M.I.R.L. Report No. 58

ZEOLITE DEPOSITS OF POSSIBLE ECONOMIC SIGNIFICANCE ON THE NORTHERN ALASKA PENINSULA

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December, 1982

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ACKNOWLEDGEMENT

My sincerest thanks to Dr. Daniel B. Hawkins and Dr. Ernest N. Wolff for their beneficial criticism of this report. I am also indebted to my field assistant, Kim Madonna, who contributed a significant amount of time and effort toward the success of this project. I also wish to thank the Mineral Industry Research Laboratory and the State Division of Geological and Geophysical Surveys whose joint funding supported this project.

ABSTRACT

Clinoptilolite, mordenite, heulandite and laumontite have been identified in possible economic concentrations on the Alaska Peninsula. Most important are: 1) a heulandite bearing water-laid tuff on Agate Island, 2) a thick sequence of terrestrial volcanics containing mordenite and clinoptilolite located between Squirrel Point and Tommy Creek, 3) water-laid tuffs containing high concentrations of clinoptilolite near Dennis Creek and 4) a heulandite bearing siltstone at Chinitna Bay.

Zeolite formation in the Iliamna Lake area was produced in "open" systems of fresh water lakes and ground water systems which have transformed vitric volcanic material into zeolites. Burial diagenesis is responsible for alteration of early formed, low temperature-pressure zeolites into high temperature-pressure varieties.

The formation of laumontite in a tuffaceous sandstone at Chinitna Bay was the result of low grade burial metamorphism. The mode of formation of heulandite in a welded tuff and siltstone unit, also located at Chinitna Bay, appears to have resulted from diagenesis alteration of terrestrial sediments.

Transportation of zeolite ore from Iliamna Lake would be by lake to Pile Bay Village then by road to Iliamna Bay and, finally, by ship to the consumer. In the Chinitna Bay area ore can be loaded directly onto ships for transportation to the consumer.

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INTRODUCTION

The realization, in the 1950's, that naturally occurring zeolites could be of commercial utility triggered a reaction in the industrial and academic worlds. The new interest resulted in a flood of publications dealing with numerous aspects of the zeolite family, including new and extensive deposits, mineralogy, modes of formation, chemical reactivities, history and uses. This close inspection revealed further industrial applications of zeolites.

As a result of growing commercial utilization, minable zeolite deposits have been developed in several countries including the conterminous United States. A number of different zeolite occurrences had been reported in Alaska by various authorities since the 1960's (Figure 3). However, the possibility of economic zeolite deposits in Alaska held little interest until 1972, when increased industrial use, including cracking catalysts in the petroleum industry, binders for mixed fertilizers and conditioners for agricultural soil stimulated a program to locate zeolite deposits of commercial value. The result of this research revealed extensively zeolitized beds of Tertiary volcanic tuff and sediments on the Northern Alaska Peninsula near Iliamna Lake (Madonna, 1973). A list of 39 other potential zeolite localities is shown in Table 4 (See Appendix for Tables).

It is the purpose of this project to investigate the more important zeolitized units reported in the Iliamna Area and locate other potentially economic deposits. Examination of each deposit includes the size, semiquantitative concentration and type of zeolite present. In addition, each deposit is briefly discussed in terms of its possible economic importance.

Background

Zeolites were first described in 1756 by Baron Cronstedt. He derived the name from the Greek Zein, meaning to boil, and Lithos, meaning stone, because of the apparent boiling which took place as he heated the minerals. Subsequent investigations revealed that zeolites are a group of tectosilicates which may be considered, chemically, as hydrated equivalents of the feldspars. Like the feldspars, the zeolite framework is composed of three dimensional (Si, Al)O_4 tetrahedra. Cavities within the framework are the sites of cations, generally Ca^{++}, Na^+ or K^+, which balance the negative charge of the structure. However, unlike the feldspars which have compact structures prohibiting removal of a cation without disrupting the structure, the zeolite framework contains wide interconnecting openings which permit easy removal of the positive ions.

An additional characteristic which differentiates zeolites from feldspars is the presence of water molecules within the cavities of the zeolite structure. This water may be removed by heating and, unlike most hydrated minerals which collapse during the dehydration process, the aluminosilicate structures of zeolites remain stable to quite high temperatures.

In the late 1920's it was discovered that the dehydrated zeolite framework, with its honeycomb of passageways, is capable of absorbing large quantities of other fluids and gases in place of the water removed. Also, because each member of the zeolite family has a unique aperture size, the molecules admitted are restricted to those of appropriate dimensions. This selective nature of the zeolite structures make them extremely useful as industrial molecular sieves.

Knowledge of the geological significance of zeolites was slow in developing in comparison to advances in understanding their chemical properties. Because molecular sieve properties make zeolites highly useful for industrial purposes and because economic deposits were unknown, chemists in the late 1930's began a program to produce synthetic zeolites. By the early 1950's, several artificial zeolites were produced which have become extremely useful as industrial molecular sieves (Breck, 1964).

About this same time (1950's) geologists began to realize the significance of zeolites formed in volcanic tuff beds deposited in marine and saline-alkaline lake environments (Hay, 1966). When several high-grade deposits were discovered, the natural zeolites were examined to determine if they might be competitive with synthetic molecular sieves. Results revealed that sedimentary zeolites have properties very similar to those of artificial zeolites, and natural zeolites showed great potential for industrial application. When the potential economic value of natural zeolites became apparent, industry began an exploration program in the continental United States which led to the identification of over 80 mineable deposits.

INDUSTRIAL UTILIZATION

At the same time that the United States began its program to uncover new zeolite deposits, other countries such as the Soviet Union, Bulgaria, New Zealand, Hungary, Australia, Germany and Japan began to develop their deposits. As new high grade deposits were discovered, technological advances surrounding the commercial utilization of naturally occurring zeolites also flourished. In a recent study of worldwide deposits and utilization of naturally occurring zeolites by Frederick A. Mumpton (1973) it was found that over 300,000 tons of zeolitized tuffs are mined and used annually. Notable among the producing deposits are the Japanese mines, which are responsible for almost thirty percent of the world's annual production. Several uses described by Mumpton (1973) are summarized below.

Japanese researchers have developed numerous industrial uses for natural zeolites. The sodium-potassium zeolite, clinoptilolite, has found application as a filler in the Japanese paper industry. The paper filled with clinoptilolite is bulkier, more opaque, easier to cut and gives less ink blotting than similar clay filled papers.

Clinoptilolite is also being used in Japan as an agglutination agent for mixed fertilizers. In addition, it tends to retain the desirable cations in the soil for longer periods of time. It is suggested that laumontite, a sodium-zeolite, may also find important use as a conditioning agent in agricultural soils (Hawkins, 1973).

Japanese researchers have found clinoptilolite and mordenite especially useful as animal nutrients. As much as 10% by weight of these zeolites have been added to the diet of pigs and chickens, with significant increases in adult weight and reduction of total cost of feed. In addition, the animals excrement is much less odorous because of the ammonium absorption by the zeolite.

Naturally occurring mordenite has recently found use in the separation of high purity oxygen from air. The oxygen, produced at Toyohashi City, is used in the smelting of pig iron for the production of Toyota automobiles. The Toyohashi City plant also produces 99% plus nitrogen by use of natural mordenite.

Clinoptilolite has recently proven useful in removing ammonium from sewage and agricultural effluents. In a recent test on a Lake Tahoe, California sewage stream, clinoptilolite was successful in removing 97% of the ammonium. The ammonium was then discharged into the air and the clinoptilolite regenerated for futher use.

Zeolitized tuffs have, for many years, found use in pozzolanic cement and concrete. Pozzolanic concrete appears to be as strong as or stronger than that produced with normal amounts of portland cement. Furthermore, hydraulic cement produced from zeolite pozzolans appears to be more resistant to underwater corrosion.

Naturally occurring clinoptilolite has found additional use as an agent in ion exchange processes which concentrate and isolate radioactive ions from waste waters generated by atomic installations. Once the clinoptilolite is saturated with the radioactive ions it can be stored or cleaned with chemicals and reused.

In addition to the uses described above, zeolites have found numerous other applications. Hungary has used refined natural mordenite as a cracking catalyst in the petroleum industry and Japan has developed a use for natural zeolites as a polishing agent for dentifrice. A list of selected references from chemical abstracts on the use and properties of natural zeolites has been assembled and presented by Hawkins (1973).

ZEOLITE GENESIS

The occurrence of zeolites in several types of geologic settings is reasonably well known. In the past twenty years a large number of publications have appeared dealing with the conditions and environments of formation. Based upon the work of many investigators, including R.J. Hay, D.S. Coombs, R.A. Sheppard, A.J. Gude, A. Lijima, M. Uteda, L.B. Sand, R.C. Surdam and M.E. Teruggi, Fredrick A. Mumpton (1973) divided zeolite deposits into the following six classes:

1. Deposits which formed from volcanic material in "closed" system of ancient and present-day saline lakes. (Example: zeolites tuffs of ancient Lake Tecopa, Shoshone, California; Sheppard and Gude, 1968).

2. Deposits which formed from volcanic material in "open" systems freshwater lakes or groundwater systems. (Example: Altered tuffs of the John Day formation, central Oregon; Hay, 1963).

3. Deposits which formed from volcanic material in near-shore or deep-sea marine environments. (Example: Massive, clinoptilolite-rich tuff near Kurdzali, Bulgaria; Alexiev, 1968).

4. Deposits formed by low-grade burial metamorphism of volcanic and other material in thick sedimentary sequences. (Example: Triassic greywackes of the Turingatura District, Southland, New Zealand; Coombs, 1954).

5. Deposits formed by hydrothermal or hot-springs activity. (Example: Altered bedded tuffs and sandstones at Wairakei, North Island, New Zealand; Steiner, 1953).

6. Deposits formed in lacustrine or marine environments without direct evidence of volcanic precursor material. (Example: Analcime zones of the Triassic Lockatong Formation, New Jersey; Van Houten, 1960).

Workers have found the zeolites formation is favored by fluids of high pH and high alkali-ion to hydrogen-ion ratios in contact with reactive silicate material such as vitric-volcanic ash and tuff. Deffeyes (1959) suggests that zeolites form in sedimentary tuff deposits by solution of volcanic glass followed by precipitation of the zeolite from the solution. Sheppard (1971) suggests that high pH conditions account for the solubility of the glass and that reactivity of alkali ions is responsible for precipitation of the zeolites.

Throughout the world, the thickest and most widespread zeolite deposits are of Triassic and younger ages. Their absence from older rocks is apparently due to the formation of authigenic albite and potash feldspar at the expense of the metastable zeolites (Hay, 1966).

Because zeolites are hydrous mineral phases of low specific gravity they are particularly sensitive to pressure and temperature changes. This gives rise to the vertical zeolite zonation found in thick sequences of tuffaceous sediments. Zonation proceeds from the most hydrous and least dense zeolites at the top (i.e. lowest pressure-temperature conditions) to the least hydrous and most dense zeolites at the bottom (i.e. highest-pressure temperature conditions). With increasing pressure and temperature the zeolites become unstable and are ultimately transformed to minerals such as the feldspars, which are stable under these conditions.

This suggests, in a general way, that three conditions must be met before extensive zeolitization is possible:

1) Presence of reactive parent material, e.g. vitric tuffs.

2) Presence of "active" fluids, e.g. marine, saline-lake, or hydrothermal fluids.

3) Passage of a geologically short time span such that previously formed metastable zeolites have not been altered to more stable phases.

These conditions are diagrammatically shown in the Venn diagram of Figure 1. The most probable localities for zeolite formation and preservation are those for which all three conditions are simultaneously satisfied. There are a number of localities in Alaska that meet these conditions and have the potential of hosting zeolite deposits (Figure 7).

THIS STUDY

Field Methods

Search strategy: The search for zeolites in the Iliamna area was restricted to those lithologic units which meet the three basic conditions for zeolite formation and preservation, as shown in Figure 1.

Sampling: Zeolites can often be recognized in the field. Laumontite, for example, can often be identified by its white color, pearly luster, and by the friable nature of its dehydration product, leonhardite, on weathered exposures. Coarse volcanogenic zeolite crystals can, in many cases, be recognized by their wavy or radiating fibrous habit. Zeolitized sedimentary rocks may be distinguished by their pale yellow, green or orange color, chalklike appearance and low specific gravity (Hay, 1966).

Fist-sized samples, exhibiting characteristics typical of zeolitized rocks, were selected from promising lithologies exposed in the areas visited. A description of each sample is presented in Table 1.

Laboratory Methods

Samples were examined by heavy-liquid separation, x-ray diffraction, thermal analysis and quantitative field test. Results are tabulated in Table 1.

Heavy-Liquid Separation: Because of their low specific gravity, generally between 2.0 and 2.4, the members of the zeolite family may be separated from heavier minerals by heavy-liquids. This procedure was conducted on the study samples to determine semiquantitatively the zeolite concentrations. Selected samples were ground and sieved and the -150 to +325 mesh fraction was weighed and then separated into light and heavy components by bromoform, which had been reduced to 2.4 specific gravity by addition of acetone. The light fraction was weighed and the approximate percentage of light material (less than sp. gr. 2.4) in each sample calculated.

X-ray Diffraction: Light fractions of heavy-liquid separates were finely powdered and then mixed with water and mounted on a glass slide. The samples were analyzed with a Norelco diffractometer using a copper X-ray tube with a nickel filter and a goniometer scan speed of two degrees per minute.

X-ray patterns of the samples were compared to a set of standard zeolite patterns and the A.S.T.M. card catalog to determine the possible presence and type of zeolites.

Thermal Analysis: The zeolites, heulandite and clinoptilolite give virtually the same X-ray pattern. Mumpton (1960), introduced a test to distinguish the two minerals: "If after heating overnight at 450°C, the mineral no longer diffracts X-rays, it should be called heulandite; if however, diffraction is maintained it should be called clinoptilolite". This procedure was employed on several samples to determine which of the two zeolites were present.

Quantitative Field Test: Culfaz, Keisling and Sand (1973) suggest a simple quantitative field test for molecular sieve zeolites, as summarized below:

Five grams of finely ground sample (below 10 mesh) is placed in an aluminum container and heated to 350°C. The sample container is then capped and allowed to cool to atmospheric temperature. Ten milliliters of water, also at atmospheric temperature, are added to the sample and stirred quickly with a thermometer. The temperature rises rapidly, reaching a maximum within 30 seconds. A high temperature rise upon the addition of water is characteris-

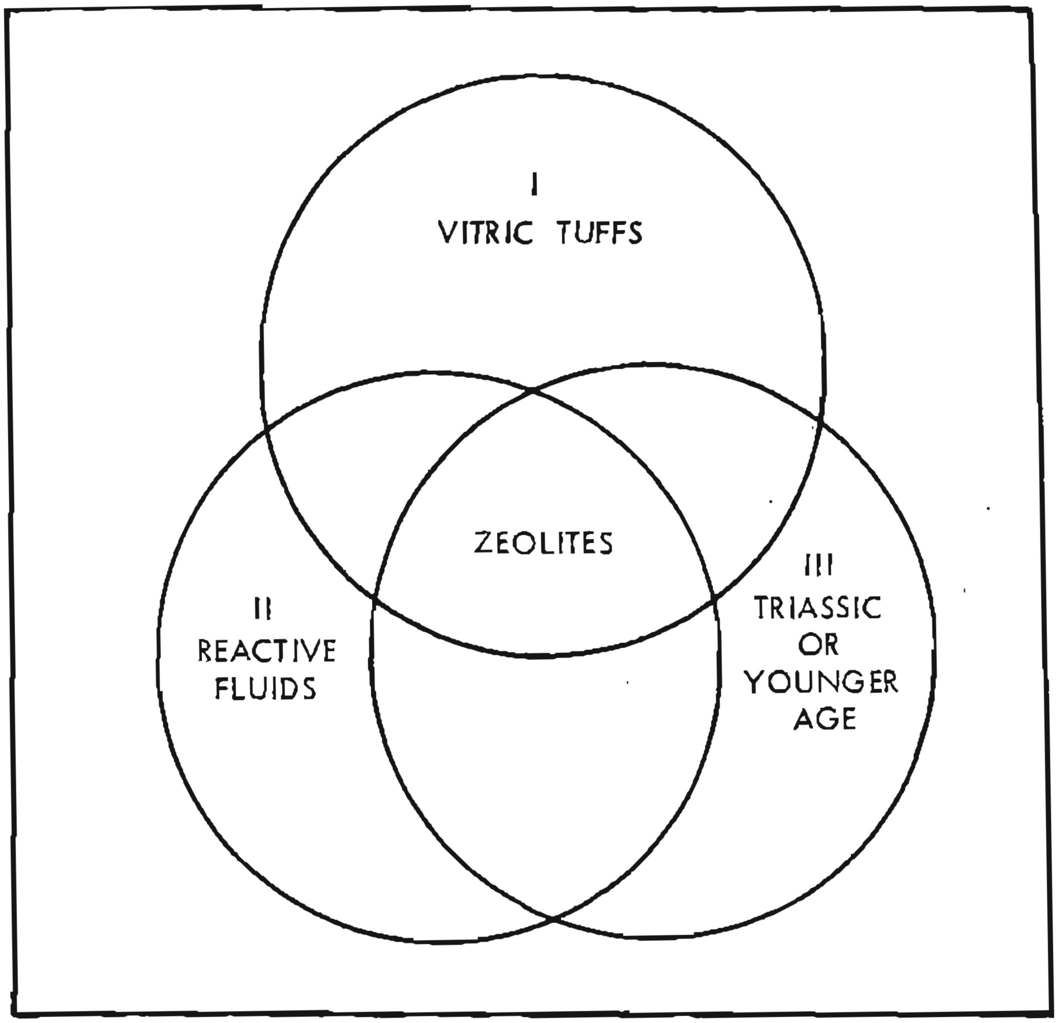

Figure 1. Venn Diagram Showing Conditions Which Favor Zeolite Formation and Preservation.

tic of the presence of zeolitic material in the sample, and the degree of temperature rise is directly proportional to the quantity of zeolite present.

Selected zeolitized samples obtained during this study were subjected to this field test in order to determine relative concentrations. The results of tests on each sample collected are listed in Table 1.

Results of Study by Area

The areas investigated and sampled include the west shore of Chinitna Bay, the Oil Bay Drainage, Iliamna Bay-Pile Bay Village Road and Iliamna Lake, including portions of the periphery and several islands.

Two localities on the south shore of Iliamna Lake appeared to be highly favorable sites for extensive zeolite formation and warranted more intensive examination. The first, located northeast of Tommy Creek, encompasses approximately eight square miles. The second, located approximately five miles northeast of Big Mountain near Dennis Creek, encompasses approximately ten square miles.

A preliminary examination, in 1983, of the Chinitna Formation, exposed at Chinitna Bay, revealed the presence of zeolites. A more thorough examination of the area was undertaken during the 1974 field season. Figure 2 shows the areas examined and the location of sample points.

Oil Bay Drainage and Iliamna Bay-Pile Bay Village Road: Lithologic units exposed in these areas consist mostly of plutonic igneous rocks unfavorable for zeolitization. Sample number 2, collected in the mountains east of Iliamna Bay, is a quartz monzonite which contains noncommercial fracture fillings of thompsonite and chabazite. No other units conducive to zeolitization were observed.

Newhalen-Iliamna Area: Lithologic units exposed along the shore of Iliamna Lake between Newhalen and Iliamna (Figure 2) consist of green, brown and gray andesitic and tuffaceous material of Tertiary age. The outcrops are low lying, reaching a maximum of twenty feet above lake level near Iliamna.

Examination of selected samples revealed the presence of several zeolitized beds. The most important are green heulandite bearing tuffs (samples 5 & 6). The high percentage of low specific gravity material (99%) combined with the rather large temperature increase (12.0°C) produced by the field test suggests that unit 5 contains a high concentration of heulandite. Similarly, unit 6 has a high percentage of low specific gravity material, however, the temperature rise produced by the field test was relatively low (5°C). The topographic characteristics of the two units, with relation to the lake level, are somewhat dissimilar. The water-laid tuff of unit 5 rises only a few feet above lake level, then gives way to a marshy environment to the north. In contrast, the andesitic tuffs of unit 6 rise approximately twenty feet above the lake level. However, this unit also gives way, gradually, to a marshy environment.

The low comparative relief of unit 5 and the marsh boundary which surrounds both units will probably prohibit profitable utilization of these deposits.

Eagle Bay-Chekok Point: Examination of felsic tuffs, rhyolite and reworked volcanics on the lake shore north of Agate Island, extending from Eagle Bay to Chekok Point (Figure 2) revealed several beds containing low to moderate zeolite concentrations. Of the units examined only number 25 show economic potential. The unit consists of a bed of mordenite bearing reworked volcanics which rises thirty feet above lake level and extends approximately one hundred feet along the lake shore. Because of excessive overgrowth it was not possible to determine the full extent of the deposit. Tests revealed 99 percent low specific gravity material in the sample and a moderate rise in temperature. This suggests that the deposit may be a possible source of mordenite.

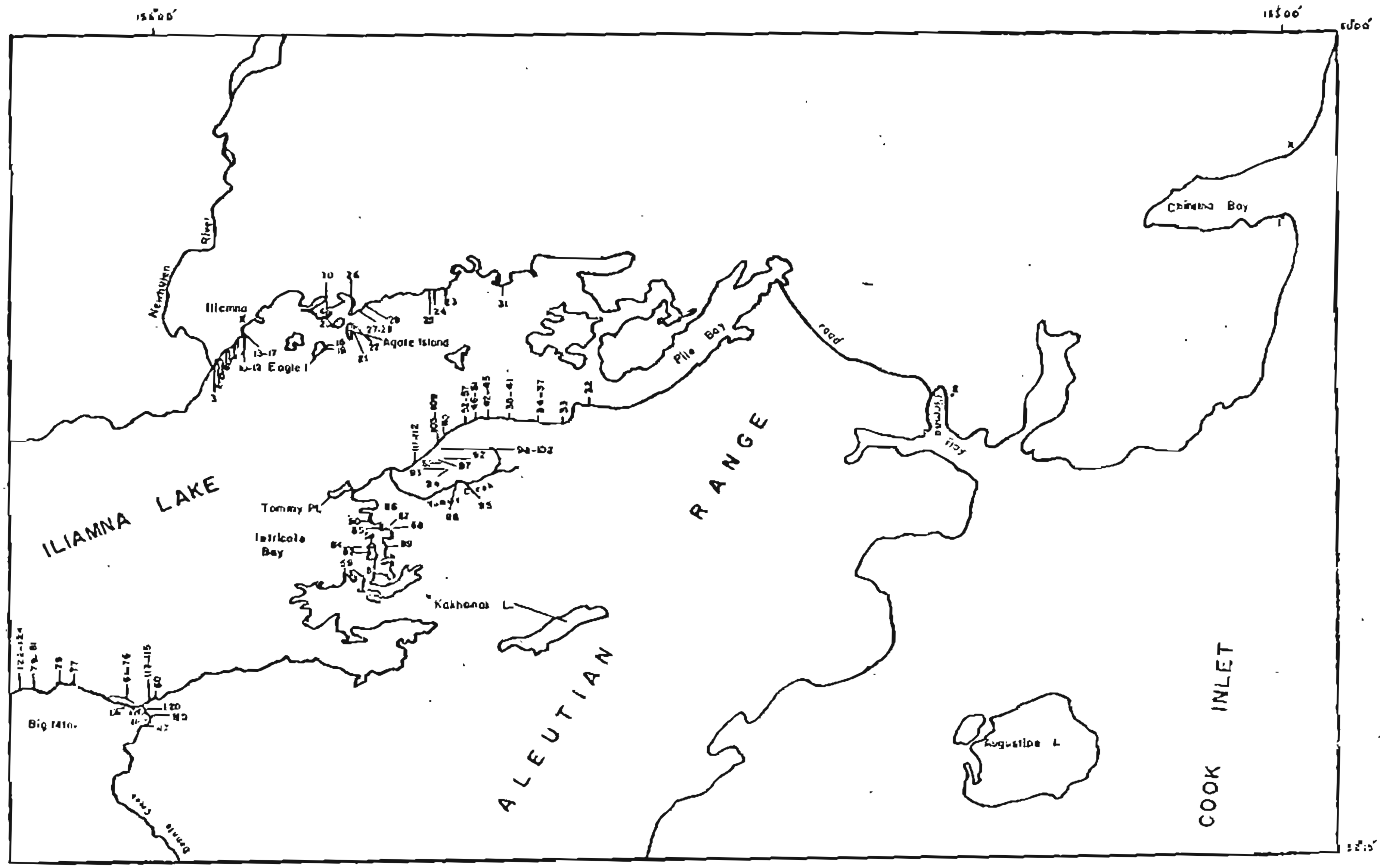

Figure 2. Location of Units Sampled During This Study.

Eagle, Eagle Bay and Agate Islands: Samples of Tertiary felsic tuffs, andesite and reworked volcanics were collected from Eagle, Eagle Bay and Agate Islands located approximately three miles southeast of Iliamna (Figure 2). X-ray examination of these samples revealed that all but one were zeolitized. However, specific gravity separations and the results of the field test suggest that only the heulandite bearing tuff (#21) which extends approximately one hundred and fifty yards across the northeastern end of Agate Island (Figure 3) is of possible economic value.

The unit is a gray to green tuff which forms cliffs rising between fifteen and twenty feet above shore line. The areal extent is shown in Figure 3. The extremely high percentage of low specific gravity material (98%) and moderate temperature increase (7°C) combined with the respectable areal extent, suggests that this material should not be overlooked as a possible source of heulandite.

Squirrel Point-Tommy Point: The preliminary investigation in 1972 of Tertiary andesites, tuffs and tuffaceous sediments on the south shore and adjacent hills of Iliamna Lake, between Squirrel Point and Tommy Creek, revealed several highly zeolitized units. A more thorough investigation of the area during this study revealed extensive beds containing high concentrations of clinoptilolite, mordenite and heulandite in addition to two laumontite bearing volcanics. Figure 4 shows a number of the more important areas examined and the outcrop patterns of the more extensively zeolitized units.

Several tuffs contain abundant mordenite in the Squirrel Point area. The highest concentrations are found in samples 44 and 56 (Figure 2). Unfortunately, the unit represented by sample 44 is a thin interlayered bed of local extent which would prohibit profitable utilization.

The unit represented by sample 56, on the other hand, is a green, fine-grained, altered tuff bed twenty feet high and one hundred and fifty feet long. The respectable results of tests shown in Table 1 and the moderate areal extent indicate that this deposit may be of economic interest as a future source of mordenite.

Other mordenite bearing tuffs outcrop on the lake shore at sample points 110 and 112 (Figure 2). Similarity in physical and mineralogical characteristics suggest that these two outcrops were originally members of the same tuff bed. Both outcrops are light green in color and contain spherical structures suggesting aggitation in an aqueous environment. Tests show that both units contain high percentages of mordenite (Table 1). In addition, strike and dip measurements suggest that these beds are on the east and west limbs of a gently folded anticline. This is further confirmed by anticlinally folded Tertiary sediments exposed on the lake shore between the two mordenite bearing units (samples 103-109, Figure 2). The mordenite units are approximately fifteen feet thick and both are exposed for approximately one hundred feet along the lake shore. The high zeolite concentration suggested by tests (Table 1) and the sizeable areal extent indicate that these units may be among the more important mordenite deposits in the Iliamna area.

Zeolitized Tertiary sediments (sample 98-101 and 103-109) are exposed along the lake shore and approximately one-half mile up a small tributary (Figure 4). The sediments vary from fine grained tuffaceous siltstone to reworked volcanics and rough, bouldery, tuffaceous conglomerates. As indicated earlier the sediments are exposed in a gently folded, north-south trending anticline. As Table 1 shows, most of the sedimentary beds are zeolitized. The most important are clinoptilolite bearing tuffaceous sandstones and reworked volcanics (samples 98, 99 and 100) exposed in the small drainage trending southeast from the lake (Figure 4). The combined thickness of the three beds is approximately sixty feet. Extensive foliage prevented measurement of the length and width of the beds. However, exposures of the sediments on the lake shore suggest a length of approximately one-half mile and, from what could be observed in the drainage, a width of approximately one-quarter mile. This deposit has possibilities of becoming a source of clinoptilolite, however, more extensive mapping would be required before firm evaluation could be made.

The mountains above and adjacent to the Tertiary sediments consist of approximately four hundred feet of mordenite bearing volcanics. These volcanics consist of green, welded and vitric tuffs which extend approximately one mile in a northeasterly direction and exhibit a width averaging one-half mile (see Figure 4). Tests on selected samples, both in 1972 and

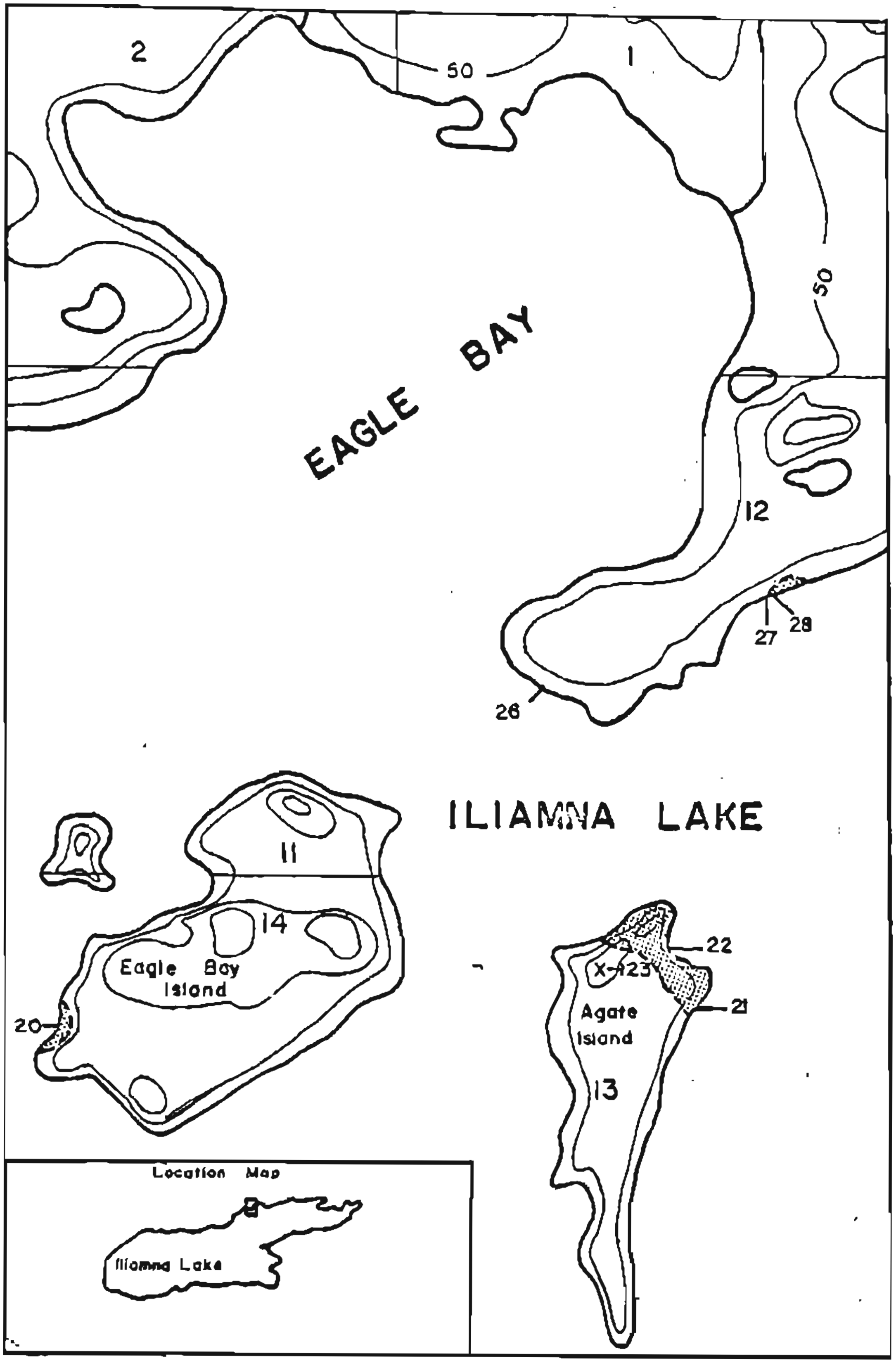

Figure 3. Zeolitized Units in the Agate Island Area.

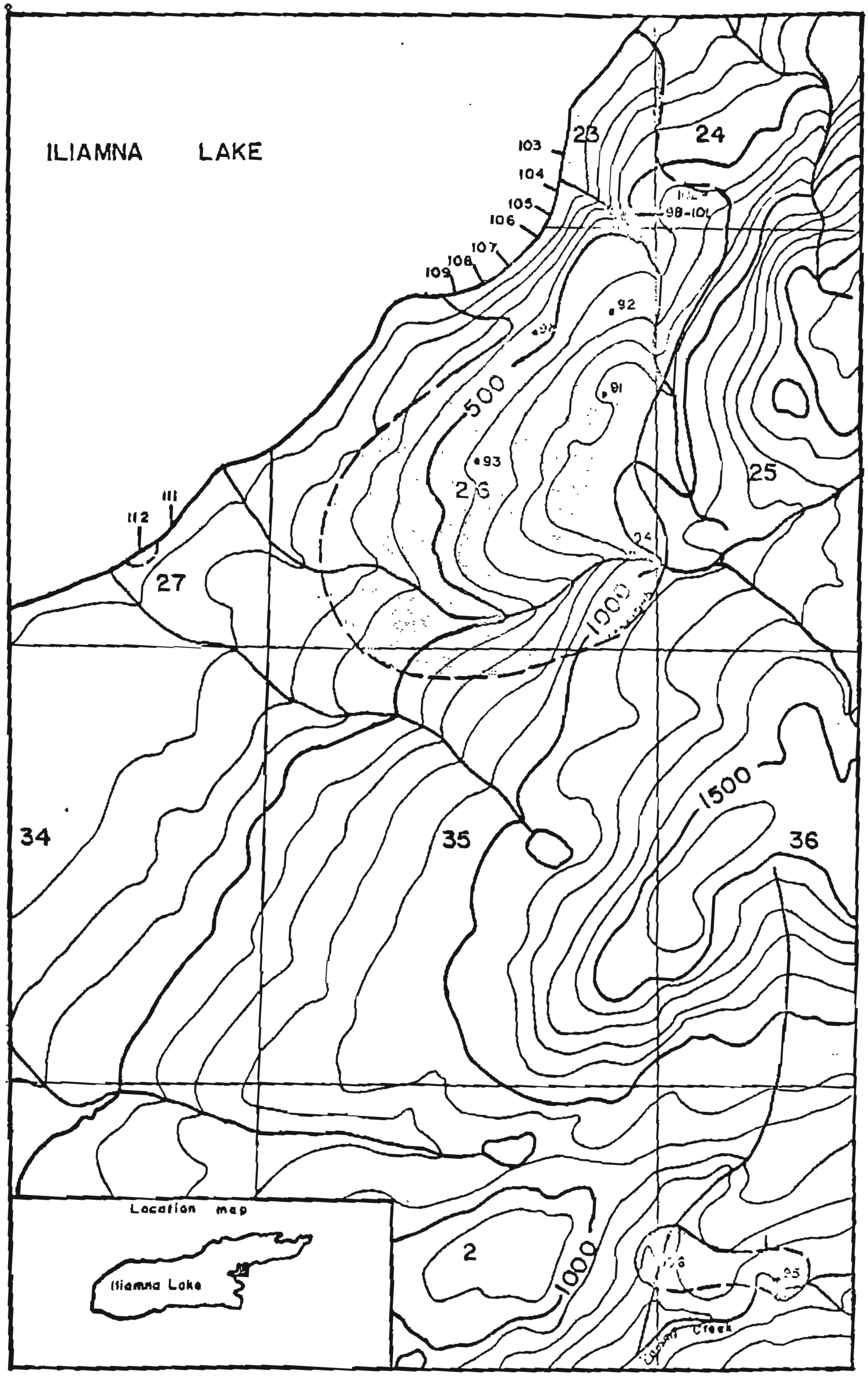

Figure 4. Zeolitized Units in the Tommy Creek Area.

during this investigation, indicate high percentages of mordenite in all but one case (Table 1). In the exception, clinoptilolite (#93) rather than mordenite was detected. From studies of pyroclastic rocks in Japan, Utada (1971) found that the occurrence of these two zeolites in the same rocks is not uncommon.

The large areal extent, extreme thickness and high percentage of zeolites in this volcanic sequence suggest that it has a high economical potential, and should be considered as a future source of mordenite and possibly clinoptilolite.

A light gray, heulandite bearing tuff (#94) outcrops in a drainage above and to the north of the mordenite bearing volcanics. The tuff bed is thirty feet high and approximately one hundred feet long. Examination of the material indicates that it is only moderately zeolitized. However, if the lower volcanic unit should be mined, this bed may become a convenient source of heulandite.

To the south two felsic welded tuffs are exposed. One on Tommy Creek (#95) and the other on a nearby tributary (#96). Sample 95 contains minor laumontite and 96 minor heulandite. Neither of these appear to have economic potential.

<u>Intricate Bay</u>: Intricate Bay is composed of numerous low lying islands and micro-bays. Table 1 shows that most of the samples of tuff selected from this area are zeolitized. Heulandite, clinoptilolite and mordenite were identified by X-ray diffraction. Additional tests as shown in Table 1 indicate that sample 85 contains significant amounts of clinoptilolite and 87 and 89 contain abundant mordenite. However, the tuff beds are low lying, rising at the most ten feet above lake level. This is probably the main factor which would prohibit profitable utilization of this material. On the other hand, this was only a preliminary investigation of Intricate Bay. Possibly, a more thorough examination of hills and rises visible a short distance from the lakeshore would reveal more extensive zeolite deposits.

<u>Big Mountain-Dennis Creek</u>: Outcrops of white and light green tuffs exposed on the lakeshore near Dennis Creek and Big Mountain contain notable quantities of clinoptilolite and heulandite. The distribution of the more important zeolitized units are shown in Figure 5. Because of the dense foliage in the area it was not possible to obtain the areal dimensions of the deposits.

Samples 61 through 76 were selected from a sixty foot outcrop of graded felsic tuff exposed along the lakeshore. Examination of the samples revealed heulandite in only minor amounts. The deposit does not appear to be of economic value.

Examination of several lithologic units in the Dennis Creek drainage revealed a green and pink welded tuff (#120) which contains a moderate amount of heulandite. The unit is sixty feet high and approximately fifty feet long. The local extent of the tuff combined with its distance from the lake (Figure 5) would prohibit profitable use of the deposit.

Results of tests on sample numbers 60 and 115 reveal that this material is among the most highly zeolitized tuffs examined from the Iliamna area. X-ray diffraction scans suggest that clinoptilolite is the predominant mineral. Heavy liquid separations and the field test both confirm the high concentration of clinoptilolite. The tuff from which sample 60 was selected is approximately twenty feet high and extends for one hundred feet along the lake shore. Similarly, the tuff bed from which sample 115 was selected is fifteen feet high and extends approximately one hundred feet along the lake shore. Unfortunately, the foliage obscures the width of these deposits and prevents a more thorough evaluation. However, because of the high concentration of zeolites in these samples they should not be overlooked as a possible source of clinoptilolite.

<u>Chinitna Bay</u>: Examination of the Chinitna Formation exposed on the west side of Chinitna Bay, during the 1973 field season, revealed the presence of laumontite in a four foot thick medium gray sandstone bed. X-ray examination suggested a high percentage of laumontite accompanied by minor quartz.

In addition to the laumontite bearing unit, zeolites were detected by D.B. Hawkins in a sample of welded tuff collected by J. Kienle from the Kenai Formation exposed on the northern shore of Chinitna Bay (personal communication, 1973).

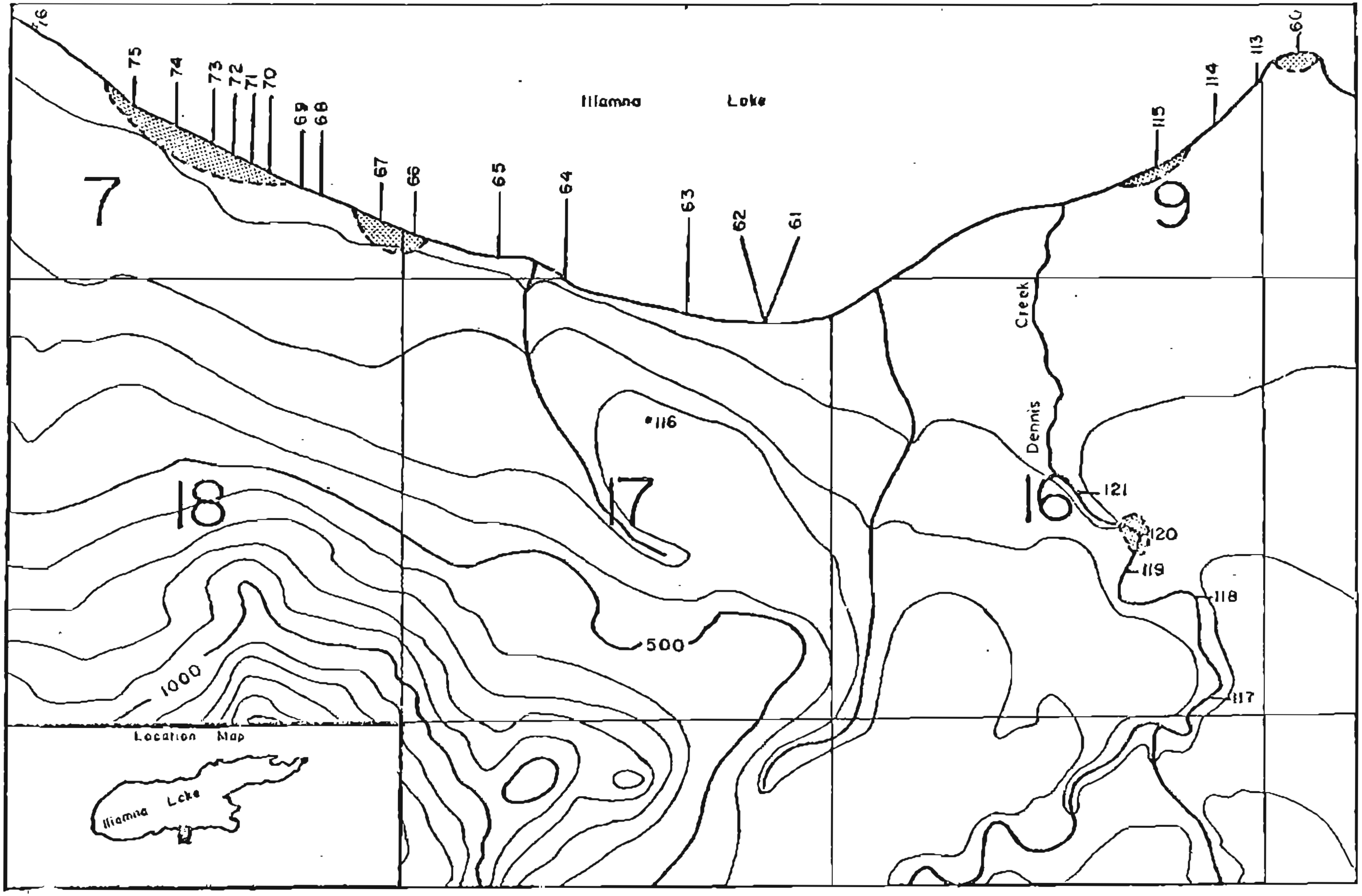

Figure 5. Zeolitized Units in the Dennis Creek Area.

In 1973 time did not permit a thorough examination of the Chinitna Bay area, however a more thorough examination of the area was carried out in 1974.

Detterman and Hartsock (1966) have presented the bedrock geology of the area, which is divided into several distinct formations. Those examined during the 1974 field season include the Lower Jurassic Talkeetna Formation, the Late Jurassic Chinitna and Naknek Formations and the Tertiary Kenai Formation.

The Talkeetna Formation consists of 5,900 to 9,000 feet of bedded volcanic rocks, which grade from interbedded tuff and tuffaceous sandstone in the upper units to massive agglomerates, volcanic breccia and lava flows near the lower extremities.

Several samples, which exhibit characteristics favorable for zeolite formation, were selected from the Upper Horn Mountain Tuff Member, which is well exposed on Horn Mountain. Results of tests show that each sample contains laumontite, but in such low concentrations as to prohibit profitable industrial utilization of the material.

The Chinitna and Naknek Formations consist collectively of from 3,500 to 7,800 feet of conglomerates, sandstones and siltstones. Several samples were selected from outcrops near Clam Cove on the north shore of Chinitna Bay and Sea Otter Point on the south shore (Figure 2). X-ray and thermal examinations indicate that most of the samples contain either laumontite or heulandite. However, the field tests suggest that concentrations are below economic proportions (Table 2).

The Kenai Formation is composed of approximately 1,000 feet of Tertiary conglomerates, sandstones and siltstones. An easily accessible exposure occurs on the seashore one and one-half miles east of Clam Cove. The outcrop is characterized by a twenty foot thick brown siltstone bed positioned unconformably between two relatively coarse conglomerate beds. An additional characteristic is the presence of several well preserved trees which span the thickness of the siltstone bed but do not extend into the conglomerate units. Locally exposed near the base of the siltstone is a thin lenticular bed of carbonaceous ash stone ranging up to two feet in thickness. The unit is exposed for approximately 100 yards on the shoreline but is concealed from view inland by foliage. However, it is suspected to have a comparatively large lateral extent.

Examination of both the ash stone and the siltstone revealed the presence of heulandite. Most samples contain between 90 and 100 percent low specific gravity material and a moderate to high temperature change. This, combined with its respectable thickness and suspected large lateral extent, suggests that the deposit may be of economic value.

GENESIS OF THE DEPOSITS

Tuffs, tuffaceous sediments and other volcanics, conducive to zeolite formation, exposed along the shoreline, on the islands, and in the mountains adjacent to Iliamna Lake, are assigned to the Tertiary Period (Detterman and Reed, 1968). The formation of zeolites in these Tertiary rocks is inherent in the overall depositional and tectonic history of the Alaska Peninsula during that time. The close of the Cretaceous was gentle as indicated by the slight disconformable contact with overlying Tertiary rocks. The Tertiary tectonic history was not one of extensive orogenic activity; the Alaska Peninsula did not become an orogenic mountain system until the Late Pliocene. Prior to this time it was basically an area of deposition which derived its topographic relief from brief vertical movements associated with igneous intrusions, and obtaining its stratigraphic thickness from massive accumulation of volcanic debris. The volcanic debris was weathered, abraded, transported and deposited in both marine and non-marine environments (Burke, 1965).

In the Iliamna Lake area Detterman and Reed (1968) report the presence of thick sequences of Tertiary, non-marine, volcanic siltstones, sandstones and conglomerates interlayered with volcanic flows and tuffs. Examples of these water-laid tuffs and reworked volcanics are exposed in numerous outcrops on the lakeshore and are interlayered with Tertiary, non-marine sediments exposed on the south shore. Tertiary vitric tuffs exposed in the mountains adjacent to the lake's southern shore, however, do not exhibit any of the characteristics typical of water-laid tuffs, and their high elevation suggest deposition in a terrestrial environment.

The zeolite deposits at Iliamna Lake were formed by the alteration of volcanic material. X-ray examinations revealed the presence of clinoptilolite, mordenite, heulandite and minor laumontite. Finally, the volcanic material was deposited in terrestrial and non-marine aqueous environments. These three parameters, mode of occurrence, mineralogy and depositional environment suggest that the Iliamna zeolites were produced from volcanic material in "open" systems of fresh water lakes and ground water systems (type 2 page 6) which transform volcanic citric material into zeolite minerals. These deposits are characterized by the presence of clinoptilolite and mordenite, and the absence of "closed" system zeolites such as erionite and chabazite. Subsequent burial of early formed low temperature-pressure clinoptilolite and mordenite appears to have been responsible for alteration into higher temperature-pressure forms. The sequence of formation found in piles of volcanic material in other parts of the world are, from low to high pressure and temperature: A) fresh glass, B) clinoptilolite-mordenite, C) analcime heulandite and D) laumontite. Assemblages representing these four zones have been detected in the Iliamna area. In addition, sample number twelve contains both heulandite and laumontite, which would be typical of the assemblage representing the isograd between the two stability fields. This suggests that burial diagenesis has been responsible for the formation of high temperature-pressure zeolites at the expense of the lower temperature-pressure varieties.

The laumontite and heulandite bearing units in the Chinitna Bay area fit the type 4 mode of zeolite formation presented by Mumpton (1973); formation by low-grade buried metamorphism of thick sedimentary sequences in which laumontite is produced at the expense of low density, more hydrous zeolites such as heulandite, as well as other silicate minerals.

TRANSPORTATION

The rugged topography and distance (180 miles) from Anchorage has made air the only practical means of transporting passengers, freight and mail to Iliamna Lake. Flights from Anchorage to Iliamna are scheduled three times a week. The aircraft stops at Iliamna and Big Mountain, then returns to Anchorage. Air and water transportation is available in Iliamna for passengers and supplies traveling to other points on the lake.

A limited amount of freight is transported by water from Anchorage and/or Homer, to Iliamna Bay, on the coast, and finally driven to Pile Bay Village on Iliamna Lake by way of a 14 mile gravel road (Figure 2). The road is maintained between May and October each year by the Alaska State Highway Department, for portage of fishing boats from Cook Inlet to Iliamna Lake where they proceed by water to Bristol Bay. A steel bridge has been constructed across Iliamna River, which is intersected by the thoroughfare. Petroleum products are available at both terminals and heavy equipment and boat repair is available at Pile Bay Village.

Transporting ore from Iliamna Lake could be achieved by loading the ore into portable dump beds and carrying them, by barge, up the lake to Pile Bay Village. The portable beds could then be loaded directly onto trucks for transport to Iliamna Bay. Here the ore could be stored in holding bins or loaded directly onto ships for delivery to Anchorage or other ports.

It is doubtful that shipping problems would be encountered in transporting the ore from the mine to Pile Bay Village, or across the road which is capable of handling several hundred tons of ore per day. However, loading problems may result from tides which leave Iliamna Bay dry for several hours each day.

CONCLUSIONS

Zeolite deposits of possible economic importance exist in the Iliamna Lake area. Most important are: 1) a heulandite bearing, water-laid tuff on Agate Island, 2) a thick sequence of terrestrial volcanics containing mordenite and clinoptilolite located between Squirrel Point and Tommy Creek, 3) water-laid tuffs containing extremely high concentrations of clinoptilolite near Dennis Creek, and 4) a heulandite bearing siltstone at Chinitna Bay.

The deposits in the Iliamna lake area were formed in an "open" system of fresh water lakes and ground water which transform volcanic vitric material into zeolites.

Burial diagenesis was responsible for altering early formed low-pressure, low-temperature zeolites into more stable high-pressure high-temperature members.

The formation of laumontite and heulandite at Chinitna Bay was the result of low grade burial metamorphism in thick sedimentary sequences.

Transporting ore from Iliamna Lake can be achieved by barging the material up the lake to Pile Bay Village, trucking it the 14 mile distance to Iliamna Bay and then shipping it to the consumer. At Chinitna Bay the material would be loaded directly onto ships.

APPENDIX

Table 1

Results of Tests on Individual Samples
See Figure 2 for Collection Point of each Sample

Sample Number	Rock Type	% less than 2.4 sp. gr.	Field Test △ T in °C	Zeolites Present
1	Tuffaceous sandstone	W.R.	4.0	Laumontite
2	Fracture filling	W.R.	–	Thompsonite Chabazite
3	Cavity filling (andesite)	W.R.	–	Water Rich Heulandite
4	Andesite	19	–	–
5	Tuff	99	12.0	Heulandite
6	Reworked volcanics	89	5.0	Heulandite
7	Tuff	17	–	–
8	Tuff	9	–	–
9	Tuff	33	4.0	Clinoptilolite
10	Tuff	14	–	–
11	Tuff	45	9.5	Laumontite
12	Reworked volcanics	42	4.0	Laumontite
13	Tuff	59	–	–
14	Tuff	11	–	–
15	Reworked volcanics	12	3.0	Heulandite
16	Reworked volcanics	76	4.5	Heulandite
17	Andesite	6.5	–	–
18	Andesite	37	–	–
19	Andesite	40	4.0	Laumontite
20	Reworked volcanics	4.1	2.0	Heulandite
21	Tuff	98	7.0	Heulandite
22	Reworked volcanics	33	3.5	Heulandite
23	Reworked volcanics	10	3.0	Heulandite
24	Tuff	5	–	–
25	Reworked volcanics	99	6.0	Mordenite
26	Reworked volcanics	50	–	–

Table 1

Continued

Sample Number	Rock Type	% less than 2.4 sp. gr.	Field Test △ T in °C	Zeolites Present
27	Reworked volcanics	61	5.0	Clinoptilolite
28	Tuff	8.3	-	-
29	Reworked volcanics	4.3	-	-
30	Tuff	13	-	-
31	Rhyolite	14	3.0	Heulandite
32	Tuff	28	-	-
33	Reworked volcanics	5.0	-	-
34	Tuff	4.8	-	-
35	Reworked volcanics	3.3	-	-
36	Reworked volcanics	1.7	-	-
37	Conglomerate	1.1	-	-
38	Tuff	2.6	-	-
39	Tuff	1.9	-	-
40	Tuff	3.5	-	-
41	Tuff	5.5	-	-
42	Andesite	29	3.0	Laumontite
43	Tuff	50	-	-
44	Tuff	84	6.0	Mordenite
45	Reworked volcanics	1.3	-	-
46	Andesite	13	-	-
47	Tuff	84	-	-
48	Andesite	1.6	-	-
49	Tuff	0.5	-	-
50	Tuff	2.3	-	-
51	Tuff	0.5	-	-
52	Andesite	0.5	-	-
53	Reworked volcanics	6.3	-	-
54	Andesite	11	3	Clinoptilolite

Table 1

Continued

Sample Number	Rock Type	% less than 2.4 sp. gr.	Field Test Δ T in ^{o}C	Zeolites Present
55	Tuff	7.8	-	-
56	Tuff	97	9.0	Mordenite
57	Sandstone	29	4.5	Clinoptilolite
58	Tuff	54	7.0	Clinoptilolite
59	Reworked volcanics	83.5	-	-
60	Tuff	100	12.0	Clinoptilolite
61	Tuff	31	-	-
62	Tuff	89	-	-
63	Tuff	32	-	-
64	Tuff	38	-	-
65	Tuff	45	-	-
66	Tuffaceous sandstone	29	3.0	Heulandite
67	Tuff	4.5	2.0	Heulandite
68	Andesite	19	-	-
69	Tuff	19	-	-
70	Tuff	45	9.0	Heulandite
71	Tuff	23	-	-
72	Tuff	55	3.0	Heulandite
73	Tuff	30	3.0	Heulandite
74	Tuff	84	4.0	Heulandite
75	Tuff	38	4.0	Heulandite
76	Tuff	38	-	-
77	Tuff	14	-	-
78	Reworked volcanics	18	-	-
79	Tuff	23	-	-
80	Tuff	40	-	-
81	Tuff	40	-	-
82	Tuff	62	7.0	Mordenite

Table 1

Continued

Sample Number	Rock Type	% less than 2.4 sp. gr.	Field Test △ T in °C	Zeolites Present
83	Tuff	85	5.0	Heulandite
84	Tuff	52	–	–
85	Tuff	99	10.0	Clinoptilolite
86	Tuff	85	–	–
87	Tuff	74	9.0	Mordenite
88	Tuff	52	3.0	Heulandite
89	Tuff	94	8.0	Mordenite
90	Rhyolite cavity fillings	71	–	–
91	Tuff	72	10.0	Mordenite
92	Tuff	79	11.0	Mordenite
93	Tuff	74	7.0	Clinoptilolite
94	Tuff	70	5.0	Heulandite
95	Tuff	36	2.5	Laumontite
96	Tuff	38	3.0	Heulandite
97	Tuff	85	10.0	Mordenite
98	Reworked volcanics	99	9.0	Clinoptilolite
99	Tuffaceous sandstone	64	4.0	Clinoptilolite
100	Reworked volcanics	95	5.0	Clinoptilolite
101	Reworked volcanics	93	3.5	Heulandite
102	Tuff	97	8.0	Mordenite
103	Breccia	68	4.0	Clinoptilolite
104	Sandstone	15	–	–
105	Mudstone	100	–	–
106	Tuffaceous sandstone	37	4.0	Clinoptilolite
107	Tuffaceous sandstone	50	4.0	Heulandite
108	Tuffaceous conglomerate	24	4.5	Heulandite
109	Reworked volcanics	50	–	–
110	Tuff	94	7.0	Mordenite

Table 1

Continued

Sample Number	Rock Type	% less than 2.4 sp. gr.	Field Test $\triangle$ T in ^{0}C	Zeolites Present
111	Andesite	74	–	–
112	Tuff	99	12.0	Mordenite
113	Ignimbrite	93	–	–
114	Fracture filling	96	–	–
115	Tuff	94	13.0	Clinoptilolite
116	Tuff	29	–	–
117	Tuff	59	–	–
118	Tuff	59	–	–
119	Rhyolite	56	–	–
120	Tuff	96	7.0	Heulandite
121	Tuff	88	–	–
122	Tuff	26	–	–
123	Tuff	38	3.0	Heulandite
124	Rhyolite	W.R.*	–	–

*W.R. = Whole Rock

Table 2

Results of Tests on Samples Collected at Chinitna Bay in 1974.

Sample Number	Rock Type	% less than 2.4 sp. gr.	Field Test Δ T in ^{o}C	Zeolites Present
C-1	Siltstone	98	9.0	Heulandite
C-2	Tuff	92	13.0	Heulandite
C-3	Tuff	43	13.0	Heulandite
C-4	Tuff	93	10.0	Heulandite
C-5	Siltstone	98	11.0	Heulandite
C-6	Siltstone	90	12.0	Heulandite
C-7	Siltstone	98	11.0	Heulandite
C-8	Sandstone	35	8.0	Laumontite
C-8'	Sandstone	30	5.0	Laumontite
C-8"	Siltstone	78	-	-
C-9	Sandstone	31	4.0	Laumontite
C-10	Sandstone	50	3.0	Heulandite
C-11	Sandstone	42	4.0	Laumontite
C-11'	Sandstone	18	4.0	Heulandite
HM-1	Tuff	72	4.0	Laumontite
HM-2	Tuffaceous S.S.	41	4.0	Laumontite
HM-3	Andesite	3	3.0	Laumontite

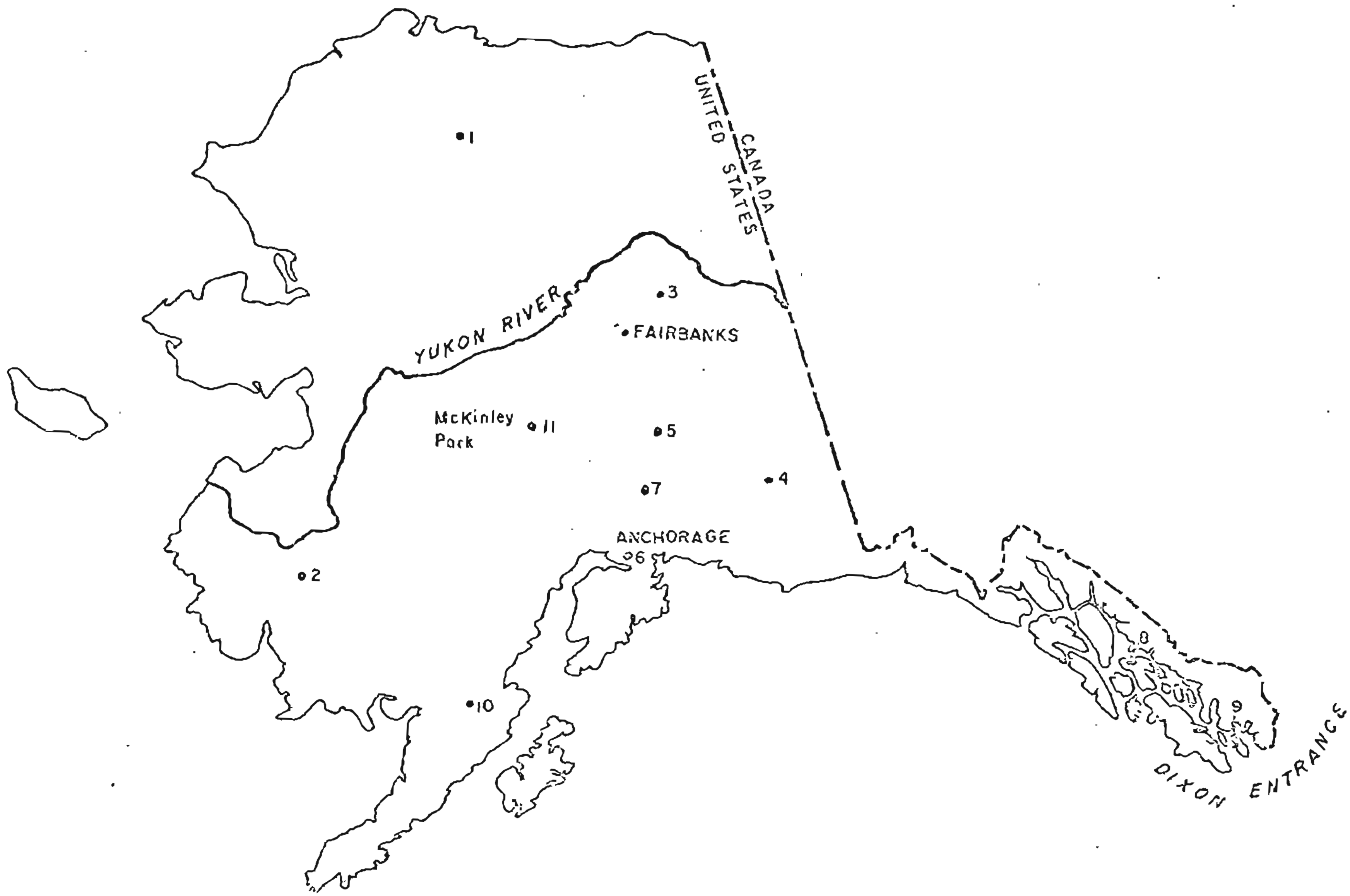

Figure 6: Location of zeolite occurrences reported in Alaska. (See Table 3 for References)

Table 3

ZEOLITE OCCURRENCES REPORTED IN ALASKA

(See Figure 6 for Location)

MAP NO.	OCCURRENCE	MINERAL	REFERENCE
1.	Sedimentary	Clinoptilolite	Reynolds & Anderson, 1967
2.	Metamorphic	Laumontite	Hoare, 1964
3.	Contact Metamorphic	Yugawralite Stilbite Laumontite	Eberlein, Weber, & Beatty, 1971
4.	Cavity Fillings	Thompsonite	Moffit and Knopf, 1910 Capps, 1916
5.	Cavity Fillings	Natrolite	Glavinovich, 1967 Unpublished Masters Thesis
6.	Metamorphic	Laumontite	Clark, 1972
7.	Metamorphic	Laumontite Analcime Heulandite Mordenite	Hawkins personal communications, 1973
8.	Cavity Fillings	Zeolites	Muffler, 1967
9.	Cavity Fillings	Zeolites	Berg
10.	Sedimentary	Mordenite Heulandite Clinoptilolite Analcite Laumontite	Madonna, 1973
11.	Sedimentary Volcanogenic	Heulandite Mordenite	Madonna, 1973

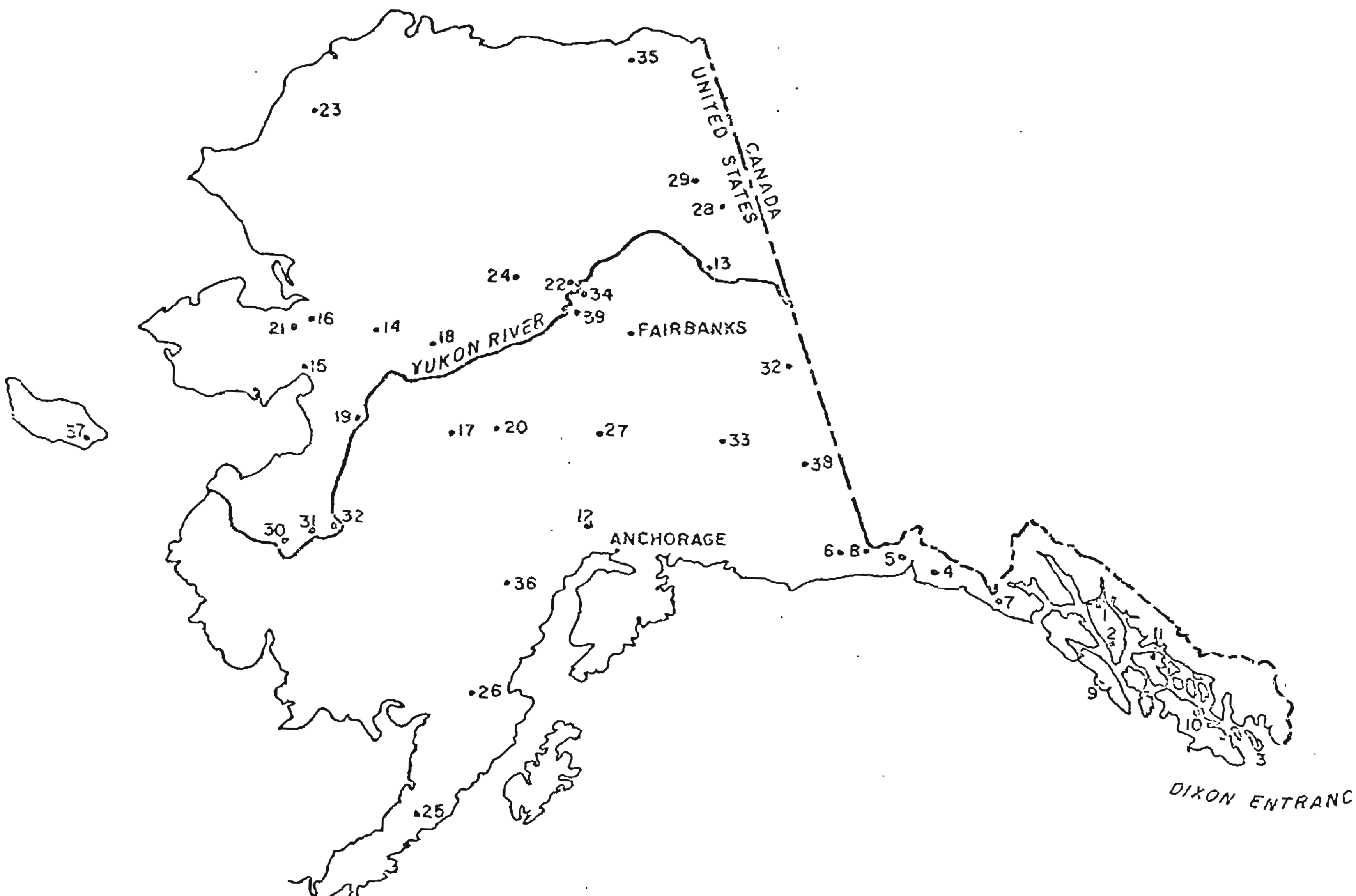

Figure 7: Possible zeolite localities in Alaska. (See Table 4 for references)

Table 4

ROCK TYPES AND REFERENCES FOR POSSIBLE
ZEOLITE LOCALITIES IN ALASKA

(See Figure 7 for Location)

AREA NO.	ROCK TYPES	REFERENCES
1.	Volcanic tuff	Lathram, Loney, Condon, Berg, 1959
2.	Tertiary volcanics	Loney, 1965
3.	marine rhyolite tuff & ash	Berg, 1969
4.	argillite and tuffs	Miller, 1961
5.	argillite and tuffs	Miller, 1961
6.	argillite and tuffs	Miller, 1961
7.	argillite and tuffs	Miller, 1961
8.	argillite and tuffs	Miller, 1961
9.	Quaternary volcanics	Loney, Pomeroy, Brew, Muffler, 1964
10.	tuff and lavas	Sainsbury, 1981
11.	Jurassic tuff beds	Buddington and Chapin, 1929
12.	Mesozoic acid flows & tuffs	Capps, 1940
13.	Tertiary volcanics (tuff)	Mertie, 1937
14.	rhyolitic tuff	Cass, 1957
15.	volcanics (tuff)	Cass, 1959
16.	volcanics (tuff)	Cass, 1959
17.	argillite and tuff	Cass, 1959
18.	rhyolite and tuff	Cass, 1959
19.	rhyolite and tuffs	Cass, 1959
20.	volcanics and tuffs	Eakin, 1918
21.	water lain tuffs	Martin, 1919
22.	metamorphosed tuffs	Eakin, 1916
23.	bentonites	Smith and Mertie, 1930
24.	Tertiary tuffs	Maddren, 1913
25.	pumice and ash	Moxham, 1951

Table 4—continued

AREA NO.	ROCK TYPES	REFERENCES
26	Tertiary tuffs	Detterman and Reed, 1957
27.	tuffs	Hawyley, Clark, and Benfer, 1968
28.	Tertiary clays with tuff	Brosge, Reiser, Dutro, Churkin, 1966
29.	tuffs and clays	Brosge and Reiser, 1962
30.	Siliceous volcanic tuffs	Hoare, 1962
31.	tuffs	Hoare, 1961
32.	tuffs	Foster, 1964
33.	Jurassic volcanic tuffs	Ferriens, 1971
34.	tuffaceous argillites	Kachadoorian, 1971
35.	tuffs and bentonite	Reiser, 1971
36.	Tertiary tuffs	Reed and Elliot, 1971
37.	tuffs	Patton, 1971
38.	non-marine tuffs	Richter, 1972
39.	volcanics	Chapman, Weber, and Tabler, 1971

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