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Zeolite-bearing Cretaceous tuff in Beaverhead County, southwestern Montana

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ABSTRACT

Clinoptilolite and mordenite are constituents of a Cretaceous pyroclastic-flow unit locally more than 1,000 ft thick that crops out intermittently around the perimeter of an area of about 50 sq mi west and southwest of Dillon, Mont. These zeolite minerals are most abundant in the parts of the unit that are least deformed and metamorphosed. Thirty-nine selected samples of the tuff from throughout the exposed area were analyzed by X-ray diffractometer. These analyses suggest that the tuff exposed along the valley of Grasshopper Creek, 1-3 mi above its mouth, is especially noteworthy because it consists predominantly of clinoptilolite and commonly some mordenite. In this area, the zeolitic rock is tens to hundreds of feet thick and in its general appearance seems to be fairly uniform. The tuff in this and possibly other localities has potentially commercial importance for local use in agriculture and mine-waste cleanup.

INTRODUCTION

The zeolites clinoptilolite and mordenite are found in substantial though variable amounts in a tuffaceous rock unit that crops out southwest of Dillon, Mont. These minerals were identified by routine X-ray diffractometer analysis of samples collected during geologic mapping. R.A. Sheppard (oral commun., 1987) has noted that clinoptilolite was identified previously by D.B. Hawkins from a locality near Badger Pass (Sheppard, 1976, p. 75). Hawkins' locality is not precisely known but could be within the same tuff unit described here. These zeolite minerals serve to characterize the unit and distinguish it from a Tertiary tuff unit that locally overlies the zeolitic tuff and with which it has been confused in the past. The abundance of zeolites in certain samples indicates that parts of the unit are of commercial grade. This report is intended as a preliminary description of the tuff and its contained zeolites; it calls attention to their presence and general distribution so that interested parties may examine it further. No tests of its properties have been made. Such tests, along with more detailed sampling and mapping, will be necessary to determine if, indeed, any part of the tuff unit will have commercial use.

Zeolites are a group of minerals that are crystalline hydrous alumino-silicates of sodium, potassium, magnesium, calcium, and other less abundant elements. The alkali and alkaline earth elements, Si:Al ratios, and water are highly variable, resulting in more than 40 separate mineral species.

Zeolite minerals form naturally in a variety of geologic environments, most commonly in association with volcanic rocks. Some zeolite minerals form as handsome crystals and crystal aggregates in cavities and along fractures in lava flows, generally basalt, whereas other zeolites, including those that have been most used commercially, form as alteration products of vitroclastic material in tuffaceous rocks. As the fragments of volcanic glass, and to a lesser extent of pyrogenic crystals of feldspar, become altered by groundwater or saline, alkaline lake water, zeolites may form. Zeolitic tuffs that are least contaminated by non-zeolite minerals and have the greatest economic potential formed in saline, alkaline playa lakes (Sheppard and Gude, 1968). In addition, many zeolite minerals used commercially are man-made.

Zeolites have diverse uses in agriculture and industry (Mumpton, 1978). To the general public, the most well known use is cat-box filler (cat litter). In industry, they are used as filters, ion-exchange materials, gas adsorbers, and odor-controlling materials in a wide variety of applications. In agriculture, they are used as additives to feed for cattle and fowl, as absorbing material for animal waste, as fertilizers, and as soil amendments.

The zeolitic tuff described here has been quarried from a pit along Montana Highway 278 just east of Badger Ridge, but not for any use that depends on special properties of the contained zeolites, as such, although these properties probably contribute to its utility. This rock has been used mainly for road metal, for which purpose it is excellent because it does not washboard badly, does not produce significant dust, is not slippery when wet, and drains well. Many secondary roads in Beaverhead County have a top dressing of crushed rock from this quarry. The tuff has also been used locally for building stone and decorative rock. The zeolite content of the tuff in the quarry along highway 278 is probably not high enough for most commercial uses, but the same unit at other localities has a higher content of zeolite minerals and appears to be more uniform in mineral composition. Thus it may be suitable for a variety of uses. Most commercial zeolite deposits are in fluviatile and lacustrine deposits that are little contaminated by epiclastic detritus; few zeolitic pyroclastic-flow deposits, such as those described in this report, have been developed commercially because they tend to be more variable in mineral composition and lower in grade.

R.A. Sheppard and G.A. Desborough have graciously shared their knowledge of zeolites and have reviewed the manuscript. D.K. Allerton and David Wilson prepared the samples and the X-ray diffraction patterns.

GEOLOGIC SETTING

Cretaceous volcanic rocks, of which the zeolitic tuff is a part, occupy a small volcanic field, or perhaps the erosional remnant of a larger one, that underlies at least 50 sq mi west and southwest of Dillon, Mont., (fig. 1) (Ivy, 1989). An unknown additional amount of these deposits may be unconformably overlain by younger deposits in the area from Ermont Gulch northward to, and perhaps beyond, Rattlesnake Creek and eastward from the present exposure of the volcanic rocks. Furthermore, an unknown amount is covered by a thrust plate to the west. In the earliest large-scale geologic mapping in this area (Myers, 1952; Lowell, 1965), these rocks were interpreted to be of Tertiary age and were regarded as such until Snee and Sutter (1979) provided evidence that their age is Late Cretaceous on the basis of potassium-argon measurements. Since then, additional age determinations by the $^{40}Ar/^{39}Ar$ technique have refined the age of the upper part of the volcanic sequence and of associated intrusive rocks to a range of about 73-80 Ma (million years) (analyses by L.W. Snee in Ivy, 1989). On the basis of these measurements, therefore, the zeolitic tuff is older than about 80 Ma, but its precise age has not been determined.

The Cretaceous volcanic rocks comprise two distinctive and dissimilar units: a lower unit of zeolitic tuff and an upper unit chiefly of intermediate volcanic breccia, lava flows, and shallowly emplaced intrusive bodies. The tuff unit will be referred to in this report as "tuff of Grasshopper Creek," and the upper unit will be referred to as "volcanics of Cold Spring Creek," as they were by Ivy (1989) and Pearson (1988). Myers (1952) called the tuff of Grasshopper Creek merely "Tuff," and Lowell (1965) referred to it as "Early tuff," as did Thomas (1981).

The Cretaceous volcanic rocks overlie, in depositional contact, conglomerate and sandstone of the Upper Cretaceous Beaverhead Group at most places. At other places, they are in contact with Mississippian limestone, but some of those contacts may be faults. The volcanic rocks are overlain unconformably, at one place or another, by rocks of three different units: (1) conglomerate and sandstone that may be Late Cretaceous or early Tertiary and that have been considered by some to be Beaverhead Group (De la Tour-du-Pin,

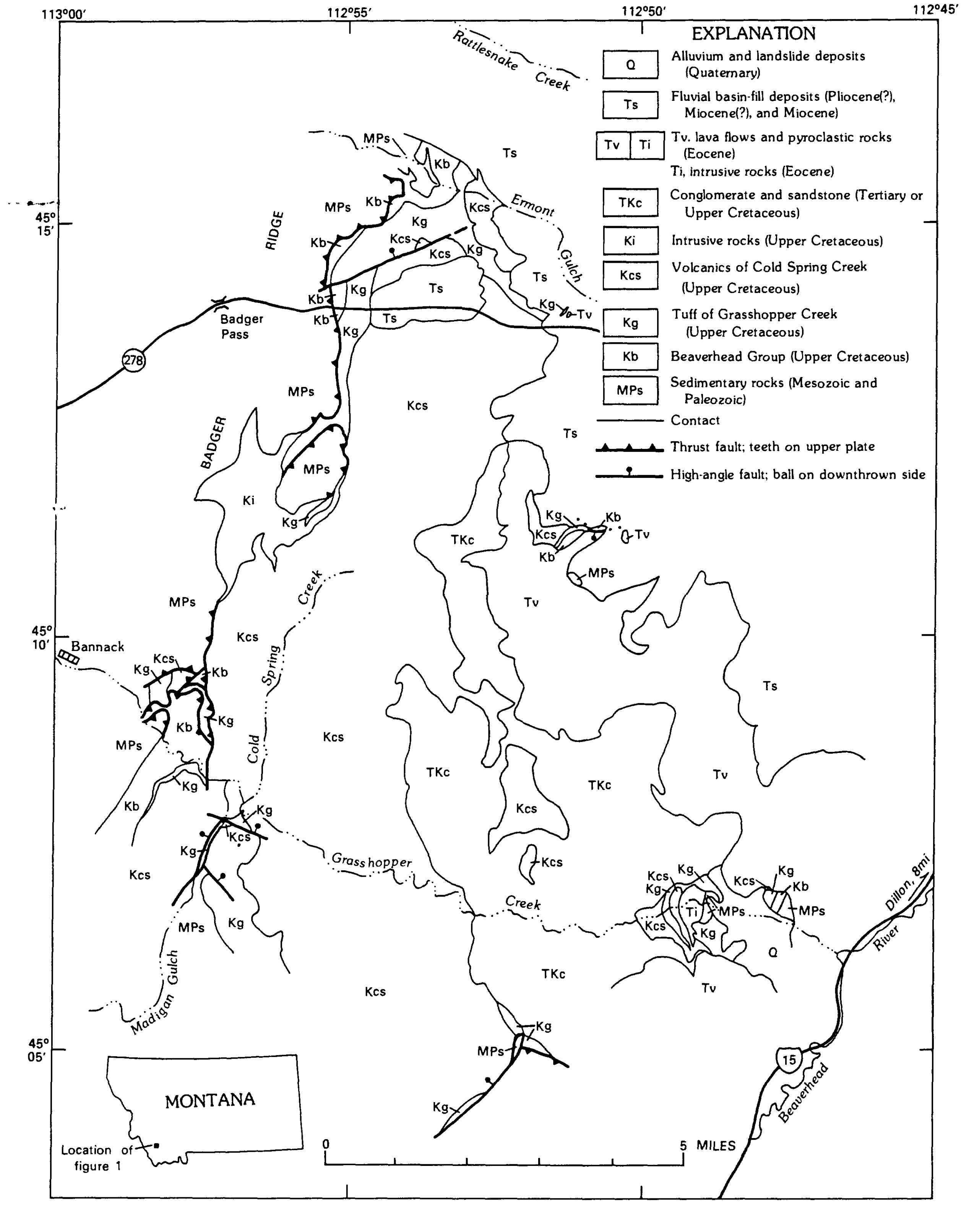

Figure 1.--Generalized geologic map of the Ermont Gulch-Grasshopper Creek area, Beaverhead County, Montana

1983; Johnson, 1986; Thomas, 1981), (2) Eocene lava flows and pyroclastic deposits, or (3) fluvial basin-fill deposits of probable Miocene age.

Structurally, the tuff of Grasshopper Creek and the volcanics of Cold Spring Creek occupy a shallow structural basin, about 3-10 mi wide and 14 mi long, that is faulted on its west side (fig. 1). In addition, a few minor faults and folds are within the basin, but generally the Cretaceous and younger rocks are only slightly deformed. At least part of the western edge of the outcrop of the Cretaceous volcanic rocks is a west-dipping thrust fault that brought Mississippian and younger strata eastward over the tuff and locally over the overlying volcanics of Cold Spring Creek. This thrust fault is best exposed about 1 mi east of Bannack on the north side of Grasshopper Creek (fig. 1). At that place, the Cretaceous volcanic rocks and Beaverhead Group have been folded or dragged to vertical beneath the overlying thrust plate. With that exception, dips of the Cretaceous volcanic rocks just east of the trace of the thrust are mostly 10°-30° east, and dips tend to flatten farther eastward and then locally to reverse to the west still farther east. Faulted and folded Paleozoic and Mesozoic sedimentary rocks that form the upper plate of the main thrust crop out on Badger Ridge, which rises to the west of the Cretaceous volcanic rocks. The ridge is a component of that part of the Montana thrust belt called the "frontal fold and thrust zone" by Ruppel and Lopez (1984).

TUFF OF GRASSHOPPER CREEK

The tuff of Grasshopper Creek crops out extensively between Montana Highway 278 and Ermont Gulch and, from that area, discontinuously southward along the east side of Badger Ridge and along the continuation of the ridge south of Grasshopper Creek (fig. 1). About 0.5 mi north of Ermont Gulch, the tuff is covered by fluvial basin-fill deposits of Miocene(?) age, and the unit has not been recognized farther north, where pre-Tertiary rocks are next exposed about 2-5 mi north and northeast of the Ermont Gulch locality. The tuff is also extensively exposed in and east of the drainage of Madigan Gulch, which is south of Grasshopper Creek and about 1 mi east of the ridge. Other exposures shown on figure 1 are: (1) in a small structurally complex area north of Timber Butte, (2) a considerably larger area near the mouth of Grasshopper Creek that contains several discrete outcrop areas, and (3) small faulted exposures about 2 mi south of Grasshopper Creek at the southern known limit of the Cretaceous volcanics. Thus, as presently known, the tuff crops out discontinuously on the periphery of a roughly triangular area that measures about 13 mi north-south and 9 mi east-west. Within the triangular area, the tuff is mainly covered by younger deposits but may well be continuous in the subsurface.

The tuff crops out in low rolling topography and is covered by thin soil. The rock is well indurated but is much less resistant than the Paleozoic limestones that are locally in contact with it, but generally it has about the same resistance as the overlying volcanics of Cold Spring Creek. Locally, the tuff stands as cliffs as much as 40 ft high in narrow gullys.

In general appearance, the tuff of Grasshopper Creek contrasts with other rocks in the area chiefly because of its light color; the overlying lavas in the volcanics of Cold Spring Creek are moderate to dark shades of gray, brown, green, and red. The tuff typically is yellowish gray, light olive gray, pinkish gray, white, very light gray, or light gray; pale red zones are common north of highway 278 and in the Madigan Gulch area. Locally, where deformed or near intrusive rocks, such as east of Bannack, the tuff has been metamorphosed, as is evident in the mineral composition (table 1), in an

Table 1.--Mineralogy of tuff of Grasshopper Creek

[Mineral abundance estimated from relative peak heights on x-ray diffractometer patterns; X, major component, probably several tens of percent. 0, minor components, several percent to a few tens of percent; t, trace, less than a few percent; ?, identification uncertain. Feldspar includes both plagioclase and potassium feldspar.]

Sample No.	Lat. N. ° ' "	Long. W ° ' "	Mordenite	Clino-ptilolite	Analcime	Feldspar	Quartz	Opal-CT	Mica	Smectite	Chlorite	Calcite	Glass
84P037	45 15 23	112 53 06	--	--	--	0	X	--	0	--	t	0	--
84P038	45 15 23	112 53 13	--	--	--	0	X	--	t	t	t	X	--
84P084	45 15 39	112 53 20	--	--	--	0	X	--	0	t	t	X	--
84P086	45 15 23	112 53 13				X	X		t	--	--	0	--
84P103A	45 12 47	112 55 07	t?	--	--	0	X	X	0	--	--	--	--
84P103B	45 12 47	112 55 07	t?	--	--	0	0	X	--	0	--	--	--
84P105	45 12 29	112 55 23	--	t	--	X	X	--	--	t	--	--	--
84P114	45 09 14	112 57 23	--	--	--	X	X	--	0	--	--	X	--
84P129	45 14 59	112 54 09	--	--	--	X	X	--	0	t	--	--	--
84P132	45 15 18	112 53 50	--	--	--	0	X	--	0	--	--	--	--
84P135	45 15 29	112 53 30	--	--	--	--	X	--	0	--	0	--	--
84P137	45 15 30	112 53 28	t	--	--	0	X	--	t	--	t	--	--
84P138	45 15 30	112 53 27	t?	t?	--	X	X	--	--	--	--	--	--
84P139	45 15 57	112 54 58	X	t	--	0	0	--	--	t	--	--	--
84P140	45 13 52	112 55 05	--	--	--	0	X	--	--	0	--	--	--
84P141	45 13 58	112 55 00	X	0	--	0	0	--	--	--	--	--	--
85P043	45 09 19	112 58 13	--	--	--	X	X	--	t	--	--	--	--
85P066	45 13 59	112 55 05	X	--	--	0	X	--	t?	--	--	--	--
85P067	45 14 02	112 55 02	X	--	--	0	X	--	t?	--	--	--	--
85P068	45 14 08	112 54 56	X	--	--	0	X	--	t?	--	--	--	--
85P069	45 14 08	112 54 55	--	0	--	0	X	--	--	--	--	--	--
85P070	45 14 07	112 54 53	--	X	--	0	X	--	--	--	t	--	--
85P071	45 14 06	112 54 52	X	--	--	0	X	--	--	t	t	--	--
85P072	45 14 08	112 54 48	X	--	--	0	X	--	--	--	--	--	--
85P073	45 14 09	112 54 46	0	--	--	0	X	--	--	t	t	--	--
85P074	45 14 08	112 54 45	0	--	--	0	X	--	--	--	t	--	--
85P075	45 14 09	112 54 43	0	--	--	0	X	--	--	--	--	--	--
85P076	45 14 14	112 54 40	--	--	--	X	X	--	--	--	--	--	--
85P077	45 14 11	112 54 39	0	--	--	0	X	--	--	--	--	--	--
85P078	45 14 12	112 54 38	X	--	--	X	X	--	--	--	--	--	--
85P130	45 11 15	112 51 11	--	--	--	X	X	--	0	--	t	0	--
85P131	45 11 22	112 50 38	--	--	--	0	X	--	0	t	--	0	--
86P021	45 07 01	112 48 50	0	X	--	0	0	--	--	t	--	--	--
86P030	45 06 10	112 49 09	?	X	--	?	0	--	--	--	--	--	--
87P005	45 06 33	112 49 28	t	X	--	--	0	--	--	--	--	--	--
87P013	45 06 16	112 48 31	--	--	--	--	0	--	--	--	--	--	X
87P023	45 05 27	112 52 24	X	X	--	0?	0	--	--	--	--	--	--
87P028	45 07 32	112 56 39	--	X	X	0	X	--	t	--	--	--	--
88P140	45 09 22	112 58 11	--	--	--	X	X	--	t	--	--	--	--

increase in brittleness, and by a change in color to a slight greenish or light brownish hue. Manganese dendrites are common, and yellowish-brown limonite coats fracture surfaces locally; traces of limonite may account for the pale yellow tint of the tuff in many places.

The tuff unit consists of massive beds a few feet to several tens of feet thick that locally alternate with thinner platy to flaggy zones that are finer grained and better sorted than the massive beds. The massive beds are interpreted as pyroclastic-flow deposits, and the platy rocks are probably fallout tuff deposits. In most of the area of outcrop, the massive beds have a compaction foliation that resulted from the collapse of pumice fragments. This structure seems everywhere to be a reliable indicator of bedding attitude. The foliated rock tends to split with a hammer and to weather around the flattened pumice and more equant accidental and non-pumiceous juvenile fragments along rough-surfaced curving planes to form lumpy, irregularly lenticular chips and plates. The flattened pumice fragments are commonly 0.2-2 in. in diameter and <0.1-0.4 in. thick. In lower Grasshopper Creek, however, the pumice fragments have not been flattened, and as a result, the rock there lacks the foliation and has a very different appearance. The flattening of pumice in some areas and lack of flattening in others is tentatively ascribed to the effects of orogenic deformation and not to compaction during welding when the deposit was hot.

The lack of flattening of pumice is probably the reason that Lowell (1965) included the tuff of Grasshopper Creek in that particular area with the overlying Tertiary (probably Eocene) tuff, which is predominantly smectitic and contains only minor amounts of zeolites. The pumice lumps are commonly ovoid and as much as several inches long. In contrast to the foliated tuff, the tuff in lower Grasshopper Creek has voids that may be original gas pockets or result from weathering-out of pumice or other weak original fragments. The specific gravity of the tuff is noticeably lower in this area. In addition to pumice and angular to rounded juvenile fragments, the tuff contains rare to abundant fragments, ranging from sand to cobble size, of sedimentary rock (generally quartzite and limestone). Some of these are accidental pyroclastic fragments, but locally the rock appears to be a tuffaceous conglomerate, and in it, limestone and quartzite fragments are probably epiclastic. Tuffaceous conglomerate may be interbedded with tuff in the Ermont Gulch area, but because of metamorphism the distinction between Beaverhead Group conglomerate and tuffaceous conglomerate in tuff of Grasshopper Creek is difficult to make. For this reason, some samples near Ermont Gulch are shown on figure 2 within the Beaverhead Group; none of these samples contains zeolites.

The thickness of the tuff unit ranges from 0 to >1,000 ft, although structural complications may have influenced both extremes. The thickness in uncomplicated sections seems to be greatest in the northwestern and northern exposures, where about 900 ft of beds are indicated by calculations from the geologic map. Along Grasshopper Creek about 2.5 mi below Bannack, a well-exposed flat-lying section is 160 ft thick, but about 1 mi north of that locality, where the unit has been turned up to vertical beneath the thrust, the unit seems to be more than 1,200 ft thick, although that thickness includes many small dikes and the rock has been deformed. In lower Grasshopper Creek, the tuff seems to have been deposited over irregular topography held up by steeply tilted beds of the Kootenai Formation and possibly of the Beaverhead Group (the tuff has not been observed in contact with the Blackleaf Formation that overlies the Kootenai in this area). The thickness in lower Grasshopper Creek ranges from <100 ft to >350 ft over a distance of 1 mi.

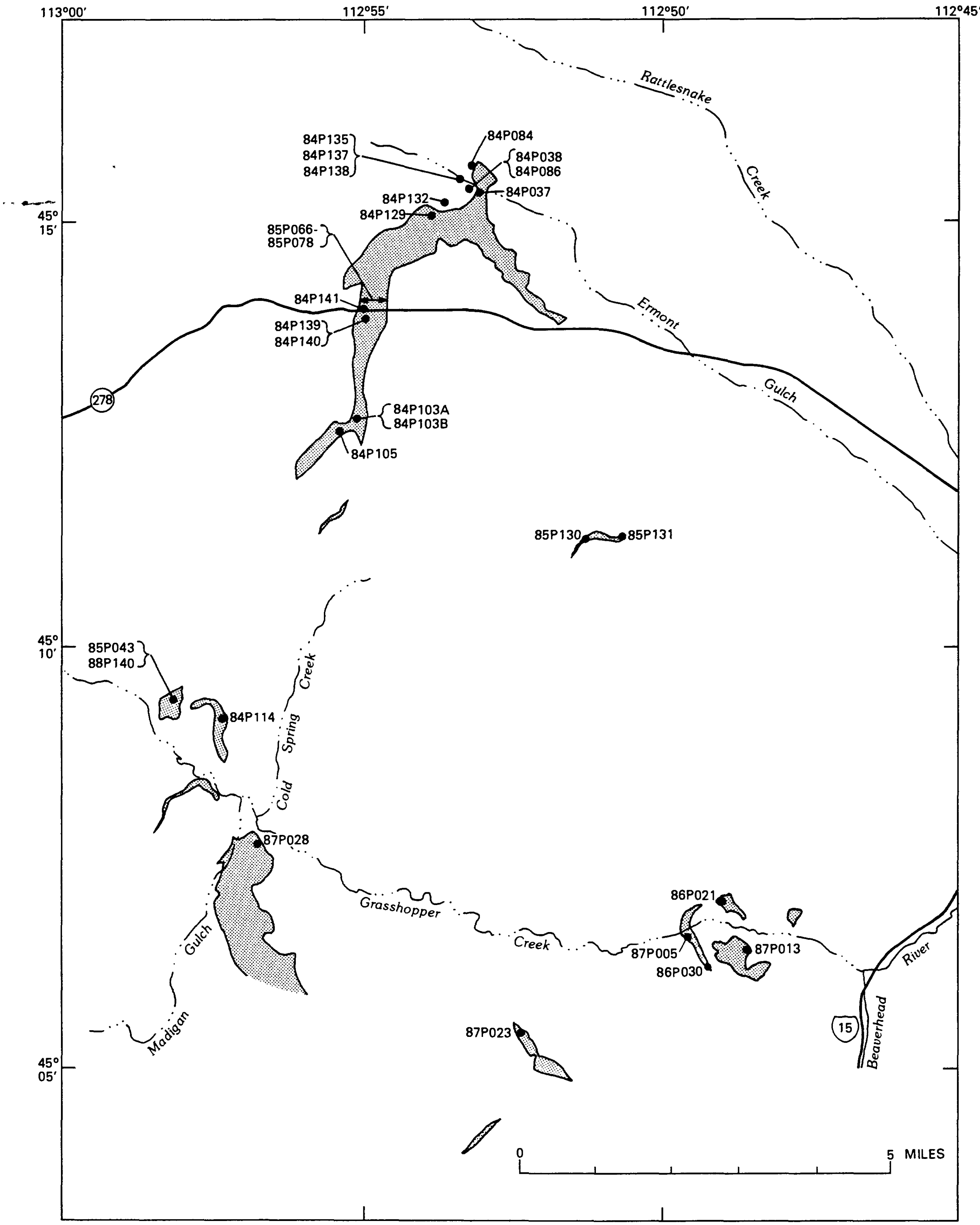

Figure 2.--Areas of outcrop of tuff of Grasshopper Creek and sample localities discussed in text

MINERALOGY AND DISTRIBUTION OF MINERALS

In thin section, the tuff is a fine-grained to very fine-grained aggregate of colorless to pale yellowish-brown, low-birefringent, authigenic minerals and a very minor amount of pyrogenic crystals, chiefly quartz. Pyrogenic plagioclase crystals are sparse and largely altered to zeolite minerals. Neither glass nor pyrogenic mafic minerals have been observed in thin section. Pyroclastic fragments, so clearly evident in hand specimen, seem to be composed of the same minerals as the matrix, although staining with sodium cobaltinitrite indicates that some fragments are rich in authigenic potassium feldspar and others are not. Any glass shards that may have been in the matrix have been completely replaced by authigenic minerals.

Hand-specimen samples and one bulk sample of the tuff were examined by X-ray diffraction techniques to determine bulk mineralogy and approximate proportions of the major constituents. The X-ray analyses were made on small samples chipped from the hand specimens and ground to a powder, selected only to exclude significant accidental fragments. The one bulk sample (86P021) weighed about 35 lbs and was collected for the purpose of extracting heavy minerals. Sample localities are shown on figure 2. Sampling density is not adequate to fully characterize the mineralogy of the tuff unit nor to identify specific localities that might be especially worthy of further investigation. The 39 samples examined, however, do seem to be sufficient to show the general regional distribution of the zeolite minerals and to suggest that lower Grasshopper Creek may contain large tonnages of potentially commercial zeolitic rock.

Mordenite and clinoptilolite are the chief zeolite minerals recognized, and they coexist in some samples. Analcime, together with clinoptilolite, is a major constituent in one sample. Mordenite is more abundant than clinoptilolite in most samples from the northern and western outcrop areas. Clinoptilolite is sporadic in those areas and is abundant in samples from the lower Grasshopper Creek area. Some samples contain little except quartz, plagioclase, and potassium feldspar; these samples are from parts of the unit that are near intrusive rocks or are more deformed by folding or faulting, such as those east of Bannack, and their mineralogy is regarded as metamorphic. Feldspars and quartz common in many other samples together with zeolites are regarded as authigenic. Opal-CT has been identified in samples from one locality (samples 84P103A and 84P103B, fig. 2). Clay minerals (mainly 14-Å clays) are identifiable in trace amounts or not at all on the X-ray traces, except for a few samples of reworked or deeply weathered tuff from the quarry south of highway 278. Minor or trace amounts of mica, chlorite, or calcite are present locally. A sample of pumice (87P013) from lower Grasshopper Creek consists almost entirely of glass having an index of refraction of slightly greater than 1.50.

The abundance of the several minerals in the tuff was estimated using relative peak heights from the X-ray diffractometer traces, but only in the most general way; these estimates are given in table 1. The amounts are categorized as major (probably a few tens of percent or more), minor (several percent to a few tens of percent), and trace (barely detectable to a few percent). All samples analyzed are mixtures, so that empirical standards were not made using the actual minerals present for the purpose of more precise determination of abundance.

The relative peak heights suggest that clinoptilolite in certain samples from lower Grasshopper Creek (86P021, 86P030, and 87P005) is in the range of about 60->90 percent of the rock. In this area the rock crops out in several discrete areas on the lower valley slopes on both sides of the creek from the valley floor to as much as 400 ft above the floor. The discrete outcrop areas are separated from one another by cover of younger deposits (volcanics of Cold Spring Creek, Tertiary lava flows and tuff and Quaternary alluvium, colluvium, and landslide deposits), by a basaltic intrusion, and by faulting within the Cretaceous volcanic rocks. The largest exposures are in the south half of sec 27. Others are in the SW 1/4 sec 22, NW 1/4 sec 26, NW 1/4 sec 27, and NE 1/4 sec 28, all in T 8 S, R 10 W. Sample 87P023 from about 1.5 mi south of Grasshopper Creek contains abundant clinoptilolite and mordenite. Both of these areas, lower Grasshopper Creek especially because of its accessibility and the extent of outcrop of the tuff unit, contain rock sufficiently rich in zeolite to be of commercial interest.

POTENTIAL USES

Testing of cation-exchange capacity and gas adsorption will be necessary to actually determine if the rock has useful properties. If the properties of the rock are satisfactory, local potential uses, in addition to those already employed, are in cattle feedlots or other places where livestock congregate and near mining activities. Around livestock, the zeolites absorb the ammonium ion and help to prevent animal waste products from entering streams and ground water supplies. Such ammoniated zeolite can then be used as fertilizer and soil amendment. Around mines, mine dumps, and mill tailings, perhaps the zeolitic tuff can ameliorate deleterious acid-water effluent and runoff and their contained undesirable metals (Jordan and others, 1988). For such undemanding uses as these, fine crushing or coarse grinding would likely be the only treatment required of the quarried zeolitic rock.

Prior to closer-spaced sampling to determine the local variability in zeolite content and testing the tuff's properties, no attempt will be made to calculate available tonnages. Judging only from the thickness of the tuff unit, its area of outcrop, and the zeolite content of samples, it is possible that many millions of tons of good grade rock may be present near the surface and hence readibly available.

CONCLUSIONS

X-ray analyses indicate that in most areas of outcrop the tuff of Grasshopper Creek contains the zeolites mordenite and clinoptilolite in varying amount, and one sample contains analcime as well. Samples from the western and northern parts of the area contain authigenic or metamorphic quartz and feldspar in addition to zeolites in some samples, or instead of them in others, most abundantly in samples associated with intrusive rocks or deformed by folding and faulting.

The highest total zeolite content and also the highest amount of clinoptilolite have been found in samples from lower Grasshopper Creek. This suggests that the tuff in that area is more likely to have properties that will be useful locally in agriculture and mine-waste cleanup. Tonnages of the zeolitic rock are very large.

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