Mordenite Occurrences in the Marysvale Area, Piute County, Utah: A Field and Experimental Study*

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ABSTRACT.—Mordenite was studied in the vicinity of Marysvale, Utah, where it occurred in three different outcrops: a pitchstone plug, the glassy margin of a rhyolite flow, and a densely welded tuff unit. Samples of mordenite and unaltered glass from each outcrop were analyzed by X-ray fluorescence, and in all cases, mordenite showed more calcium and less silica than the glass. A strong positive correlation exists between the Ca:Na:K ratios of a particular mordenite sample and the Ca:Na:K ratios of the unaltered glass of the same outcrop.

Glass from the pitchstone plug outcrop was altered in the laboratory in a series of experiments in which mordenite was synthesized over a wide spectrum of OH^- concentrations at a constant Na^+ concentration. Phillipsite, analcime, and alkali feldspar, as well as an unidentified phase, also crystallized in the course of the experiments. It was observed that mordenite and analcime coexisted in a metastable condition. However, the presence of mordenite retarded the growth rate of analcime.

Projecting zeolite growth patterns through time indicates that after 39 days, mordenite will not persist at any pH within the limits of this experiment. This finding is attributed to the high Na^+ activity of the solutions. Other experiments indicate that minimum Na^+ concentrations required for mordenite synthesis may vary inversely with the pH of the solution.

Geologic sketches of the three mordenite localities of this study led to models of emplacement of the glass and subsequent mordenitization. The profound influence of permeability resulting in the mordenite mineralization of glass was observed on both large and small scales.

Glasses from each outcrop were altered experimentally to determine the susceptibility of each to mordenitization. Results are nearly identical for all glasses tested, with the exception of a brown variety of glass found in the Beaver Creek rhyolite flow, which proved to be significantly more resistant to the formation of mordenite. This difference is attributed to a higher degree of silica polymerization.

Secondary silica appears to have precipitated from ascending hydrothermal solutions contemporaneously with mordenitization of the glasses. Such solutions were most likely high in calcium and mildly alkaline.

INTRODUCTION

Zeolites are tectosilicates with a three-dimensional framework of $(Si,Al)O_4$ tetrahedra that does not collapse with dehydration. Zeolites are hydrated under normal atmospheric conditions, with water molecules occupying large interconnected cavities. With heat, water vapor may be driven off, and thus they may appear to "boil." The word *zeolite* means *boiling stone.*

In the past, zeolites were considered to be little more than mineral curiosities and were valued only by museums and mineral collectors. However, in recent decades, zeolites have been brought out of obscurity to find diverse uses in industry as molecular sieves, desiccants, soil conditioners, paper fillers, lightweight aggregates, crackers of hydrocarbons, fertilizers, and so forth (Mumpton 1978). At present most commercial zeolites are made synthetically.

Mordenite and clinoptilolite, both identified in the Marysvale volcanic field, are among eight zeolite varieties currently mined for industrial purposes (Mortier and others 1978). Steven and Cunningham (1979) mapped and evaluated the economic potential of clinoptilolite in the Cove Fort area and reported the occurrence and general distribution of clinoptilolite in the Three Creeks Reservoir area.

Zeolites in the immediate area of Marysvale were first recognized by Kerr and others (1957) in association with argilliza-

tion in ore veins. They described mordenite alteration of rhyolitic glass dikes as being very similar to the mineralization of the pitchstone plug outcrop described in the present work. Kerr considered his study of mordenite to be somewhat cursory and indicated a need for further investigation (Kerr and others 1957).

In this work, three distinct outcrops in the Marysvale area containing mordenite were studied: a hydrated glass plug, the chilled margin of a rhyolite flow, and a welded tuff unit (fig. 1). These occurrences of mordenite were compared and contrasted in terms of mineralogy, field relationships—and degree of alteration. Various models for the emplacement and subsequent zeolization of such outcrops are proposed in this work, utilizing experimental data combined with field observations.

PREVIOUS WORK

Zeolite mineralization was studied somewhat incidentally as it pertained to associated uranium and alunite deposits by Kerr and others (1957). The specific zeolites they identified (besides mordenite) were thomsonite, natrolite, chabazite and stilbite. They mapped zones of argillic, alunitic, silicic, and zeolitic alteration with the most extensive zeolite alteration being in the
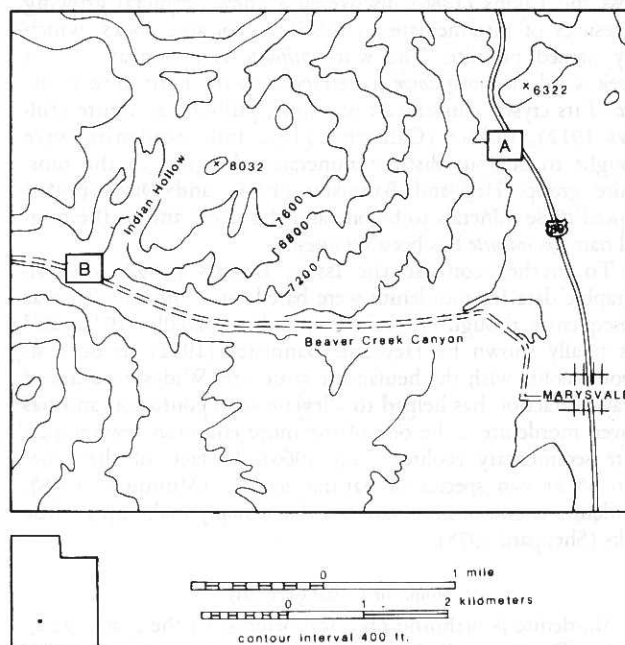

FIGURE 1.—Index map of known mordenite occurrences near Marysvale, Utah. Study area A: Pitchstone vent area. Study area B: Beaver Creek rhyolite flow overlain by welded tuff unit.

Silica Hills area in the form of amygdaloidal filling and veins in intermediate volcanic rocks.

They also identified mordenite (formerly called ptilolite) in rhyolitic glass dikes but did not give specific locations of its occurrence. Their zeolite zones do not include those of this thesis. They concluded that such zones result from alteration of volcanic rocks by alkaline solutions with excess silica and that some former zeolite zones are now altered to clay.

Steven and Cunningham (1979) identified clinoptilolite in the "zeolite tuff" of the Bullion Canyon Volcanic Complex at Cove Fort and in the Joe Lott Tuff in the Mt. Belknap Volcanic series of the Three Creeks Reservoir area.

The study areas of this thesis are in the Delano Peak Northeast Quadrangle and the Marysvale Northwest Quadrangle. The most recent geologic maps of these areas are by Cunningham and Steven (1979a,b). These maps were used as a reference in mapping the geology of the immediate study areas on a much larger scale.

Part of this thesis involves the synthesis of mordenite under various conditions. Barrer (1948) was first to describe the synthesis of Na-mordenite, and he added greatly to the knowledge of synthetic zeolites in succeeding papers (Barrer and White 1952, Barrer and others 1959). Others who have contributed to the understanding of zeolite synthesis are Campbell and Fyfe (1960), Coombs and others (1959), Hay (1963, 1964, 1966), Gogishvili and others (1973), Hawkins (1981), Mariner and Surdan (1970), Senderov (1963), Sheppard and Gude (1973), and Wirsching (1976, 1981).

MORDENITE

History

Mordenite was first described by How (1864) as a fibrous mineral in radial aggregates. More than twenty years later, Cross and Eakins (1886) discovered a "new" mineral growing in vesicles of intermediate to subsilicic volcanic rocks, which they named ptilolite. The word *ptilolite* is a derivative of a Greek word meaning *down* in reference to the light, downy nature of its crystal clusters. At one time, ptilolite, arduinite (Billows 1912), flokite (Callisen 1917), and mordenite were thought to be four distinct minerals belonging to the mordenite group. Hey and Bannister (1934) and Davis (1958) showed these minerals to be one and the same, and so the original name *mordenite* has been retained.

To further confuse the issue, Dana's (1892) crystallographic data for mordenite were based on a mineral that was subsequently thought to be clinoptilolite (Schaller 1932) and was finally shown by Hey and Bannister (1934) to be a siliceous zeolite with the heulandite structure. Widespread use of X-ray diffraction has helped to alleviate such confusion and has proven mordenite to be one of the more common low-temperature sedimentary zeolites (Hay 1966). In fact, of the more than 35 known species of natural zeolites (Mumpton 1978), mordenite is one of nine varieties that usually make up zeolitic rocks (Sheppard 1975).

Mordenite Crystal Chemistry

Mordenite is orthorhombic and belongs to the space group Cmcm. The unit cell content for mordenite is approximately $(Na_2,K_2,Ca)_4Al_8Si_{40}O_{96} \cdot 28H_2O$ with alkalies normally dominant over Ca. Passaglia (1975) concluded that of the fifteen samples he analyzed himself and six other analyses he found in the literature, most contained approximately equal amounts of Na and Ca and minor amounts of K. Unlike some zeolites, mordenite varies only slightly in chemical composition, and variations mainly involve extraframework cations (Passaglia 1975).

Samples of mordenite were collected from the pitchstone vent, the Beaver Creek rhyolite flow, and the welded tuff unit. The locations of these outcrops are shown in figure 1.

X-ray powder patterns were run for mordenite from each of the three locations using a General Electric XRD-5 X-ray powder diffractometer, using nickel filtered CuK_α radiation, and an internal standard of either synthetic CaF_2 (a = 5.4626) or silicon metal (a = 5.4301). Two-theta values obtained from such patterns and from the literature (Kerr and others 1957) were used as a basis for unit cell refinements, using the least squares computer program of Evans and others (1963) (table 1).

TABLE 1

UNIT CELL DIMENSIONS FOR RESPECTIVE MORDENITE OUTCROPS

Location	a	b	c
Pitchstone plug	18.16(1)*	20.47(2)	75.42(1)
Beaver Creek rhyolite	18.04(2)	20.41(2)	75.15(1)
Welded tuff	18.06(2)	20.34(2)	75.31(1)
Rhyolitic glass dike (Kerr and others 1957)	18.05(2)	20.40(1)	75.10(1)

*Numbers in parentheses are standard deviations in the last decimal place cited.

Weight percents of major oxides were determined using a Phillips PW 1100 X-ray fluorescence spectrometer. Samples were pulverized and prepared, as outlined by Norrish and Hutton (1965), by fusing 2.25g flux, 0.42g rock sample, and 0.03g LiNO, to produce glass buttons. Two buttons were made for each sample to check the sample preparation procedure and precision. Accuracy was monitored by analyzing at least one known standard periodically during the analyses. X-ray fluorescence data were reduced to weight percent oxides on a VAX computer using a program written locally. It was impossible to avoid some contamination of mordenite samples from unaltered glass or quartz. Thin-section studies reveal quartz and mordenite to be intimately associated, especially in samples from the Beaver Creek rhyolite. A heavy liquid was used to separate mordenite from unaltered glass of the pitchstone vent area. Undoubtedly, some silica contamination, in the form of quartz or unaltered glass invalidated, to some extent, $Si/(Al + Fe^{3+})$ ratios of all mordenite samples analyzed by X-ray fluorescence.

Passaglia (1975) demonstrated a negative correlation between the b cell dimension and $Si/Si^+Al^+Fe = R$. From this relationship, he derived the following formula:

$$R + .0113 = 8.12391 - 0.35632b.$$

Although variations in chemistry are slight, mordenite from the welded tuff shows more Ca and higher Si/Al than that from either the pitchstone vent or the Beaver Creek rhyolite, which are almost identical.

Mordenite from all locations shows much more Ca and slightly less Na and K than the unaltered glass. There proves to be a direct correlation between the specific $Na^+:K^+:Ca^{2+}$ ratios of the mordenite and those of the glass from which each was derived (fig. 2). This would indicate that the composition of the glass controls, to some extent, the composition of the mordenite, but the chemistry of the altering solutions certainly affects the final cation ratios as well.

EXPERIMENTAL PROCEDURE

All laboratory experiments involving the synthesis of zeolites and other minerals from natural glass were carried out at

200° C. Although mordenite has been synthesized at temperatures as high as 300° C, the stability range of sodium-rich mordenite was determined by Senderov (1963) to be 150-230°C. This is consistent with Gogishvili and others (1973), who placed the upper limit at 220°C.

The only elevated pressure involved in the synthesis of zeolites in these experiments was due to H_2O vapor and may be considered negligible. Gogishvili and others (1973) determined that pressures up to 2000atm have no effect on the stability of the zeolite varieties synthesized in these experiments.

Glass from the pitchstone vent area was used for the synthesis of zeolites because unaltered samples of the glass were readily available. The composition of this glass is shown in table 2. Twelve bombs of the author's design were utilized in the experiments (fig. 3). In all bombs, the liquid:solid ratio (ml of altering solution to gms of glass) was 4:15, or approximately ¼.

After being heated for a specific time period, the contents of the bombs were analyzed for zeolite growth by the X-ray powder diffraction method. After the bomb was quenched in cold water, the inner capsule was opened and a small amount of material was removed and smeared on a slide for X-ray diffraction. For each check approximately the same amount of material was removed from each bomb and smeared over approximately the same surface area on a slide, so that X-ray peak heights would be somewhat comparative from one bomb to the next.

For convenience, two characteristic peaks of a given mineral that did not interfere with peaks of other phases were chosen to gauge the growth of that particular mineral. The following major peaks were used for identification (CuK radiation):

Mineral name	2θ's	
phillipsite	12.40	17.50
mordenite	9.70	22.10
analcime	15.77	52.70
K-feldspar	20.95	29.80

The heights of the representative peaks for a given mineral were measured in arbitrary units and averaged to give a number that could be used for semiquantitative estimates of zeolite growth.

After the smear was analyzed, the material was scraped off the slide and returned to the teflon chamber.

ZEOLITE GROWTH CURVES AT VARIOUS OH⁻ ACTIVITIES

The following experiment demonstrates the nature of zeolite growth over a wide spectrum of OH⁻ activities at a fixed Na^+ concentration (one molar), and under the conditions pre-

TABLE 2
WEIGHT PERCENT OXIDES

Glass from Pitchstone Plug		Mordenite from Pitchstone Plug	
SiO_2	72.07	SiO_2	67.36
TiO_2	.14	TiO_2	.14
Al_2O_3	12.00	Al_2O_3	12.53
Fe_2O_3	1.23	Fe_2O_3	1.07
MnO	.10	MnO	.01
MgO	.39	MgO	.40
CaO	.41	CaO	2.63
Na_2O	5.85	Na_2O	3.52
K_2O	3.99	K_2O	2.24
P_2O_5	.03	P_2O_5	.03
LOI	4.37	LOI	8.31
Total	100.58	Total	98.04

Glass from Beaver Creek Rhyolite		Mordenite from Beaver Creek Rhyolite	
SiO_2	71.11	SiO_2	69.15
TiO_2	.14	TiO_2	.16
Al_2O_3	10.14	Al_2O_3	11.89
Fe_2O_3	.93	Fe_2O_3	1.24
MnO	.40	MnO	.09
MgO	.30	MgO	.25
CaO	.77	CaO	2.44
Na_2O	6.55	Na_2O	3.31
K_2O	3.37	K_2O	1.92
P_2O_5	.48	P_2O_5	.03
LOI	4.90	LOI	8.71
Total	99.09	Total	99.19

Glass from Beaver Creek Rhyolite (brownish orange)		Mordenite from Beaver Creek Rhyolite (buff)	
SiO_2	70.20	SiO_2	64.64
TiO_2	.13	TiO_2	.13
Al_2O_3	11.37	Al_2O_3	12.12
Fe_2O_3	.83	Fe_2O_3	.82
MnO	.23	MnO	.30
MgO	.30	MgO	.30
CaO	1.17	CaO	3.73
Na_2O	6.80	Na_2O	4.80
K_2O	2.64	K_2O	.38
P_2O_5	.52	P_2O_5	.56
LOI	5.14	LOI	11.10
Total	99.33	Total	98.88

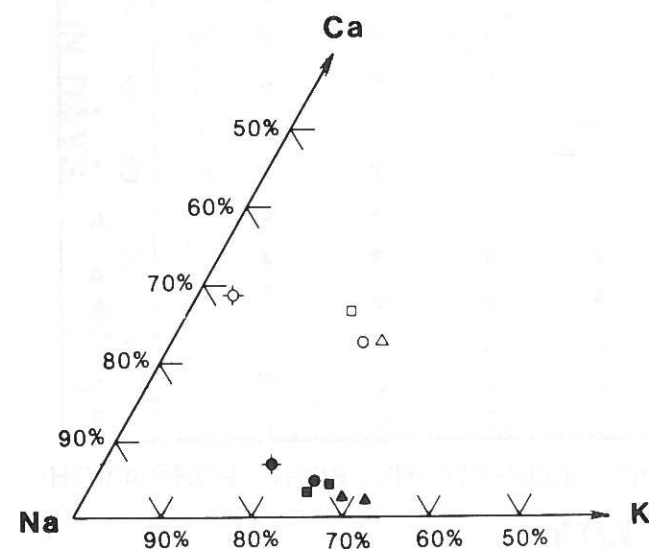| Glass from Welded Tuff		Mordenite from Welded Tuff	
SiO_2	71.97	SiO_2	66.46
TiO_2	.14	TiO_2	.05
Al_2O_3	12.14	Al_2O_3	12.80
Fe_2O_3	.88	Fe_2O_3	1.15
MnO	.05	MnO	.05
MgO	.02	MgO	.59
CaO	.58	CaO	3.26
Na_2O	6.04	Na_2O	3.61
K_2O	3.26	K_2O	1.77
P_2O_5	.02	P_2O_5	.04
LOI	3.88	LOI	10.55
Total	98.98	Total	100.33

FIGURE 2.—Distribution of exchangeable cations in moles fractions. Solid symbols represent glass; open geometric symbols, mordenite. Triangles, pitchstone plug outcrop; circles, Beaver Creek rhyolite flow (circles with crosses represent brownish orange glass or buff colored mordenite; without crosses, dark green colored glass or pale green mordenite); and squares, welded tuff unit.

viously described. Altering solutions of one molar concentra-
tion were prepared from various mixtures of NaOH and NaCl
as indicated in figures 4, 5, 6.

The contents of the bombs were analyzed, as described
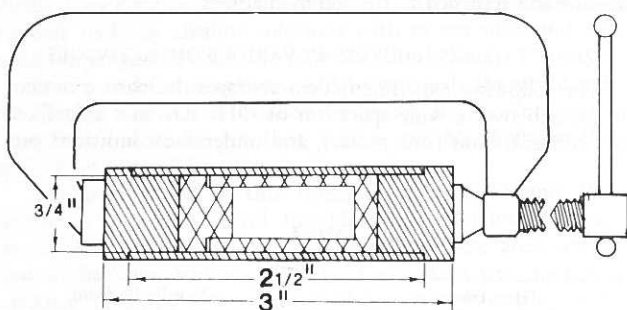above, at time intervals indicated in figures 4, 5, and 6.

FIGURE 3.–Design of bombs in which minerals were synthesized. Diagonal
lines = components of aluminum, and cross-hatch lines = components
of teflon. Inner chamber has capacity of approximately 20 ml. Bomb held
together with C-clamp, which pinches teflon cap to teflon cylinder to seal
inner chamber. Teflon gasket helps insure tight seal.

Every 24 hours, old solutions were filtered off and fresh so-
lutions were added in their place to simulate an "open system."
An open-system model was chosen for this experiment to accel-
erate growth rates (Wirsching 1976) and to focus on the ef-
fects of the initial solution chemistry and not on the composi-
tion of the glass or variations (through time) in solution
chemistry that may occur with alteration. For example, pH
consistently dropped as glass dissolved.

A rather wide variety of minerals grew from the same par-
ent glass where the only variables were time and OH⁻ activity.
Presumably the chloride ion has no effect on the dissolution of
glass or the formation of zeolites because it does not fit into
any zeolite structure. A discussion of the various minerals syn-
thesized and the possible reasons for their growth follows.

ZEOLITE AND FELDSPAR GROWTH PATTERNS

Phillipsite

Phillipsite (fig. 7) has a relatively low Si/Al ratio and is
therefore unstable in silica-rich hydrothermal solutions (Haw-
kins 1981). Its formation in rhyolitic glass may be explained by
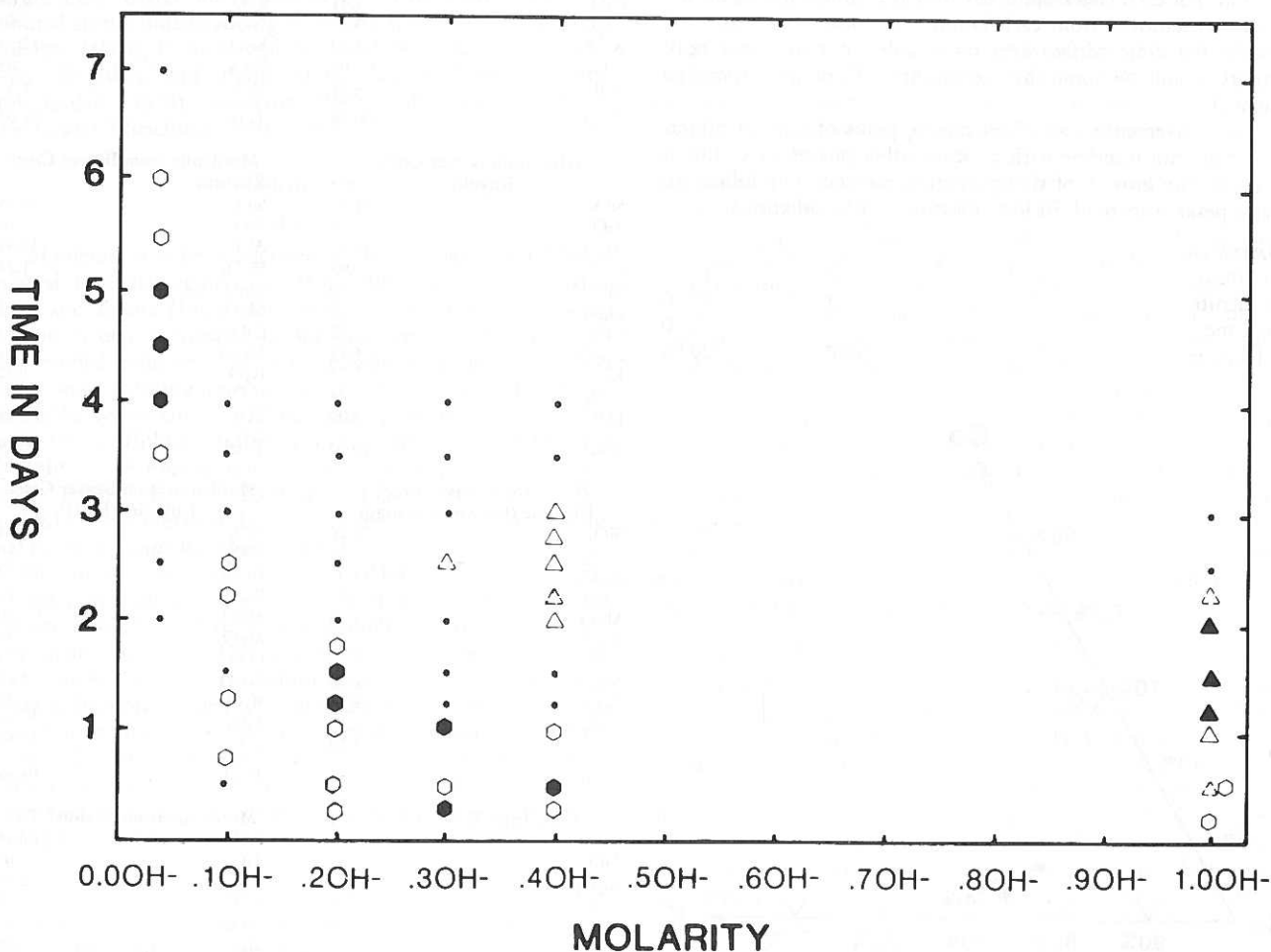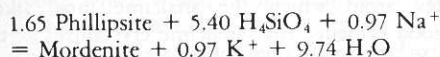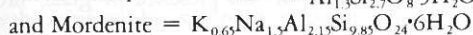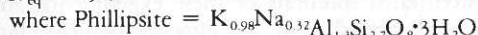the initial "incongruent dissolution" of glass, creating an

FIGURE 4.–Growth patterns of phillipsite and alkali feldspar synthesized at 200°C in 1M solutions. Hydroxide ion concentration is indicated in diagram as result of
the dissociation of NaOH. Proper amounts of NaCl were added to yield 1M Na⁺ concentrations for all solutions. (Solutions were filtered off and renewed
every 24 hours). Hexagons represent phillipsite and triangles represent alkali feldspar growth. Solid figures represent abundant growth; open figures, moderate
growth; dashed figures, slight growth as determined by X-ray diffraction. Small dots represent times at which samples were analyzed, but no growth was de-
termined. Note: Alkali feldspar is more stable at extreme OH⁻ concentrations, and phillipsite persists longer at much lower hydroxide concentrations, but
both are unstable.

aluminum-rich, silica-poor environment favorable for the crystallization of phillipsite (Holler and Wirsching 1978). Phillipsite appears to nucleate early and grow quickly. Its presence prior to other phases, with the exception of an unidentified clay mineral, may be explained as a function of kinetics alone.

Phillipsite appeared and disappeared and appeared again in several runs (fig. 4). This may best be explained in terms of ionic activity. Because Na^+ is the only cation introduced by the mineralizing solutions, K^+ required for phillipsite to crystallize must come from the initial dissolution of glass. As glass dissociates and phillipsite forms, the K^+/Si ratio of the solution decreases, favoring the formation of a more sodium-rich zeolite, such as mordenite. In the process of converting phillipsite into mordenite, K^+ is released into solution as outlined by Hawkins (1981):

1.65 Phillipsite + 5.40 H_4SiO_4 + 0.97 Na^+
= Mordenite + 0.97 K^+ + 9.74 H_2O

log K_{eq} = 19.8

where Phillipsite = $K_{0.98}Na_{0.32}Al_{1.3}Si_{2.7}O_8 \cdot 3H_2O$
and Mordenite = $K_{0.65}Na_{1.5}Al_{2.15}Si_{9.85}O_{24} \cdot 6H_2O$

Consequently, the K^+ activity of the solution increases, which favors the recrystallization of phillipsite.

Other experiments indicate that the stability field of phillipsite is larger at lower temperatures and in more potassium-rich solutions (Hay 1964; Wirsching 1976, 1981; Hawkins 1981).

Mordenite

Mordenite (figs. 8, 9) consistently appears as an early phase in all runs except in nearly pure NaCl solutions, where no growth was detected in runs of 10 days or longer, presumably because of the inability of saline solutions with neutral pH to dissociate glass (Gogishvili and others 1973).

Coombs and others (1959) grouped mordenite with the highly siliceous zeolites which are stable only in solutions supersaturated in silica with reference to quartz. In other words, if the dissolved silica in solution was in equilibrium with quartz, the silica activity would not be sufficiently high for mordenite to crystallize. More recent studies indicate that mordenite growth requires silica supersaturation with respect to amorphous silica (Gogishvili and others 1973). Such an ex-
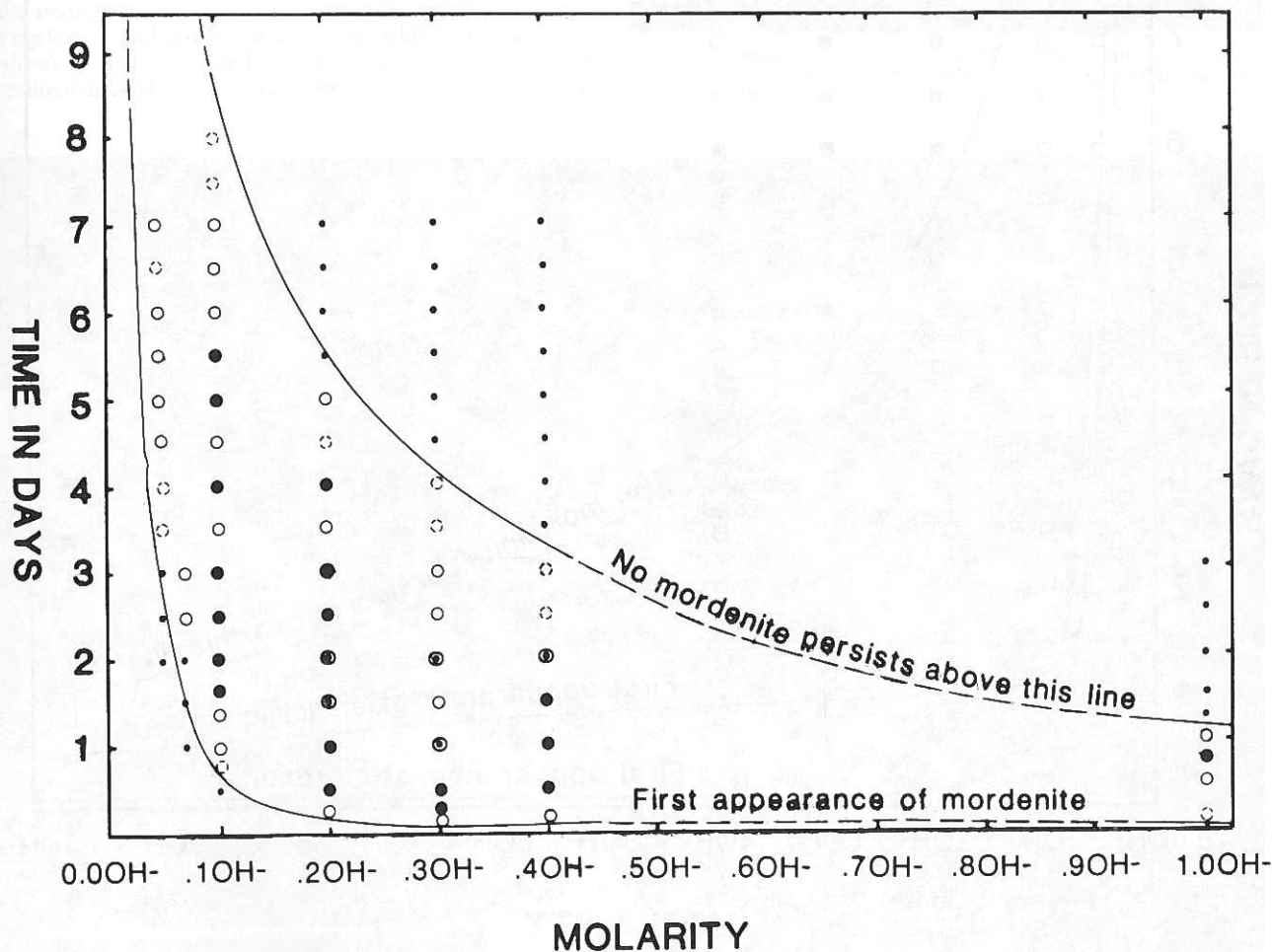

FIGURE 5.–Growth patterns of mordenite synthesized at 200°C in 1M solutions. Hydroxide ion concentration is indicated in diagram as a result of dissociation of NaOH. Proper amounts of NaCl are added to yield 1M Na^+ concentrations for all solutions. Black circles encompassed by larger circles represent most abundant growth; black circles, abundant growth; open circles, moderate growth; dashed circles, slight growth. Small dots, times at which samples were analyzed, but no growth was determined. Lower curve represents first appearance of mordenite; upper curve, last occurrence of mordenite. Above this line, mordenite does not persist. Note: Extrapolation of these curves shows they cross after 39 days, indicating that mordenite will not persist in any of these solutions regardless of pH, undoubtedly because of the high Na^+ activity.

treme concentration of silica theoretically occurs at the boundary layer of the glass and solution (Gogishvili and others 1973). Others believe zeolites may form indirectly from a gel (Mariner and Surdan 1970) or from solution by direct precipitation (Deffeyes 1959). Figure 9 is a scanning electron microscope photograph, which shows a glass shard encased in a crystalline network of mordenite. It appears that, as the glass shard dissolved, mordenite precipitated from the highly siliceous zone immediately surrounding the shard.

Dibble and Tiller (1981) observed that early-forming "disordered minerals," (nonalacimic zeolites), such as mordenite and phillipsite, form early in the presence of glass to reduce the free energy of the system but eventually yield to more stable phases, with slower growth rates, such as analcime and feldspars. In these experiments, mordenite was short lived, especially in highly alkaline runs, where glass dissolution was most rapid, and mordenite presumably disappeared when the glass had been totally dissolved. Because of the accelerated transformations under the conditions of the experiments, phases, such as mordenite, analcime, and alkali feldspar, clearly coexist (fig.

10) in an ephemeral, metastable relationship that may not occur in nature.

Senderov (1963) concluded that mordenite is not stable if the alkalinity is too high, which is consistent with the results of this investigation. Although at high pH silica is more soluble, the OH⁻ ion polymerizes the dissolved silica, thereby reducing the effective amount of free silica in solution (Hay 1964).

Analcime

Analcime is sodium rich and silica poor with respect to mordenite. Therefore, it is favored by increasing the sodium concentration and by the complete dissolution of glass. Photomicrographs of synthetic analcime are shown in figures 10 and 11. Close correlations between Si/Al ratios of analcime and that of suspect zeolites, from which the analcime most likely formed, provide good evidence that analcime crystallizes at the expense of pre-existing zeolites (Sheppard and Gude 1969). In the highly concentrated solutions of these experiments, analcime probably does crystallize in the presence of glass, most
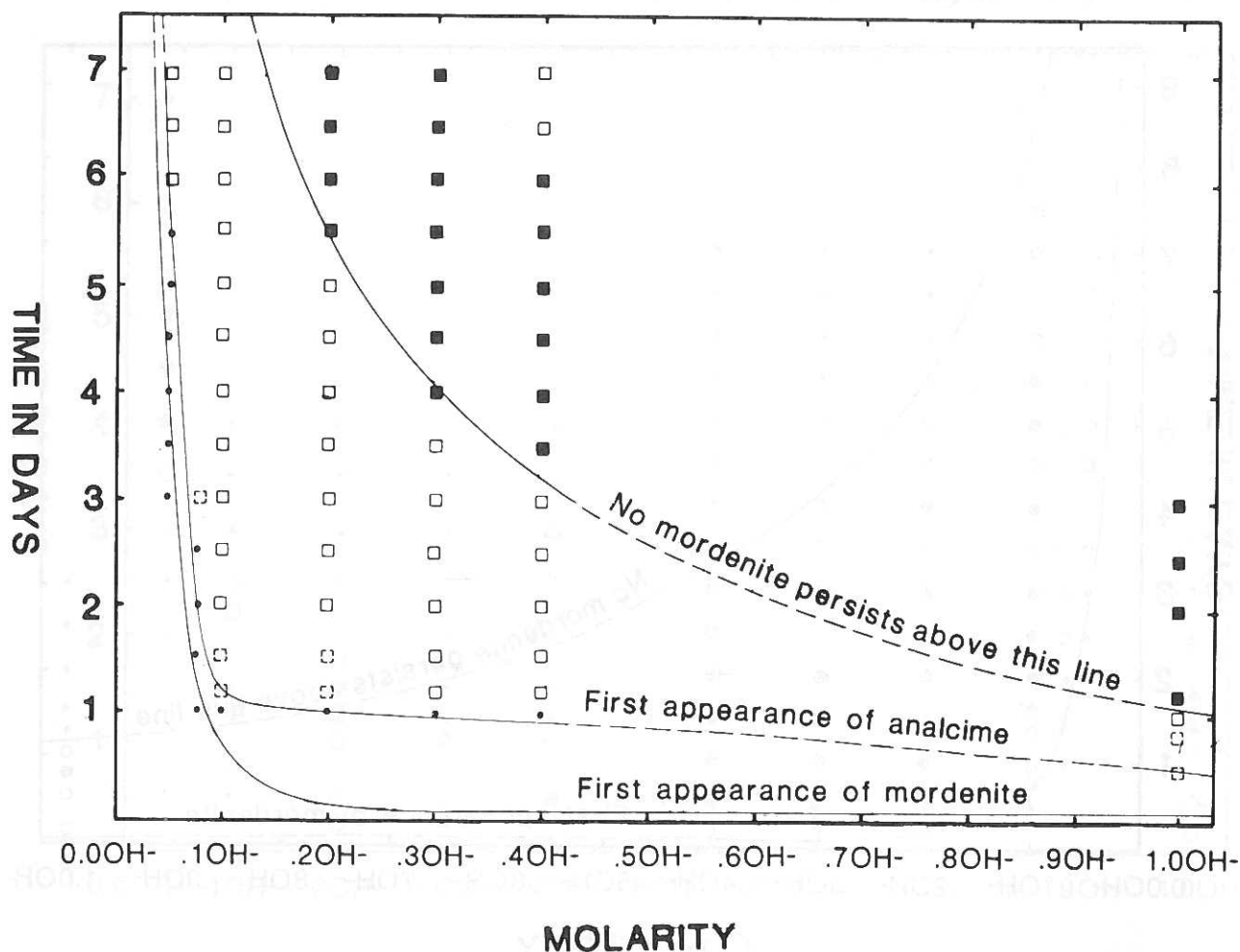

FIGURE 6.—Growth patterns of analcime synthesized at 200°C in 1M solutions. Hydroxide ion concentration is indicated in diagram as a result of dissociation of NaOH. Proper amounts of NaCl were added to yield 1M Na⁺ concentrations for all solutions. Black squares represent abundant growth; open squares, moderate growth; dashed squares, slight growth. Small dots, times at which samples were analyzed, and no growth was determined. Lower curve represents the first appearance of analcime. Superimposed on this chart are curves representing first and last appearance of mordenite as indicated. Note: Appearance curve of analcime curves steeply upward in lower alkaline region, where mordenite is more stable. Note also strong correlation of abundant analcime growth and disappearance of mordenite. Both examples indicate growth of analcime is slowed by presence of an intermediate, metastable-phase mordenite.

likely from pre-existing mordenite or even alkali feldspar (fig. 11). However, once mordenite disappears, which may indicate the complete solution of glass, the crystallization of analcime is suddenly accelerated (fig. 6).

In these experiments, analcime is the only existing phase, once mordenite disappears, in solutions that are 0.4 molar NaOH or less. The fact that analcime forms over a broad range of pH is well demonstrated.

Alkali Feldspar

Alkali feldspar forms only in highly alkaline solutions (fig. 4). Perhaps rapid dissociation of glass at higher pH is sufficient to produce enough potassium activity for alkali feldspar crystallization. Also, as pH increases, activity of H_2O decreases (Zhdanov 1968), which would favor a nonhydrous phase, such as alkali feldspar over analcime.

In natural lacustrine systems, alkali feldspars form adjacent to zeolites in the most alkaline portions of the lake but not in the presence of glass (Sheppard and Gude 1973). This finding is substantiated by scanning electron photographs of alkali feldspar and analcime, which show the glass has virtually disappeared in samples containing alkali feldspar (fig. 10). In natural systems, analcime may become unstable and disappear with the nucleation and growth of the more stable feldspars. Figure 10 shows an analcime crystal partially dissolved and partially recrystallized as alkali feldspar. In these experiments, however, al-

kali feldspar eventually yields to analcime, contrary to the typical sequence in natural systems (Sheppard and Gude 1973), probably as the result of a continued influx of sodium-rich solutions.

FIGURE 8.—Fibrous mordenite with unidentified mineral synthesized at 200°C in .2M (50% NaOH, 50% NaCl solution) after 7 days (no renewal of solution). Bar represents 20 μm.
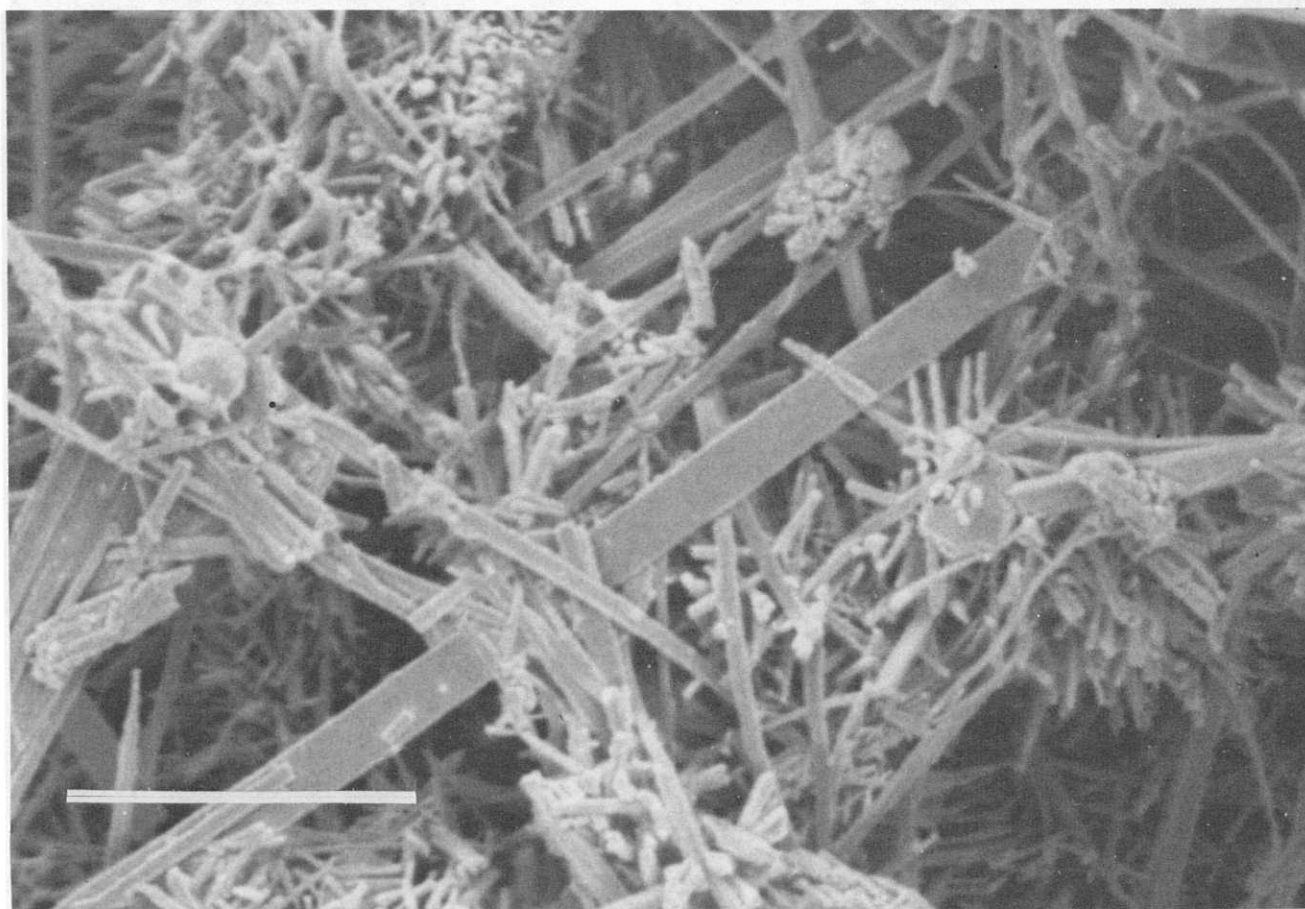

FIGURE 7.—Long prismatic crystals of phillipsite with fibrous mordenite synthesized at 200°C in 1M (7.5% NaOH, 92.5% NaCl) solution after 3 days—fresh solution every 24 hours. Scale bar represents 10 μm.

GROWTH CURVES

Interpretation of Mordenite Growth Patterns

In order to predict the growth patterns of the minerals synthesized over a wide spectrum of OH⁻ concentrations, mineral growth was recorded on graphs (figs. 4, 5, 6). The abscissa represents time, and the ordinate represents solution concentration.

For each solution, a point on the graph was estimated for the first appearance of a mineral and the disappearance of a previously existing mineral based on the intensity of the X-ray pattern of the mineral at the time it was first detected or the last time it was detected before it disappeared. Such points were used in a best fit power curve program to obtain the following equations for curves denoting the appearance and disappearance of mordenite plotted against time and solution concentration:

Appearance curve: $Y = 19.77^x - 2.26$
Disappearance curve: $Y = 225.76^x - .84$

Where x = hours and Y = OH⁻ molarity in tenths. These equations were used as a basis for projecting the growth pattern of mordenite through time in solutions of low OH⁻ concentrations in which mordenite growth is very slow. The two curves cross, however, after 39 days, which indicates that under the conditions of this experiment, mordenite is metastable and will eventually disappear, regardless of the pH. This undoubtedly is due primarily to the high Na⁺ concentration (1 molar) of the mineralizing solutions, which favors a sodium-rich phase such as analcime (Senderov 1963, Holler and Wirsching 1978).

Similar curves were also calculated for analcime. The appearance curve for analcime rises sharply as the OH⁻ concentration decreases below .2 molarity (fig. 6). This sharp rise may be explained by the sudden slowdown of the dissolution of glass at lower pH and in terms of relative stabilities of mordenite and analcime. Mordenite is relatively more stable at low pH. Therefore, the formation of analcime is delayed owing to the persistence of a metastable phase, such as mordenite. Metastable phases are believed to delay the formation of more stable assemblages tens of millions of years in natural systems (Dibble and Tiller 1981). As soon as mordenite disappears, in the experimental system, analcime growth is markedly increased.

Growth Curves at Various Na⁺ Concentrations

The following experiment was designed to test the growth of mordenite, using a series of solutions with a constant NaOH, i.e., OH⁻ concentration. Curves denoting the appearance of mordenite were estimated for altering solutions of 1/10, 2/10, and 3/10 NaOH molarities. The Na⁺ activities varied according to the relative proportions of NaCl and H₂O as shown in figure 12.

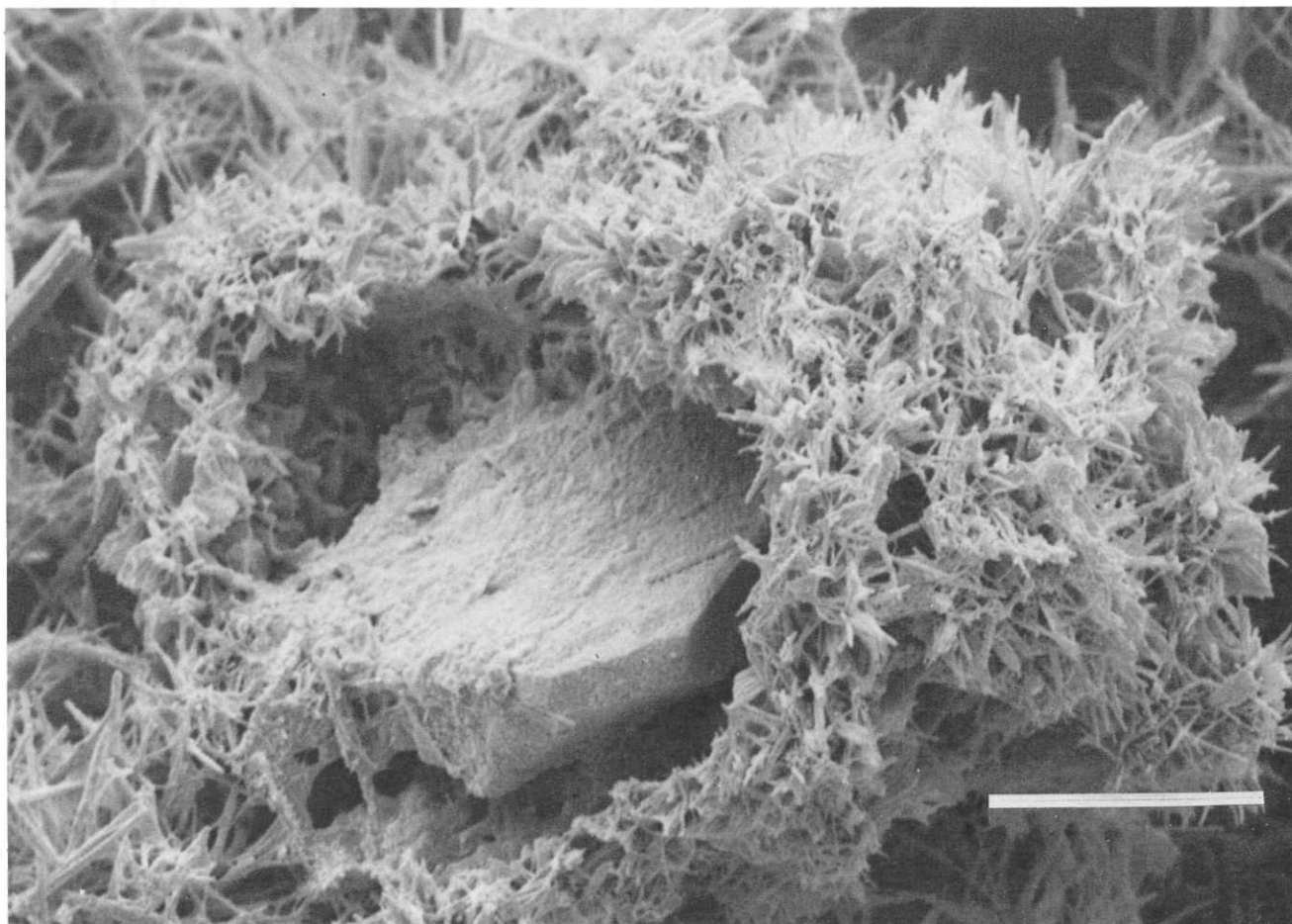The results were somewhat predictable. Curves shifted ver-

FIGURE 9.—Mordenite (confirmed by X-ray diffraction pattern) crystallizing in zone of silica supersaturation immediately around a dissolving glass shard. Bar represents 20 μm.

tically up with decreasing OH⁻ activities. In other words, for a given sodium concentration, reaction rates are increased at higher pH consistent with previous experiments. Each curve also shows an increase in the rate of mordenite formation at higher Na⁺ activities. This indicates that silica solubility rates increase with the increasing ionic concentration of the solution (Mariner 1971). This increase has been attributed to the polymerization of monosilicic acid in solution induced by Na⁺ (or other cations in solution), thus preventing a condensed silicic acid layer that would otherwise form on the surface of silica grains (Mariner 1971).

Data gathered, using NaOH as a source of hydroxide ion, show increased rates of mordenite formation at higher salinities (Na⁺) and pH, also observed by Hay (1966), Mariner (1971), and Dibble and Tiller (1981). The curves for the various OH⁻ activities appear to approach different asymptotes that shift to the right (higher Na⁺ concentrations) with increasing OH⁻ concentrations. Therefore, in a general sense, minimum Na⁺ concentrations (salinity) required to form mordenite may depend on the pH (alkalinity) of the solution. Solution chemistry, which may be considered the most important factor in the zeolitization of volcanic glass (Hay 1966), will be discussed further as it applies to the mordenite outcrops near Marysvale.

Other factors to be considered in conjunction with field observations include permeability, extent of hydrothermal activity, susceptibility of various glasses to mordenite alteration, and the relationship of silicification and mordenitization.

PITCHSTONE PLUG

About 3.2 km north of Marysvale along U.S. 89, are several outcrops of massive pitchstone (A in fig. 1). The most obvious outcrop forms a prominent cliff face adjacent to the highway and is here referred to as the "pitchstone plug" (fig. 13). Additional bodies of pitchstone crop out higher in the hillside and extend for several hundred meters along the south side of the ridge.

The pitchstone plug was dated (K-Ar) by Bassett and others (1963) to be 17.8 m.y. Outcrops of rhyolite appear at the base of the southeast side of the pitchstone plug and directly below other pitchstone outcrops at several locations. It appears that the pitchstone plug is only part of a vent much larger than the present study area. Evidence that the pitchstone represents the chilled caps of ascending magmas is found in vertical flow layering in the basal rhyolite and lower parts of the pitchstone and in the fact that the glass crops out above and below individual stratified units at the western end of the study area (fig. 13). The original shape and extent of the vent are obscured by erosion. Pitchstone outcrops are terminated to the south and west by major faults. A minor fault downdrops the eastern half of the pitchstone outcrops 15 meters or more.

The largest exposure of the basal rhyolite is on the south side of the ridge about 30 m west of the highway. The lowest part of the exposure consists of a rhyolite breccia containing fragments of rhyolite a few tens of centimeters across in random orientations. Both the rhyolite matrix and the rhyolite
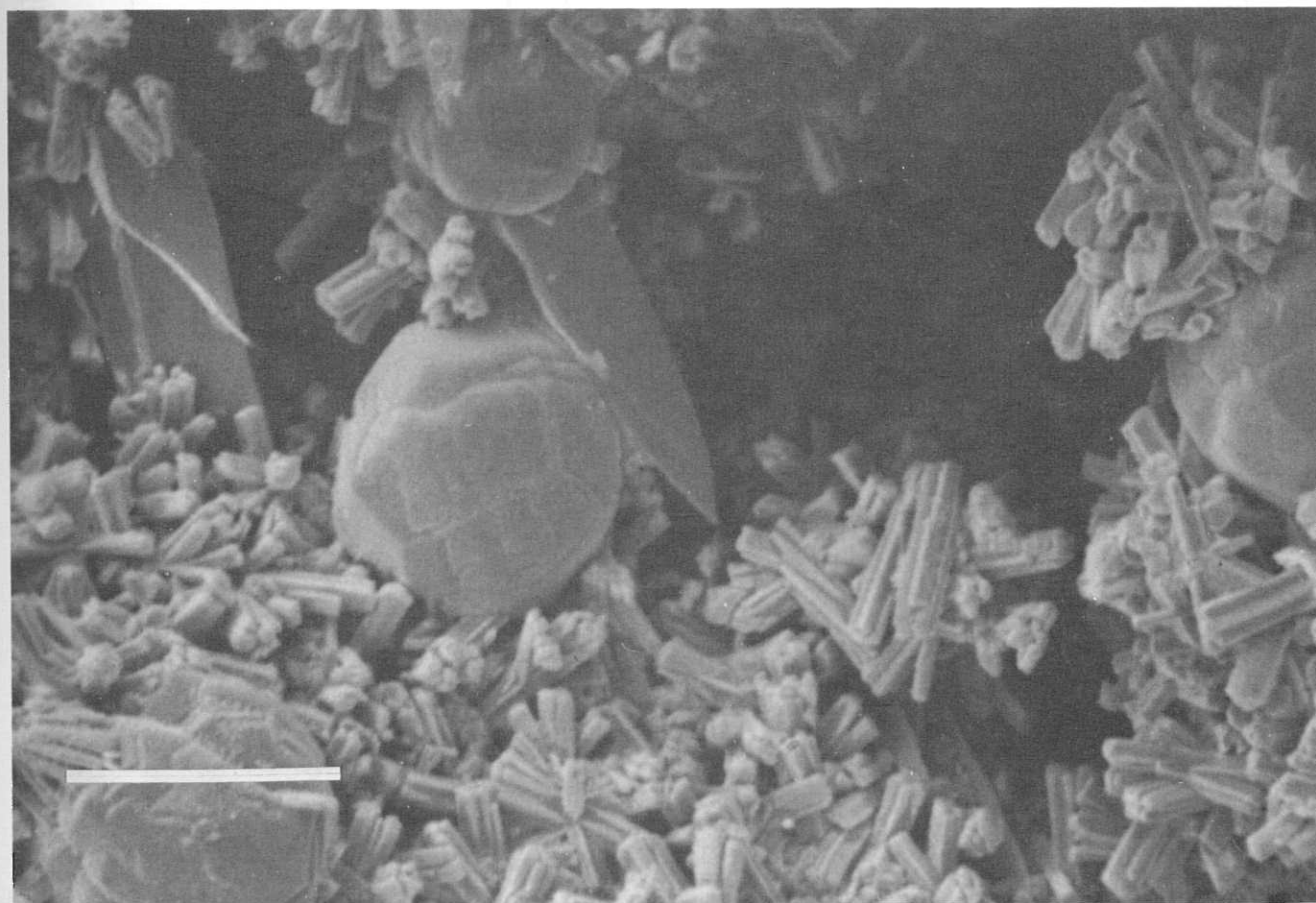

FIGURE 10.—Short, stubby K-feldspar crystals, isometric analcime crystals, and what is likely a bladed form of mordenite synthesized at 200°C in 1M NaOH solution after 3 days (no solution change). Note K-feldspar growing at the expense of analcime in lower left corner. Scale bar represents 10 μm.

clasts have been highly altered and etched by weathering along the flow layers. Higher in the exposure, clasts disappear. The basal rhyolite is characterized by vertical flow layering and silicified flow banding, which include cherty concretions.

Above the basal rhyolite is the pitchstone body, the medium for mordenite growth. The fracturing of the pitchstone plug undoubtedly aided mordenitization. Some of the fractures have been healed by veins of light reddish purple chert. Large portions of the plug appear to have been autobrecciated, resulting in what appears at first glance to be a conglomerate. Closer inspection reveals the "pebbles" to be of the same glass as the matrix. Mineralizing solutions have altered the glassy matrix to accent the unaltered glassy fragments, which have, in turn, been somewhat rounded by mordenite mineralization. Solutions attacked the sharp edges and rounded the clasts, just as weathering along joint systems will produce rounded rock bodies in the process of spheroidal weathering.

Zeolitization

Mordenite, which appears as a green discoloration of the glass, is localized immediately around cherty veins and concretions and on a microscopic scale is concentrated in perlitic cracks. In general, the lower part of the pitchstone plug is considerably more mineralized and silicified than the upper portion. Vertical, parallel cherty veins and associated concretions along flow layers (fig. 14) in the rhyolite can be traced into the

pitchstone, where they eventually disappear. Glass between such veins is invariably altered to mordenite. In the upper portions of the plug, cherty veins are fewer and restricted to the fractures. A small outcrop of black, unaltered pitchstone is situated on the west side of the plug and probably represents the outermost portion of the plus being relatively unfractured and unaffected by mineralizing solutions.

Model for Emplacement

The emplacement of the pitchstone plug and associated glass bodies is subject to diverse interpretations. In some outcrops, there seems to be a contact plane between basal rhyolite and pitchstone, which would be somewhat surprising if the pitchstone and rhyolite cooled from the same melt.

If the rhyolite predated the pitchstone, it is difficult to explain how the melt from which the pitchstone formed pushed through the solidified rhyolite without including xenoliths of rhyolite in the glass. On the other hand, if the pitchstone had cooled first at the surface, the ascending rhyolitic magmas of a second event most likely would have destroyed the pitchstone during eruption. Vertical cherty flow layers of identical characteristics in the rhyolite and the glass strongly suggest that rhyolite and pitchstone cooled from the same melt. The relatively sharp contact may best be explained by the following scenario. A body of rhyolitic magma ascended and began to cool at the surface to form a rhyolite plug with a glassy margin. Be-
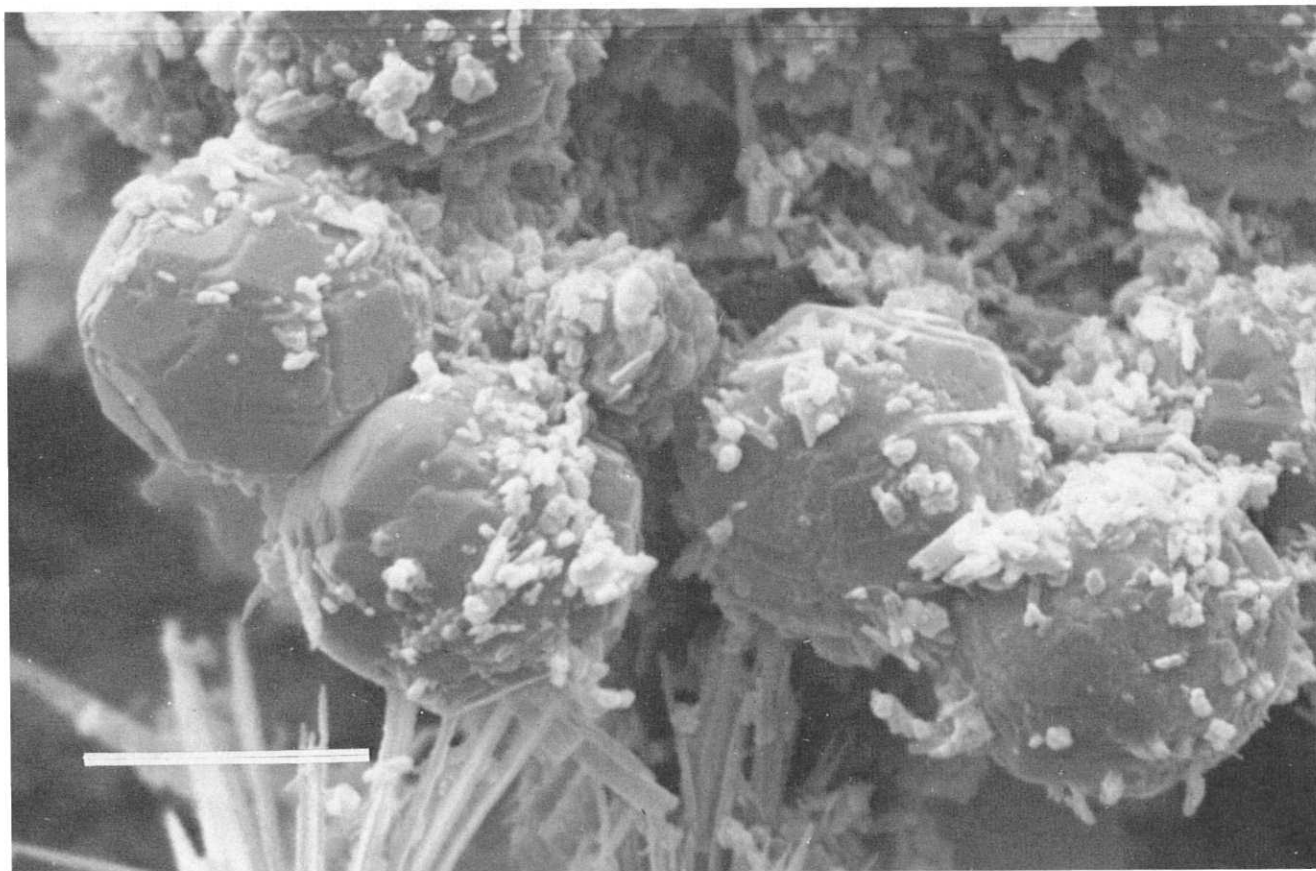

FIGURE 11.—Isometric crystals of analcime with associated bladed mordenite and grossly dissolved feldspar crystals. Synthesized at 200°C, 1M NaOH after 5 days (no solution change). Scale bar represents 10 μm. Note: In figure 10, feldspar formed as analcime dissolved. In nature, feldspar usually succeeds analcime at high alkalinities, but considering the extreme Na^+ concentration of this solution, analcime appears to be the more stable phase.
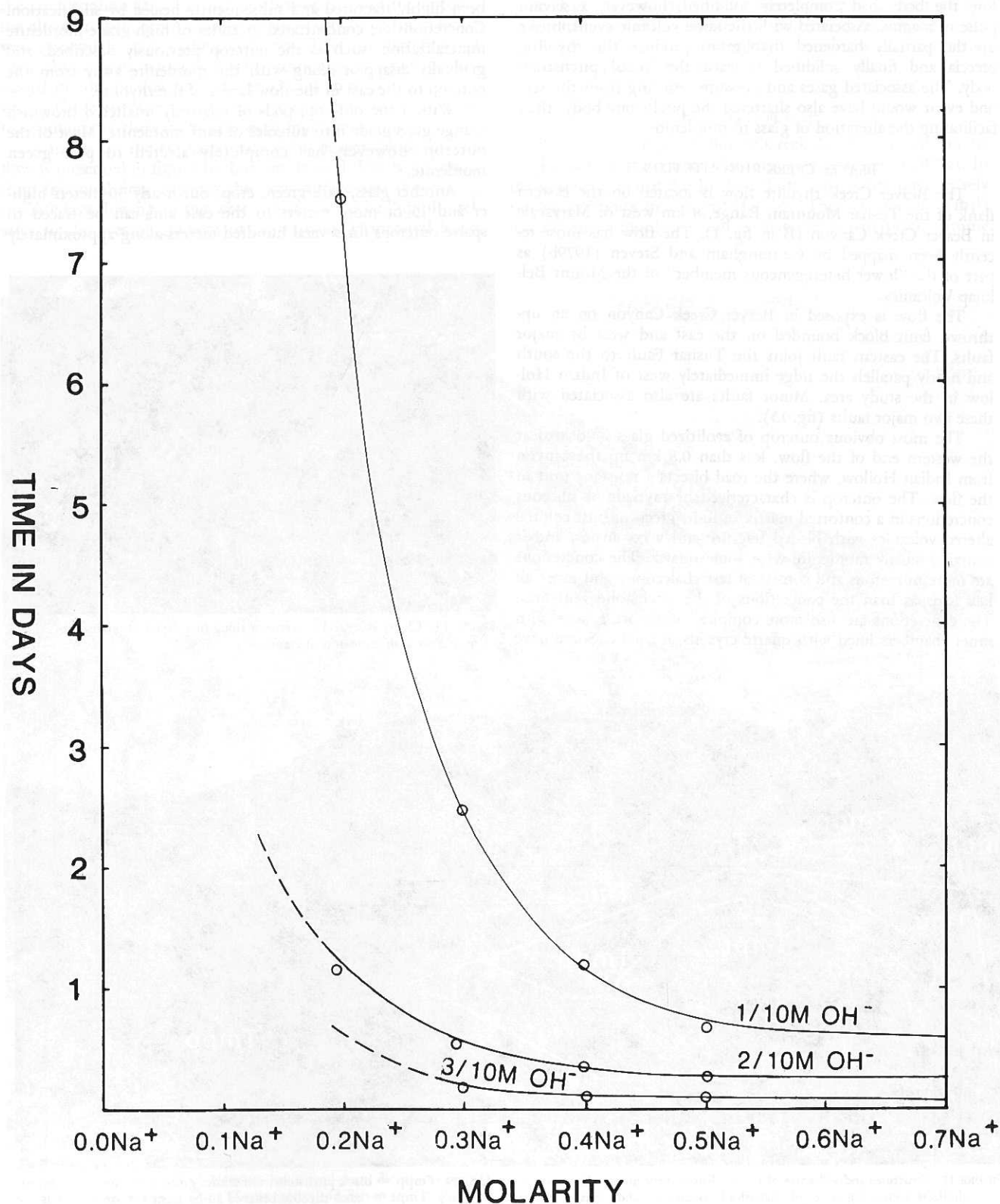
FIGURE 12.—Curves designate the first appearance of mordenite. Molar Na$^+$ concentrations are indicated assuming 100 percent dissociation of NaCl and NaOH in solution. Each curve represents mordenite growth patterns at a constant OH$^-$ concentration as indicated. Note: Mordenite forms first in solutions with a high concentration of OH$^-$ for any given Na$^+$ concentration. Also, curves appear to approach different asymptotes that shift to the right as OH$^-$ concentrations decrease.

fore the body had completely solidified, however, a second pulse of magma, associated with the same volcanic event, broke up the partially hardened rhyolite to produce the rhyolitic breccia and finally solidified beneath the initial pitchstone body. The associated gases and pressure resulting from the second event would have also shattered the pitchstone body, thus facilitating the alteration of glass to mordenite.

BEAVER CREEK RHYOLITE FLOW

The Beaver Creek rhyolite flow is located on the eastern flank of the Tushar Mountain Range, 8 km west of Marysvale in Beaver Creek Canyon (B in fig. 1). The flow has most recently been mapped by Cunningham and Steven (1979b) as part of the "lower heterogeneous member" of the Mount Belknap Volcanics.

The flow is exposed in Beaver Creek Canyon on an upthrown fault block bounded on the east and west by major faults. The eastern fault joins the Tushar Fault to the south and nearly parallels the ridge immediately west of Indian Hollow in the study area. Minor faults are also associated with these two major faults (fig. 15).

The most obvious outcrop of zeolitized glass is located at the western end of the flow, less than 0.8 km up the canyon from Indian Hollow, where the road bisects a resistant unit in the flow. The outcrop is characterized by myriads of siliceous concretions in a contorted matrix of light green or buff colored altered volcanics with bladed fracture and waxy luster, and it contains mostly mordenite with some quartz. The concretions are more numerous and consist of less chalcedony and more alkali feldspar than the concretions of the pitchstone vent area. The concretions are also more complex. Many are geodes with inner chambers lined with quartz crystals or calcite. Some have

been highly fractured and subsequently healed by silicification. Concretions are concentrated in zones of high-grade mordenite mineralization, such as the outcrop previously described, and gradually disappear along with the mordenite away from the outcrop to the east in the flow layers of the rhyolite.

Within the outcrop, pods of relatively unaltered brownish orange glass grade into aureoles of buff mordenite. Most of the outcrop, however, has completely altered to pale green mordenite.

Another glass, dark green, crops out nearly 30 meters higher and 15 or more meters to the east and can be traced to sparse outcrops for several hundred meters along approximately

FIGURE 14.—Cherty veins and concretions along flow layers in pitchstone associated with mordenite alterations.
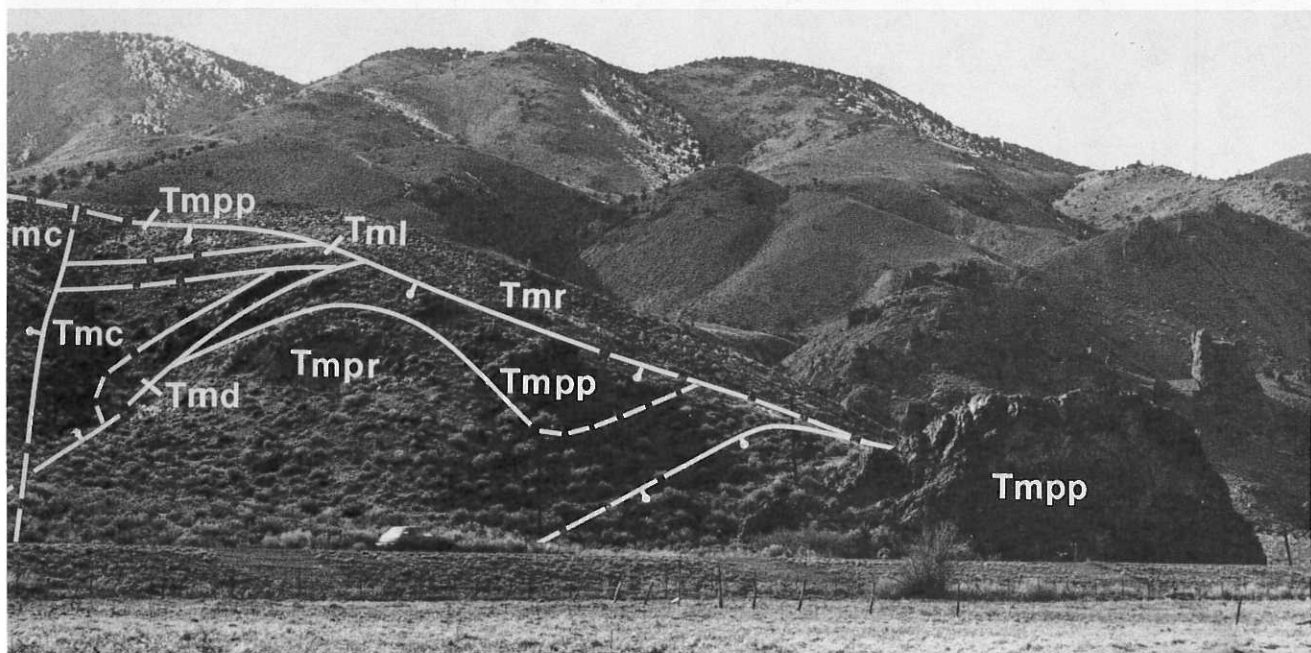

FIGURE 13.—Structures and volcanics of the pitchstone vent area looking east across U.S. 89. **Tmpp** = black pitchstone, sometimes green from mordenite mineralization, containing zones of chalcedony concretions and veins. K-Ar age is 17^+ m.y. **Tmpr** = basal rhyolite believed to be from the same melt as the **Tmpp**. Lower portions are brecciated. Flow layers are characteristically silicified with associated concretions. **Tml** = light green lapilli ash flow tuff approximately 1.5 m thick containing 25 percent lithic fragments. **Tmd** = rhyolitic dike, reddish black on weathered surface and reddish brown on fresh surface, contains approximately 25 percent phenocrysts of plagioclase and K-feldspar. **Tmc** = crystal-rich member—partly to densely welded, reddish brown, alkali-rhyolite ash flow tuff containing 30 percent phenocrysts; quartz (3 percent), anorthoclase (24 percent), sodic plagioclase (2 percent), and biotite (1 percent) (Cunningham and Steven 1979b). K-Ar age is 19.0 ± 1.2 m.y. (Steven and others 1979). **Tmr** = Red Hills Tuff Member—crystal-poor, welded, white to red, alkali-rhyolite ash-flow tuff containing 7–8 percent phenocrysts of anorthoclase, quartz, sodic plagioclase, and minor biotite (Cunningham and Steven 1979).

the same contour (fig. 16, top). As before, most of the outcrop has altered to pale green mordenite. No buff colored mordenite was observed in any of these outcrops. The interpretations of such observations relevant to the various glasses will be discussed in conjunction with the model of emplacement of the Beaver Creek rhyolite and the experiments designed to test the susceptibility of the various glasses to mordenitization.

A model for the emplacement of the Beaver Creek rhyolite flow is presented in figure 16, bottom. Folded flow layers result from frictional drag between the flow surface and the viscous rhyolite lava flowing to the west, which would be "uphill" relative to the present gradient of the canyon. Horizontal layers exposed in the roadcuts in the eastern portion of the flow begin to turn upward in the central portion of the flow and are nearly vertical near the mordenitized roadcut, which represents the glassy margin of the leading edge of the flow.

WELDED TUFF UNIT

The rhyolite flow of Beaver Creek Canyon is overlain by the Joe Lott Tuff Member (Cunningham and Steven 1979a). In the lower portion of the Joe Lott Tuff two continuous, densely welded tuff units are mapped (fig. 15). The lowest unit (**Tmjl**) has altered to mordenite and is characterized by black fiamme
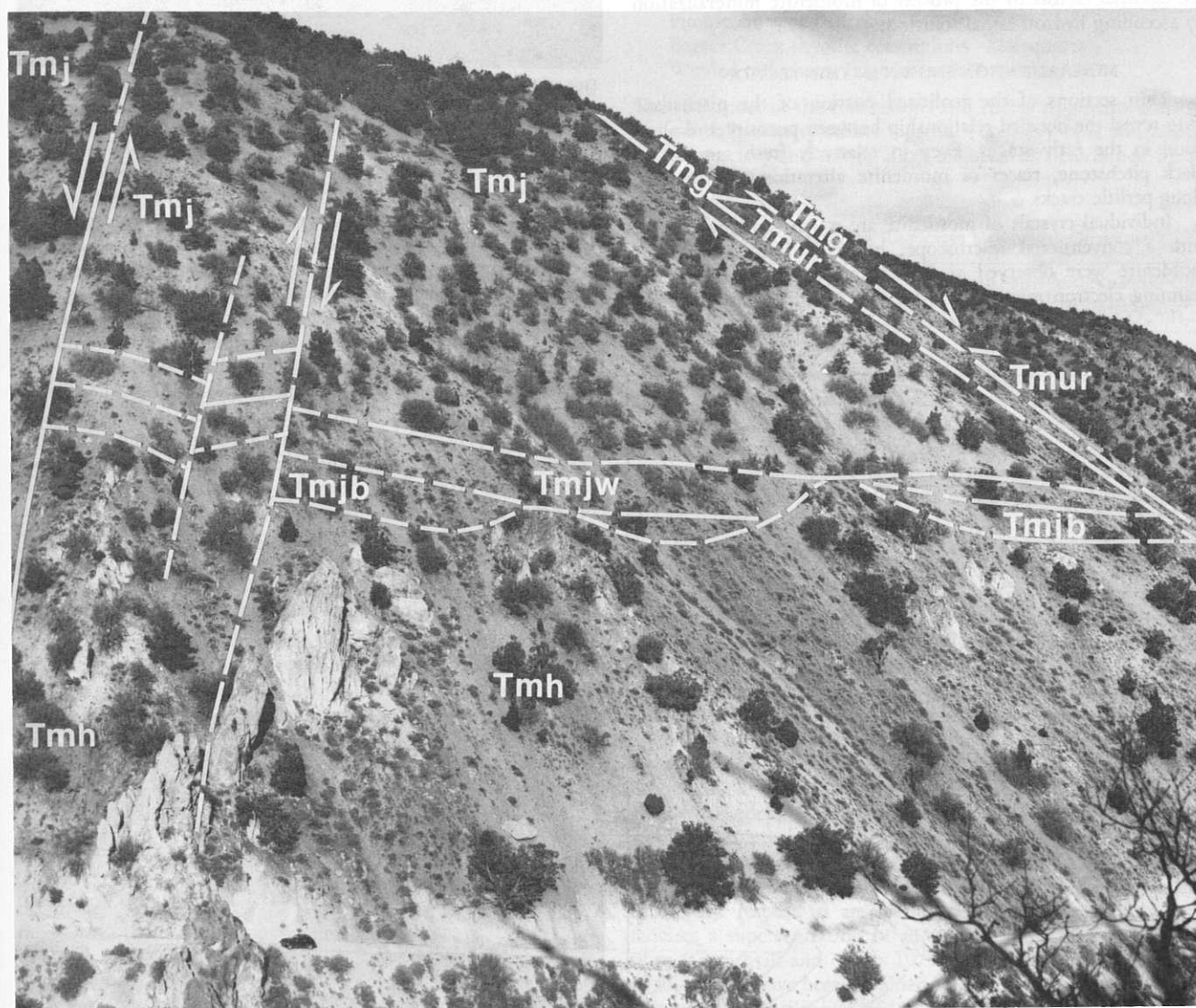

FIGURE 15.–Structure and volcanics of Beaver Creek rhyolite flow area looking north from across the canyon. **Tmg** = Gray Hills Rhyolite Member–light gray (pinkish gray in this area), spherulitically devitrified alkali-rhyolite lava flow. Contorted flow layering is characteristic (Cunningham and Steven 1979a). **Tmur** = Upper Red Tuff Member–red, crystal-poor, densely welded, ash-flow tuff characterized by black fiamme (in this area fiamme are dark reddish brown) as much as 3 cm long (Cunningham and Steven 1979a). **Tmj** = Joe Lott Tuff Member–crystal-poor, partly welded, light gray, alkali-rhyolite ash-flow tuff containing 1–2 percent phenocrysts of quartz, sodic plagioclase, and sanidine, and traces of biotite (Cunningham and Steven 1979c). **Tmjw** = welded tuff unit near the base of the Joe Lott Tuff Member characterized by black fiamme as large as 10 cm long in a matrix of black welded glass. Unit contains mordenite and less than 5 percent chert and lithic clasts. **Tmjb** = heterogeneous unit that includes a densely welded tuff unit containing 5 to 10 percent cherty and lithic fragments and is characterized by black fiamme, as large as 10 cm in a black or brownish orange matrix, that weather orange. Unit also bleaches yellow and contains greater than 5 percent lithic fragments near the base. **Tmh** = lower heterogeneous member–sequence of rhyolitic lava domes, lava flows, subordinate ash-flow tuffs, and volcanic sedimentary rocks, in part overlain by the Joe Lott Tuff Member (Cunningham and Steven 1979a).

up to 10 cm long. Cherty clasts are ubiquitous, and the matrix is sometimes orange, accenting the black fiamme. The upper unit (**Tmjw**) is so densely welded that some sections are composed entirely of black welded glass in which the fiamme can be distinguished from the matrix only on surfaces etched by weathering.

Mineralization

X-ray diffraction shows mordenite (characteristically orange) to be concentrated in the cherty basal tuff and immediately around quartz veins or chert nodules. However, traces of mordenite are disseminated throughout the welded tuff, with the exception of the black fiamme, which are essentially nonporous. It appears, once again, that porosity and permeability are essential factors in the process of mordenite mineralization by ascending hydrothermal solutions.

MINERALIZATION SHOWN IN THIN SECTION

Thin sections of the zeolitized portion of the pitchstone plug reveal the detailed relationship between porosity and alteration in the early stages. Even in relatively fresh samples of black pitchstone, traces of mordenite alteration can be seen along perlitic cracks.

Individual crystals of mordenite are much too small to see with a conventional microscope; however, fibrous wisps of mordenite were observed at 2300X magnification under the scanning electron microscope (fig. 17). Mordenite in thin sec-

FIGURE 17.—Photomicrograph of natural mordenite from the pitchstone plug. Mordenite appears as fibrous growths. Bar represents 10 μm.

tion appears as turbid, irregular, optically anisotropic growths showing essentially no pleiochroism. Alteration begins along perlitic cracks and proceeds inward toward the centers of the spheres (fig. 18). A number of altered spheres observed in thin sections from the pitchstone plug contained slender, low birefringent, length-fast crystals that are probably cristobalite.

Thin sections from the Beaver Creek rhyolite flow demonstrate a more advanced stage of alteration where mordenite is restricted to a very limited zone along the perlitic cracks, and the remainder of what was once glass is now fine-grained anhedral quartz (fig. 19). The grains are coarsest in the center of the spheres. The crystallization of this form of quartz is believed to be subsequent to mordenite formation and, perhaps, aided by the excess silica from the glass after it has altered to mordenite.

Secondary alkali feldspar is ubiquitous in the mordenite zone of the Beaver Creek rhyolite flow and appears as brown plumose growths or radiating spheres. The feldspar formed after mordenite and may grow seemingly unrestrained by previous growths or structures, or may be controlled to some extent by perlitic cracks.
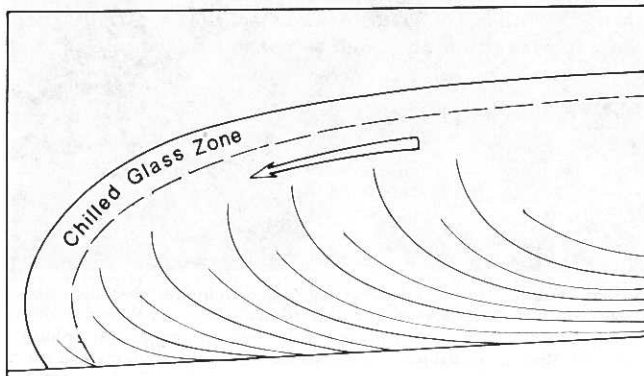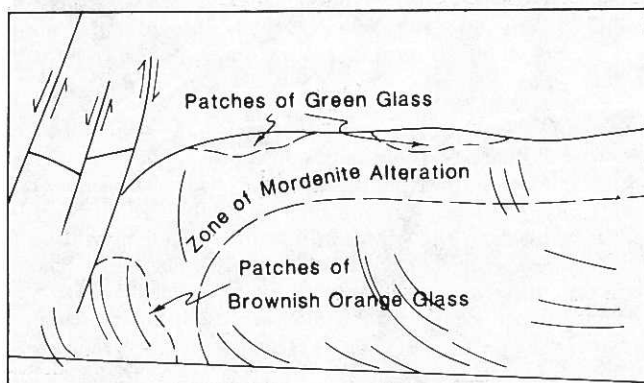

FIGURE 16.—Top: Actual flow layers and glass zones, as mapped from a photograph of the Beaver Creek rhyolite flow. Near horizontal line shows present location of road. Bottom: An idealized model of emplacement of the Beaver Creek rhyolite flow, showing flow direction to the west.
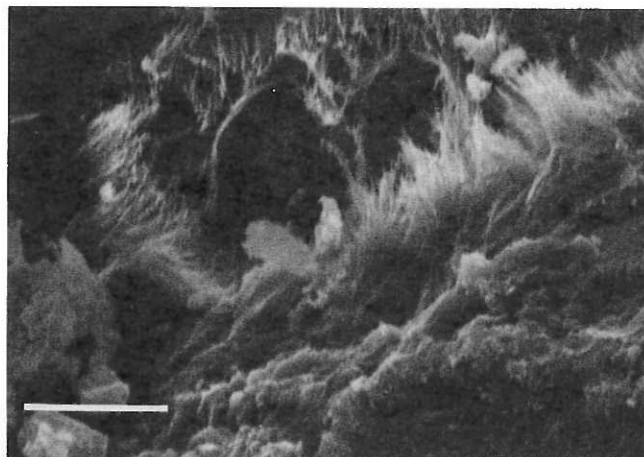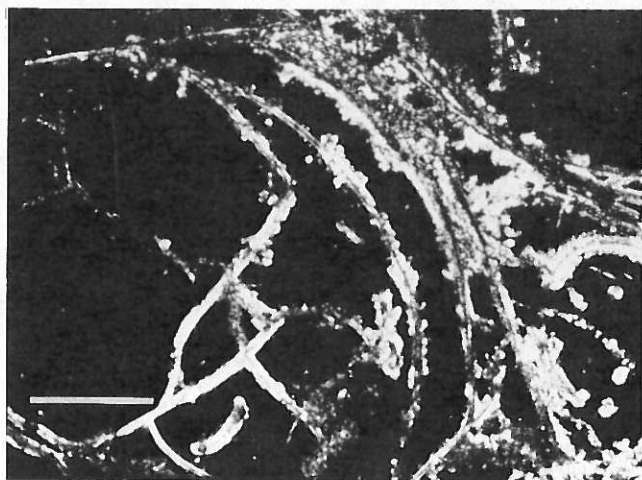

FIGURE 18.—Thin section from the pitchstone plug as viewed at 100 magnification under polarized light. Mordenite (light colored) alteration progresses inward from perlitic cracks. Bar represents 0.5 mm.
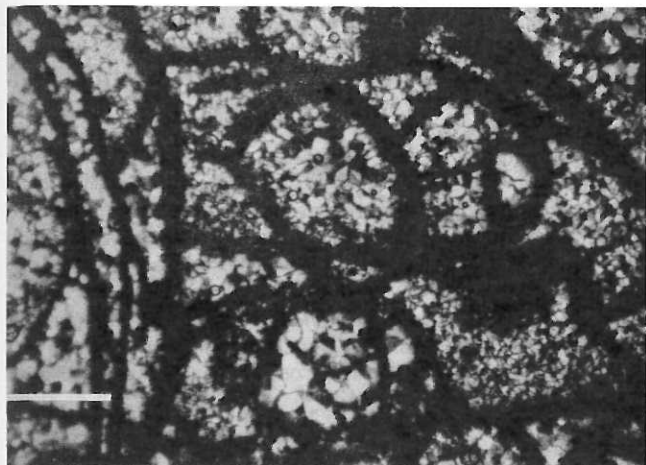
FIGURE 19.—Thin section of mordenite in the Beaver Creek rhyolite flow under polarized light. Alteration is more advanced than in figure 18. Centers of the spheres, defined by perlitic cracks, have crystallized to quartz. Mordenite is concentrated immediately around perlitic cracks. Bar represents 0.5 mm.

In the welded tuff unit mordenite forms in altered shards and along perlitic cracks in some black fiamme. The cherty clasts are primary, as evidenced by the shards that conform to the shape of the clasts. Mineralization is intensified around most of the clasts and along veins of crystalline silica.

COMPARATIVE ALTERATION OF GLASS VARIETIES

One of the few tangible components relating to mordenite alteration is the unaltered glass. Weight percent oxides of major elements for each of the glasses are listed in table 2. The susceptibility of each glass to mordenite alteration was determined by experimentation.

Unaltered glass samples from each of the three major outcrops were powdered and subjected to identical conditions of hot alkaline solutions (1 molar solutions, 1/5NaOH-4/5NaCl at 200 C) using procedures previously described. The progress of alteration was monitored by X-ray diffraction.

Green and brownish orange glasses from the pitchstone vent area, welded tuff unit, and Beaver Creek rhyolite flow altered to mordenite after 15, 18, and 39 hours respectively. Not only did mordenite take twice as long to form in the brownish orange Beaver Creek rhyolite glass, but once formed, it did not yield as strong an X-ray pattern for mordenite as did the other glasses. On the other hand, the brownish orange glass favored more abundant growth of analcime, compared to the other glasses. In all three glasses, analcime formed after 30 hours.

This experiment demonstrates that differences in the degree of mordenite alteration at the three major outcrops cannot be accounted for by variations in the susceptibility of glasses to mordenitization, with the exception of the brownish orange glass from the Beaver Creek rhyolite flow. This glass occurs in isolated pods within the mordenite roadcut at the western end of the flow. The glass has resisted alteration except for the rim of buff colored mordenite encompassing the pods. (The brownish orange glass altered experimentally to buff colored mordenite as well.) Conversely, the green glass, which originally constituted the bulk of the outcrop, has entirely altered to green mordenite. Green glass crops out at the top of the flow where it was somewhat shielded from ascending hydrothermal solutions.

The glasses are chemically similar (table 2). The greater re-

sistance of the brownish orange glass to mordenite alteration may be attributed to a higher degree of polymerization of silicate tetrahedra, which slowed the dissolution of silica. This would explain why the glass altered to a less siliceous zeolite, analcime, and was a relatively poor media for the synthesis of a highly siliceous zeolite, mordenite.

MORDENITE AND SILICIFICATION

Forms of silica other than glass were studied in relationship to mordenite alteration. Concretions from the pitchstone vent area and the Beaver Creek rhyolite flow, and cherty fragments from the welded tuff unit were quantitatively analyzed for quartz, using an X-ray diffraction technique described by Ballard and others (1940), with the following results:

Pitchstone vent concretions—27% quartz
Beaver Creek rhyolite concretions—22% quartz
Welded tuff cherty fragments—26% quartz

The remainder of the concretions and cherty fragments consists of essentially noncrystalline material (probably opal and poorly crystalline clay) and minor alkali feldspars as determined by X-ray diffraction.

TABLE 3
CHEMICAL FORMULAS FOR RESPECTIVE MORDENITE OUTCROPS

Pitchstone plug	$(Na_{.865}K_{.384}Ca_{.375})Al_{2.042}Si_{9.969}O_{24}\cdot nH_2O$
Beaver Creek rhyolite	$(Na_{.913}K_{.342}Ca_{.375})Al_{1.791}Si_{10.156}O_{24}\cdot nH_2O$
Welded tuff	$(Na_{.869}K_{.276}Ca_{.427})Al_{1.557}Si_{10.332}O_{24}\cdot nH_2O$

To determine the amount of free silica, powdered samples of the concretions and cherty clasts were altered in 1M NaOH solutions at 200°C. After three days, each of the samples altered to analcime and alkali feldspar. However, all attempts to alter the samples to mordenite failed. A control sample of powdered quartz was subjected to identical conditions, but showed no signs of alteration when the experiment was terminated after five days. This experiment demonstrates that the concretions and cherty clasts contain forms of silica other than quartz that are at least partially soluble. However, they were not soluble enough to obtain the levels of silica supersaturation required to form mordenite. This finding is further substantiated by the fact that concretions, chalcedony veins, and cherty fragments did not naturally alter to mordenite in the study area, although they were clearly associated with mordenite alteration.

These forms of silica were observed to concentrate in highly mordenitized zones, suggesting that concretions and chalcedony veins formed from the same solutions that altered the glass to mordenite. Dissolved silica in hydrothermal solutions would have precipitated as opal (cristobalite) before crystallizing to chalcedony (Campbell and Fyfe 1960). As opal precipitated, the solutions would have eventually obtained equilibrium with respect to amorphous silica. Mordenite, however, requires a supersaturation of silica with respect to amorphous silica (Gogishvili and others 1973). Such a high concentration of silica must have been obtained in the pore spaces of the glass surrounding the silicified veins.

Ellis (1960) grew mordenite in a natural system within a bore hole from rhyolitic glass reacting with circulating waters that contained only 550 ppm SiO_2. Such solutions are not highly supersaturated, even with respect to quartz. Therefore, mordenite must have resulted from higher concentrations of silica in the pore space of the rhyolitic glass. Pore solutions may contain several orders of magnitude more silica than the general circulating waters (Hay 1966).

The fact that mordenite forms a halo around isolated concretions of the pitchstone plug suggests that the formation of the concretions enhances mordenite growth. As silica precipitates, alkalies and calcium are concentrated in residual solutions, which in turn, favor zeolite growth. If such solutions, or successive solutions, were alkaline, they would facilitate the crystallization of opal to quartz (Campbell and Fyfe 1960) and, at the same time, dissociate silica in the glass to help provide the necessary supersaturation of silica required for mordenite formation.

Concretions of similar dimensions are associated with clinoptilolite in an altered tuff of the John Day Formation in central Oregon. Such concretions are believed to have formed from the hydration of pumice fragments, which act as a nucleus and subsequently alter to montmorillonite, which, in turn, raises the pH and ionic activities of associated solutions (Hay and Sheppard 1977). Perhaps a similar relationship exists with the concretions of this study area, if part of the material comprising the concretions that does not yield an X-ray pattern is, in fact, a poorly crystalline clay.

It has been observed that the cation ratios of natural and synthetic zeolites are similar to the cation ratios of the altering solutions (Hay 1966, Mariner 1971). The chemical environment of diagenesis may be deciphered with some caution by contrasting the chemistry of the zeolite and the unaltered glass. The diagenetic solutions of the Marysvale area appear to have been relatively calcium rich (fig. 2).

The concentration of Ca^{2+} in solution is somewhat dependent on the pH (Mariner 1971). The terms *pH* and *alkalinity* have very similar meanings. Alkalinity is defined by Stumm and Morgan (1970) as:

$$HCO_3^- + 2CO_3^{2-} + OH^- - H^+$$
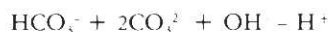
If the altering solutions were highly alkaline, the Ca^{2+} ion would combine with the CO_3 ion to precipitate $CaCO_3$. Mariner (1971) associated high Ca^{2+} activities in solutions with low alkalinity. No evidence of primary calcification was found in the present study area, suggesting that solutions were mildly alkaline. Kerr and others (1957) found evidence to suggest that hydrothermal solutions in the Marysvale area were originally acidic at depth but eventually became alkaline as they ascended and reacted with the country rock.

A mildly alkaline solution necessarily requires higher salinity (higher activities or K^+, Na^+, of Ca^{2+} to alter fresh glass to mordenite than more alkaline solutions, as demonstrated by the present experiments (fig. 12). Therefore, mildly alkaline solutions that altered the mordenite in the study areas most likely contained high ionic activities with Ca^{2+} as the principle ion (fig. 2). If the Na^+ activity of the solutions was very high, analcime would be expected, as demonstrated in the experiments.

MODEL FOR MORDENITIZATION

The following is a model for the alteration of rhyolitic glass within the study area. Ascending hydrothermal solutions rich in silica and alkalies moved along joint systems, fault planes, and flow layers. The solutions approached the surface and experienced sudden losses in pressure and temperature, both of which resulted in silica coming out of solution in solutions saturated with silica under previous conditions. According to Campbell and Fyfe (1959), such precipitation is especially pressure sensitive, and therefore the presence of amorphous silica could easily be explained in the shattered plug of the pitchstone vent area. Coombs and others (1959) state that silica sud-denly becomes insoluble as saturated solutions drop in temperature below 300°C. The theoretical temperature range of mordenite stability is estimated to be 150–230°C (Senderov 1963). Therefore, silica could theoretically precipitate along flow layers and in fractures at temperatures favorable for mordenite formation. As silica precipitates, the solution is concentrated in cations such as Ca^{2+}, Na^+, and K^+ with Ca^{2+} being the dominant cation. Early-forming clays may have raised the pH of the altering solutions. Increasing the pH and ionic strength of the solution would aid in the solution of glass and, therefore, mordenite crystallization.

Alkali feldspar formed within the concretions and on the edges of chalcedony veins, but high silica activities sufficient to form mordenite could be attained only in the surrounding pore fluids within the rhyolitic glass.

CONCLUSION

The experimental data of this thesis, which concentrated on hydrothermal solution chemistry, were combined with field observations to formulate the following conclusions:

1. Experimental alteration of volcanic glass in highly saline solutions of varying OH^- activities at a constant Na^+ concentration demonstrates the incompatibility of certain zeolite species. Phillipsite consistently disappears just before or shortly after the appearance of analcime. Mordenite and analcime coexist in a metastable condition, but, once mordenite disappears, the growth rate of analcime increases dramatically. Photomicrographs clearly show alkali feldspar growing at the expense of analcime; however, this order may be reversed through time with the continued influx of sodium-rich solutions.

2. Mordenite will not persist in solutions of one molar Na^+ regardless of the pH. Analcime is the end product under such conditions and crystallizes at the expense of mordenite. The absence of analcime may indicate that the zeolitizing solutions in the study areas had a relatively low sodium activity, or at least Na^+ is not the dominant cation in solution.

3. It appears that minimum concentrations of cations, specifically Na^+, required to form mordenite may vary with pH. Higher concentrations of Na^+ are required to form mordenite at lower pH. Thus, the low alkaline hydrothermal solutions, which altered the glass in the study area, would necessarily have a high ionic strength (particularly Ca^{2+}).

4. Mordenite from the study area was restricted to rhyolitic glasses and, to a lesser extent, to the flow layers of the Beaver Creek Rhyolite flow. Glasses showing various degrees of susceptibilities to mordenite alteration were found within the Beaver Creek rhyolite flow. Such differences are attributed to differing degrees of silica polymerization.

5. All occurrences of mordenite in the study area demonstrate the profound influence of permeability on mordenite mineralization. Zeolitized outcrops are bounded by major faults, which may have been the avenues for ascending hydrothermal solutions that disseminated throughout the glass bodies along fractures and perlitic cracks.

6. Secondary silicification is closely associated with mordenite mineralization. Silica would most likely precipitate from hot solutions with decreases in temperature and pressure, within a temperature range favorable for mordenite formation. As silica precipitates, Na^+, K^+, and Ca^{2+} activities of the residual solutions increase, with Ca^{2+} as the major cation, to aid in the zeolitization process. Mordenite formed in the pore spaces of the glass, where high silica concentration of the solution was attained.

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