# ZEOLITES IN EOCENE BASALTIC PILLOW LAVAS OF THE SILETZ RIVER VOLCANICS, CENTRAL COAST RANGE, OREGON

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Abstract—Zeolites and associated minerals occur in a tholeiitic basaltic pillow lava sequence that makes up part of the Eocene Siletz River Volcanics in the central Coast Range, Oregon. Regional zoning of zeolite assemblages is not apparent; the zeolites formed in joints, fractures, and interstices, although most occur in central cavities of basalt pillows. The zeolites and associated minerals identified, in general order of paragenetic sequence, are smectite, pyrite, calcite (small spheres), thomsonite, natrolite, analcime, scolecite, mesolite, stilbite, heulandite, apophyllite, chabazite, mordenite, calcite (scalenohedra and twinned rhombohedra), laumontite, and amethystine quartz. Common three-mineral assemblages are: natroliteanalcime-stilbite, stilbite-heulandite-chabazite, stilbite-apophyllite-chabazite, and natrolite-mesolite-laumontite.

Alteration of basaltic glass, which was initially abundant, appears to have been an important factor in formation of the zeolites. Isotopic data suggest that zeolitization occurred during a low-temperature ( $60^{\circ}$ - $70^{\circ}$ C) submarine hydrothermal event, or by reactions of cold (~ $10^{\circ}$ C) meteoric water with basalt over a long time. The occurrence of different mineral assemblages in cavities of adjacent basalt pillows indicates that these minerals crystallized in closed systems that were isolated as fractures and joints were sealed by deposition of smectite and early zeolites. Although the total chemical composition of the mineral assemblages in cavities is similar, different mineral species formed because of the sensitivity of zeolite minerals to slight variations in physical and chemical conditions within individual cavities.

Key Words-Analcime, Apophyllite, Isotope abundance, Laumontite, Mesolite, Pillow lava, Smectite, Zeolites.

#### INTRODUCTION

A variety of zeolites and associated minerals occur in a basaltic pillow lava sequence of the early and middle Eocene Siletz River Volcanics in the central Coast Range, Oregon (Figure 1). Similar mineral assemblages in similar geologic environments have been described from Iceland (Walker, 1960a; Betz, 1981), Ireland (Walker, 1960b), India (Sukheswala et al., 1974; Kostov, 1981), Newfoundland (Bay of Fundy) (Carpenter, 1971), and the United States (New Jersey) (Fenner, 1910; Schaller, 1932). Although a regional zeolite zonation was recognized for most of these major occurrences, it has not been recognized in the Siletz River Volcanics. The present study describes the occurrence of the zeolites and associated minerals in the basaltic pillow lavas of the Siletz River Volcanics and attempts to explain their origin.

## GEOLOGIC SETTING

During early and middle Eocene time, the coastline of Oregon and Washington was far to the east of its present location, and an island arc trending nearly north-south occupied the area of the present Oregon Coast Range (Snavely and Wagner, 1963; Lyttle and Clarke, 1975). The Siletz River Volcanics (Snavely et al., 1968) make up the island-arc rocks in the central Oregon Coast Range and thickness varies from about 3 km in the shallower parts to as much as 6 km near volcanic centers. The great thickness of the volcanic rocks and the shallow character of the interbedded sedimentary layers suggest that the sequence was deposited in a constantly subsiding basin. Snavely et al. (1968) divided the Siletz River Volcanics into two petrochemical units: (1) a lower unit that consists of early Eocene submarine flows of tholeiitic basaltic pillow lavas and breccias; and (2) an upper unit of middle Eocene subaerial and submarine alkalic rocks. The volcanic rocks interfinger complexly with marine basaltic tuffaceous siltstone and sandstone. In both units pillow lavas and breccias are common, and zeolitization has taken place throughout the entire sequence.

Pillow structure in basaltic lavas has been attributed to the subaqueous cooling of lava (Moore, 1975). As the hot lava comes in contact with cold water, pillows are formed which have outer shells of glass due to quenching by cold water. Central cavities are formed when fluid lava drains from the pillows before the interior of the pillows cools (see Ballard and Moore, 1977; Francheteau *et al.*, 1980). Pillows with similar large central cavities but without zeolitic alteration were described by Waters (1960) in the Columbia River Basalt Group where the pillows formed in shallow lakes and are palagonitized but not zeolitized. Grenne and Roberts (1983)



Figure 1. Map showing location of study area and general distribution of Siletz River Volcanics in the central Coast Range of Oregon (after Snavely *et al.*, 1968).

described Ordovician pillow basalts with large central cavities in Norway and suggested that seawater entered the cavities immediately after the lava drained out, thus chilling the interior of the cavities to glass.

Parts of the Siletz River Volcanics have been uplifted and folded into numerous broad, elongate anticlines and synclines (Snavely and Wagner, 1964). Numerous northwest- and northeast-trending, high-angle normal and reverse faults having displacements of a meter to hundreds of meters, and westto northwest-trending, strike-slip faults cut the volcanic sequence (Snavely and Wagner, 1964). Post-Eocene mafic dikes and sills have intruded the Siletz River Volcanics.

The area of this study is an eastern exposure of basaltic pillow lavas that were deposited in a shallow marine backarc basin between the island-arc axis to the west and the Eocene coastline to the east. Thin-bedded tuffaceous sedimentary rocks and thin sills and dikes are locally associated with the basaltic pillow lavas. The lower unit of the Siletz River Volcanics in this area is exposed in a northeast-trending anticlinel uplift bounded by northeast-trending, steeply-dipping faults roughly parallel to the anticlinal axis (Figure 2).

## **EXPERIMENTAL**

Quarries for road rip-rap provided excellent rock exposures in an otherwise heavily vegetated region.



Figure 2. Map showing generalized geology and location of quarries sampled in this study.

Five quarries containing unusually large and abundant secondary minerals were selected for detailed study. Alteration and secondary mineral distribution were mapped in the quarries, but lack of exposures precluded any continuous mapping between quarries. Other quarries irregularly distributed through the Siletz River Volcanics in the study area have exposed pillow lavas that are barren or nearly barren of secondary minerals. Quarry maps of secondary mineral distribution and descriptive mineralogy of the zeolites and related minerals from four of the quarries were given by Clark (1964).

Samples were studied with the binocular microscope to determine paragenetic sequences and assemblages. The refractive-index oil-immersion technique was used to determine optical properties of the alteration minerals, and observe any overgrowths or inclusions that might exist. X-ray diffraction (XRD) using the Debye-Scherrer powder method provided films for mineral identification. The smectite was identified from XRD powder diffractograms using a goniometer equipped with a graphite crystal and focussing monochromator. Five minerals were hand-picked for chemical analyses by wet chemical techniques and flame photometry for major oxides, and by visual direct-reader spectrometry for semi-quantitative trace-element analyses. Samples of quartz, calcite, apophyllite, and altered basalt were analyzed for stable isotopes of oxygen, and the calcite for isotopes of carbon, using a mass spectrometer.

# RESULTS

Alteration minerals occur: (1) as replacements of plagioclase phenocrysts in the basalt; (2) in large central cavities of the basalt pillows; (3) along joints and fractures within the basalt pillows and the interstices between pillows; (4) within brecciated areas where pillows broke apart during emplacement, and (5) along fractures through the basaltic pillow lava sequence; and (6) in fractures through thin, interbedded, tuffaceous siltstone and sandstone beds. Plagioclase phenocrysts in the zeolitized areas of pillow basalt are partly or completely replaced by zeolites and dark-green smectite. Smectite occurs in the cores of the phenocrysts or as thin green bands outlining internal zones within the phenocrysts.

The largest and best-crystallized zeolites were deposited in the central cavities of basaltic pillow lavas. In cross section the basalt pillows are round to slightly elliptical having diameters of about 30 cm to 2.5 m but averaging about 1 m. They are piled on each other with little space between. The space between pillows is filled mostly with smectite and minor amounts of calcite and zeolites, which are alteration products of basaltic glass. Most of the pillows are solid to the core and show radial cooling joints. About 20% of the pillows in the localities studied have one or more cavities located just above the center of the pillow (Figure 3), and the outcrop distribution of the pillows containing central cavities is irregular. The cavities are typically elliptical and have a rounded top and flattened base indicating the orientations of the pillows when they cooled. Maximum dimension of the cavities is from a few centimeters to about 60 cm. At the JayTe'el and Soap Creek quarries, pillows commonly contain 2 to 4 small cavities (Figure 3-upper); those at the Coffin Butte and Kings Valley quarries characteristically have only one large central cavity (Figure 3-lower). All cavities found contained zeolites and associated secondary minerals. The cavities are lined with a thin layer (0.5-2 mm thick) of dark-green smectite upon which the secondary minerals were deposited. Some of the zeolites crystallized all the way around the inside of a cavity, but others crystallized only on the bottom. Acicular zeolites in pillow cavities are as long as 60 mm, tabular crystals are as long as 25 mm, equant analcime crystals are as large as 60 mm in diameter, and twinned calcite rhombohedra are as large as 200 mm on a side. Cavities are usually not completely filled but are vuggy. For example, in one pillow at the Coffin Butte quarry, a layer of stilbite covers the bottom of the cavity, and chabazite, which crystallized later, coats the stilbite and the sides and top of the cavity. Crystallization appears to have occurred prior to regional



Figure 3. Altered basaltic pillows showing central cavities that contain secondary minerals. Upper—pillow from the JayTe'el quarry has several small elliptical cavities containing mostly mesolite. Pillow is not in place; top is toward left. Note radial cooling joints. Lower—large central cavity lined mostly with stilbite in a pillow at the Coffin Butte quarry. Note flat bottom and rounded sides and top of the cavity.

folding of the pillow lavas because secondary mineral deposits follow the configuration of the cavities and are not deposited at an angle to the flat cavity bottoms.

The most common 3-phase assemblages of secondary minerals in the pillow cavities are as follows, in order of deposition:

> natrolite-analcime-stilbite stilbite-heulandite-chabazite stilbite-apophyllite-chabazite natrolite-mesolite-laumontite.

Locally, only two phases are commonly found in a cavity, and rarely four are found. In addition to the minerals mentioned, calcite is generally the last mineral deposited in larger cavities. A definite layering of the minerals in the cavities of most pillows has been noted, indicating that the major phases were not codepositional but changed during the alteration process. Later minerals are, with few exceptions, deposited upon fresh crystal surfaces of already existing crystals, and corrosion of early-formed crystals is generally not apparent. The corrosion of early-deposited natrolite at



Figure 4. Unbroken basaltic pillow showing zeolites outlining cooling fractures.

the Coffin Butte and Kings Valley quarries where spheroidal clusters of twinned analcime include remnants of earlier natrolite (Staples, 1946) is the only evidence of later-stage reactions affecting already existing secondary minerals.

The outcrop distribution of zeolite assemblages in pillow cavities of the Siletz River Volcanics appears to be random, and no regional distribution was evident. Adjacent pillows commonly contain different mineral assemblages. For example, one pillow may contain natrolite-analcime-stilbite, and an adjacent one may contain stilbite-heulandite-chabazite. Careful plotting of pillow assemblages at two quarries showed that local concentrations of similar assemblages could be mapped (Clark, 1964), but the assemblages did not give any pattern of regional zoning.

Radial cooling joints and fractures within pillows are filled with zeolites in areas such as the JayTe'el and Soap Creek quarries, where zeolite and clay alteration of the basalt is extensive (Figure 4). At the Coffin Butte and Kings Valley quarries, the basalt is not so highly altered and only minor zeolites have been found along radial joints, even though the central cavities may contain abundant zeolites. Interstices between the rounded basalt pillows are commonly filled with massive darkgreen smectite containing small amounts of massive analcime, natrolite, stilbite, and/or calcite. Locally the zeolites between pillows are small but occur as welldeveloped crystals rather than in masses. Brecciated areas where pillows broke apart during extrusion are pervasively altered to smectite, and abundant zeolites (generally analcime and natrolite) and calcite cements the breccia. Fractures through the basaltic pillow lava were found only at the JayTe'el quarry, where the frac-



Figure 5. Outcrop of zeolitized basaltic pillow lava at the JayTe'el quarry cut by vertical fractures (arrows) that filled with zeolites and calcite.

tures extend from the ground surface about 2.5 m downward into the quarry wall cutting through several pillows (Figure 5). These fractures are filled with mesolite, laumontite, and calcite. Thin-bedded tuffaceous sandstone and siltstone beds 15 to 100 cm thick are interlayered with the pillow lavas and contain zeolites, usually stilbite, replacing glass of the tuff fragments, and in 1-2 mm wide veinlets cross-cutting the bedding planes.

The general paragenetic sequence of the secondary minerals is the same at the 5 quarries, and nearly all minerals occur at each locality although the relative amounts are different. The general paragenetic sequence combined from the individual quarries is shown on Figure 6. Locally there appears to be codeposition, and analcime, apophyllite, and calcite formed during at least two periods of major deposition.

# Chemistry

Chemical analyses for major oxides and semiquantitative spectrographic analyses for trace elements for five minerals are shown in Table 1. The analyzed apophyllite has an exceptionally high F content and is therefore fluorapophyllite, according to the nomencla-



Figure 6. General paragenetic sequence of zeolites and associated minerals. Solid bars represent relative time of main deposition; dashed lines between bars represent minor intermittent deposition.

ture of Dunn *et al.* (1978). The analcime is nearly pure end-member Na-analcime with only traces of K and Ca; its Si/Al ratio is 2.13. Chabazite contains minor amounts of Na and K, and trace amounts of Ba and Sr, and has a Si/(Al + Fe<sup>3+</sup>) ratio of 2.06, placing it in the range of "normal" chabazites, as defined by Sheppard and Gude (1970). The analyzed mesolite is slightly more Ca-rich than midway between natrolite and scolecite, but within the range for mesolite indicated by Alberti *et al.* (1982). Mesolite and scolecite occur as overgrowths on natrolite in several of the quarries. The analyzed stilbite is higher in Si than most stilbites, but within the range of normal composition (Černý, 1965); its Si/Al ratio is 3.18.

Generally the minerals contain low concentrations of trace elements; 30 elements were looked for but not detected (Table 1). Whole rock major oxide and selected trace element analyses of unaltered basalt from near the JayTe'el and Coffin Butte quarries are shown in Table 2.

## Isotopes

The minerals and rocks analyzed are greatly enriched in <sup>18</sup>O and <sup>13</sup>C (Table 3). A sample of tholeiitic basalt from the freshest part of a pillow has a  $\delta^{18}$ O of +8.11‰, which is a small enrichment from the usual +6.0‰ of unaltered basalt (Taylor, 1968). A highly altered part of the same pillow adjacent to the internal cavity consisting mostly of smectite has a  $\delta^{18}$ O value of +16.87‰. The oxygen isotopes show that all of the lava has undergone some alteration.

Although the quartz and calcite  $\delta^{18}$ O values plot at

	Apophyllite	Analcime	Stilbite	Mesolite	Chabazite
(Wt. %) <sup>1</sup>					
SiO <sub>2</sub>	52.96	55.98	57.89	44.46	47.05
$Al_2O_3$	0.18	22.54	15.56	27.39	19.51
Total Fe					19101
as Fe <sub>2</sub> O <sub>3</sub>	0.10	0.09	0.08	0.10	0.08
MgO	nd	0.14	nd	nd	nd
CaO	24.80	0.02	7.76	9.29	9.33
$Na_2O$	0.07	13.42	0.86	6.46	1.02
K <sub>2</sub> O	3.97	0.02	0.02	0.08	0.33
$H_2O^+$	16.65	8.03	16.18	11.92	17.29
$H_2O^-$	0.17	0.04	2.25	0.53	5.16
F	2.01	< 0.01	< 0.01	< 0.01	< 0.01
Total	100.91	100.28	100.60	100.23	99 77
O≡F	0.84			100.25	<i></i>
	100.07				
Si/Al	~	2.13	3.18	3.79	2.07
(ppm) <sup>2</sup>					
Ba	2	<2	<2	<2	150
Sr	2	1	7	30	1500
Cu	7	50	10	15	5
Ga	<0.7	<0.7	< 0.7	15	< 0.7
Ti	7	2	5	1.5	10
v	50	<1	<1	<1	<1

Table 1. Chemical analyses of secondary minerals from the Siletz River Volcanics, Oregon.

<sup>1</sup> Analysts: J. H. Christie,  $K_2$  and  $Na_2O$  by flame photometer; S. T. Neil, other major oxides and F by wet chemistry. <sup>2</sup> Analyst: C. Heropoulos; 6-step semi-quantitative spectrographic analysis; additional elements looked for but not detected with limit of detection (in part). We can be a set of the set of t

listed with limit of detection (in ppm): Mn <0.7, Ag <0.7, As <100, Au <7, B <2, Be <0.7, Bi <7, Cd <7, Ce <50, Ci <1, Cr <0.7, Cu <0.7, Eu <50, Ge <7, Hf <50, In <1.5, La <7, Li <100, Mo <2, Nb <10, Ni <0.7, Pb <7, Pd <1, F <5, Re <7, Sb <20, Sc <0.7, Sn <2, Ta <50, Te <300, Th <150, Tl <3, U <150, W <10, Y <7, Yb <0.7, Zn <15, Z <3.

nd-not detected.

Table 2. Whole rock chemical analyses, recalculated waterfree, of unaltered tholeiitic basaltic pillow lavas of the Siletz River Volcanics, Oregon (Snavely *et al.*, 1968).

	Tholeiite Jay Te'el quarry	Tholeiite Coffin Butte quarry
(Wt. %)		
SiO <sub>2</sub>	48.6	48.4
$Al_2O_3$	14.7	14.1
$Fe_2O_3$	4.3	5.2
FeO	6.7	8.5
MgO	8.6	5.7
CaO	12.9	11.9
Na <sub>2</sub> O	2.1	2.7
K₂O	0.10	0.17
TiO <sub>2</sub>	1.7	2.9
$P_2O_5$	0.16	0.29
MnO	0.19	0.30
Total	100.05	100.16
(ppm)		
Ba	7	70
Со	70	70
Cr	150	70
Cu	70	150
Ga	7	15
Ni	150	150
Sc	15	15
Sr	300	300
$\mathbf{V}$	70	150
Zr	70	70

300°C on the temperature of deposition curve of Friedman and O'Neill (1977), geologic evidence indicates this temperature is much too high. Calcite and quartz were likely not deposited in equilibrium with each other in the pillow lavas.

#### DISCUSSION

Zeolites may have formed in the basaltic pillow lavas of the Siletz River Volcanics by: (1) a hydrothermal mechanism; (2) low-grade regional metamorphism; or (3) alteration of basalt by cold meteoric water. Regional metamorphism at low-grade (zeolite facies) conditions, as defined by Coombs *et al.* (1959), should have resulted in a regional zeolite zonation, but such zoning has not been recognized in the present study. Likewise, no geologic evidence of regional burial metamorphism of the Siletz River Volcanics has been found.

Alteration by the reaction of cold meteoric waters at  $25^{\circ}-35^{\circ}$ C and the abundant basaltic glass was considered by Nashar and Davies (1960) and Nashar and Basden (1965) for similar assemblages in other areas. Alteration by meteoric waters at  $25^{\circ}-35^{\circ}$ C should take place at a shallow burial depth and thus alteration by such meteoric waters should have resulted in a regional distribution and zonation of secondary minerals, at least below a regional water table. This pattern was not recognized in the study area.

Alternatively, such low-temperature hydrothermal

Table 3. Isotopic compositions of selected minerals and altered pillow lava.

	δ <sup>18</sup> Ο <sup>1</sup> (‰)	δ <sup>13</sup> C <sup>2</sup> (‰)
Quartz	+25.21	<u> </u>
Calcite	+22.0	+7.73
Apophyllite	+9.89	
Very altered basalt of pillow ad- jacent to interior cavity	+16.87	
Least altered part of same pil- low	+8.11	

<sup>1</sup> vs. SMOW.

<sup>2</sup> vs. PDB.

Analyst: L. D. White.

conditions may have been superimposed on the pillow lavas by localized heat sources such as individual eruptive centers. This type of heat source would have resulted in patchy alteration which extended throughout the area of island-arc volcanism. Westercamp (1981) described an irregular distribution of zeolites and other minerals in amygdules in pillow lavas, hyaloclastite tuffs, and associated rocks on the island of Martinique, French West Indies. He concluded that the distribution resulted from areas of well-defined heat flow with sufficient available fluids. He referred to these as "heat flow domes" (Westercamp, 1981). The concept of localized heat flow also seems to be a reasonable explanation of the irregular distribution of zeolites and related minerals in the Siletz River Volcanics. Other processes of zeolitization which depend on intrusive heat sources, such as plutons, dikes, and sills, and on fracture controls have been observed by the authors in the western Cascade Range of Oregon and Washington. Alteration in the Siletz River Volcanics, however, was probably not related to large intrusive bodies because none have been recognized in the area and geophysical data do not suggest their existence. Dikes and sills occur within the pillow lavas, but are not specifically associated with zeolites. Some dikes and sills may have locally been barriers to circulating hydrothermal fluids and thereby may have structurally controlled alteration.

Fault control of hydrothermal fluids is possible in this anticlinal area bounded by faults; more faults probably exist in the area than were recognized in the field. Indeed, laumontite, mesolite, and calcite occur along vertical fractures through basaltic pillow lavas at the JayTe'el quarry (Figure 5); however, no concentrations of zeolites were noted near or along the major faults. Fault control of hydrothermal alteration was therefore minimal.

Factors enhancing zeolitic alteration include the abundance of water, the abundance of glass in the host rocks, permeability for the circulation of altering alkaline to neutral fluids, and temperatures less than about 250°C. Temperatures within the Siletz River Volcanics hydrothermal system could not have been very high because greenschist-facies minerals were not observed. From a consideration of the crystallization temperatures of similar minerals in Icelandic geothermal holes (Kristmannsdóttir and Tómasson, 1978), the maximum temperature of crystallization of the earliest deposited secondary minerals was probably about 150°C; chabazite was the lowest temperature zeolite and was probably deposited at about 70°C.

Laumontite has generally been regarded as a hightemperature zeolite (Liou, 1971; Kristmannsdóttir and Tómasson, 1978); however, Sukheswala et al. (1974) related the laumontite zone in the Deccan trap lavas of India to structural deformation of the lavas and to dikes intruding the lavas. A similar explanation may account for laumontite in the Siletz River Volcanics where deformation is obvious and dikes are common. In the basaltic pillow lavas of the Siletz River Volcanics, however, the laumontite is invariably a late-formed mineral. When the pillows and fractures containing laumontite were first exposed to air, the laumontite crystals were transparent. Within minutes to hours of exposure to air, the laumontite dehydrated. The clear laumontite crystals could not have formed at very elevated temperatures; in fact, they must have formed at very low temperatures. Boles (1977), in his review of laumontite stability, suggested low-temperature crystallization for some laumontites. McCulloh et al. (1981) described laumontite precipitated from hot springs in California between 89° and 43°C.

The hydrothermal fluids to be considered in the zeolitization must have been seawater, meteoric water, or a mixture of the two. The active geothermal systems producing zeolites in most of Iceland are dominantly meteoric waters (Kristmannsdóttir and Tómasson, 1978). Zeolitic alteration and the variety of zeolite minerals such as are found in the pillow lavas of the Siletz River Volcanics are scarce in similar submarine pillow lavas (Mottl, 1983). Submarine hydrothermal alteration usually results in widespread greenschist-facies mineralogy rather than zeolite assemblages (Mottl and Holland, 1978); however, hydrothermally altered tholeiitic basalts containing analcime, wairakite, natrolite, thomsonite, chabazite, laumontite, stilbite, and heulandite, as well as smectite and mixed-layer chlorite/ smectite, have been described from the Mid-Atlantic Ridge (Miyashiro et al., 1971; Aumento et al., 1971). Melson et al. (1968) described a zeolite-bearing altered basalt which occurs only along a level approximately midway between the axial valley and the crest of the Mid-Atlantic Ridge.

Permeability was likely an important factor in the alteration and especially in the deposition of the different zeolite assemblages. The initial permeability of the Siletz River Volcanics was probably generally high because of spaces between rounded pillows, radial cooling joints in pillows, and interlayered thin beds of tuff-

aceous sandstone and siltstone. As alteration progressed, secondary minerals were deposited in open spaces, thus decreasing overall permeability. If hydrothermal fluids of an open system had been sealed in the pillow cavities by crystallization of clay minerals and zeolites, the individual cavities would have become closed systems. Then, as the trapped residual fluid became cooler and more alkaline, secondary minerals would have crystallized as the reactions progressed to completion. The sensitivity of zeolite minerals to slight changes in various physical and chemical conditions, such as temperature, solution chemistry, amount of solutions involved in the reactions (water/ rock ratio), and permeabilities, was pointed out by Höller and Wirsching (1978). Arnórsson et al. (1983) noted a change in composition of geothermal systems in response to rate of leaching of primary constituents, rate of fluid flow, and rate of precipitation of secondary minerals, factors that were particularly pronounced at low temperatures. The total chemical composition of the different assemblages in the pillow cavities is similar, but when an individual cavity became a closed system for any length of time the secondary mineral assemblage within that cavity reflected the closed system environment.

The chemical components of the zeolites and associated minerals were likely derived mainly from the basalts, particularly the basaltic glass. Field observations show that the amount of secondary mineralization is proportional to the extent of alteration of the host rocks. Plagioclase phenocrysts in the interior of pillows adjacent to central cavities are commonly replaced by zeolites. Early smectite replacement of the basaltic glass released Ca, Na, and K to the hydrothermal fluids, but the Fe and Mg remained in the clay portion of the altered rock. The source of F and K to form apophyllite in the late stage of secondary mineral crystallization is not certain. The basaltic lava must have been the main source of these components even though it contains only 0.1 to 0.2 wt. % K<sub>2</sub>O (Table 2). Temperatures may have been too low to form potassium-bearing clays and adularia. No data are available on the F content of the unaltered basaltic rocks or the interlayered marine sediments, but the basaltic lavas were most likely the source of F also. Likewise, small amounts of Ba and Sr contained in basaltic lavas (Table 1) were probably leached and selectively concentrated in chabazite.

The depositional sequence in the Siletz River Volcanics consists of small amounts of initial Ca-rich phases (e.g., calcite and thomsonite), changing to abundant Na-rich phases (e.g., natrolite and analcime) (Figure 7). The mineral sequence then progressed gradually to Ca-Na phases and again to abundant Ca-rich minerals as the latest deposits. The water content of the secondary minerals generally increased as the crystallization sequence progressed (Figure 8).



Figure 7.  $SiO_2$ -(K,Na)<sub>2</sub>O-CaO variation diagram of zeolites, apophyllite, and unaltered tholeiitic basalt in the Siletz River Volcanics. Circles represent minerals analyzed for this study (Table 1), squares are representative zeolite compositions, and triangles are unaltered basaltic lavas from Coffin Butte quarry (CB) and JayTe'el quarry (J) (Table 2).

Quartz and mordenite are scarce and were late to crystallize. These minerals probably were deposited from water which became locally enriched in silica at a late stage of alteration. The quartz shows several growth stages without any other minerals deposited between periods of quartz precipitation. Most calcite in the pillow cavities is later than chabazite, which suggests low temperatures if chabazite crystallized at 70°C or below as in Icelandic geothermal systems (Kristmannsdóttir and Tómasson, 1978). Therefore, calcite probably formed from dissociation of bicarbonate in HCO<sub>3</sub>-rich waters into carbonate ion, which combined with Ca leached from the basalt.

Carbonates in hydrothermal ore deposits show an increase in  $\delta^{13}$ C with succeedingly younger stages of deposition and with cooling (Rye and Ohmoto, 1974). Only one ore deposit, however, cited by these authors had late calcite with a  $\delta^{13}$ C as high as +5‰; the  $\delta^{13}$ C of calcite from the Pine Point deposit was as high as +10‰. Rye and Ohmoto (1974) attributed this value to an increase in methane which caused a decrease in the oxidation state of the late fluids. A slow rate of crystallization also concentrates the heavy isotopes in carbonates (O'Neil *et al.*, 1969). The +7.73‰ <sup>13</sup>C and +22.0‰ <sup>18</sup>O of the calcite determined in the present study suggest a very low-temperature alteration system perhaps involving carbon derived from marine carbonates or seawater (Lawrence *et al.*, 1979).

Whether the alteration fluids were low-temperature hydrothermal seawater or cold meteoric waters cannot be determined with certainty on the basis of available data. The heavy isotopes may be a result of seawater alteration at temperatures below 100°C, and probably 60°-75°C (Taylor, 1974; Friedman and O'Neil, 1977). Temperatures for cool meteoric waters indicated by the enrichment in heavy isotopes would have to be



Figure 8.  $SiO_2-H_2O-(K_2O + Na_2O + CaO)$  variation diagram of zeolites and apophyllite in the Siletz River Volcanics.

below about 10°C. Therefore, temperatures analogous to the Icelandic geothermal systems could only be attained using seawater as the alteration fluid on the basis of the isotope data.

#### SUMMARY AND CONCLUSIONS

The assemblages of zeolites and associated minerals in the basaltic pillow lavas of the Siletz River Volcanics are similar to other major zeolite occurrences in basaltic pillow lavas. The lack of regional zeolite zoning in the Siletz River Volcanics in contrast to places where it has been described in India, Ireland, and Iceland may be explained by differences in heat source and heat flow. The paragenetic sequences and relative abundances of secondary minerals, however, are not the same at all localities worldwide, which reflects the sensitivity of zeolite minerals to slight changes in physical and chemical conditions during deposition.

The permeability of the pillow lavas was high until clay alteration from the basaltic glass filled joints and fractures. Sealing may have begun in an open system and compartmentalized the altering pillow lavas into numerous closed systems as secondary minerals closed the fractures and joints. Slight differences in fluid composition, temperatures, pH, amount of fluid, and size of cavity in the individual closed systems probably affected the type of zeolite species that formed and adjacent cavities developed different secondary mineral assemblages. Isotope data suggest low-temperature alteration of basalt, but whether hydrothermal seawater at 60°-75°C or cold meteoric water at <10°C was the reacting fluid is inconclusive.

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Резюме — Цеолиты и связанные с ними минералы встречаются в толеитовой базальтовой подушковой лаве, которая является частью эоценовых вулканических пород Сайлетз Ривер в центральной области орегонского побережья. Районирование цеолитовых отложений не является очевидным; цеолиты формировались в узлах, тпецинах и целях, но самое большое их количество находится в центральных пустотах базальтовых подушек. Цеолиты и связанные с ними минералы находятся в следующем общем порядке парагенетической серии: смектит, пирит, кальцит (малые шарики), томсонит, натролит, анальцим, сколесит, месолит, стильбит, гейландит, апофиллит, хабазит, морденит, кальцит (разносторонние тречгольники и спаренные ромбоздры), ломонит, и аметистовый кварц. Обычные трех-минеральные составы это: натролит-анальцим-стильбит, стильбит, стильбит

Изменение базальтового стекла, которое сначала находилось в большом количестве, кажется значительным фактором в процессе формирования цеолитов. Изотопные данные указывают на то, что цеолитизация происходила во время низко-температурного подводного гидротермального превращения, или путем реакции холодной (~10°C) атмосферической воды с базальтом в течение длинного периода времени. Залегание различных минеральных отложений в пустотах соседних базальтовых подушек указывает на то, что эти минералы кристаллизировались в замкнутых системах, которые были отвелены в виде трещин и узлов, уплотненных осаждением смектита и первоначальных цеолитов. Хотя полная химическая композиция минеральных отложений в пустотах являетсая подобной, различные минералы формировались в результате чувствительности цеолитовых минералов к небольшим изменениям в физических и химических условиях внутри индивидуальных пустот. [Е.G.]

Resümee-Zeolithe und Begleitminerale treten in einer tholeitbasaltischen Abfolge von Pillowlaven auf, die einen Teil der eozänen Siletz River Vulkane, Central Coast Range, Oregon, darstellt. Eine regionale zonare Verteilung der Zeolithvergesellschaftungen ist nicht zu beobachten; die Zeolithe bildeten sich in Klüften, Spalten, und Zwischenräume, obwohl die meisten in zentralen Hohlräumen der Basaltpillows auftreten. Die identifizierten Zeolithe und Begleitminerale sind in der allgemeinen paragenetischen Abfolge: Smektit, Pyrit, Calcit (kleine Kugeln), Thomsonit, Natrolith, Analcim, Skolezit, Mesolith, Stilbit, Heulandit, Apophyllit, Chabasit, Mordenit, Calcit (Skalenoeder und verzwillingte Rhomboeder), Laumontit, und Amethyst-artiger Quarz. Häufige Vergesellschaftungen aus drei Mineralen sind Natrolith-Analcim-Stilbit, Stilbit-Heulandit-Chabasit, Stilbit-Apophyllit-Chabasit, und Natrolith-Mesolith-Laumontit.

Die Umwandlung von basaltischem Glas, das ursprünglich sehr häufig war, scheint bei der Zeolithbildung ein wichtiger Faktor gewesen zu sein. Isotopen-Daten deuten darauf hin, daß die Zeolithisierung während eines niedrig temperierten (60°–70°C) submarinen hydrothermalen Ereignisses stattgefunden hat, oder durch die Reaktion von kaltem (etwa 10°C) meteorischem Wasser mit dem Basalt über eine lange Zeit. Das Auftreten verschiedener Mineralvergesellschaftungen in den Hohlräumen benachbarter Basaltpillows deutet darauf hin, daß diese Minerale in geschlossenen Systemen kristallisierten, die voneinander getrennt waren, da die Spalten und Klüfte durch die Ablagerung von Smektit und früh gebildeten Zeolithen verschlossen waren. Obwohl der Gesamtchemismus der Mineralvergesellschaftungen in den Hohlräumen ähnlich ist, bildeten sich verschiedene Mineralarten. Der Grund ist die Empfindlichkeit der Zeolithminerale gegenüber geringen Änderungen der physikalischen und chemischen Bedingungen innerhalb der einzelnen Hohlräume. [U.W.]

**Résumé** – Des zéolites et minéraux associés se trouvent dans une séquence de laves "coussins" tholéiitiques basaltiques qui constitue une partie des roches volcaniques Eocènes de la Rivière Siletz dans la Coast Range Centrale, Oregon. Un zoning régional d'assemblages de zéolites n'est pas apparent; les zéolites se sont formées dans des joints, fractures et interstices, quoique la plupart se trouvent dans des cavités centrales de coussins de basalt. Les zéolites et minéraux associés identifiés, en ordre général de séquence paragénétique sont smectite, pyrite, calcite (petites sphères), thomsonite, natrolite, analcime, scolecite, mésolite, stilbite, heulandite, apophyllite, chabazite, mordénite, calcite (scalénohédrons et rhombohédrons jumellés), laumonite, et quartz amethystine. Des assemblages de 3 minéraux communs sont natrolite-analcime-stilbite, stilbite-heulandite-chabazite, stilbite-apophyllite-chabazite, et natrolite-mésolite-laumonite.

L'altération de verre basaltique, qui était abondant initialement, semble avoir été un facteur important dans la formation de zéolites. Les données isotopiques suggèrent que la zéolitisation s'est passée pendant un évenement hydrothermique sousmarin à basse température (60°-70°C), ou par des réactions d'eau météorique froide avec du basalt pendant longtemps. L'emplacement de différents assemblages minéraux dans les cavités de coussins de basalt adjacents indique que ces minéraux se sont cristallisés dans des systèmes fermés qui étaient isolés, comme les fractures et les joints étaient hermétiquement fermés par le dépôt de smectite et des premières zéolites. Quoique la composition chimique totale des assemblages minéraux dans les cavités est semblable, des espèces de minéraux différents se sont formées à cause de la sensitivité des minéraux zéolites à de légères variations dans les conditions physiques et chimiques au sein des cavités individuelles. [D.J.]