei, sandy limestone is underlain by a 5-m thick, tuff bed composed of mordenite (60%) and lesser amounts of calcite, quartz and chlorite (Edbrooke and Brook, 2009). At Puketotara in the Kaipara area, a 90 cm thick tuff bed in the deep marine, Timber Bay Formation contains mainly erionite with lesser amounts of chabazite and clinoptilolite. The erionite is silica-poor ((Si/Al^{+}Fe^{+3} = 2.79), with alkalis dominant over alkaline earths (Sameshina, 1978). Minor amounts of analcime are found in tuffaceous beds in the Kaipara area, and in the matrix of andesitic grit in the Colville Formation at Fletcher Bay. Analcime constitutes up to 30% of the matrix of the Albany Conglomerate, which crops out north of Auckland (Sameshina, 1978). The Parnell Grit in the Auckland metropolitan area contains chabazite in thin tuff beds at Takapuna Beach and at Karaka Bay, clinoptilolite in Auckland City, and phillipsite between Auckland and Leigh, 60 km to the north (Sameshina, 1978). Davidson and Black (1994) described a strong lithologic control on diagenetic zeolite assemblages in the Waitemata Group, with clinoptilolite + mordenite + chabazite ± erionite as a cement in volcaniclastic sandstones, analcime + clinoptilolite + chabazite ± erionite in rhyolitic tuff beds, and analcime cement in conglomerate beds.

Zeolites in weakly metamorphosed marine tuffs and volcaniclastic sandstones of Triassic-Jurassic age in Southland and southwest Auckland

Thick bedded deposits of laumontite and thinner beds containing clinoptilolite/ heulandite or analcime have been described in tuffs and volcaniclastic sandstones of the Triassic Murihiku Supergroup strata of the Taringatura Hills of Southland (Coombs, 1954; Coombs, 1959). The largest deposit, containing up to 70% laumontite with fine quartz, feldspar, clay and chlorite minerals, forms a steeply dipping bed about 3 m thick and several kilometres long. A thicker bed, containing a lesser laumontite content, extends for about 14 km along the full length of the North Range between Mossburn and Lumsden (Coombs, 1959).The clinoptilolite/ heulandite- or analcime-bearing beds are stratigraphically above the laumontite-rich beds, and on the basis of this sequence a zeolite metamorphic facies, comprised of the mineral assemblages of laumontite-albite grading up to clinoptilolite-heulandite-analcime, was recognised by Coombs et al. (1959). Zeolite alteration in the

Murihiku Supergroup rocks of Southland is further described and discussed by Boles and Coombs (1975, 1977).

Zeolitic tuffs and volcaniclastic sandstones also occur in Triassic-Jurassic Murihiku Supergroup rocks between Port Waikato and Marokopa, south of Auckland (Coombs et al., 1959; Black et al., 1993; Woldemichael and Black, 2002). Laumontite, occurring as a cement and replacing feldspar and lithic clasts, is the dominant zeolite in volcaniclastic sediments of Late Triassic to Middle Jurassic age, whereas heulandite, as cavity fillings or replacing volcanic glass, is the more common zeolite in Middle-Late Jurassic sequences (Black et al., 1993; Woldemichael and Black, 2002). Laumontite-rich tuff beds, 30-50 mm thick, occur in the Triassic Ngutunui Formation of the Murihiku Supergroup at Marokopa (MacFarlan, 1998). Near Port Waikato, Late Jurassic volcaniclastic sandstones contain a stilbite-heulandite-analcime assemblage and a vitric tuff bed contains phillipsite-analcime-celadonite (Black et al., 1993).

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