U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

DIAGENETIC ALTERATION OF BASALTIC TEPHRA IN LACUSTRINE DEPOSITS, SOUTHWESTERN IDAHO AND SOUTHEASTERN OREGON

by

Richard A. Sheppard

Open-File Report 96-697

Denver, Colorado
1996

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Richard A. Sheppard

ABSTRACT

The Chalk Hills Formation of the western Snake River Plain, Idaho, and an unnamed sedimentary deposit near Harney Lake, Oregon, provide a rare opportunity to study the alteration of both rhyolitic and basaltic tephra that were deposited in the same depositional environment and were probably exposed to the same diagenetic fluids and processes. Both deposits are Miocene and lacustrine. Rhyolitic tephra in both deposits were investigated previously, and the basaltic tephra in the upper parts of both deposits is the subject of the present study. The diagenetic mineralogy of the altered basaltic tephra was determined by X-ray diffractometer analyses supplemented by scanning electron microscopy and thin section study. The chemical composition of the diagenetic minerals was determined by electron microprobe analyses supplemented by energy-dispersive X-ray analyses.

Basaltic tephra is dark gray to black where fresh and yellow, orange, or brown where altered, generally 2-10 cm thick, and shows normal graded bedding. An assemblage of smectite+heulandite is common in altered basaltic tephra in the Chalk Hills Formation, but smectite+phillipsite is common in the unnamed deposit near Harney Lake. The basaltic tephra in the Chalk Hills Formation also may contain minor chabazite, trace amounts of opal-CT, and rare, trace amounts of erionite. The basaltic tephra in the unnamed deposit near Harney Lake also may contain trace to minor amounts of chabazite and trace amounts of analcime or erionite. Smectite (nontronite) is generally more abundant than zeolite in the altered basaltic tephra from both deposits.

Relative to basaltic tephra, the diagenetic alteration of rhyolitic tephra resulted in an overall more siliceous mineral assemblage, greater abundance of zeolites, higher Si:Al ratios for individual zeolite species, and the early formation of montmorillonite rather than nontronite. Thus, for tephra exposed to the same diagenetic fluids and processes, the original composition of the tephra had a major influence on the genesis of the diagenetic mineral assemblage in the lacustrine deposits.

INTRODUCTION

The alteration of volcanic glass has received much attention lately for both academic and practical reasons. Common alteration products of the glass are zeolites and clay minerals that have economic importance, and these minerals formed chiefly by the reaction of volcanic glass with pore water of various compositions (Hay, 1966). Although basalt is by far the most abundant volcanic rock, the ratio of basaltic pyroclastic material to non-pyroclastic material is less than that for other volcanic rocks (Fisher and Schmincke, 1984). The most widespread and predominant pyroclastic materials deposited on land originated from silicic sources. Basaltic tephra and tuffs commonly have not been recognized in lacustrine deposits, partly because the basaltic beds are thin (generally less than 10 cm thick), altered, and inconspicuous in outcrop.

During investigations of zeolite-rich silicic tuffs in two Miocene lacustrine basins of southwestern Idaho (Sheppard, 1991) and southeastern Oregon (Sheppard, 1994), numerous thin beds of basaltic tephra (both relatively fresh and altered) were recognized but were not studied in detail because they had no apparent commercial value. In 1995, however, the basaltic tephra of both basins was sampled and studied to complement the investigations of silicic tephra. These studies provided the opportunity to examine the influence the original chemical composition of the glass had on the subsequent diagenetic mineral assemblages and on the chemical composition of individual authigenic silicate phases. Inasmuch as the above investigations (Sheppard, 1991; 1994) showed that the two lacustrine units were deposited in water of different composition, there was also an opportunity to examine this effect on the alteration of the contrasting basaltic and rhyolitic glasses.

GEOLOGIC SETTING

Samples for this present investigation came from two Miocene lacustrine deposits: (1) the Chalk Hills Formation south of Oreana, Owyhee County, Idaho, along the southwestern margin of the western Snake River Plain (fig. 1) and (2) an unnamed volcaniclastic unit east of Harney Lake, Harney County, Oregon (fig. 2). These two lacustrine deposits contain much silicic tephra throughout, and both have thin beds of basaltic tephra in their upper parts. Previous studies (Sheppard, 1991; 1994) indicated that the depositional environment of the Chalk Hills Formation was characterized by lake water which had a lower pH and salinity than that of the lacustrine deposit near Harney Lake.

Chalk Hills Formation, Idaho

The Chalk Hills Formation is about 100 m thick and consists chiefly of mudstone, siltstone, sandstone, diatomite, and numerous relatively thin tephra beds. The formation is chiefly lacustrine and was deposited along the southwestern margin of the western Snake River Plain, an intermontane rift basin that received several thousand meters of volcanic and sedimentary deposits in Miocene and later time. The Chalk Hills Formation commonly dips about 3-10 degrees northeastward and is cut by numerous northwest-trending faults. Throughout most of the outcrop belt, the tephra beds are unaltered or altered to smectite, but south of Oreana, Idaho, the tephra is altered mainly to zeolites with or without smectite and opal-CT (Sheppard, 1991).

Most of the tephra in the formation are silicic and vitric, and this tephra is the most conspicuous and continuous strata. Fresh silicic tephra is gray, fine to medium grained, friable, and easily disaggregated with the fingers. Altered silicic tephra is white, yellow, or light brown, relatively hard, and dull or earthy. Basaltic tephra (table 1) occurs only in the upper part of the formation, is dark gray to black and coarse grained, and generally shows normal graded bedding. Altered basaltic tephra is yellow, orange, or brown, and relatively soft (fig. 3). Fission-track dating of the silicic tephra indicated ages of about 8.5-5.5 Ma (Smith and others, 1982).

The zeolites and coexisting authigenic silicate minerals in the Chalk Hills Formation formed during diagenesis by hydrolysis and dissolution of volcanic glass by pore water that was trapped in the tephra during and after lacustrine sedimentation. Where the tephra is still unaltered, the original lake water probably was fresh. The zeolitic sediments probably coincide with a part of the ancient lake that had a low to moderate salinity (about 300-3000 mg/L) and a pH of 7-9 (Sheppard, 1991).

Unnamed Miocene Volcaniclastic Rocks near Harney Lake, Oregon

The volcaniclastic rocks near Harney Lake are part of the now abandoned Danforth Formation of Piper and others (1939), which also included interstratified silicic ash-flow tuffs and local basalt flows. Walker (1979) abandoned the Danforth Formation and formally named three regionally extensive ash-flow tuffs (from bottom to top): the Devine Canyon, Prater Creek, and Rattlesnake Ash-flow Tuffs. The interstratified volcaniclastic sedimentary rocks and the basalt flows still remain unnamed. Volcaniclastic rocks near Harney Lake occur between the Devine Canyon and Rattlesnake Ash-flow Tuffs and include a local nonwelded facies of the Prater Creek Ash-flow Tuff. An age of 9.3-6.5 Ma for these chiefly lacustrine rocks is constrained by the dated Devine Canyon and Rattlesnake Ash-flow Tuffs (Walker, 1979).

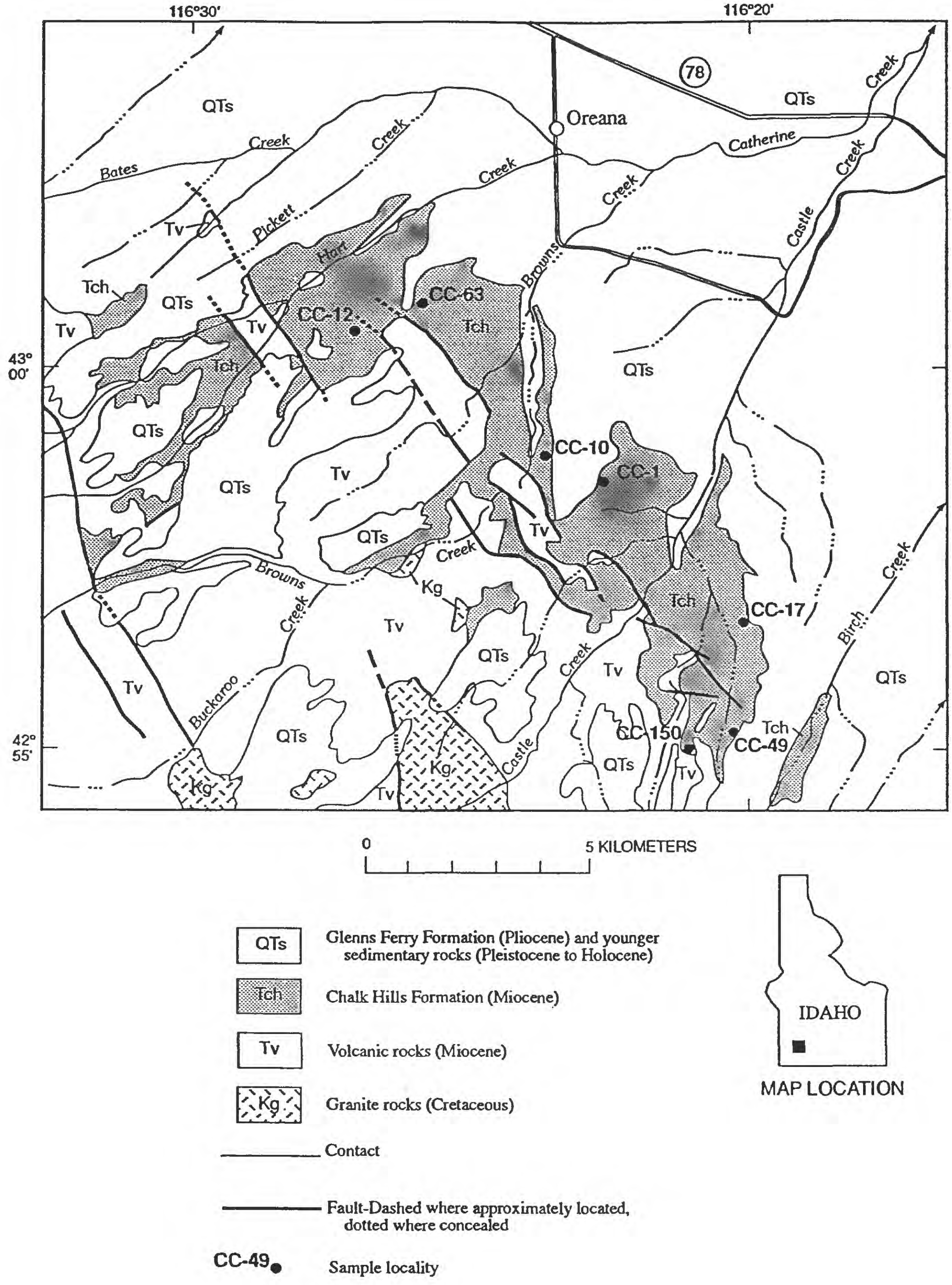

Figure 1. Generalized geologic map showing sample localities in the Chalk Hills Formation south of Oreana, Owyhee County, Idaho; modified from Sheppard (1991). Mineralogic composition of samples, as estimated from X-ray diffractometer patterns, is given in table 3.

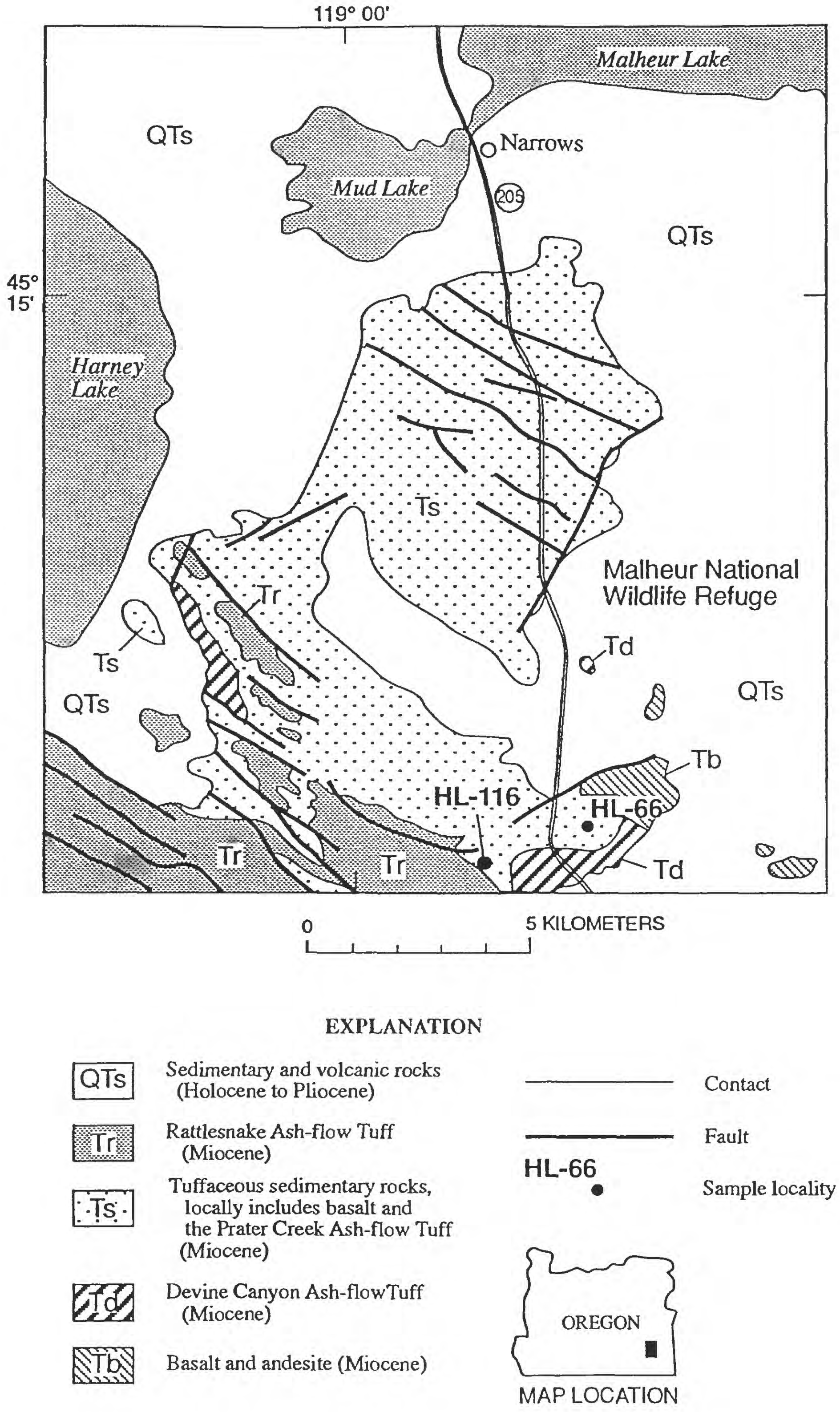

Figure 2. Generalized geologic map showing sample localities in unnamed Miocene lacustrine rocks near Harney Lake, Harney County, Oregon; modified from Sheppard (1994). Mineralogic composition of samples, as estimated from X-ray diffractometer patterns, is given in table 3.

Table 1. Chemical analysis of basaltic glass from tephra in the Chalk Hills Formation near Oreana, southwestern Idaho.

[Sample CC-150C collected between Castle Creek and Birch Creek, SE1/4NW1/4 sec. 9, T. 6 S., R. 1 E. A, average of 11 electron microprobe analyses by Isabelle K. Brownfield, H_2O calculated by difference; B, analysis calculated anhydrous and normalized to 100 percent]

	A	B
SiO_2	46.81	47.99
Al_2O_3	14.04	14.40
FeO	13.11	13.44
MgO	6.63	6.80
CaO	10.24	10.50
Na_2O	2.61	2.68
K_2O	0.61	0.63
TiO_2	2.70	2.77
P_2O_5	0.61	0.62
MnO	0.17	0.17
H_2O	2.47	----
Total	100.00	100.00

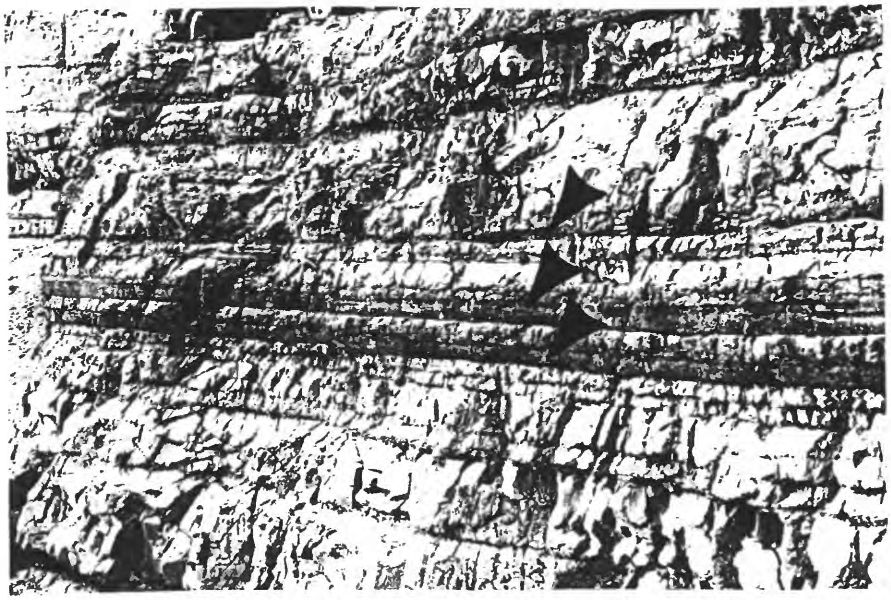

Figure 3. Natural exposure of the upper part of the Chalk Hills Formation, Idaho, showing thin beds of altered basaltic tephra (arrows) at sample locality CC-10, about 0.5 km east of Browns Creek. Geologic pick (28 cm long) shown for scale.

Figure 4. Scanning electron micrograph showing rhombohedra of chabazite that grew on spherulitic phillipsite (Ph); basaltic tephra near Harney Lake, Oregon.

The Miocene volcaniclastic rocks near Harney Lake have a maximum thickness of about 120 m but thin southward to about 5 m. The sedimentary rocks are chiefly lacustrine but are locally fluviatile, particularly near the southern margin of the depositional basin. The lithologies include mudstone, siltstone, sandstone, tephra, chert, limestone, and rare dolomite. In addition to the numerous discrete beds of tephra, most epiclastic rocks have a volcaniclastic component. The ash-flow tuffs and volcaniclastic sedimentary rocks commonly dip 8-20 degrees northeastward and are cut by numerous northwest-trending faults of slight (commonly 10-100 m) displacement.

Most of the tephra in the Miocene lacustrine rocks east of Harney Lake originally was vitric and silicic, and most show some alteration. Relatively unaltered silicic tephra is light gray and friable, and the vitric material has a characteristic vitreous luster. Altered tephra generally is zeolitic, resistant, and commonly ledge forming. Zeolitic silicic tephra is white, light gray, yellow, orange, brown, or green, relatively hard, and dull or earthy.

Basaltic tephra is present in a 12-m interval beneath a basalt flow (table 2) in the upper part of the Miocene lacustrine rocks southeast of Harney Lake. The tephra is brown to dark gray, coarse grained, poorly sorted, and poorly indurated. The tephra consists almost entirely of angular clasts of vesicular, glassy basalt that are 0.5-8 mm long. Most of the clasts are altered to smectite, zeolites, and calcite.

The zeolites and coexisting authigenic silicate minerals in the silicic volcaniclastic rocks undoubtedly formed during diagenesis by hydrolysis and dissolution of silicic glass by interstitial water (Sheppard, 1994). The pattern of alteration and the lateral gradation of almost unaltered (fresh) glass to an assemblage of smectite, opal-CT, zeolites, and (or) potassium feldspar strongly indicated that the interstitial water causing the alteration was the alkaline and saline water trapped in the tephra during lacustrine deposition and that the lake water was laterally chemically zoned, being fresh or freshest in the southern part of the area where unaltered silicic glass is most abundant. Examination of ostracodes suggested original lake water that had a pH as high as 9.4-11.0 and total dissolved solids as high as 15-100 g/L.

MATERIALS AND METHODS

Following detailed investigations of zeolite-rich silicic tuffs in the Chalk Hills Formation of southwestern Idaho (Sheppard, 1991) and an unnamed volcaniclastic unit east of Harney Lake, southeastern Oregon (Sheppard, 1994), about 50 samples of basaltic tephra (both relatively fresh and altered) were collected in 1995. The beds of basaltic tephra are relatively thin (about 2-160 cm thick), but most are 2-10 cm thick.

The mineralogy of bulk samples was determined by X-ray diffraction analysis. Samples were first ground to a powder and then back packed in aluminum sample holders, exposed to copper radiation, and scanned at 2° 2θ per minute over a range of 2°-40° 2θ. Relative abundances of the minerals were visually estimated from the diffractometer patterns following the procedure outlined by Sheppard and Gude (1968, p. 2-3). Estimates are probably less reliable for samples containing glass or opal-CT because these materials yield rather poor X-ray records. The clay mineralogy was determined by standard techniques on the less than 2-µm fraction of the altered tephra that was sedimented on glass slides.

Textures and paragenetic relationships of the diagenetic minerals were examined in thin sections and immersion oil mounts by transmitted-light microscopy and by scanning electron microscopy of freshly broken fragments. Samples to be studied by scanning electron microscopy were coated with carbon and then recoated with a film of gold (about 300 Å thick) just prior to examination.

The chemical composition of bulk samples was determined by standard X-ray fluorescence analysis. The H_2O content was determined by weight loss on ignition at 925°C. A semiquantitative energy-dispersive X-ray unit, attached to the scanning electron

Table 2. Chemical analysis of basalt lava flow from an unnamed Miocene lacustrine deposit near Harney Lake, southeastern Oregon.

[Sample HL-66-13 collected from Saddle Butte, NW1/4NW1/4 sec. 18, T. 28 S., R. 31 E. X-ray fluoresence analysis by ACTLABS, Inc.; H_2O determined by weight loss on ignition. A, bulk analysis; B, analysis calculated anhydrous and normalized to 100 percent]

	A	B
SiO_2	46.08	47.93
Al_2O_3	15.9	16.53
Fe_2O_3	11.62	12.08
MgO	8.48	8.82
CaO	9.15	9.52
Na_2O	2.36	2.45
K_2O	0.74	0.77
TiO_2	1.37	1.42
P_2O_5	0.28	0.29
MnO	0.18	0.19
H_2O	4.68	----
Total	100.84	100.00

microscope, was used to determine the Si:Al ratios of selected zeolites. The chemical compositions of basaltic glass shards, smectite, and zeolites were determined with a JEOL (model JXA-8900) electron microprobe on polished thin sections that had been coated with carbon.

RESULTS

Diagenetic Petrology of the Basaltic Tephra

The mineralogy of the altered basaltic tephra was determined mainly by study of X-ray diffractometer powder patterns of bulk samples (table 3), supplemented by thin section study and scanning electron microscopy. Thin section study and scanning electron microscopy were especially useful for determining the age relationships of the authigenic minerals, but these techniques were not used until the mineralogy was determined by X-ray methods.

Basaltic tephra consisting entirely of unaltered vitric material was not recognized in either study area, although some tephra consists of about 90 percent glass. Most tephra lacks glass or consists of relict glass and variable amounts of authigenic smectite, zeolites, and opal-CT. The zeolite content ranges from a trace to 30 percent, and the smectite content is 10-70 percent. Relict glass commonly coexists with authigenic smectite, but glass rarely coexists with smectite + zeolites. Heulandite is the common authigenic zeolite in tephra from the Chalk Hills Formation, but phillipsite is common in tephra near Harney Lake. Minor to trace amounts of chabazite are especially common in basaltic tephra near Harney Lake. Trace amounts of erionite rarely coexist with the other zeolites in tephra from both areas. Trace to minor amounts of analcime were identified by X-ray diffraction only in the tephra near Harney Lake, but the analcime rarely was recognized in thin sections.

The basaltic tephra consists chiefly of angular, vesicular glass (or pseudomorphs of glass) and generally less than two percent angular crystal and rock fragments. Plagioclase (An_{60-70}) is the chief crystal fragment recognized, and basalt is the main rock fragment. Locally, the basaltic tephra contains as much as 30 percent detrital grains, including plagioclase, quartz, biotite, muscovite, epidote, and hornblende. Diatoms are present locally in the basaltic tephra from the Chalk Hills Formation. The basaltic glass generally has a marginal alteration, about 5 µm thick, of smectite. In completely altered tephra, the smectite forms pseudomorphs after the vitric material. Zeolite occurs either as a cement that grew on the smectite or as a filling of vesicles in the vitroclastic material.

Diagenetic Mineralogy

Analcime

Analcime is a relatively rare zeolite in the basaltic tephra and was identified only in the tephra near Harney Lake (table 3) where it commonly is present in only trace amounts. The analcime is present as subhedral trapezohedra that are 40-440 µm in size.

Chabazite

Although chabazite was recognized from both areas, it is most common in tephra near Harney Lake where most samples contain only a trace. In the Chalk Hills Formation, it coexists with heulandite, but near Harney Lake, it coexists with phillipsite. Chabazite occurs as nearly cubic rhombohedra that are 3-60 µm in size (fig. 4). Electron microprobe analyses of chabazite near Harney Lake (table 4) showed that the Si:Al ratio is about 2.0-2.3 and that Ca is the major cation. Energy-dispersive X-ray analyses indicated that some chabazites in altered basaltic tephra near Harney Lake have Si:Al ratios as high as about 2.7.

Table 3. Mineralogic composition of basaltic tephra from southwestern Idaho and southeastern Oregon, as estimated from X-ray diffractometer patterns of bulk samples

[X-ray analysis results given in parts per 10. Leaders (--), looked for but not found; Tr, trace. Other is chiefly opal-CT; samples CC-12-5C, CC-12-5D, and CC-12-5F contain 1 part detrital quartz; sample CC-17Y contains 3 parts apatite; sample CC-150D contains a trace of detrital quartz]

Sample No.	Thickness of tephra, in centimeters	Glass	Smectite	Phillipsite	Chabazite	Heulandite	Erionite	Analcime	Plagioclase	Calcite	Gypsum	Other
Locality CC-1: near Castle Creek; NE1/4SE1/4 sec. 19, T. 5 S., R. 1 E.; Owyhee County, Idaho												
CC-1-XXA	35	--	5	--	1	3	--	--	1	--	--	--
CC-1-XXB	35	--	5	--	--	3	--	--	1	--	1	Tr
Locality CC-10: near Browns Creek; NE1/4NE1/4 sec. 24, T. 5 S., R. 1 W.; Owyhee County, Idaho												
CC-10-3D	6	--	7	--	--	2	Tr	--	1	--	--	--
CC-10-3E	10	--	5	--	--	3	--	--	2	--	Tr	--
CC-10-3J	6	--	6	--	--	3	Tr	--	1	--	--	Tr
CC-10-3K	7	--	7	--	--	2	--	--	1	--	Tr	--
CC-10-3L	8	--	7	--	--	2	Tr	--	1	--	--	--
CC-10-3M	10	--	7	--	--	2	--	--	1	--	--	--
CC-10-3N	3	--	6	--	--	2	--	--	2	--	--	Tr
CC-10-4E	3	--	7	--	--	2	--	--	1	--	--	--
CC-10-4F	8	--	6	--	--	3	--	--	1	--	--	Tr
Locality CC-12: near Hart Creek; NE1/4NE1/4 sec. 9, T. 5 S., R. 1 W.; Owyhee County, Idaho												
CC-12-5A	4	7	2	--	--	--	--	--	1	--	--	Tr
CC-12-5B	2	8	2	--	--	--	--	--	Tr	--	--	--
CC-12-5C	22	5	2	--	--	--	--	--	2	--	--	1
CC-12-5D	6	4	3	--	--	--	--	--	2	--	--	1
CC-12-5E	6	9	1	--	--	--	--	--	Tr	--	--	Tr
CC-12-5F	5	6	1	--	--	--	--	--	2	--	--	1
CC-12-5G	12	8	2	--	--	--	--	--	Tr	--	--	Tr
Locality CC-17: near Castle Creek; NE1/4SE/4 sec. 33, T. 5 S., R. 1 E.;' Owyhee County, Idaho												
CC-17-3A	6	6	4	--	--	--	--	--	1	--	--	--
CC-17Y	3	3	3	--	--	--	--	--	1	--	--	3
CC-17X	4	6	2	--	--	--	--	--	1	--	1	--
Locality CC-49: between Castle Creek and Birch Creek; NE1/4NE1/4 sec. 9, T. 6 S.,R. 1 E.; Owyhee County Idaho												
CC-49A	10	5	5	--	--	Tr	--	--	Tr	--	--	--

Sample No.	Thickness of tephra, in centimeters	Glass	Smectite	Phillipsite	Chabazite	Heulandite	Erionite	Analcime	Plagioclase	Calcite	Gypsum	Other
Locality CC-63: near Hart Creek; SE1/4SE1/4 sec. 3, T. 5 S., R. 1 W.; Owyhee County, Idaho												
CC-63C	4	5	4	--	--	--	--	--	1	--	--	--
CC-63X	3	3	2	--	--	--	--	--	1	--	4	--
CC-63Z	13	3	2	--	--	--	--	--	1	--	4	--
Locality CC-150: between Castle Creek and Birch Creek; SE1/4NW1/4 sec. 9, T. 6 S., R. 1. E.; Owyhee County, Idaho												
CC-150A	20	6	2	--	--	--	--	--	2	--	--	--
CC-150B	20	7	2	--	--	--	--	--	1	--	--	--
CC-150C	10	9	1	--	--	--	--	--	Tr	--	--	--
CC-150D	8	6	2	--	--	--	--	--	2	--	--	Tr
Locality HL-66: Saddle Butte; NW1/4NW1/4 sec. 18, T. 28 S., R. 31 E., Harney County, Oregon												
HL-66-10B	6	--	4	2	Tr	--	--	Tr	1	3	--	--
HL-66-10E	3	--	5	1	1	--	--	--	Tr	3	--	--
HL-66-10F	7	--	5	3	Tr	--	--	Tr	Tr	2	--	--
HL-66-10G	7	--	6	2	Tr	--	--	Tr	Tr	2	--	--
HL-66-10H	3	--	4	3	Tr	--	--	Tr	1	2	--	--
HL-66-10I	5	--	7	2	Tr	--	--	--	Tr	1	--	--
HL-66-12E	160	3	5	Tr	--	--	--	--	2	Tr	--	--
HL-66-12F	160	2	5	1	Tr	--	Tr	--	2	--	--	--
Locality HL-116: near Saddle Butte; NE1/4SE1/4 sec. 14, T. 28 S., R. 30 E.; Harney County, Oregon												
HL-116A	--	--	5	--	Tr	--	--	2	Tr	3	--	--
HL-116B	--	--	6	Tr	Tr	--	--	1	2	1	--	--

Table 4. Chemical analyses of chabazite from basaltic tephra in unnamed Miocene lacustrine deposit near Harney Lake, southeastern Oregon.

[Electron microprobe analyses by Isabelle K. Brownfield. H_2O calculated by difference. Unit-cell contents based on 24 oxygen atoms]

Sample	1	2
Chemical analyses		
SiO_2	50.33	55.90
Al_2O_3	21.52	20.41
Fe_2O_3	0.53	0.15
MgO	0.17	0.03
CaO	9.06	8.94
BaO	0.28	0.24
Na_2O	0.46	0.61
K_2O	4.08	3.37
H_2O	13.57	10.35
Total	100.00	100.00
Unit-cell contents		
Si	7.92	8.36
Al	3.99	3.60
Fe^{3+}	0.06	0.02
Mg	0.04	0.01
Ca	1.53	1.43
Ba	0.02	0.01
Na	0.14	0.18
K	0.82	0.64
H_2O	7.12	5.16
$Si:(Al+Fe^{3+})$	1.96	2.31

Sample locations

1. Sample HL-66-10B; near Saddle Butte; NW1/4NW1/4 sec. 18, T. 28 S., R. 31 E.
2. Sample HL-66-10F; near Saddle Butte; NW1/4NW1/4 sec. 18, T. 28 S., R. 31 E.

Erionite

Erionite is relatively rare in basaltic tephra from both areas, and it occurs only in trace amounts. Erionite is present as acicular or fibrous crystals that are 2-80 µm long. The length:width ratio is about 20-70. Scanning electron microscopy shows that some well-formed hexagonal prisms are teminated by pinacoidal faces (fig. 5). Erionite coexists with all other zeolites in the tephra. Chemical analyses could not be performed by electron microprobe because the crystals are too thin. Energy-dispersive X-ray analyses, however, indicate that the Si:Al ratio is about 3.5-3.7, and Ca and K are the major cations.

Heulandite

Heulandite was identified only in basaltic tephra from the Chalk Hills Formation where it coexists with erionite and rarely with chabazite. The heulandite occurs as well-formed platy, tabular, or blocky crystals that are about 8-375 µm long (fig. 6) and length fast. Most heulandite occurs as cement that coats the originally vitric particles with a single layer of crystals growing perpendicular to the particles' surfaces. Electron microprobe analyses showed that the Si:Al ratio is about 3.7-3.9 (table 5) and that Ca is the major cation. Additional energy-dispersive X-ray analyses indicated Si:Al ratios of about 3.2-3.6.

Thermal stability has been used as a simple way to distinguish clinoptilolite from heulandite; both are members of the heulandite structural group. Mumpton (1960) suggested overnight heating in an oven at 450 °C, followed by examination by X-ray diffraction, as a mean to differentiate the zeolites. Under these conditions, Mumpton found that the X-ray diffractometer pattern for clinoptilolite was essentially unaffected but the pattern for heulandite was destroyed. Later workers showed that the thermal behavior was complex and was affected by the Si:Al ratio and the content of divalent cations in the zeolite. Thus, Allietti (1972) proposed that the overnight heating test of Mumpton be increased to 550 °C. Four samples of zeolite-bearing basaltic tephra from the Chalk Hills Formation were heated in an oven at 550 °C for 15 hours. After cooling to room temperature, the samples were examined by X-ray diffraction. The diffractometer pattern for all samples showed only an amorphous record and indicated that the zeolite was heulandite rather than clinoptilolite.

Phillipsite

Phillipsite was identified only in basaltic tephra near Harney Lake where it is the most common zeolite and coexists with analcime, chabazite, and erionite. Except for a rare occurrence as individual acicular crystals that are 2-25 µm long, phillipsite occurs as length-slow spherulites or partial spherulites (fig. 7) that are 85-360 µm in diameter. The spherulitic phillipsite cements the basaltic vitroclasts and fills vesicles in them. Many of the spherulites have mutually interferred with one another during their growth, but where a spherulite projects into a still-unfilled intergranular void, crystal terminations show the typical twinned habit (fig. 8). Most spherulites show an optical zoning. Electron microprobe analyses show that the Si:Al ratio is about 2.2-2.3 and that Ca and K are the major cations (table 6). Additional energy-dispersive analyses indicate an even wider range of Si:Al ratios of about 2.0-2.5.

Opal-CT

Opal-CT was recognized only in the tephra from the Chalk Hills Formation and only in trace amounts. Scanning electron microscopy shows that opal-CT occurs chiefly as small (2-20 µm in diameter) lepispheres (fig. 9). X-ray diffractometer patterns show a major broad peak near 4.07 Å.

Smectite

Smectite is a ubiquitous authigenic mineral in the basaltic tephra from both areas, even in chiefly unaltered tephra. The content ranges from 10 to 70 percent but is generally

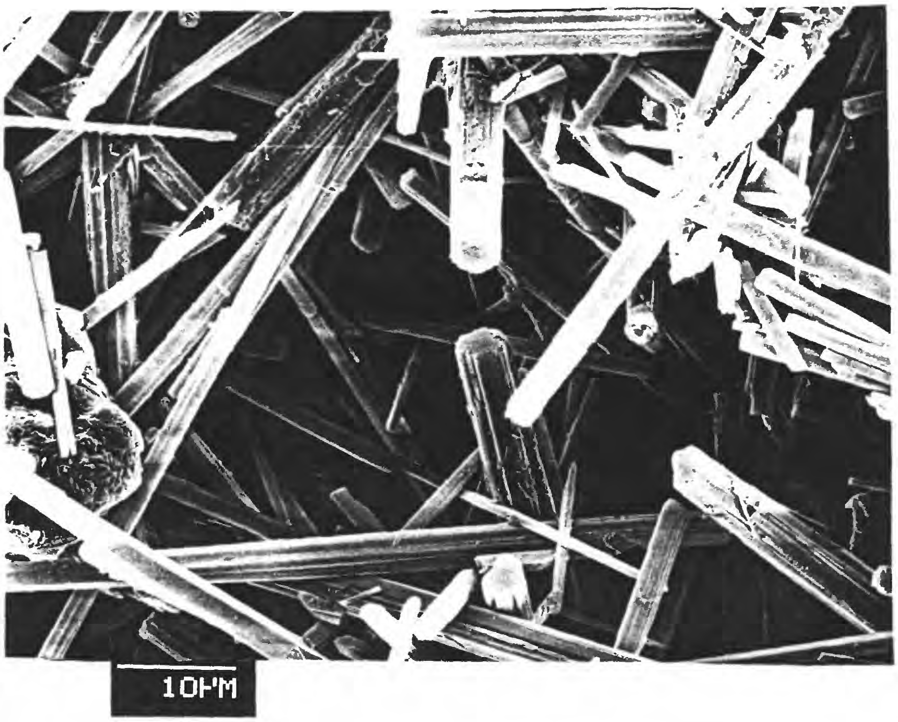

Figure 5. Scanning electron micrograph showing well-formed hexagonal prisms of erionite that are terminated by pinacoidal faces; basaltic tephra from the Chalk Hills Formation, Idaho.

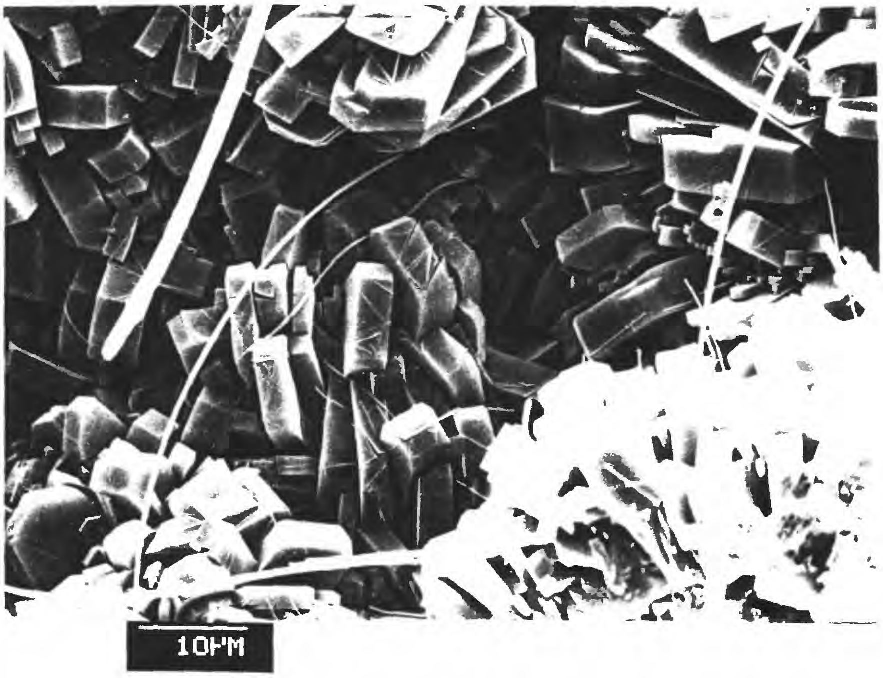

Figure 6. Scanning electron micrograph showing fibers of erionite that grew on tabular to blocky heulandite; basaltic tephra from the Chalk Hils Formation, Idaho.

Table 5. Chemical analyses of heulandite from basaltic tephra in the Chalk Hills Formation near Oreana, southwestern Idaho.

[Electron microprobe analyses by Isabelle K. Brownfield. H_2O calculated by difference. Unit-cell contents based on 72 oxygen atoms]

Sample	1	2
Chemical analyses		
SiO_2	66.70	64.73
Al_2O_3	14.36	14.62
Fe_2O_3	0.27	0.24
MgO	1.06	1.47
CaO	3.41	3.91
BaO	0.09	0.18
Na_2O	1.55	0.89
K_2O	0.95	0.36
H_2O	11.61	13.60
Total	100.00	100.00
Unit-cell contents		
Si	28.85	28.57
Al	7.32	7.60
Fe^{3+}	0.09	0.08
Mg	0.68	0.96
Ca	1.58	1.85
Ba	0.02	0.03
Na	1.30	0.76
K	0.52	0.20
H_2O	16.74	20.01
$Si:(Al+Fe^{3+})$	3.89	3.72

Sample locations

1. Sample CC-1-XXA (average of two analyses); near Castle Creek; NE1/4SE1/4 sec. 19, T. 5 S., R. 1 E.
2. Sample CC-10-3D; near Browns Creek; NE1/4NE1/4 sec. 24, T. 5 S., R. 1 W.

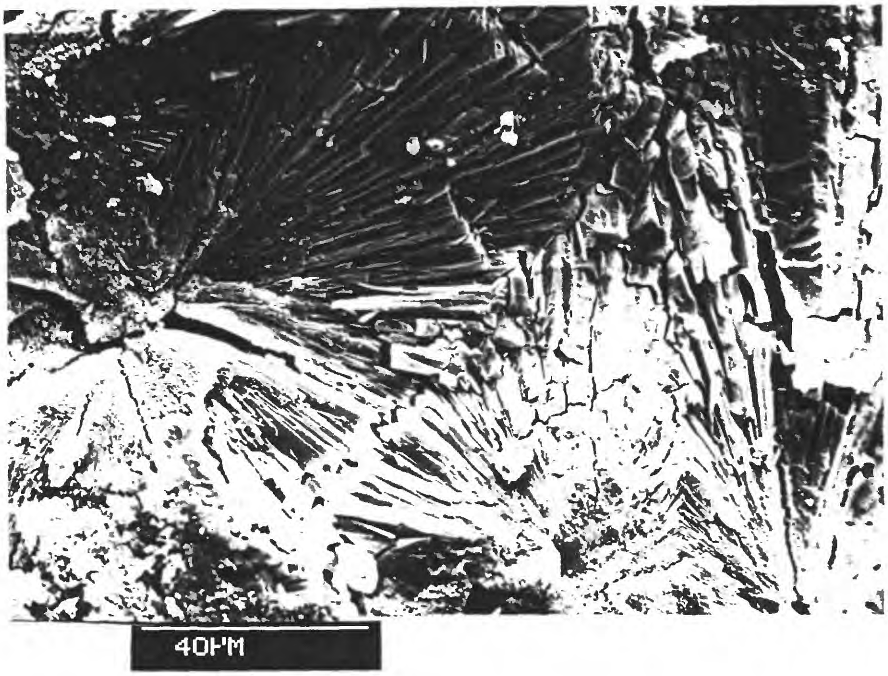

Figure 7. Scanning electron micrograph showing growth of mutually interfering spherulites of phillipsite; basaltic tephra near Harney Lake, Oregon.

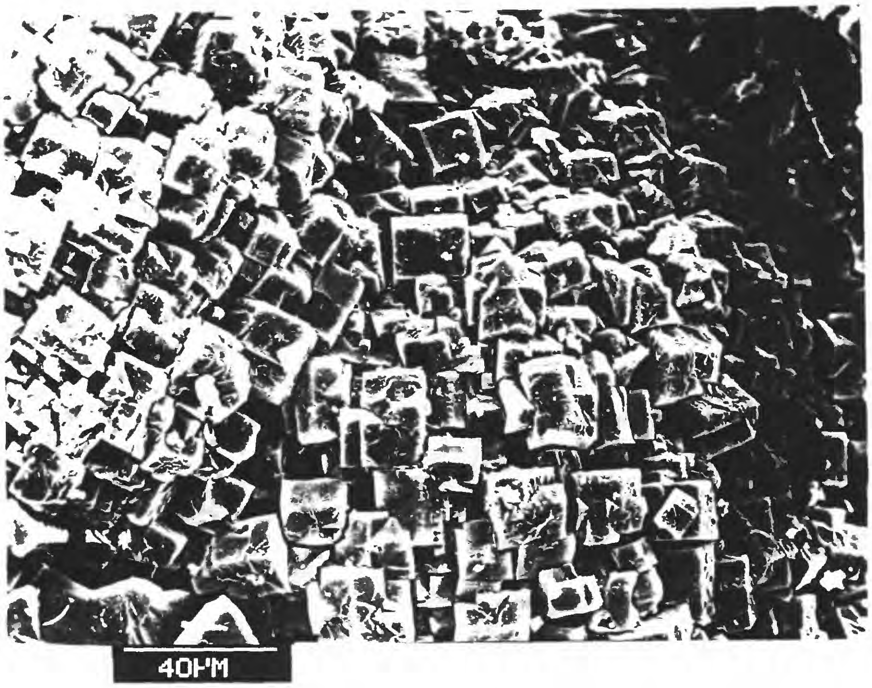

Figure 8. Scanning electron micrograph showing twinned crystal terminations on a spherulite of phillipsite; basaltic tephra near Harney Lake, Oregon.

Table 6. Chemical analyses of phillipsite from basaltic tephra in unnamed Miocene lacustrine deposit near Harney Lake, southeastern Oregon.

[Electron microprobe analyses by Isabelle K. Brownfield. H_2O calculated by difference. Unit-cell contents based on 32 oxygen atoms]

Sample	1	2
Chemical analyses		
SiO_2	49.96	51.00
Al_2O_3	19.18	19.05
Fe_2O_3	0.08	0.19
MgO	0.04	0.08
CaO	5.49	6.70
BaO	0.15	0.19
Na_2O	1.74	0.82
K_2O	5.17	3.28
H_2O	18.19	18.69
Total	100.00	100.00
Unit-cell contents		
Si	11.03	11.17
Al	4.99	4.91
Fe^{3+}	0.01	0.03
Mg	0.01	0.03
Ca	1.30	1.57
Ba	0.01	0.02
Na	0.74	0.35
K	1.46	0.92
H_2O	13.39	13.64
Si:(Al+Fe^{3+})	2.21	2.26

Sample locations

1. Sample HL-66-10B (average of four analyses); near Saddle Butte; NW1/4NW1/4 sec. 18, T. 28 S., R. 31 E.
2. Sample HL-66-10F; near Saddle Butte; NW1/4NW1/4 Sec, 18, T. 28 S., R. 31 E.

Figure 9. Scanning electron micrograph showing a lepisphere of opal-CT that grew on fibers of erionite; basaltic tephra from the Chalk Hills Formation, Idaho.

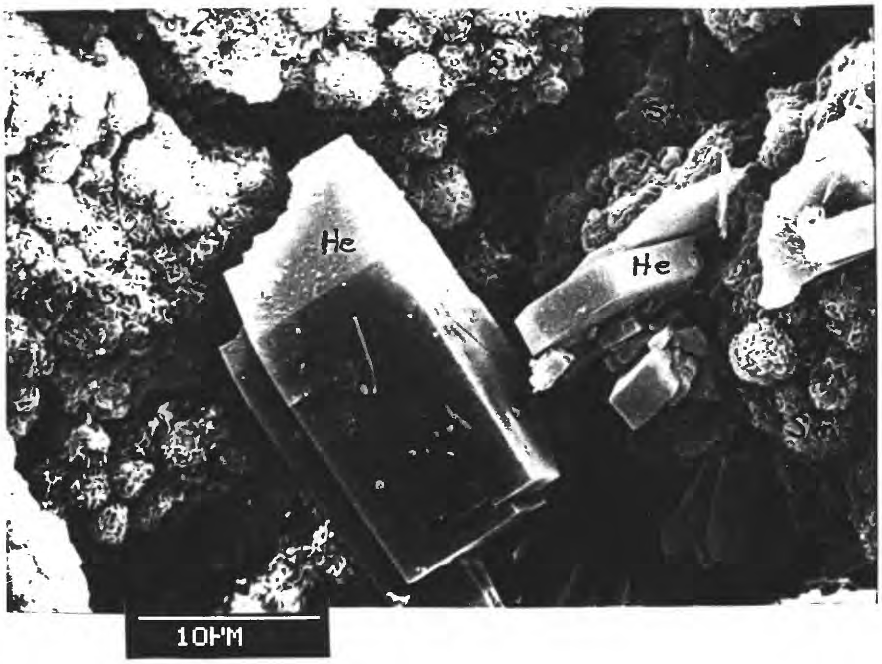

Figure 10. Scanning electron micrograph showing tabular heulandite (He) that grew on a mat of crenulated smectite (Sm); basaltic tephra from the Chalk Hills Formation, Idaho.

20-50 percent. Where smectite is the major constituent of the altered tephra, a punky "popcorn" coating is typical of weathered natural exposures. Scanning electron micrographs of smectite show the characteristic crenulated to flaky morphology (fig. 10). Smectite is yellow to reddish brown in transmitted light. The smectite has a first-order basal spacing of about 13.0-14.9 Å for oriented, air-dried samples and of 17.0-17.2 Å for oriented, glycolated samples. The (060) reflection is about 1.52-1.53 Å. A chemical analysis of smectite from altered basaltic tephra in the Chalk Hills Formation (table 7) shows that the smectite is iron and magnesium rich. On the basis of the position of the (060) reflection and the chemical composition, this smectite can be termed a magnesium-rich nontronite. Except for the relatively high magnesium and potassium contents, the composition of this smectite is similar to nontronites given by Weaver and Pollard (1973, p. 76).

Calcite and Gypsum

Calcite makes up as much as 30 percent of basaltic tephra near Harney Lake, and gypsum makes up as much as 40 percent of tephra in the Chalk Hills Formation. Both minerals were the last to form in the tephra, and they locally have replaced all earlier authigenic minerals.

Paragenesis

The relative age relationships of diagenetic minerals in basaltic tephra from both areas were determined by the sequence of filling of intergranular voids and in vesicles of the vitroclastic grains and by replacement relationships. The minerals in the interior of a void or vesicle presumably crystallized later than the mineral(s) nearer the periphery. The following sequences of crystallization were determined on the basis of thin section and scanning electron microscopy examination (the earliest mineral is listed first):

Smectite---gypsum
Smectite---heulandite
Smectite---heulandite---erionite
Smectite---chabazite---heulandite---erionite
Smectite---phillipsite---chabazite---calcite
Smectite---heulandite---erionite---gypsum
Smectite---heulandite---erionite---opal-CT
Smectite---chabazite(?)---analcime---calcite

The paragenetic sequences show that smectite consistently crystallized prior to any of the zeolites. Heulandite, chabazite, and phillipsite are early zeolites, and erionite and analcime are late zeolites. Where phillipsite and chabazite coexist, chabazite consistently postdated phillipsite. Calcite and gypsum seem to have been the latest minerals to form in the tephra.

Chemical Changes During Diagenetic Alteration

Chemical analyses of bulk samples of altered basaltic tephra from the Chalk Hills Formation are given in table 8, along with an analysis of a relatively unaltered basaltic tephra. Relative to the anhydrous composition of unaltered basaltic glass, smectite- and zeolite (heulandite)-bearing tephra show consistent gains of K_2O and SiO_2 and losses of CaO and MgO. There also appears to be locally minor losses of Na_2O and Fe_2O_3 and locally a minor gain of TiO_2. Thus, the most obvious chemical changes during the alteration of basaltic glass to an assemblage of smectite and zeolites are gains of potassium, silica, and water and losses of alkaline earth elements. Zeolite-bearing tephra, in particular, shows large gains of potassium and water and large losses of calcium and magnesium.

Table 7. Chemical analysis of smectite from basaltic tephra in the Chalk Hills Formation near Oreana, southwestern Idaho.

[Sample CC-10-3D collected near Browns Creek, NE1/4NE1/4 sec. 24, T. 5 S., R. 1 W. Average of three electron microprobe analyses by Isabelle K. Brownfield. H_2O calculated by difference]

SiO_2	40.60
Al_2O_3	7.17
Fe_2O_3	19.09
MgO	6.91
CaO	0.90
BaO	0.12
SrO	0.00
Na_2O	0.77
K_20	2.21
H_20	22.23
Total	100.00

Table 8. Chemical analyses of fresh and altered basaltic tephra from the Chalk Hills Formation near Oreana, southwestern Idaho.

[X-ray fluorescence analyses by J.S. Mee and ACTLABS, Inc.; H_2O determined by weight loss on ignition. A, bulk analysis; B, analysis calculated anhydrous and normalized to 100 percent]

	1		2		3	
	A	B	A	B	A	B
SiO_2	47.49	49.04	50.8	53.94	51.6	59.79
Al_2O_3	14.29	14.76	13.7	14.55	11.9	13.79
Fe_2O_3	14.0	14.46	12.8	13.59	11.6	13.44
MgO	5.12	5.29	2.82	2.99	1.73	2.01
CaO	9.31	9.61	6.34	6.73	3.82	4.43
Na_2O	2.35	2.43	2.26	2.40	1.43	1.65
K_2O	0.67	0.69	1.01	1.07	1.42	1.64
TiO_2	2.7	2.79	3.19	3.39	2.45	2.83
P_2O_5	0.7	0.72	0.63	0.67	0.17	0.20
MnO	0.2	0.21	0.63	0.67	0.19	0.22
H_2O	1.22	----	5.33	----	12.7	----
Total	98.05	100.00	99.51	100.00	99.01	100.00

Sample locations

1. Sample CC-150B (chiefly unaltered glass); between Castle Creek and Birch Creek; SE1/4NW1/4 sec. 9, T. 6 S., R. 1 E.
2. Sample CC-63C (unaltered glass and smectite); near Hart Creek; SE1/4SE1/4 sec. 3, T. 5 S., R. 1 W.
3. Sample CC-10-3E (chiefly smectite and heulandite); near Browns Creek; NE1/4NE1/4 sec. 24, T. 5 S., R. 1 W.

DISCUSSION

Compared to diagenetically altered silicic tephra in the same depositional (and presumably same chemical) environment, the altered basaltic tephra is characterized by a relatively silica-poor mineral assemblage. Table 9 gives a comparison of characteristics for altered basaltic and rhyolitic tephra from the two deposits that were studied. An assemblage of smectite+heulandite is common for basaltic tephra in the Chalk Hills Formation, but smectite+phillipsite is common for the unnamed deposit near Harney Lake. Altered basaltic tephra in the Chalk Hills Formation also may contain minor chabazite, trace amounts of opal, and rare trace amounts of erionite (table 3). Altered basaltic tephra in the unnamed deposit near Harney Lake also may contain trace to minor amounts of chabazite and trace amounts of analcime or erionite. Smectite (nontronite) is generally more abundant than zeolite.

The diagenetic mineral assemblage in the associated rhyolitic tephra is commonly characterized by smectite+clinoptilolite+opal-CT in the Chalk Hills Formation (Sheppard, 1991) and by smectite+clinoptilolite+erionite+opal-CT in the unnamed deposit near Harney Lake (Sheppard, 1994). Altered rhyolitic tephra in the Chalk Hills Formation also may contain trace amounts of mordenite, rare phillipsite, and rare trace to minor amounts of erionite. Altered rhyolitic tephra in the unnamed deposit near Harney Lake also may contain trace to major amounts of chabazite, phillipsite, mordenite, and potassium feldspar and rarely trace to major amounts of analcime and quartz. Zeolites are commonly more abundant than smectite (montmorillonite) in the rhyolitic tephra.

Relative to basaltic tephra, the diagenetic alteration of rhyolitic tephra resulted in an overall more siliceous mineral assemblage, greater abundance of zeolites, and early formation of montmorillonite rather than nontronite. Thus, for tephra exposed to the same diagenetic fluids and proceses, the original composition of the tephra had a major influence on the genesis of the diagenetic mineral assemblage in the lacustrine deposits.

The original composition of the tephra also had a pronounced effect on the composition, particularly the Si:Al ratio, of individual diagenetic zeolite species. Although clinoptilolite and heulandite are members of the heulandite structural group, clinoptilolite was recognized only in the rhyolitic tephra, and heulandite was recognized only in the basaltic tephra. The clinoptilolite is generally alkali rich with Si:Al ratios of about 4.0-5.0 (Sheppard, 1991; 1994), and the heulandite is calcic with Si:Al ratios of about 3.2-3.9. Mordenite, a siliceous zeolite, was recognized only in rhyolitic tephra where it is alkali rich and has Si:Al ratios of about 4.6-5.2 (Sheppard, 1991). Chemical data were obtained only for chabazite in tephra from the unnamed lacustrine deposit near Harney Lake where the Si:Al ratio is about 3.5-4.0 in rhyolitic tephra (Sheppard, 1994) and about 2.0-2.7 in basaltic tephra. Ca is the major exchangeable cation in chabazite from basaltic tephra. Although the exchangeable cations were not determined for the rhyolitic tephra, data from other deposits indicate that both alkali-rich and alkaline earth-rich varieties of chabazite are known from rhyolitic tephra (Gude and Sheppard, 1978). Chemical data were obtained only for phillipsite from the unnamed lacustrine deposit near Harney Lake. Phillipsite in rhyolitic tephra is alkali-rich and has Si:Al ratios of about 3.2-3.5 (Sheppard, 1994), but phillipsite in basaltic tephra contains major Ca and K and has Si:Al ratios of about 2.0-2.5. Only energy-dispersive X-ray data are available for erionite from both kinds of tephra in both areas. Erionite in rhyolitic tephra is rich in Na and K and has Si:Al ratios of about 3.2-3.8, but erionite in basaltic tephra is rich in Ca and K and has Si:Al ratios of about 3.5-3.7. Analcime was recognized only in the tephra from the unnamed lacustrine deposit near Harney Lake but was not analyzed. Thus, in a general way, diagenetic zeolites in rhyolitic tephra are alkali rich and have relatively high Si:Al ratios, whereas those in basaltic tephra are calcic and have relatively low Si:Al ratios.

Even the chemical changes during diagenetic alteration of tephra seem influenced by the original composition of the tephra. As mentioned above, smectite- and zeolite-bearing

Table 9. Comparison of characteristics for altered basaltic and rhyolitic tephra.

Characteristic	**Basalt**	**Rhyolite**
Common thickness	2-10 cm	0.2-12.0 m
Color	Yellow or brown	White, gray, or green
Common grain size of vitroclastic material	Coarse	Fine
Induration	Poor	Good
Predominant authigenic mineral	Smectite	Zeolite
Presence of opal	Rare	Common
Smectite mineral	Nontronite	Montmorillonite
Zeolite content	Trace to 30 percent	Trace to 100 percent
Common zeolites	Heulandite, phillipsite, chabazite, analcime	Clinoptilolite, phillipsite, chabazite, mordenite, erionite, analcime
Si:Al ratio of zeolites	Low	High

basaltic tephra show consistent gains of Si and K and losses of Ca and Mg. Zeolitic alteration of rhyolitic tephra, however, shows consistent gains of Ca and Mg and losses of Si and K (Sheppard, 1991). Both varieties of tephra, of course, show large gains of H_2O.

Inasmuch as the lake water trapped during the deposition of the tephra was, at least partly, responsible for the diagenetic alteration of the basaltic tephra, differences in water chemistry would be expected to result in differences in the resultant diagenetic zeolites that crystallized. Experimental work by Mariner and Surdam (1970) indicated that the Si:Al ratio of zeolite is controlled by the Si:Al ratio of the solution from which the zeolite crystallized. Their experiments showed that the Si:Al ratio of the solution increases as the pH decreases. Thus, relatively siliceous zeolites, such as heulandite, are favored over aluminous zeolites, such as phillipsite and chabazite as the pH decreases. The lake water of the Chalk Hills Formation was characterized by a significantly lower pH than the water of the unnamed deposit near Harney Lake (Sheppard, 1991; 1994). The common heulandite in basaltic tephra of the Chalk Hills Formation versus the common phillipsite near Harney Lake probably was caused by the lower pH of the lake water where the Chalk Hills tephra was deposited.

ACKNOWLEDGMENTS

Grateful appreciation is expressed to Gary L. Skipp who provided the detailed characterization of the smectite in the altered basaltic tephra and to Isabelle K. Brownfield who performed electron microprobe analyses of glass, smectite, and zeolites in the basaltic tephra.

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