Genesis of Zeolites, Nevada Test Site

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ABSTRACT

At the Nevada Test Site, zeolites, cristobalite, quartz, feldspar, and clay minerals were deposited by ground water that leached vitric volcanic rocks in the unsaturated zone and reacted with similar vitric rocks just above permeability barriers where the rocks are nearly saturated. Zeolite zoning occurred contemporaneously with zeolitization by a separation of cations according to solubility.

Zeolite zoning, chemistry of the zeolitized rocks, and lack of correlation of zones with depth below surface require that ground water moved downward through unsaturated vitric rocks. Vitric rocks were leached and the ground water increased in cation content and pH.

Water movement was reduced, saturation was increased, and reactions with vitric rocks occurred just above one of the following permeability barriers to form zeolites and other authigenic minerals: (1) Relatively impermeable welded tuffs, lava flows, and Paleozoic clastic rocks, (2) clay minerals formed by leaching of vitric rocks just above relatively permeable Paleozoic carbonate rocks, and (3) zeolitized rocks formed by ground-water reactions just above one of the aforementioned permeability barriers.

Zeolitization progressed upward through the vitric rocks by ground-water reactions just above impermeable zeolitized rocks. Ground-water movement through the zeolitized rocks, though greatly impeded, caused a redistribution of cations by charge and size and formed zeolite zones contemporaneously with the progressive thickening of the zeolitized rocks. A triangular plot of Ca plus Mg, K, and Na in zeolite-rich rocks shows that Ca and Mg are concentrated in the uppermost part of the zeolitized rocks, K in the middle part and Na in the lowermost part.

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Ground-water alteration of vitric rocks at the Nevada Test Site has produced zeolites, cristobalite, quartz, K-feldspar, and clay minerals. The altered rocks, in which clinoptilolite or analcime is usually predominant, are present in most of an area covering several thousand square miles and range from a few hundred to more than 6000 ft in thickness. Locally chabazite, mordenite, K-feldspar, or clay minerals predominate as alteration products.

Figure 1 shows the outcrop patterns of pre-Tertiary sedimentary and intrusive rocks, Tertiary volcanic rocks, and postvolcanic Tertiary(?) and Quaternary alluvium at the Nevada Test Site. Zeolitized rocks crop out or underlie most of the volcanic outcrops, the alluvial basins, and also large areas north and west of the test site. Data from drill holes (Fig. 1), nuclear test tunnels, and outcrops have provided the information for this paper. The contribution of data gathered by co-workers for other purposes is herewith gratefully acknowledged.

Zeolites can form by alteration of vitric rocks by: (1) hydrothermal alteration, (2) burial metamorphism (Coombs, 1961), (3) reaction of glass and water in a saturated system (below a water table), and (4) leaching and deposition in an unsaturated system (above a water table).
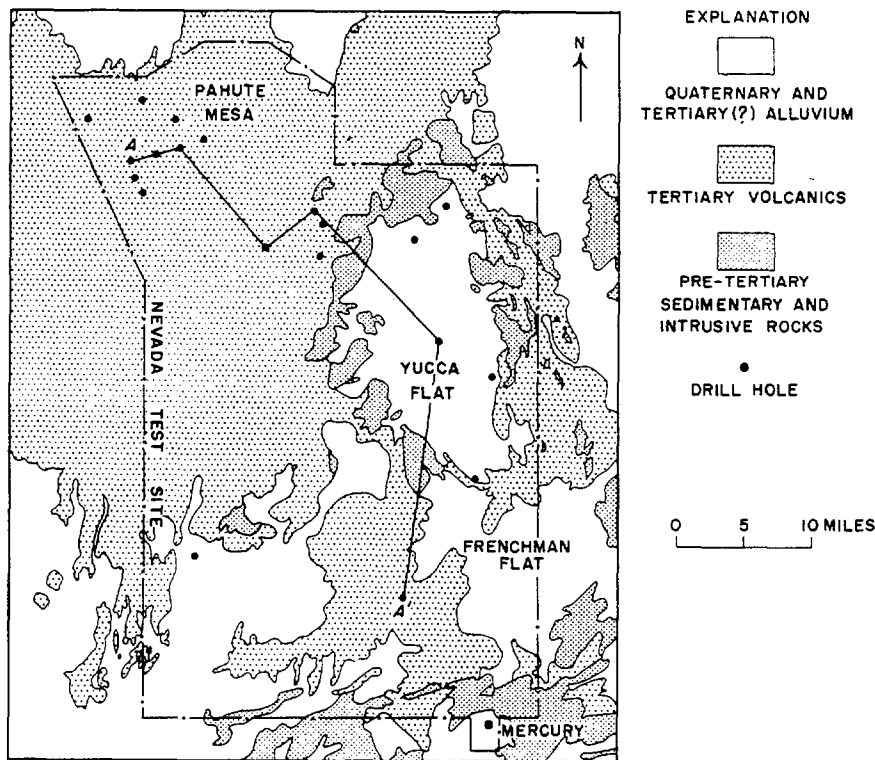

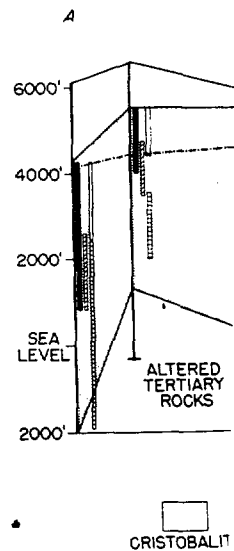Figure 1. Map showing generalized geology of the Nevada Test Site.

Figure 2. Cross levels of volcanic ro‹ lines) and rocks not terned). Line of secti

Figure 2 is a di Flat and south sh‹ chabazite or clay r overlie the clinopt a montmorillonite‹ rocks. Cristobalite higher zones. Sec‹ abundant in the l‹ is most abundant

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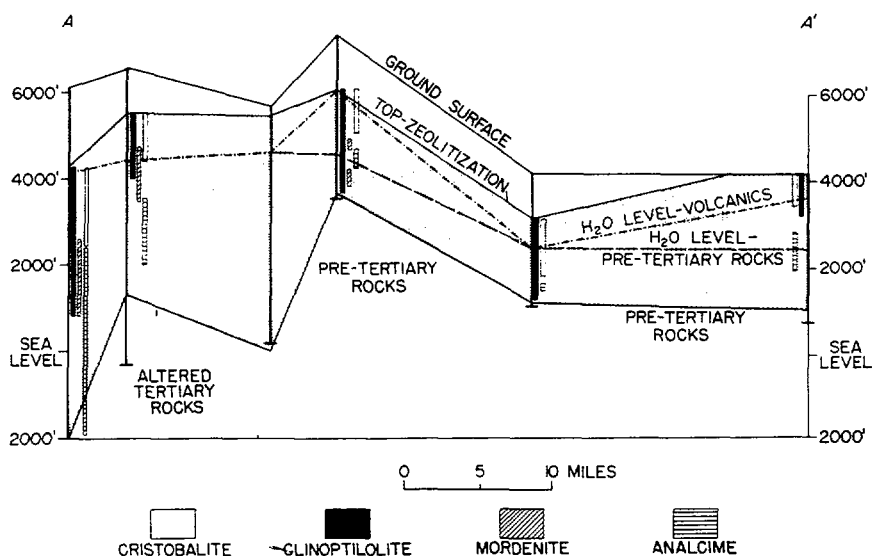
Figure 2. Cross section showing relationship of the zeolite zones, regional water levels of volcanic rocks (dotted and dashed lines), and of pre-Tertiary rocks (dashed lines) and rocks not susceptible to zeolitization underlying the zeolitized rocks (patterned). Line of section and drill holes used for control are shown on Figure 1.

Figure 2 is a diagrammatic cross section from Pahute Mesa east to Yucca Flat and south showing the zeolite zoning at the Nevada Test Site. Locally chabazite or clay minerals such as montmorillonite, illite, or mixed-layer clays overlie the clinoptilolite zone. Above highly permeable Paleozoic carbonates, a montmorillonite-illite zone as much as 200 ft thick underlies the zeolitized rocks. Cristobalite is restricted to the upper part of the clinoptilolite zone and higher zones. Secondary quartz and K-feldspar are ubiquitous, but are more abundant in the lower part of the clinoptilolite zone and lower zones. Quartz is most abundant in the analcime zone.

Preliminary studies of thin sections indicate that clay minerals were formed first, followed by clinoptilolite, mordenite, and analcime, respectively. Replacement of one zeolite by another is rarely apparent, but position within solution cavities and pore spaces clearly indicates the stated sequence. On a local microscopic scale, deposition of minerals and clinoptilolite is cyclic, indicating small-scale variations in chemistry of the altering solutions.

The zeolite zoning would seem to imply temperature and pressure controls, but zoning is the same for intervals from 1000 to more than 6000 ft thick at the same restored depths. Temperatures in the zeolitized rocks measured in drill holes are 25° to 65° C., and there is no evidence for higher temperatures during zeolitization. This temperature range is below the presently known stability field of analcime and is very narrow for the zoning. Thus, a hydrothermal or burial metamorphic (Coombs, 1961) origin is unlikely.

The relationship between the zeolitized rocks, the regional water level, stratigraphy, and hydrothermally altered volcanic rocks and pre-Tertiary sedimentary rocks underlying the zeolitized rocks is shown in the diagrammatic cross section from Pahute Mesa east to Yucca Flat and south (Fig. 3).

The top of the zeolitized rocks and the zeolite zoning both cut across stratigraphic boundaries, such as welded tuff of the Grouse Canyon Member of the Belted Range Tuff and welded tuff of the Rainier Mesa Member of the Timber Mountain Tuff. The zeolitized top is subparallel to underlying hydrothermally altered Tertiary volcanic rocks or pre-Tertiary sedimentary and intrusive rocks which are not susceptible to zeolitization. Furthermore, the zeolitized top corresponds in a general way to the configuration of present water levels in the volcanic rocks. These facts would imply that zeolitization is related to a regional water level.

Locally, water levels in most of the volcanic rocks are perched because of the extremely low permeabilities of the zeolitized rocks. Regional water levels in Paleozoic sedimentary rocks are from 500 to 2000 ft below the top of the zeolitized rocks. Geologic evidence indicates that the water levels at the Nevada Test Site were probably highest during late Pleistocene time. Formation of zeolites at that time below a regional water level seems unlikely because: (1) subsequent water levels would have to drop as much as 2000 feet; (2) vitric pumice still exists in the oldest alluvium below the projected highest water levels; and (3) fault displacement of the top of the zeolitized rocks in Yucca Flat would require more than 1000 ft of movement since the period of highest water levels.
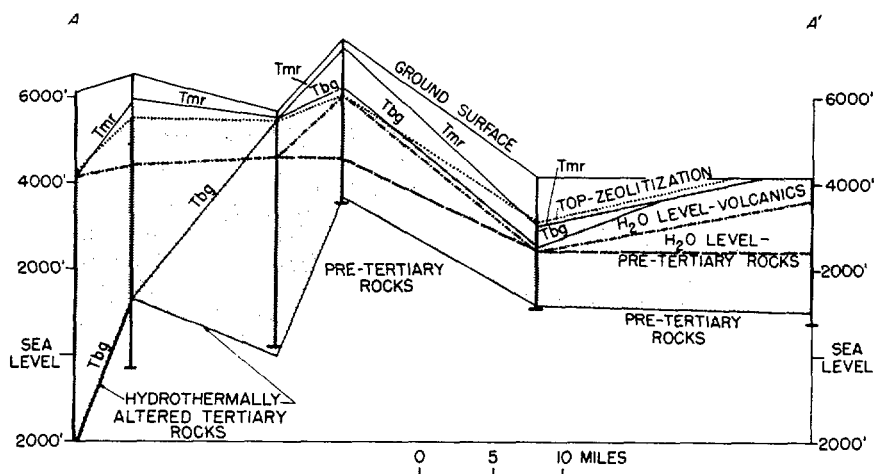

Figure 3. Cross section showing relationship of the top of the zeolitized rocks (dotted line), regional water levels of volcanic rocks (dotted and dashed lines), and of pre-Tertiary rocks (dashed line). Tmr, base of welded tuff of Rainier Mesa Member of Timber Mountain Tuff; Tbg, base of welded tuff of Grouse Canyon Member of Belted Range Tuff. Line of section and drill holes used for control are shown on Figure 1.

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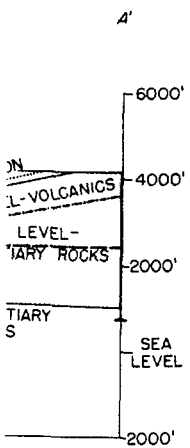ı Member of Belted
·n on Figure 1.

More evidence for the lack of a higher regional water level is furnished by the thick clay zone overlying more highly permeable Paleozoic carbonates. Below a water table vitric rocks soon alter to zeolites. Clay minerals can form only if the cations released by hydrogen exchange are flushed out. To flush out the cations would mean increasing the rate of downward water movement in the lower part of a saturated section because the cation content of the water is greatest in the lowest part of the vitric rocks. This would create an impossible hydrologic situation in saturated rocks. Thus, the vitric rocks can alter to clay minerals only if they are unsaturated and are draining rapidly into the highly permeable Paleozoic carbonates. Similarly, clay minerals are formed above the zeolitized rocks where lack of saturation is indicated by glass within and below the clay zone. Zeolites form above the basal clay zone where saturation and cation content increases because of the low permeability of the clay zone. Above Paleozoic clastics and hydrothermally altered Tertiary volcanics with low permeabilities, clay minerals are formed in small amounts or not at all.

The chemistry of hydrated glass and mineralogy of the zeolite zones indicate that the cation concentration and pH of the ground water increase downward. Recent studies of Campbell and Fyfe (1960) and Fyfe and McKay (1962) indicate that the rate of change of cristobalite to quartz increases as OH^- concentration increases. Thus, the downward replacement of cristobalite (Fig. 2) by quartz indicates a downward increase in pH.

The process of zeolitization begins with glass hydration, which can be divided into two stages: (1) Addition of water of hydration up to about 3 percent, with small changes in Na, Ca, and Mg; (2) further hydration up to a maximum of about 7 percent with large changes in Na, Ca, Mg, Si, and grain density. Glass containing more than 7 percent water of hydration is virtually unknown at the Nevada Test Site.

Changes in grain density and alumina with increasing water of hydration are shown on Figure 4. Large changes in density during zeolitization necessitate comparison of chemical analyses in terms of units per unit volume if absolute changes are to be discussed. Comparison of changes in matched pairs of vitric and zeolitized rocks calculated by using bulk density, constant alumina, and Barth's standard cell (Hoover, 1966) demonstrated that the latter two methods can result in apparent changes differing by as much as an order of magnitude from changes calculated using density. For SiO_2 a reversal of the direction of change was found in one sample when comparing the standard cell and density calculations. Although 10 to 20 percent changes in Al_2O_3 were previously noted in matched pairs of vitric and zeolitized rocks (Hoover, 1966) new data indicate that such changes are local and are probably caused by special conditions of pH and permeability.

Comparison of analyses in terms of grams per cubic centimeter can be expressed in two ways — by calculating all analyses in gm/cc, and by comparing analyses with standard weight percent curves equivalent to constant gm/cc.

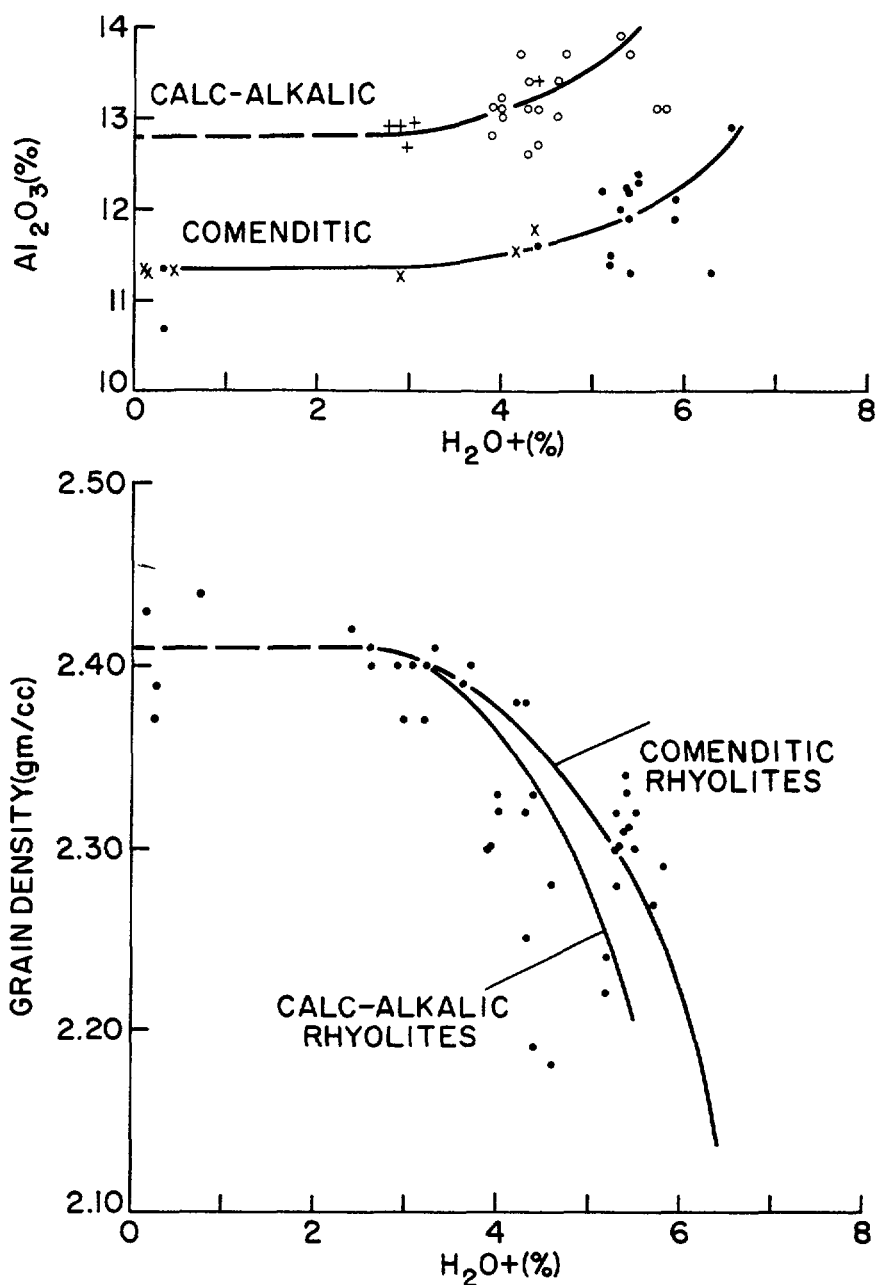Figure 4. Diagrams showing relationships of Al_2O_3 in weight percent and grain density (gm/cc) to $H_2O + (110°C)$ weight percent in vitric rocks. Curves in grain density diagram constructed from alumina curve by assuming total amount of alumina remains constant (constant gm/cc = grain density times Al_2O_3 weight percent). Al_2O_3 weight percent corrected for total H_2O and $CaCO_3$. Al_2O_3 diagram: O, ●, calc-alkalic and comenditic ash falls, respectively; +, X, calc-alkalic and comenditic ash flows respectively. Grain density diagram ●, grain density of rhyolitic glasses.

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If a nonhydrated glass contains W percent of a constituent and has a density of D gm/cc then a hydrated glass which contains D_1 gm/cc of the constituent must contain WD/D_1 weight percent if the constituent is to remain constant. Similarly if the hydrated glass contains W_1 weight percent of a constituent it must have a density of WD/W_1 gm/cc if the constituent is to remain constant.

The grain density curves (Fig. 4) were calculated in the following manner:

(1) Al_2O_3 content in the nonhydrated (W) and hydrated (W_1) glass were assumed to remain constant because of the extremely low solubility of Al_2O_3. For comenditic glasses, WD = 11.35 percent times 2.41 gm/cc (for nonhydrated glass) = 0.2735 gm/cc.

(2) Points on a curve through the Al_2O_3 analyses (drawn by inspection) were used to calculate grain densities at the same H_2O+ content by using the formula $D_1 = WD/W_1$.

(3) Curves were then drawn through the calculated grain densities to establish the grain density curves. Although the measured grain density data are scattered because of varying phenocryst content, the general agreement between the calculated curves and the measured data indicates that Al_2O_3 remains constant during hydration of glass.

Weight percent curves equivalent to constant gm/cc of K_2O, Na_2O, CaO plus MgO, and SiO_2 versus H_2O+ (Fig. 5) were calculated for comenditic glasses. Comenditic glasses were used because they have very little variation in original composition and have a very low feldspar phenocryst content. The weight percent curves equivalent to constant gm/cc were calculated in the following manner:

(1) A constant gm/cc content (K) was calculated from K = WD where W is the weight percent of a constituent in nonhydrated glass and D is the grain density of nonhydrated glass. For K_2O, K = 4.55 percent times 2.41 gm/cc = 0.1097 gm/cc.

(2) Weight percents equivalent to constant gm/cc (W_1) at calculated grain densities (D_1) were calculated from $W_1 = WD/D_1$.

(3) Curves were then drawn through the calculated weight percents to establish a weight percent curve equivalent to constant gm/cc of a constituent (Fig. 5). Analyses of hydrated glasses can be directly compared with the calculated weight percent curves to determine absolute changes during hydration.

Lipman (1965) postulated that potassium increases during glass hydration, but the curve for constant K_2O content (Fig. 5) indicates that the increase is probably apparent rather than real. The loss of sodium during glass hydration has been noted previously (Lipman, 1965), but the size of the loss was not apparent because of data scatter. Calcium and magnesium (Fig. 5) behave similarly during glass hydration and data on their oxides were combined to improve the contrast of the diagram. Lipman (1965) attributed increases in Ca and Mg to the presence of montmorillonitic clay. Recent studies by Truesdell (1966) indicate that the exchange on glass in dilute solutions is in the order of preference — hydrogen, potassium, calcium, magnesium, and finally
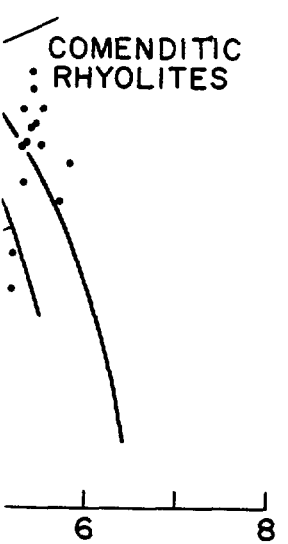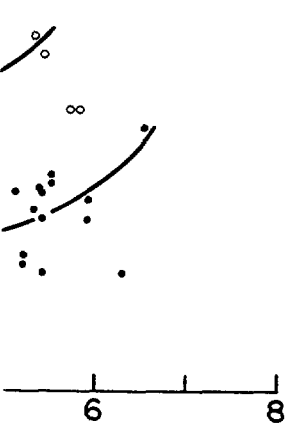
sodium. This would explain the loss of sodium and the gain of calcium and magnesium with increasing hydration of glass. Relative changes in calcium and magnesium during hydration are the largest changes of any of the constituents, but the source of the calcium and magnesium to account for the increase is not known.
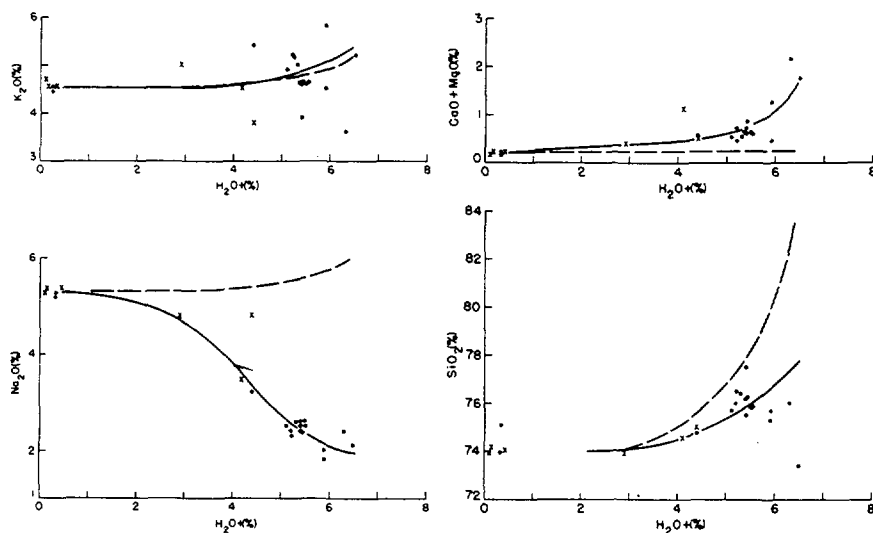

Figure 5. Diagrams showing relationships of K_2O, Na_2O, CaO plus MgO, and SiO_2 weight percent in vitric comenditic rocks. Weight percentages of oxides corrected for total H_2O and $CaCO_3$. ●, ash fall; ×, ash flow. Solid line, amount of constituent in hydrated glass (drawn by inspection); dashed line, amount of constituent equivalent to constant gm/cc of constituent [derived from calculated grain density curve for comenditic rocks (Fig. 4)].

Major cation oxide contents of the four zeolite zones are shown on Figure 6. All the analyses are of rhyolitic rocks which in X-ray diffractograms appear to contain more than 50 percent zeolite. Calcium and magnesium are concentrated in the upper chabazite zone (or persist from previous concentration during glass hydration) and sodium is leached. At single locations calcium and magnesium are concentrated in the upper part of the clinoptilolite zone. However, cation ratios in the clinoptilolite zone are greatly dependent on permeability, and calcium and magnesium may persist in rocks of low permeability at depths where these cations are usually replaced by potassium and sodium. In the deeper zeolite zones calcium and magnesium are replaced by sodium which reaches a maximum in the analcime zone. Potassium apparently is leached in the upper and lower parts of the zeolitized rocks, but a trend line through the analyses is nearly parallel to a constant K_2O line. The replacement of calcium and magnesium by sodium with depth reflects the increasing cation content of the ground water because two sodiums are required to replace one calcium or magnesium in zeolites.

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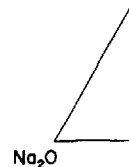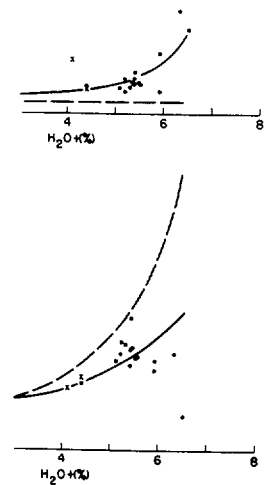and appear
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The relations between the zeolite zones, silica, and alumina are not clear and appear to be greatly affected by local variations in permeability and porosity. Locally silica is concentrated relative to alumina in the upper and lower parts of the zeolitized rocks, but variations such as opalized beds, K-feldspar-rich rocks, and clay-rich intervals with low alumina contents need further investigation.

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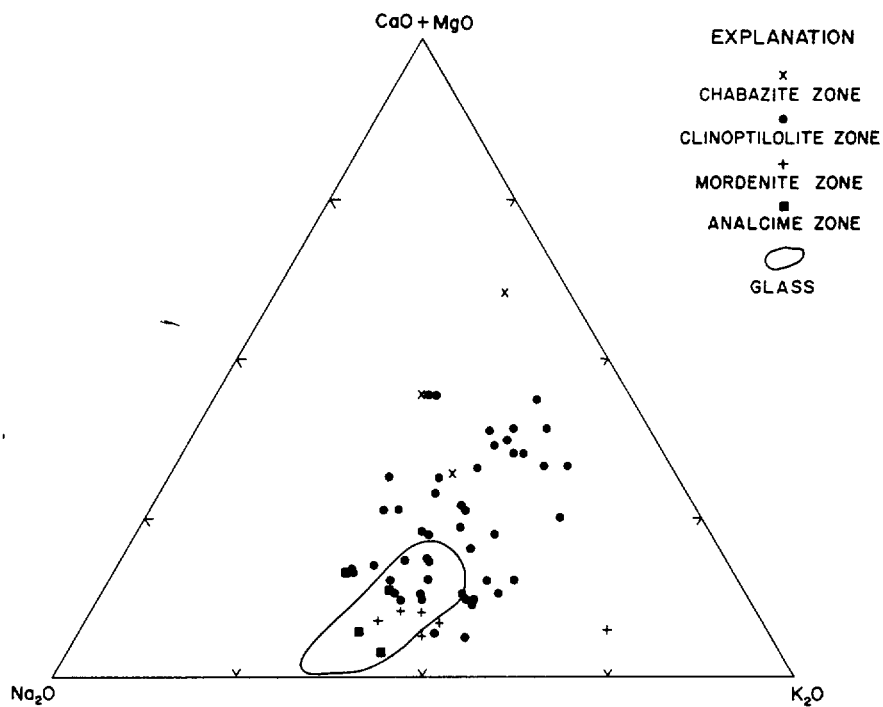density curve for comen-

Figure 6. Ternary diagram showing CaO plus MgO, Na₂O, and K₂O in rhyolitic rocks containing more than 50 percent zeolites estimated from X-ray diffractograms. Weight percentages used to calculate ratios are corrected for total H₂O and CaCO₃.

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In summary, the geology, hydrology, mineralogy, and chemistry indicate that zeolitization at the Nevada Test Site took place in an unsaturated environment in which vitric rocks were altered by leaching and deposition. Zeolites were formed just above permeability barriers where the cation content of the ground water and the saturation of vitric rocks were high enough to produce zeolites. Zeolite zoning took place after the formation of clinoptilolite and consisted mostly of a replacement of calcium and magnesium by sodium.

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