INDUSTRIAL ZEOLITES IN THE PRINCETON BASIN
(92H)

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INTRODUCTION

Recent developments in the agricultural, horticultural and industrial applications of natural zeolites have sparked interest in the occurrence of these minerals in the Princeton basin of south-central British Columbia. A previous study conducted by Read (1987) reported the occurrence of zeolites in five distinct tephra lenses of the Allenby Formation of the Princeton basin: Sunday Creek tephra, Snowpatch ash, Asp Creek ash, Tailings ash and Bromley Vale tephra. The zeolites, formed in an open hydrologic system, replace original glass shards in waterlain rhyolite tuff and volcanic breccia layers. The objectives of this study are twofold: to determine the extent of zeolitization in selected horizons of the Allenby Formation, and to investigate their potential for economic application, particularly in agriculture and horticulture.

Based on the results of Read's study, Tailings ash and Bromley Vale were chosen for further research. During fieldwork in September 1988, two Tailings ash sections (VM88-9 and VM88-10) and one Bromley Vale section (VM88-11) were sampled (Figure 3-6-1). These sections correspond to Z7, Z4 and Bromley Vale Adit No. 1 respectively in Read (1987). This report summarizes the results of the fieldwork and preliminary laboratory characterization. Future work will include further laboratory, greenhouse and field studies.

GENERAL GEOLOGY

Encompassing 170 square kilometres of south-central British Columbia, the Princeton basin is a half-graben bounded on the east by the north-northeasterly trending, west-dipping Boundary fault (Figure 3-6-1), and filled with Tertiary sediments of the Princeton Group. As proposed by Hills (1965), the stratigraphy of the Princeton Group consists of the Lower Volcanic Formation and the Allenby Formation. The Lower Volcanic Formation, predominately intermediate in composition, is comprised of greater than 1370 metres of interbedded flows, breccias, tuffs and volcaniclastic sediments. It is overlain by the Allenby Formation: a 1600 to 2000-metre sequence of sandstone, shale, waterlain rhyolite tephra and coal. Broken by northwesterly to westerly trending folds and faults south of Princeton, the shallower northern half of the trough is sediment dominated, while the southern half is predominantly volcanic (Read, 1987).

STRATIGRAPHY

The geology of the basin has been mapped at 1:50 000 scale (McMechan, 1983), and the zeolitized tephra horizons and the surrounding sedimentary stratigraphy at 1:25 000 (Read, 1987). Fieldwork conducted in 1988 for this project concentrated on producing finer stratigraphic detail on the selected exposures, and obtaining representative samples across each section: in each case, samples were taken at 1.0-metre intervals, with the exception of the upper 10 metres of VM88-10 where the interval was 2.5 metres. The stratigraphic sections are summarized in Table 3-6-1.

Detailed correlation of the Tertiary rocks in the basin is restricted by the rarity of good exposures. It has been suggested, however, that Bromley Vale tephra should correlate with Tailings ash if the Asp Creek fault (Figure 3-6-1) has a right-lateral strike-slip displacement of roughly 1200 metres (Read, 1987).

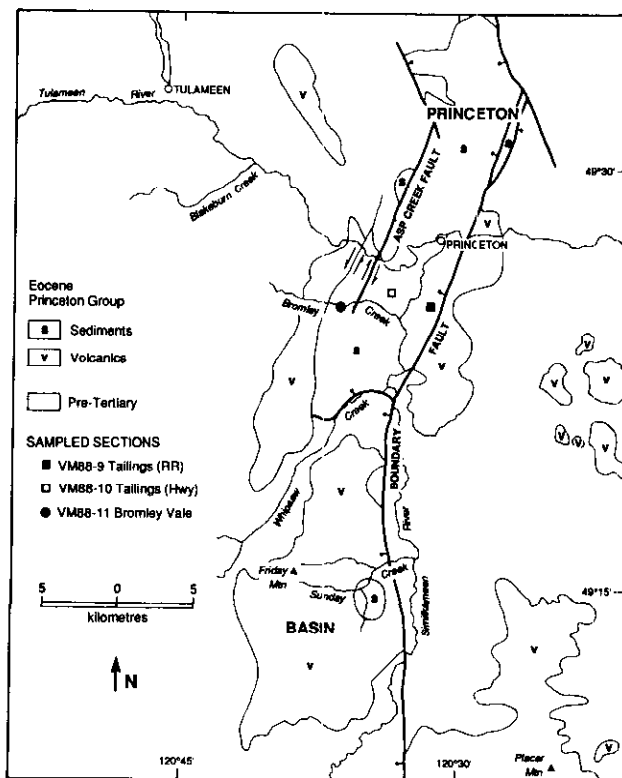Tailings ash is exposed on the south limb of the westerly trending Tailings syncline, from the left bank of the Similka-

Figure 3-6-1. Simplified geological map of the Princeton basin showing location of studied exposures. Modified from Read (1987).

Section: VM88-9 (Tailings ash on Railway)		
BED	DESCRIPTION	THICKNESS(m)	HEIGHT(m)*
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3	tuff, vitric rhyolite, buff; massive; ze, pl, ksp, qz, bi, mm; no fossils	10	4.05
2	mudstone, grey, fine; thin bedded, ripple marks, flame structures, nodules; qz, ksp, pl, mm clc; no fossils	0.05	4
1	tuff, vitric-crystal, buff to light grey; massive; ze, pl, ksp, qz, mm; no fossils	4	0

Section: VM88-10 (Tailings ash on Highway)		
BED	DESCRIPTION	THICKNESS(m)	HEIGHT(m)*
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5	tuff, vitric-crystal, light grey to buff; coarse bedded to blocky, fining upward; ze, mm, mus, pl, ksp, qz, bi; no fossils	12	11
4	ash, unconsolidated, light grey,; ze, mm, pl, ksp, qz, bi; no fossils	2	9
3	tuff, vitric-crystal, light grey; medium to coarse bedded, fining upward; pumice; ze, qz, pl, ksp, mm, mus; wood fragments (.5 to 5cm)	3	6
2	breccia, rhyolitic, buff, fine; massive; rock fragments (to 2cm), pumice; ze, pl, ksp nt, qz; wood fragments (to 10cm)	2	4
1	tuff, mixed, grey; massive; subangular rock fragments; pl, ksp, ze, qz, nt; no fossils	1	3

Section: VM88-11 (Bromley Vale)		
BED	DESCRIPTION	THICKNESS(m)	HEIGHT(m)*
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3	tuff, vitric-crystal, light grey to cream; thin to medium bedded, few rock fragments; ze, qz, pl, ksp, mm, bi; wood fragments (.1 to 1cm)	8	1
2	ash, unconsolidated, buff; pumice, angular rock fragments; ze, ksp; wood fragments	0.2	0.8
1	tuff, fine, dark grey, massive; ze, pl, ksp, mm, qz; no fossils	0.8	0

* Height refers to height above base of exposure.
N.B. Refer to Table 2 for mineral abbreviations.

Table 3-6-1. Stratigraphic sections.

meen River to the abandoned Copper Mountain railway grade. VM88-9 corresponds to a 14-metre section of this outcrop along the grade. The section consists of 4 metres of vitric crystal tuff overlain by 10 metres of vitric rhyolite tuff. Both tuffs contain zeolite (clinoptilolite), but the thin mudstone unit separating them does not. Expandable clays are present throughout the section.

On the opposite limb of the syncline, VM88-10 is exposed in a roadcut on the northwest side of Highway 3, approximately 600 metres east of a side-road along Bromley Creek and 100 metres northeast of a gravel pit. Due to obliteration by slumping, 3 metres at the base of the exposure were not included in this section.

A mixed tuff underlies a 2-metre-thick, fine rhyolite breccia which is overlain by a thick montmorillonite-bearing vitric crystal tuff.

VM88-11 corresponds to an exposed section of Bromley Vale tephra along Bromley Creek upstream from Adit No. 1. With the exception of a massive tuff and an ash layer at the base of the outcrop, the section consists of an 8-metre-thick, thin to medium-bedded, vitric crystal tuff. As in VM88-10, the presence of wood fragments in some strata indicates deposition by water (Read, 1987), and neither the top nor the bottom contact of the zeolitized horizon is exposed.

MINERALOGY

The mineralogy of the samples (Table 3-6-2) was determined by a Rigaku Geigerflex x-ray diffractometer under the following operating conditions: copper K-alpha radiation,

step scan mode, 4 second count time, 0.02° step width. In order to prepare powder presses, the samples were first powdered using a Retsch pulverizer.

Contrary to earlier findings of clinoptilolite and lesser amounts of stilbite (Z.D. Hora, personal communication, 1988), clinoptilolite is the only zeolite present in the samples studied. Plagioclase and potassium feldspars, quartz and mica (biotite, muscovite) are the most common accessory minerals. The presence of natrolite in some samples and ill-defined peaks intermediate to those for clinoptilolite and feldspar indicate the possible presence of poorly crystalline feldspathoidal minerals. Diffraction peaks associated with expandable clay minerals have been attributed to montmorillonite, however, further x-ray diffraction studies are necessary for the precise characterization of the clay mineralogy.

ZEOLITE CONTENT

Although x-ray diffraction permits the identification of the zeolite species, quantitative analysis is restricted by the interference of other phases and the non-proportional nature of peak intensities. As a result, the zeolite content of the samples was estimated from their cation exchange capacity (CEC); that is, the availability of exchangeable cations loosely held within the tetrahedral framework of their crystal structure (Mumpton, 1984). Natural zeolites have characteristically high cation exchange capacities.

In this study, the method for determining cation exchange capacity is based on clinoptilolite's high selectivity for

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SAMPLE	CEC (meq/100g)	MINERALOGY*
VM88-9 (Tailings ash on Railway):		
13-14m	157	ze,pl,ksp,qz,mm
12-13m	170	ze,ksp,qz
11-12m	123	ze,pl,ksp,bi,mm
10-11m	149	ze,pl,ksp,mm
9-10	129	ze,pl,qz,bi,mm
8-9m	159	ze,ksp,pl,qz,mm
7-8m	145	ze,ksp,pl,qz,mm,nt
6-7m	155	ze,ksp,mm
5-6m	146	ze,ksp,qz
4-5m	133	ze,ksp,qz,mm
3-4m	147	ze,pl,ksp,qz,mm
2-3m	156	ze,pl,ksp,qz,mm
1-2m	157	ze,pl,ksp,qz
0-1m	152	ze,pl,ksp,qz,mm
VM88-10 (Tailings ash on Highway):		
17.5-20m	89.3	qz,pl,ksp,bi,mm
15-17.5m	105	ze,pl,mus
12.5-15m	91.1	ze,pl,mus
10-12.5m	83.5	ze,pl,ksp,mm,mus
9-10m	75.0	ze,pl,ksp,qz mus,mm,
8-9m	64.3	pl,ksp,ze,bi,ksp
7-8m	83.1	ze,mm
6-7m	78.1	pl,ksp,ze,mus,qz
5-6m	137	ze,pl,ksp,qz,mm
4-5m	110	ze,pl,ksp
3-4m	109	ze,pl,ksp,qz
2-3m	118	alb,ze,pl,ksp,qz
1-2m	114	ze,pl,ksp,qz,nt
0-1m	104	ksom,ze,pl,ksp,qz,
VM88-11 (Bromley Vale):		
8-9m	125	ze,pl,ksp,qz,mm
7-8m	139	ze,pl,ksp,qz
6-7m	139	ze,pl,ksp,qz
5-6m	132	ze,pl,ksp,mm
4-5m	135	ze,pl,ksp,mm
3-4m	103	ze,pl,ksp,mm,bi
2-3m	142	ze,pl,bi,mm
1-2m	153	ze,ksp
0-1m	78.1	ze,pl,ksp,qz,mm

* alb=albite, bi=biotite, ksp=K feldspar, kspm=
microcline, mm=expandable clay mineral,possibly
montmorillonite, mus=muscovite, nt=natrolite,
pl=plagioclase, qz=quartz, ze=clinoptilolite.
Underlined mineral is predominant

Table 3-6-2. Mineralogy of samples from stratigraphic sections (See Table 3-6-1).

NH_4^+. One gram of powdered sample was shaken for five days in 50 millilitres of 1 molar NH_4Cl. After washing out the excess NH_4^+ with distilled water, the ammonium-saturated samples were twice exchanged with 50 millilitres of 1 molar KCl. The supernatants from both exchanges were collected in a 250-millilitre volumetric flask and brought up to volume with 1 molar KCl. The solutions were then analysed for NH_4^+-N using a Technicon colorimetric auto-analyser. The cation exchange capacity was calculated from this concentration. Values for duplicates of each sample were averaged and are presented in Table 3-6-2 and illustrated in Figure 3-6-2.
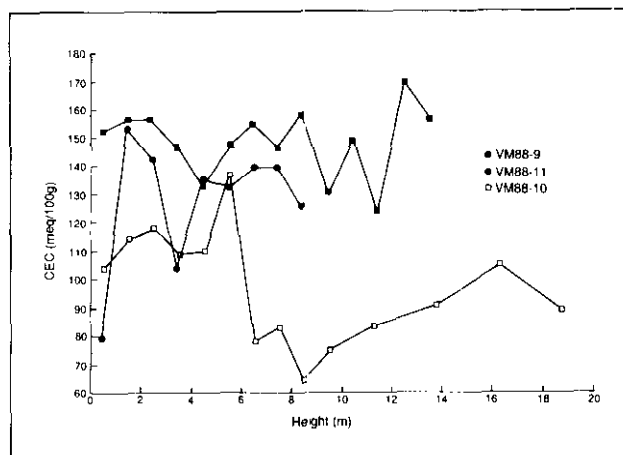

Figure 3-6-2. Plot of cation exchange capacity versus height illustrating extent and uniformity of zeolitization across VM88-9, VM88-10 and VM88-11.

The accuracy of zeolite content, as estimated by this method, is restricted by the presence of such minerals as feldspars, feldspathoids and expandable clays which contribute to the total cation exchange capacity of the sample. Furthermore, exchange capacity is a function of the degree of Al^{3+} substitution for Si^{4+} in the crystal framework of the zeolite; yet the ratio of Si:Al is not constant (Mumpton, 1984). It is possible, however, to estimate the zeolite content by assuming a cation exchange capacity of 220 meq per 100 grams for pure clinoptilolite, and disregarding the effects of secondary minerals.

The zeolite content of the studied samples ranges from 29 to 77 per cent. VM88-9 shows the least variability with 56 to 77 per cent clinoptilolite across the section, excluding the mudstone layer which is not zeolitized. In Tailings ash on Highway 3 (VM88-10), the rhyolitic breccia has the highest zeolite content (50 per cent), and that of the vitric crystal tuff in VM88-11 is about 60 per cent, generally decreasing upwards. As previously noted, however, these estimates may be high due to the presence of secondary minerals, particularly expandable clay minerals.

ECONOMIC GEOLOGY

In 1980, world production of natural zeolites was 270 000 tonnes: European production accounted for one-half of this total and Japanese for 80 000 tonnes (Sersale, 1985). The industrial applications of natural and synthetic zeolites differ owing to the uniformity, efficiency, performance quality, design parameters and high cost of synthetic zeolites; natural zeolites are better suited for less sophisticated, large-scale uses.

The most profitable applications of zeolites utilize their adsorption, ion exchange and molecular sieve properties. Present applications are in the following fields: construction industry as pozzolan; agriculture as soil conditioners, fertilizer regulators, deodorizers and feed supplements; aquaculture in filtering systems; treatment of heavy metals and waste water; oxygen separation; solar energy storage; and domestic use as deodorizers and pet litter. Clinoptilolite has demonstrated varied success in each of these applications:

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proper utilization requires careful characterization of the material with respect to type and amount of zeolite, variability within the deposit and associated mineralogy.

CONCLUSIONS

Tailings ash and Bromley Vale horizons of the Allenby Formation are potential economic deposits of natural zeolite owing to their high clinoptilolite content (estimated 26 to 77 per cent), uniformity, thickness and accessibility. Samples taken across VM88-9 (Tailings ash on railway) show the least variability and the highest cation exchange capacity values.

The preliminary results of this study warrant further characterization of the deposits, including clay mineralogy and zeolitization using scanning electron microscopy and x-ray diffraction. The potential application of these zeolites in agronomy and horticulture, based on their high cation exchange capacity and affinity for NH_4^+, will also be investigated.

ACKNOWLEDGMENTS

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