Zeolite deposits in lacustrine tuffs, Ngakuru, Taupo Volcanic Zone

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Abstract

In the Ngakuru area zeolite deposits occur in late Quaternary lacustrine vitric tuffs of the Ngakuru Formation and two of the deposits are being mined. The Ngakuru Formation overlies the Ohakuri Ignimbrite dated at c. 240 ka, and is overlain by younger alluvial sands and gravels. Individual zeolite deposits contain 50-80% zeolite over a thickness of up to 45 m in thinly stratified vitric tuffs and are localized along NE-trending normal faults. Glass shards in the tuffs are replaced by the silica-rich zeolites mordenite and clinoptilolite. Amorphous silica (opal A), opal-CT, K-feldspar and smectite are also present. The zeolites and other minerals are very fine grained (<10 ìm), with open meshes of crystals that result in high porosities (52-70%) in mordenite-rich tuffs. Zeolitic tuff samples typically have cation exchange capacities of 80 to 110 meq/100 g and internal surface areas of 25-58 m^2/g, which combine to give high liquid and odour absorption capacities. The first zeolite deposit (Mangatete) was found in 1992, and this and the Twist Road deposit are worked by quarry benching into the side of hills. The zeolitic tuffs are dried and crushed to produce a variety of products including adsorbents for soaking up oil/chemical spills and animal wastes, animal feed supplements, water treatment, and sports turf and slow release fertilizer. The Ngakuru zeolite deposits formed at shallow depth (<100 m) along fault zones from reaction of glass-rich tuff beds with groundwater-diluted geothermal water during the late Quaternary, and are as young as 8500 yr BP from ^{14}C dating of plant material in sinter associated with the Mangatete deposit.

Keywords: *mordenite, clinoptilolite, late Quaternary, vitric tuffs, adsorbents, animal feeds, fertilizer.*

Introduction

Mordenite and clinoptilolite deposits occur within a sequence of late Quaternary lake sediments and ignimbrites in the Ngakuru district within the Taupo Volcanic Zone (TVZ) (Fig. 1). The first deposit was found in 1992 at Mangatete Road and commercial production followed soon after granting of a mining permit and resource consent in late 1992 (Merchant unpublished report, 1993; Roberts, 1997). Other zeolite deposits in the Ngakuru area near Parsons Road and near Twist Road (Davies Farm) were subsequently discovered by NZ Natural Zeolite Ltd (Mowatt, 1999). Quarries at the Mangatete and Twist Road deposits are currently in production. Uses for the Ngakuru zeolite include: 1) adsorbents for soaking up oil/chemical spills and animal wastes (e.g. pet litter), 2) animal feed supplements, 3) water treatment, and 4) conditioners for sports turf and slow release fertilizer.

Most naturally occurring zeolites are formed at temperatures below 200°C under hydrous conditions at neutral to alkaline pH. The main occurrences of zeolites are in tuffs and volcaniclastic rocks in lakes or deep sea basins (Hay & Sheppard, 2001). Zeolites are also common in low

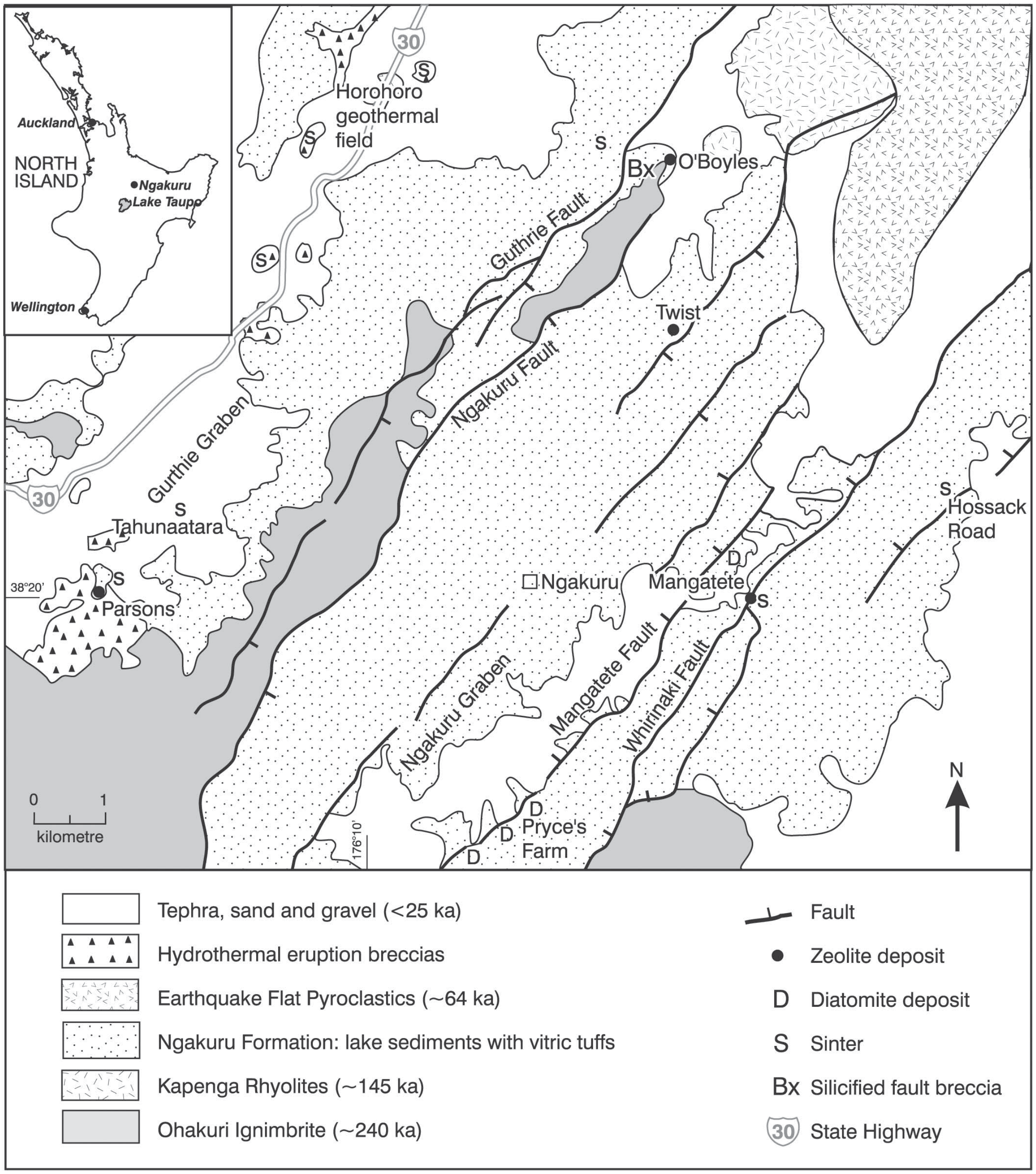

Figure 1. Geological map of the Ngakuru area, Taupo Volcanic Zone. Modified after Grindley (1960), Rutherford and Fransen (1990), Villamor and Berryman (2001) and Brathwaite (2003). $^{40}Ar/^{39}Ar$ ages for the Ohakuri Ignimbrite and Kapenga Rhyolites from G. Leonard (pers. comm., 2004).

temperature hydrothermal alteration zones in geothermal and epithermal systems (Utada, 2001). Hydrothermal zeolites mordenite, clinoptilolite, laumontite and wairakite occur in active and extinct geothermal fields of the Taupo Volcanic Zone (TVZ), such as Wairakei (Steiner, 1977; Simmons et al., 1992) and Ohakuri (Henneberger & Browne, 1988).

The geology, mineralogy and geochemistry of the Ngakuru zeolite deposits have been described by Brathwaite (2002, 2003). This paper summarizes that work and also the exploration, mining and processing of the zeolite.

Geological setting

The Ngakuru area lies within the Taupo Fault Belt, a NE-trending belt of active extension on the western side of the TVZ (Grindley, 1960; Villamor & Berryman, 2001). The TVZ contains calc-alkaline volcanic rocks less than 2 Myr old, with voluminous tephras, ignimbrites and rhyolites, and minor dacite and andesite lavas (Wilson et al., 1995). Within the TVZ there are numerous lakes, some associated with caldera volcanoes (e.g. Rotorua and Taupo), which are depocentres for tephras and volcaniclastic sediments. Lakes also existed during the late Quaternary, as indicated from the occurrence of diatomaceous silts, pumice sands and tuffs (Huka Group of Grindley, 1960) over an area of 110 by 40 km (Smith et al., 1993). The TVZ is a region of elevated heat flow, predominantly by hydrothermal convection through thin crust (15 km) intruded by magma. The heat flow is manifested by high-temperature geothermal fields, which are mainly confined to the eastern side of the TVZ. There is a still active geothermal field at Horohoro in the northern part of the Ngakuru area (Fig. 1).

Most of the Ngakuru area is underlain by the Ohakuri Ignimbrite, mainly consisting of non-welded pumice lapilli tuff dated by $^{40}Ar/^{39}Ar$ at c. 240 ka (G. Leonard pers. comm., 2004). Several domes of the Kapenga Rhyolites of Nairn (2002), dated by $^{40}Ar/^{39}Ar$ at c. 145 ka (G. Leonard pers. comm., 2004), crop out in the north of the area.

The Ohakuri Ignimbrite is overlain by the Ngakuru Formation, which was mapped by Grindley (1960) as formation hu2 (u_2 of Nairn, 2002) of the Huka Group. The Ngakuru Formation is a 100-300 m-thick sequence of siltstone, vitric tuff, pumiceous tuff, diatomite, sandstone and conglomerate. Bedding is essentially flat lying and the distribution of the formation is disrupted by still-active, NE-trending normal faults, which separate it along a horst block of Ohakuri Ignimbrite into the Ngakuru and Guthrie grabens (Fig. 1). The Ngakuru Formation is overlain by the c. 64 ka Earthquake Flat Pyroclastics and alluvial sands and gravels of the Hinurera Formation, which are overlain by the Tere Tephra (c. 24 ka) or Okareka Tephra (c. 21 ka) of Nairn (1992).

Zeolite deposits

Vitric tuff beds in the Ngakuru Formation are the main host rocks for the zeolite deposits, some of which are localized adjacent to faults (e.g. Mangatete and Twist road zeolite deposits, Fig. 1). Individual zeolite deposits contain 50-80% zeolite over thicknesses of up to 45 m in thinly stratified vitric tuffs (Fig. 2). The zeolitic tuffs are white, with iron staining along joints, and are locally interbedded with siltstone and mudstone. The primary components in the tuffs are glass shards and pumice clasts, with minor volcanic plagioclase, quartz and biotite crystals. Some of the zeolite deposits are adjacent to sinters and hydrothermal eruption breccias. The Mangatete zeolite deposit is overlain by about 25 m of weakly silicified crystal-lithic tuffs and pumice-rich sand, with a 2 m-thick sinter capping the top of this sequence. Plant material in the sinter has a ^{14}C age of 8498 ± 60 yr BP (Brathwaite, 2003).

The mineralogy, from X-Ray diffraction (XRD), consists of the silica-rich zeolites mordenite and clinoptilolite, with lesser amorphous silica (opal-A), opal-CT and K-feldspar (Brathwaite, 2003). Mordenite occurs as a mesh of crystals replacing glass shards (Fig. 3A), and as fibres coating platy crystals of clinoptilolite (Fig. 3B). Mordenite is more abundant than clinoptilolite in the lower beds within individual deposits, and is the dominant zeolite in the Twist Road deposit. Both the mordenite and clinoptilolite are very fine grained (1-10 ìm, Figs. 3A, 3B). Smectite occurs in trace to common amounts, and is abundant in intercalated mudstone laminae. Chemically the vitric tuffs are of rhyolitic composition (Brathwaite, 2003).

Figure 2. Thin bedded zeolitic tuffs exposed over a thickness of about 30 m in quarry benches at the Mangatete Road zeolite deposit.

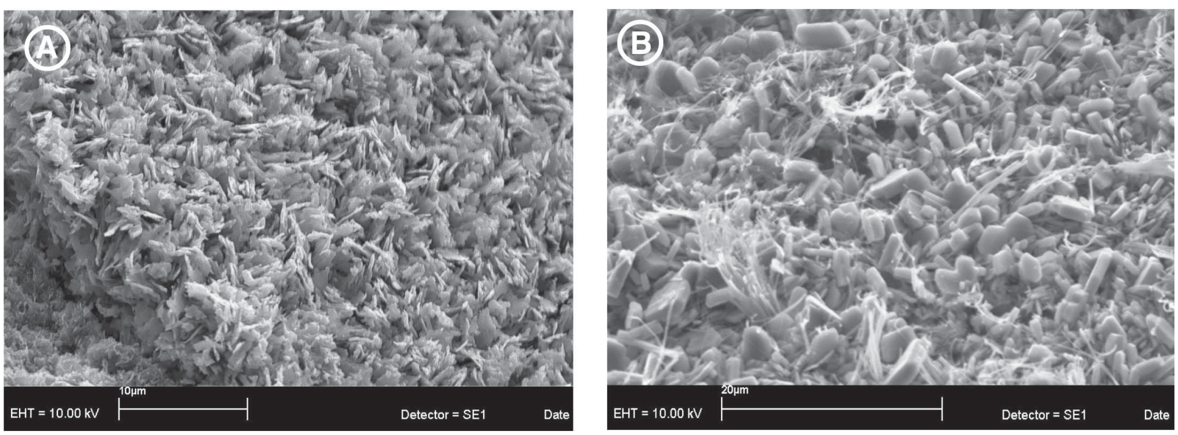

Figure 3. Scanning electron microscope images of zeolites in zeolitic tuff from Mangatete zeolite deposit. (A) mesh of mordenite crystals. (B) tabular crystals of clinoptilolite with minor fibrous mordenite. Scale bars shown in microns.

Properties of the zeolitic tuffs

Dry bulk densities are mainly in the range of 0.66-1.12 g/cm^3 (Brathwaite, 2003). Mordenite-rich samples generally have the lowest densities (0.66-0.99 g/cm^3), whereas those containing clinoptilolite are higher (1.0-1.33 g/cm^3). Measured porosities are inversely related to densities and range from 45-73%, and are particularly high (52-73%) in samples from the Twist Road deposit. The very low densities are due to the voids created by the open mesh structure of the mordenite crystals (Fig. 3A).

Cation exchange capacity (CEC) and ammonium exchange capacity (AEC) values for samples from the Mangatete deposit are in the range of 70-97 meq/100 g for CECs and 88-118 meq/100 g for AECs (Roberts, 1997). Mowatt (1999, 2000) noted that Ngakuru zeolitic tuffs typically have CECs of 76-113 meq/100 g and internal surface areas of 25-58 m^2/g, which combine to give high liquid and odour absorption capacities.

Formation of the zeolite deposits

The presence of sinter, hydrothermal eruption breccia and/or silicified fault breccia in the vicinity of the zeolite deposits suggests that they are associated with geothermal activity similar to some at the active geothermal systems in the TVZ. The Wairakei geothermal system contains mordenite (Steiner, 1977) and clinoptilolite, which formed at temperatures of 60-160°C. The main fluid type at Wairakei is a dilute alkali chloride water of near neutral pH (e.g. Hedenquist, 1986). By analogy, mordenite and clinoptilolite in the Ngakuru deposits probably formed at similar temperatures as a result of interaction groundwater-diluted alkali chloride water with glass shards in the vitric tuffs (Brathwaite, 2003).

Exploration, mining and processing

The Mangatete zeolite deposit was found in February 1992 by R.J. Merchant and P.J. Roberts during a survey for zeolite in hydrothermal alteration zones in the Rotorua-Taupo region. A quarry was developed at Mangatete in October 1992 by Mining Assets Ltd and was subsequently acquired by FERNZ. The Mangatete zeolite deposit crops out on a hillside (Fig. 2) along a fault zone. Exploration of the deposit was carried out by mapping and sampling, including digging of pits with an excavator. The zeolite contents of the samples were estimated from semiquantitative XRD analyses.

Following acquisition of the Mangatete quarry and associated processing plant in Tokoroa from FERNZ in 1998, NZ Natural Zeolite has expanded the operations and made significant improvements to the processing plant. Additional occurrences of zeolitic tuffs including the Twist Road deposit, were discovered by C. Mowatt of NZ Natural Zeolite (Mowatt, 1999). A quarry and covered drying pad have been developed at Twist Road. The quarries are worked by benching with hydraulic excavators on a campaign basis, mainly in the summer to facilitate drying of the zeolitic tuff. The raw material is crushed and screened on site and placed in stockpiles (~40 000 m^3) for drying in the open air, or on the covered 5000 m^2 drying pad during wet months, before carting to the secondary processing plant at Tokoroa 25 km away. Secondary processing involves gas-fired kiln drying of the zeolite followed by a crushing and screening to produce a range of products of different particle size ranges and densities. Further processing by nutrient loading onto granular zeolite for the animal feed and fertilizer industries is carried out at the parent company's (Resource Refineries Ltd) Waharoa facility, 105 km north of Ngakuru (Hill, 2005).

The high cation exchange and open pore structure with high internal surface areas of the Ngakuru zeolite make it very effective in applications such as ammonium removal from waste water, and in animal feeds and fertilizers by providing an ideal host for loading with beneficial organic or inorganic liquids. The same characteristics provide for an extremely efficient mechanism for the absorption of liquids and odours (predominantly ammonia) for the pet litter and oil spill markets. The sports turf market also makes use of these two main attributes, but also requires a material that is resilient to mechanical breakdown to allow it to be blended with sand. The Twist Road deposit provides these characteristics, and the recently constructed Wellington and Waikato sports stadiums both include ~8% zeolite in the turf root zone to aid nutrient and moisture retention.

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Dave Hill holds an NZCE (Mech & Prod) and has spent 20 years in the mining & quarrying industries, five of these in the USA & UK. He is the General Manager and a director for Resource Refineries Ltd and is a director for Rocktec Ltd, an engineering solutions company to the quarrying & mining industries.