COMMERCIAL-GRADE MORDENITE DEPOSITS OF THE HORN MOUNTAINS, SOUTH-CENTRAL ALASKA

By
D.B. Hawkins

SPECIAL REPORT 11

STATE OF ALASKA

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COMMERCIAL-GRADE MORDENITE DEPOSITS OF THE HORN MOUNTAINS, SOUTH-CENTRAL ALASKA

By D.B. Hawkins[1]

ABSTRACT

The Horn Mountains, in south-central Alaska, have zeolitized tuff beds 14 kilometers long and at least 30 meters thick and that consist of 50 percent mordenite. This mordenite tuff is of commercial grade and shows promise as a sulfur-dioxide sorbent.

Both the individual tuff beds and the entire tuff unit are graded. The double grading implies that the tuff was formed by a large undersea volcanic (dacitic?) explosion.

Mordenite and other zeolites such as heulandite, laumontite, and analcime, which occur in other rock units of the area, were formed by chemical reactions controlled by the composition and permeability of the parent material and the composition of pore water. During zeolite formation the volcanic pile was subjected to fluid pressures of 0.5 to 3 kilobars and temperatures less than 200°C.

INTRODUCTION

The Horn Mountains are located in townships 22 and 23 north, ranges 11 and 12 east, Seward Meridian, on the eastern flank of the Talkeetna Mountains in the Nelchina area (pl. 1). The geology of this area was described by Grantz (1965). The present study is concerned with deposits of the zeolite mordenite in the Horn Mountains and is a continuation of that reported by Hawkins (1973, 1976). The previous studies established the presence of mordenite and other zeolites such as heulandite, laumontite, and analcime, and delineated an apparent zeolite zonation in the rocks of the Horn Mountains area. The purpose of the present study was to determine the extent and grade of the mordenite deposit in the area. To this end, fist-sized samples were collected from numerous outcrops of tuff and tuffaceous wackes for subsequent laboratory studies. Plate 1 shows the sample localities.

GEOLOGY

As described by Grantz (1965), the Horn Mountains structurally are a horst consisting of Lower Jurassic Talkeetna Formation volcanic rocks. Little folding exists, suggesting shallow burial at the time of tectonism. The younger rocks surrounding the horst are sandstones of the Middle Jurassic Tuxedni Formation and sandstones and argillites of the Cretaceous Matanuska Formation. A geologic map, modified from Grantz (1965), was prepared as part of the present study and is shown as plate 1. Splays associated with the Caribou fault, a major fault in the area, delineate the Horn Mountains horst.

The present work was confined to the Talkeetna Formation, which in the area consists of about 2,500 feet of tuffs, flows, and sandstone. The rock units mapped were recognized mainly on the basis of topographic expression and stratigraphic relation to the distinctive mordenite-bearing tuffs. The lithology of the various units is quite similar in that they consist of andesite and basalt flows, interbedded with tuffaceous wackes and vitric tuffs.

Rock units designated Jtk-a, Jtk-b, Jtk-c, Jtk-d, and Jtk-e (pl. 1) were recognized. These differ from those previously mapped (see table below) because of the larger area studied in the present work.

This Study	Previous Study
Jtk-a	Not recognized
Jtk-b	Jtk-1
Jtk-c	Jtk-2, Jtk-3
Jtk-d	Jtk-3, Jtk-4
Jtk-e	Jtk-5

UNIT Jtk-e

Map unit Jtk-e, the southernmost and stratigraphically lowest unit, consists mainly of volcanic sandstone, basalt and andesite flows, and some tuffs. Montmorillonite is abundant in these rocks, and landslides commonly occur in this unit. Zeolitization is not pronounced, although void fillings of heulandite are evident in the coarser sandstones. Mordenite is present in several thin (2-meter-thick) tuffs of this unit (e.g., samples 17b and 79; Hawkins, 1976). Unit Jtk-e forms a series of low, northeast-trending ridges immediately adjacent to Alfred Creek, and is particularly well exposed at South Lake. Throughout much of the study area, unit Jtk-e is in fault contact with the stratigraphically higher unit Jtk-d. At sample locality 42, on the north shore of South Lake, the pelecypod Gryphaea cf. G. *cymbium* Lamarck was found in sandstone float from the ridge immediately north of South Lake. The pelecypod is an index to the Pliensbachian Stage (Imlay 1955).

[1]Geology department, University of Alaska, College, AK 99701.

UNIT Jtk-d

Map unit Jtk-d is characterized by tuffaceous wackes and by andesite and basalt(?) flows with subordinate pumiceous and vitric tuffs. This unit is a ridge former. The lowest member of the unit is a coarse-grained tuffaceous wacke, which is well exposed at the narrows of the east fork of Alfred Creek and at the placer mine on Albert Creek. The unit is extensively zeolitized, with void fillings and veinlets of heulandite especially common in the coarser lithologies. The uppermost member of this unit is a sequence of tuffaceous wackes interbedded with thin andesite flows. Both the wackes and flows have been extensively altered to the assemblage calcite, analcime, and heulandite. Subordinate laumontite is present in the form of laumontite, calcite, and quartz veins.

UNIT Jtk-c

Map unit Jtk-c, the mordenite-bearing tuff unit, is the principal object of this study. This unit conformably overlies unit Jtk-d. The mordenite tuff weathers to a tannish-white color and characteristically forms rounded, rubble-crop noses on ridges extending down from the summit of Horn Mountain. These rubble crops do not support vegetation. They consist of thin (2-cm-thick) plates about 10 cm or less in length. Often, thin rosettes of radiating mordenite crystals 0.5 to 1 cm in diameter are present in the tuff partings. These crystals are an excellent field guide to this unit. When walked on, the tuff makes a musical "clinking" sound that belies the highly siliceous nature of the material. Typical exposures of this tuff are shown in figures 1, 2, and 3.

The western extremity of the tuff is in the Flume Creek drainage. Here, a typical rubble crop of tuff is exposed partly down the ridge on the west side (opposite) of the saddle (fig. 3). The tuff is terminated here by several faults, with the final exposure being a thin (6-meter-thick) sliver of tuff at the headwaters of a draw immediately below the summit of Horn Mountain. At the eastern extremity in the east fork of North Creek, the tuff has a greenish cast and appears to be more argillaceous than elsewhere.

In thin section, the North Creek tuff is indistinguishable from the lower members of this unit at sample locality 12 (see below). X-ray diffraction reveals, however, that the tuff here is no longer mordenite bearing but contains heulandite instead. The transition in this tuff from mordenite to heulandite occurs somewhere in North Creek. For the most part, the mordenite tuff is nonfossiliferous, although a few fragments and casts of wood can be found in the tuff at the headwaters of Albert Creek. At North Creek, however, in the eastern-

Figure 2. Basin at headwaters of west fork of Alfred Creek showing mordenite tuff rubble crops in left and right foreground, capping ridge leading down from the summit of Horn Mountains. See photograph locality B on plate 1.

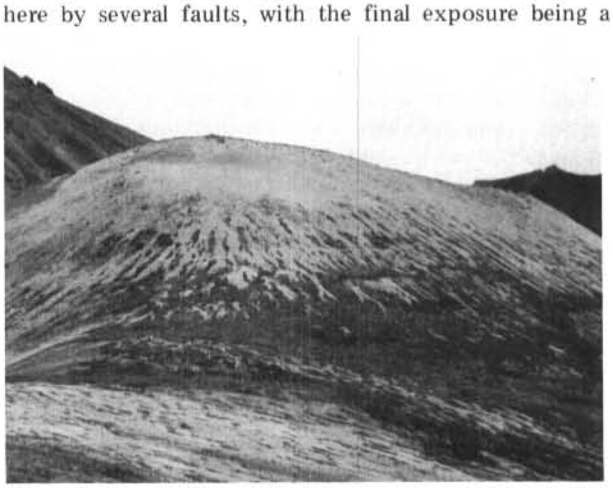

Figure 1. Mordenite tuff rubble crop at the headwaters of Albert Creek. See photograph locality D on plate 1.

Figure 3. Mordenite tuff and talus on ridge dividing the headwaters of the west fork of Alfred Creek from Flume Creek. See photograph locality A on plate 1.

most exposure, the tuff contains abundant, handsome fossils of the ammonite *Haugia sp.* This genus is restricted to the middle(?) and upper Toarcian stage of the Lower Jurassic. The presence of these ammonites and the previously mentioned Gryphaea and graded bedding in the tuffs (see below) provide excellent stratigraphic control—control that was lacking at the time of the previous work (Hawkins, 1976) and which resulted in a misinterpretation of the stratigraphic relations in that report.

The thickness of the tuff exceeds 30 meters over most of its 14-kilometer length. A well-exposed section at the headwaters of the east fork of Alfred Creek was sampled (series 12) at 6-meter intervals. The total length of the traverse directly across strike was 46 meters. As shown in plate 1, the dip of the beds was 23 degrees; thus the calculated exposed thickness of this unit was 30 meters. At this locality, the tuff is fine grained and well sorted. Figure 4 is a photograph of a typical hand specimen from the upper 10 meters of this unit. About 40 percent of the bottom member of the tuff unit consists of whole or broken crystals of plagioclase (An_{28}), the largest of which are about 0.2 mm long. The rest of the rock consists of small pumice fragments in a devitrified ash matrix.

Although mordenite and quartz are major constituents as shown by X-ray diffraction, neither is evident petrographically. The tuff becomes progressively finer grained and less plagioclase rich toward the top of the unit. The top 10 meters consist of very fine-grained devitrified ash, with some ($\leq$5%) small (<0.024-mm) plagioclase fragments. From bottom to top of this unit, the relative quantity and grain size of plagioclase decreases and the quantity of devitrified ash increases. Ferromagnesian minerals are very rare in this unit (as they are in all but Jtk-a). Some of the coarser units contain fragments of andesite, the ferromagnesian minerals of which have been extensively altered to iron oxides and montmorillonite. Apparently, most of the ferromagnesian minerals in these units have been destroyed since deposition.

A sequence of tuff samples collected from locality 30 (pl. 1; fig. 5) show interesting sedimentary and metamorphic textures not evident at locality 12. As shown in figure 5, small-scale bedding planes can be seen which in some cases are cross bedded and which also show evidence of soft-sediment slumping. The individual beds are composed of a layer rich in plagioclase fragments overlain by fine-grained pumiceous material. Thus, there is both a small-scale and a large-scale grading in this sequence. As Fiske and Matsuda (1964) have pointed out, such doubly graded bedding is a property of marine pyroclastics. Figure 6 is a photograph of hand specimen 30-11 from the top of the tuff unit and shows the development of incipient calcite-analcime(?) porphyroblasts, which appear to postdate the formation of mordenite and quartz in the tuff.

Figure 5. Mordenite tuff showing thin beds, some of which are cross bedded. Sample number 30-9.

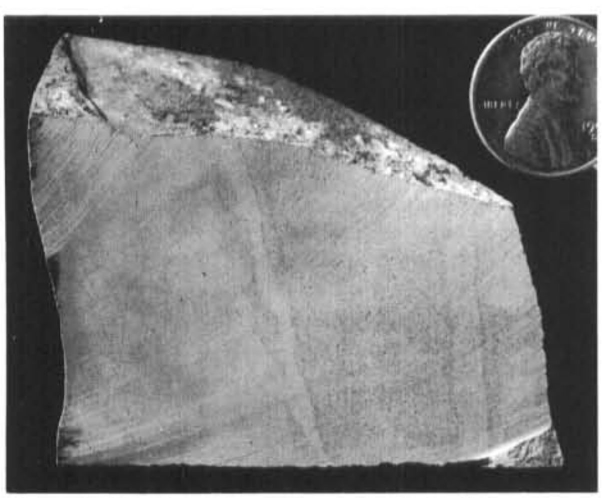

Figure 4. Hand specimen of mordenite tuff from upper 10 meters of tuff and at sample locality 12.

UNIT Jtk-b

Map unit Jtk-b, which conformably overlies unit Jtk-c, is topographically—though not stratigraphically—the highest unit in the Horn Mountains horst. It is characterized by volcanic sandstone, basalt and andesite flows. The unit is extensively zeolitized and contains abundant veins of chalky laumontite and large (2- to 4-cm) void fillings of heulandite, an example of which is shown in figure 7. The mineral assemblages calcite-heulandite-analcime, heulandite-analcime, and quartz-laumontite either with or without calcite are common. Montmorillonite accompanies all the above assemblages. The zeolite assemblages are similar to those in the underlying Jtk-d unit although laumontite is much more common in the upper unit. Mordenite is lacking in the Jtk-b unit. Figures 8 and 9 are photomicrographs

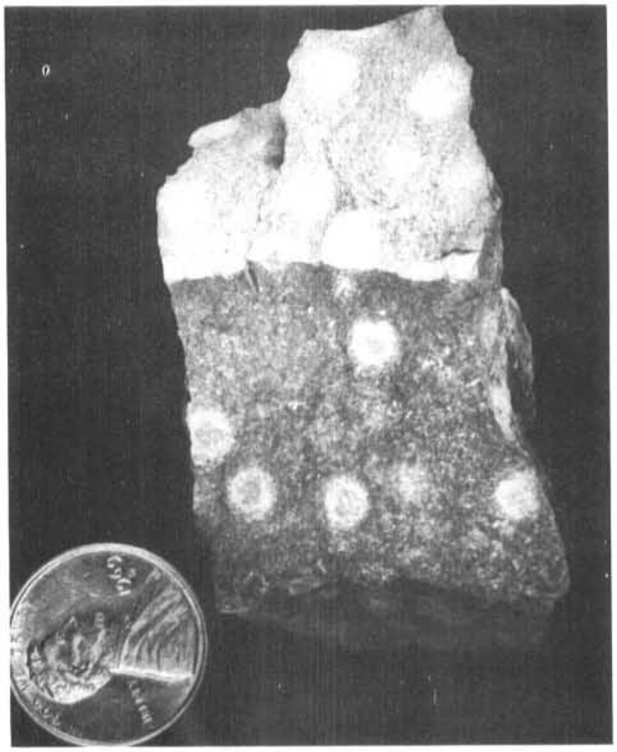

Figure 6. Mordenite tuff from sample locality 30-H, showing development of incipient calcite-analcime porphyroblasts.

showing the assemblages calcite-heulandite and heulandite-analcime.

UNIT Jtk-a

Map unit Jtk-a consists of pumiceous crystal wackes interbedded with andesite flows. This unit is in fault contact with the underlying Jtk-b unit. The contact is often well defined, as can be seen in figure 10, a photograph of the north face of Horn Mountains. Compositionally, ferromagnesian minerals such as augite and iron oxide pseudomorphs after pyroxene are more abundant than in the underlying units. Analcime with or without calcite and laumontite characterizes this unit. Analcime often occurs as an alteration product of plagioclase. Microcrystalline quartz is present as cement in several samples. Heulandite is present but is not as abundant as in other units. No mordenite was observed in this unit.

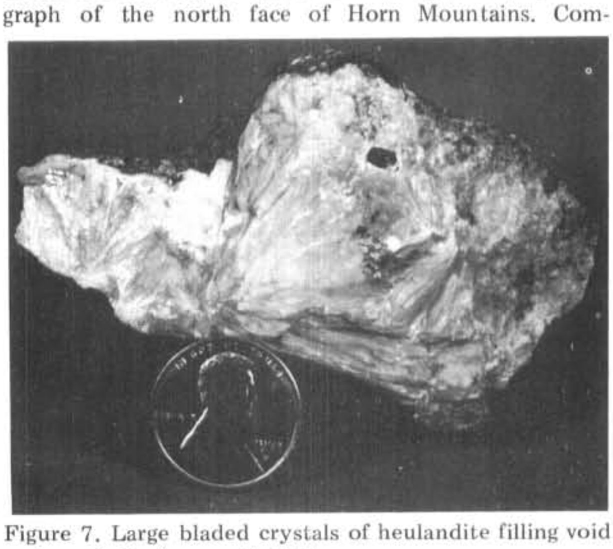

Figure 7. Large bladed crystals of heulandite filling void in andesite from unit Jtk-b.

LABORATORY STUDIES

Each sample collected was split; one part was ground for laboratory studies and the other was used to make a thin section. X-ray diffraction patterns of the ground samples were obtained as described previously (Hawkins, 1973). Samples containing zeolites of the heulandite family were heated following the method of Alietti (1972) to distinguish between heulandite and the more siliceous, alkali-metal dominant clinoptilolite. Samples containing clay minerals were treated with ethylene glycol and X-rayed again to determine if expanding-lattice clay minerals were present. The results of these analyses, supplemented by petrographic examination, are given in table 1. Several samples were suspended in bromoform-ethanol solutions of the requisite specific gravity to separate and concentrate the minerals present. In this way, analcime in sample 20 was separated from heulandite (specific gravity of <2.21) and quartz, calcite, and plagioclase (specific gravity of >2.40). Following the method of Coombs and Whetten (1967), the separated analcime was mixed with silicon, and the resultant mixture was ground fine and X-rayed. Eight X-ray diffraction scans over the analcime$_{639}$ and silicon$_{331}$ diffraction peaks were made at a scan speed of 1/4 degree per minute. The average $\triangle 2\theta$ ($\triangle 2\theta = 2\theta$ analcime$_{639}$ - 2θ silicon$_{331}$) for this analcime was found to be 1.84 ± 0.04 degrees. From Coomb's and Whetten's curve, this value corresponds to an ideal anhydrous analcime composition of $Na_{15.2}Al_{15.2}Si_{32.8}O_{96}$.

Heulandite from samples 39 and 40 was concentrated in the <2.21 specific-gravity fraction of these samples. Heating tests clearly established that this heulandite belonged to Alietti's Group 1 heulandites inasmuch as the 020 diffraction peak completely disappeared after heating for 16 hours at 550°C.

All samples were examined petrographically, with particular attention being paid to the heulandite crystals. Boles (1972) showed that heulandite can exhibit either positive or negative elongation, depending on whether the Si-Al ratio is ≥ 3.57 or ≤ 3.52, respectively. In the present study, most of the heulandites were "length fast," that is, silica poor. Two of the samples, 31-11 and 37, both from unit Jtk-b slightly above the mordenite tuff, were "length slow," indicating that these heulandites were more silica rich than the others.

Finally, the field test for zeolites devised by Culfaz and others (1973) and described previously (Hawkins,

1976) was carried out on all samples. The results of this test are presented in table 1.

DISCUSSION
ORIGIN AND DISTRIBUTION OF ZEOLITES

The distribution and origin of the zeolites in the rocks of the Horn Mountains area were extensively discussed previously (Hawkins, 1975). A pronounced zeolite zonation was evident: a zeolite-free quartz zone was overlain by a heulandite zone, which in turn was overlain by a mordenite zone, followed by another heulandite zone, and finally by a laumontite zone. Only two analcime-bearing samples were observed—both were from the first heulandite zone. The sequence was attributed to burial metamorphism, with the laumontite representing the most deeply buried rocks. This, coupled with a lack of sedimentary and fossil control, led to a misinterpretation of the stratigraphy of the area. From the present work it is clear that the above-mentioned laumontite zone is in the stratigraphically highest rock unit of the four. Furthermore, although a zeolite zonation is still present, laumontite is now known to occur in both heulandite zones, although it is more abundant in the upper zone. Analcime is much more common than was previously thought and mordenite is restricted mainly to the tuffaceous Jtk-c unit, with tuff horizons in the Jtk-e unit. It is now clear that simple burial diagenesis with the topographically higher units being subjected to increased pressure-temperature conditions cannot explain the zeolite distribution observed. The particular diagenetic mineral assemblage observed is almost certainly a result of local chemical conditions prevailing with a given rock unit. As discussed previously (Hawkins, 1976), the rocks of the area encountered water pressures during burial of about 0.5 to 3 kilobars and temperatures not exceeding $200^{\circ}C$—possibly about $100^{\circ}C$ (Read and Eisbacher, 1974).

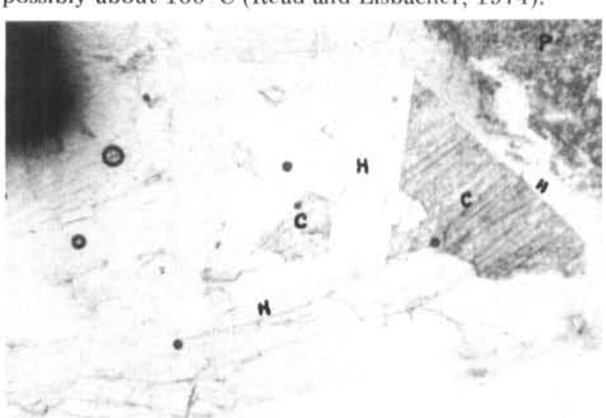

Figure 8. Photomicrograph of sample 31-4 showing sharp, angular calcite crystals (C), filling spaces between heulandite (H) blades. Pumice fragment (P) in upper right corner. The length of largest calcite crystal is about 2 mm.

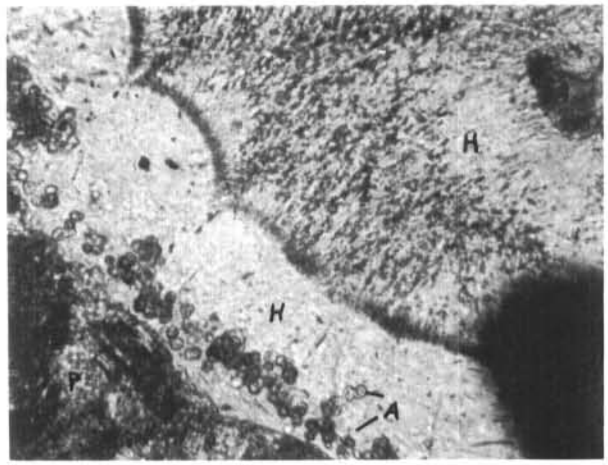

Figure 9. Photomicrograph of sample 31-6 showing small (0.02-mm) beads of analcime (A) at edge of vein in pumice (P). The analcime is enclosed in heulandite, two generations of which are present. Note the foreign particles being excluded at the recrystallization interface.

Mordenite is a very siliceous zeolite and requires a high activity of silica for its formation. As discussed in the previous report, mordenite in unit Jtk-c was formed by the alteration of a relatively impermeable vitric tuff. Plagioclase compositions in this tuff are within the andesine compositional range. This suggests that the tuff from which the mordenite formed may have been richer in silica than the other units.

Zeolite assemblages such as those described here have been extensively studied elsewhere and most recently reported on by Ghent and Miller (1974), Read and Eisbacher (1974), and Boles and Coombs (1975). Boles and Coombs suggest laumontite may form by the dehydration and desilication of heulandite:

Figure 10. The north face of Horn Mountains showing the faulted contact in the swale between the massive cliff forming unit Jtk-b (left) and the more permiceous Jtk-a unit (right). Photograph locality C on plate 1.

Table 1. *Sample number, hand-specimen description, mineralogy,*[1] *and results of field test.* (See plate 1 for sample locations.)

Sample	Description	Mineralogy[2]		ΔT (°C)
1	Andesite porphyry	Plagioclase, quartz, montmorillonite		0.0
2	Andesite	Plagioclase, quartz, mordenite(?)		0.5
3	Pumiceous wacke	Plagioclase, quartz, laumontite		0.4
4	Basalt	Plagioclase, quartz		0.7
5-A	Pumiceous crystal wacke	Plagioclase, quartz, heulandite, calcite		1.6
5-B	Pumiceous tuff	Plagioclase, quartz		1.8
6	Vitric tuff	Plagioclase, quartz, laumontite		6.1
7-A	Coarse pumiceous wacke	Plagioclase, quartz, heulandite		2.6
7-B	Pumiceous crystal wacke	Plagioclase, analcime, heulandite, calcite, montmorillonite		2.0
8	Pumiceous crystal wacke	Plagioclase, quartz, heulandite, montmorillonite		2.1
9-A	Pumiceous crystal wacke	Plagioclase, quartz, heulandite		3.2
9-B	Pumiceous tuff	Plagioclase, quartz, prehnite(?)		2.0
10	Vitric tuff	Plagioclase, quartz, mordenite		8.1
11-A	Pumiceous crystal tuff	Quartz, laumontite		0.4
11-B	Pumiceous crystal tuff	Quartz, laumontite		1.0
12-O	Vitric tuff	Quartz, plagioclase, mordenite	0[3]	6.7
12-A	-------- do --------	------------- do ---------	6	7.5
12-B	-------- do --------	------------- do ---------	12	7.0
12-C	-------- do --------	------------- do ---------	18	10.5
12-D	-------- do --------	------------- do ---------	24	9.8
12-E	-------- do --------	------------- do ---------	30	9.0
12-F	-------- do --------	------------- do ---------	36	9.8
12-G	-------- do --------	------------- do ---------	42	5.5
12-H	-------- do --------	------------- do ---------	46	6.2
13	Vitric tuff	Quartz, plagioclase, mordenite		6.0
14	Vitric tuff	Quartz, plagioclase, mordenite		4.4
15	Pumiceous crystal wacke	Plagioclase, quartz, heulandite		0.0
16	Pumiceous crystal wacke	Calcite, heulandite		0.2
17-1	Andesite (altered)	Plagioclase, quartz, analcime		0.0
17-2	Andesite (altered)	Plagioclase, quartz, analcime		0.0
17-3	Pumiceous crystal tuff	Plagioclase, quartz, laumontite		1.8
17-4	Andesite porphyry (altered)	Plagioclase, quartz, analcime		0.0
17-5	Andesite porphyry (altered)	Plagioclase, quartz, analcime		0.0

[1] Mineralogy determined principally by X-ray diffraction, supplemented by optical microscopy.
[2] Underlines denote zeolites.
[3] Distance in meters from top contacts, series 12 only.

Table 1. *Sample number, hand-specimen description, mineralogy, and results of field test*—Continued

Sample	Description	Mineralogy	ΔT (°C)
18-B	Andesite porphyry (altered)	Plagioclase, montmorillonite	0.0
18-M	Altered silicified pumice	Plagioclase, quartz, heulandite, mordenite, calcite, montmorillonite	- -
18-T	Pumiceous crystal wacke	Plagioclase, quartz, heulandite, laumontite, calcite, montmorillonite	6.2
19	Andesite porphyry	Plagioclase, quartz, montmorillonite	1.8
20	Basalt	Plagioclase, analcime, heulandite, calcite	1.6
21	Pumiceous wacke	Plagioclase, quartz, heulandite	2.4
22	Pumiceous crystal wacke	Plagioclase, quartz, heulandite	7.0
23	Vitric tuff	Plagioclase, quartz, mordenite	12.0
24	Vitric tuff	Plagioclase, quartz, mordenite	10.1
25	Pumiceous crystal wacke	Plagioclase, quartz, heulandite, montmorillonite	2.7
26	Pumiceous wacke	Plagioclase, quartz, heulandite, montmorillonite	2.5
27	Pumiceous wacke	Plagioclase, quartz, mordenite, montmorillonite(?)	7.0
28	Pumiceous crystal wacke	Plagioclase, quartz, heulandite	3.5
29-1	Pumiceous tuff	Laumontite, calcite	2.6
29-2	Pumiceous crystal wacke	Plagioclase, analcime, calcite, montmorillonite	2.7
29-3	Andesite porphyry	Plagioclase, montmorillonite	2.3
29-4	Quartz-laumontite-calcite vein	Quartz, laumontite, calcite	1.1
29-5	Andesite porphyry	Plagioclase, montmorillonite, analcime (tr)	2.2
29-6	Pumiceous wacke	Plagioclase, quartz, montmorillonite, analcime (tr), calcite (tr)	2.3
29-7	Pumiceous crystal wacke	Plagioclase, quartz, montmorillonite, analcime (tr)	1.5
29-8	Pumiceous crystal wacke	Plagioclase, quartz, vein quartz, montmorillonite	1.0
29-9	Andesite porphyry	Plagioclase, quartz, heulandite, montmorillonite	3.4
29-10	Pumiceous tuff	Plagioclase, quartz, vein quartz, analcime, calcite	2.5
29-11	Pumiceous tuff	Plagioclase, quartz, heulandite, analcime, mordenite, calcite	3.0
30-1	Pumiceous tuff	Plagioclase, quartz, heulandite, analcime	2.0
30-2	Pumiceous crystal tuff	Plagioclase, quartz, mordenite, calcite, analcime	5.6
30-3	Pumiceous tuff	Plagioclase, quartz, analcime, mordenite	6.1
30-4	Pumiceous crystal wacke	Plagioclase, quartz, mordenite	9.2
30-5	Pumiceous tuff	Plagioclase, quartz, mordenite	9.7
30-6	Pumiceous wacke	Plagioclase, quartz, montmorillonite	2.2
30-7	Vitric tuff	Plagioclase, quartz, mordenite	10.4
30-8	Pumiceous crystal wacke	Plagioclase, quartz, montmorillonite	2.6
30-9	Pumiceous tuff	Plagioclase, quartz, mordenite	6.6
30-10	Pumiceous tuff	Plagioclase, quartz, mordenite, analcime (tr)(?)	9.1
30-11	Pumiceous tuff	Plagioclase, quartz, mordenite, calcite	7.7
30-12	Vitric tuff	Plagioclase, quartz, mordenite	7.1
30-13	Vitric tuff	Plagioclase, quartz, mordenite, heulandite (tr)(?)	8.7
30-14	Vitric tuff	Plagioclase, quartz, mordenite	8.2
31-1	Andesite porphyry	Plagioclase, quartz, montmorillonite, laumontite, calcite	1.8
31-2	Pumiceous crystal wacke	Plagioclase, quartz, montmorillonite, heulandite, analcime (tr)	4.4

Table 1. *Sample number, hand-specimen description, mineralogy, and results of field test*—Continued

Sample	Description	Mineralogy	ΔT (°C)
31-3	Pumiceous crystal wacke	Plagioclase, quartz, heulandite	3.7
31-4	Pumiceous tuff w/heulandite vein	Quartz, heulandite, calcite	5.9
31-5	Pumiceous tuff	Quartz, laumontite	2.2
31-6	Pumiceous crystal wacke	Plagioclase, quartz, heulandite, analcime, montmorillonite	4.1
31-7	Pumiceous crystal wacke	Plagioclase, quartz, heulandite, montmorillonite	3.1
32	Vitric tuff	Plagioclase, quartz, mordenite	10.2
33-1	Pumiceous crystal wacke	Plagioclase, quartz, mordenite, heulandite	7.3
33-2	Pumiceous crystal wacke	Plagioclase, quartz, mordenite, heulandite	7.3
33-3	Tuffaceous wacke	Plagioclase, quartz, heulandite, montmorillonite	0.8
33-4	Pumiceous crystal wacke	Plagioclase, quartz, heulandite, analcime, montmorillonite	7.6
34-1	Vitric tuff	Quartz, heulandite, analcime (tr)	6.7
34-2	Pumiceous crystal wacke	Plagioclase, quartz, mordenite	2.4
34-3	Pumiceous crystal wacke	Plagioclase, quartz, mordenite	7.2
35	Vitric tuff	Plagioclase, quartz, mordenite	7.6
36	Pumiceous crystal wacke	Plagioclase, quartz, heulandite, analcime, calcite	3.2
37	Pumiceous crystal wacke	Plagioclase, quartz, heulandite	3.1
38	Pumiceous crystal wacke	Plagioclase, quartz, heulandite(?), montmorillonite	7.4
39	Vitric tuff	Plagioclase, quartz, heulandite, montmorillonite	11.2
40	Vitric tuff	Plagioclase, quartz, heulandite, montmorillonite	8.7
41	Vitric tuff	Plagioclase, quartz, heulandite, montmorillonite	10.4
42	Vitric tuff	Plagioclase, quartz, heulandite, montmorillonite	7.1

$$CaAl_2Si_7O_{18}\cdot 6H_2O = CaAl_2Si_4O_{12}\cdot 4H_2O + 3\ SiO_2 + 2\ H_2O \quad (1)$$

(Heulandite) (Laumontite) (Quartz) (Water)

Neither in the present study nor in those of Ghent and Miller or Read and Eisbacher is there evidence that this reaction occurred. Rather it appears that laumontite formed in these situations by deposition from silica-poor, calcium-rich pore water.

A common diagenetic assemblage observed in the present study is heulandite-analcime with or without calcite. As Zen (1961, 1974) and Ghent and Miller (1974) discuss, the formation of zeolites is affected by the partial pressure of carbon dioxide (pCO_2) in the system. At a high pCO_2, calcium-zeolite assemblages are replaced by the assemblage clay-calcite-quartz, as shown by the following reaction (for example, Ghent and Miller, 1974):

$$CaCO_3 + Al_2Si_2O_5\cdot 4H_2O + 2SiO_2 + 2\ H_2O = CaAl_2Si_4\cdot 4H_2O + CO_2 \quad (2)$$

(Calcite) (Kaolinite) (Quartz + Water) (Laumontite) (Carbon Dioxide)

As discussed by Ghent and Miller, the conditions for an equilibrium assemblage of calcite and laumontite require that if the activity of silica is fixed by quartz saturation, these minerals would be in equilibrium in an alkaline, calcium-rich, CO_2-deficient fluid. Ghent and Miller point out that these conditions are seldom observed in natural hydrothermal systems.

That similar conditions must apply for the mutual stability of calcite and heulandite can be seen by combining equations (1) and (2) to yield (3), a reaction strictly analogous to (2):

$$CaCO_3 + Al_2Si_2O_5\cdot 4H_2O + 5\ SiO_2 + 4H_2O = CaAl_2Si_7O_{18}\cdot 6H_2O + CO_2 \quad (3)$$

(Calcite) (Kaolinite) (Quartz) (Water) (Heulandite) (Carbon Dioxide)

A calcite-heulandite assemblage is shown in figure 8, from which it appears that heulandite formed first, followed by calcite, which apparently did not form at the expense of the heulandite. This observation, coupled with the data for the calcite-laumontite stability, suggests that the calcite-heulandite assemblage is not an equilibrium assemblage.

Analcime in the assemblage analcime-heulandite with or without calcite could have been formed from heulandite as described by Boles (1971). Figure 9 shows an analcime-heulandite assemblage and seems to indicate that the analcime formed first, probably by reaction between the vein fluid and the vitric ash and plagioclase, with the heulandite forming at a later stage. There is no textual evidence from other samples to suggest that the analcime formed from heulandite (or clinoptilolite) was silica rich, that is, that it bore the signature of the siliceous parent regardless if quartz was present. Analcime from sample 20, the same locality discussed previously (Hawkins, 1976) was shown to have an ideal anhydrous composition ($Na_{15.2}Al_{15.2}Si_{32.8}O_{96}$). This composition would place the analcime in the silica-poor group C of Coombs and Whetten (1967); that is, having been formed by direct precipitation or by direct reaction of highly alkaline water with sediment. Thus, on the basis of textual evidence and composition, it appears that the analcime in the Horn Mountains rocks was not formed from a heulandite precursor. Rather, it seems that the observed assemblage analcime-heulandite-calcite is not an equilibrium assemblage but is probably a paragenetic assemblage with calcite the last phase to form and analcime possibly the first.

DEPOSITIONAL ENVIRONMENT OF HORN MOUNTAIN ROCKS

Fiske and Matsuda (1964) have described a sequence of volcanic rocks from the Tokiwa area in Japan that bears a striking resemblance to the volcanic sequence at Horn Mountain. In particular, the authors discuss the unusual vertical grading of the tuffs: each individual bed is graded and the entire sequence of beds is graded. The authors attribute this grading to a large undersea volcanic eruption in fairly deep water, coupled with the repetitive sorting of settled debris by turbidity currents. Because of a) the general similarity of the Horn Mountains volcanic sequence to that of Tokiwa, b) the particular similarity in which doubly graded beds are present in the mordenite tuff, and c) the marine affiliation of the mordenite tuff as shown by the presence of ammonites, it is concluded that the Horn Mountains rocks are the result of undersea volcanism and that the mordenite tuffs are the result of a large undersea volcanic (dacitic?) explosion. The mordenite formed subsequently by diagenetic action of pore water on the vitric material.

ECONOMIC POTENTIAL OF MORDENITE TUFFS

As discussed previously (Hawkins, 1976), the mordenite tuffs were thought to be of commercial grade and extent. The results of the present work emphasize this point. Table 2 is a summary of the results of the zeolite field test for mordenite-bearing samples. These results may be used as a rough guide to the mordenite content of the deposit. Assuming that a pure mordenite sample would show a ΔT value of 16.3°C and that ΔT increases linearly with increasing concentration of mordenite in the sample, the mean and standard deviation values of 8.05 ± 1.89°C correspond to an average mordenite concentration of 49 percent that varies from 26 to 72 percent for two standard deviations about the mean value. As mentioned in the previous report, this grade is comparable to that mined at Union Pass, Mohave County, Arizona, and Malheur County, Oregon (Mumpton, 1973). In addition, sulfur-dioxide sorption studies

TABLE 2. *Results of heating tests on samples from mordenite tuff. (Data from table 1.)*

Sample	ΔT (°C)[1]	
10	8.1	
12-0	6.7	
12-A	7.5	
12-B	7.0	
12-C	10.5	
12-D	9.8	
12-E	9.0	
12-F	9.8	
12-G	5.5	
12-H	6.2	
13	6.0	
14	4.0	
23	12.0	
24	10.1	
27	7.0	
30-2	5.6	
30-3	6.1	
30-4	9.2	
30-5	9.7	
30-7	10.4	
30-9	6.6	
30-10	9.1	
30-11	7.7	
30-12	7.1	
30-13	8.7	
30-14	8.2	
32	10.2	
35	7.6	
n = 28		
Mean		8.05
Standard deviation		1.89
[2]Synthetic sodium mordenite		16.3

[1]Temperature differential (p. 4).
[2]Hawkins, 1973, table 3.

are being carried out on this tuff at Worcester Polytechnic Institute. Preliminary results (L.B. Sand, written commun., 1975) indicate that the Horn Mountains mordenite has a high SO_2-sorption capacity and, as a consequence, it was one of three mordenites chosen for further study. In addition, the Horn Mountains mordenite showed the favorable property of having the greatest abrasion resistance of the mordenites studied. Probably the most striking feature of the Horn Mountains mordenite deposit is its size—some 14 kilometers in length and at least 30 meters thick, with a relatively uniform grade throughout. The deposit appears to be much larger than those in the conterminous United States and rivals the Japanese deposits in size. This is probably the largest known high-grade mordenite deposit in North America.

The procedure for filing a zeolite claim was discussed in a previous report (Hawkins, 1973) where it was pointed out that zeolites are subject to the sodium-potassium lease law. The validity of a placer claim versus a Federal lease has subsequently been tested in court by the Union Carbide Corporation. In this instance, the placer claim was given precedence, at least for the zeolite chabazite. The situation is still not clarified, however. At present, it appears that the best procedure would be to file a lode or placer claim followed by application for a Federal lease (Keith Papke, written commun., 1975).

CONCLUSIONS

The Horn Mountain mordenite deposit is of economic size and grade and warrants development.

The tuff in which the mordenite occurs is the result of an undersea volcanic explosion and is essentially the undersea equivalent of a subaerial ash-flow tuff. The observed zeolite assemblages in the rocks of the Horn Mountains were not temperature controlled; rather, the particular assemblages were produced by chemical reactions that were controlled by the composition and permeability of the parent material and the composition of intrastratal fluids. During zeolite formation, the volcanic pile was subjected to fluid pressures of about 0.5 to 3 kilobars, and temperatures less than 200°C, probably around 100°C.

SUGGESTIONS FOR FURTHER WORK

The properties, particularly gas-sorptive properties, of the Alaskan mordenite must be evaluated with respect to certain industrial applications.

Mordenite deposits should be sought at other localities where Talkeetna Formation rocks occur. Exposures of Talkeetna Formation rocks in the Chugach Mountains just south of Sheep Mountain (Grantz, 1965; Hawkins, 1973) and in the Talkeetna Mountains at the headwaters of Caribou Creek, and at Oshetna and Little Oshetna Rivers (Grantz, 1965) should be investigated.

Much detailed work remains to be done in the Horn Mountains. Detailed mineralogical and petrologic studies and chemical analyses of the various rocks and minerals are particularly needed.

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REFERENCES CITED

Alietti, A., 1972, Polymorphism and crystal chemistry of heulandites and clinoptilolites: Am. Mineralogist 57, p. 1448-1462.

Boles, J.R., 1971, Synthesis of analcime from natural heulandite and clinoptilolite: Am. Mineralogist 56, p. 1724-1734.

____ 1972, Composition, optical properties, cell dimensions, and thermal stability of some heulandite group zeolites: Am. Mineralogist 57, p. 1463-1493.

Boles, J.R., and Coombs, D.C., 1975, Mineral reactions in zeolitic Triassic tuff, Hokonui Hills, New Zealand: Geol. Soc. America Bull. 86, p. 163-173.

Coombs, D.C., and Whetten, J.T., 1967, Composition of analcime from sedimentary and burial metamorphic rocks: Geol. Soc. America Bull. 78, p. 269-282.

Culfaz, A., Kiesling, C.H., and Sand, L.B., 1973, A field test for molecular sieve zeolites: Am. Mineralogist 58, p. 1044-1048.

Fiske, R.S., and Matsuda, T., 1964, Submarine equivalent of ash flows in the Tokiwa Formation, Japan: Am. Jour. Sci. 262, p. 76-106.

Ghent, E.D., and Miller, B.E., 1974, Zeolite and clay-carbonate assemblages in the Blairmore Group (Cretaceous), southern Alberta foothills, Canada: Contr. Mineralogy and Petrology 44, p. 313-329.

Grantz, A.M., 1965, Geologic map and cross sections of the Nelchina area, south-central Alaska: U.S. Geol. Survey open-file report.

Hawkins, D.B., 1973, Sedimentary zeolite deposits of the upper Matanuska Valley, Alaska. Alaska Div. Geol. and Geophys. Surveys, Spec. Rpt. 6.

____ 1976, Mordenite deposits and zeolite zonation in the Horn Mountains area, south-central Alaska: Alaska Div. Geol. and Geophys. Surveys Spec. Rpt. 9.

Imlay, R.W., 1955, Characteristic Jurassic molluscs from northern Alaska: U.S. Geol. Survey Prof. Paper 274-D, p. 69-96.

Imlay, R.W., and Detterman, R.L., 1973, Jurassic paleobiogeography of Alaska: U.S. Geol. Survey Prof. Paper 801, 34 p.

Mumpton, F.A., 1973, Worldwide deposits and utilization of natural zeolites: Indus. Minerals 73, October, p. 2-11.

Read, P.B., and Eisbacher, G.H., 1974, Regional zeolite alteration of the Sustut Group, north-central British Columbia: Canadian Mineralogist 12, p. 527-541.

Zen, E-An, 1961, The zeolite facies: An interpretation: Am. Jour. Sci. 259, p. 401-409.

____ 1974, Burial metamorphism: Canadian Mineralogist 12, p. 445-455.