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by

Nels Forsman

Report of Investigation No. 87
North Dakota Geological Survey
Sidney B. Anderson,
Acting State Geologist
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ABSTRACT

Volcanic tuffs occur in the sequence of strata comprising the Killdeer Mountains of Dunn County, North Dakota. Glass grains remain the dominant components of each tuff unit, with identifiable phenocrysts, and accessory or accidental volcanic rock fragments also present, together with variable amounts of epiclastic grains. A sequence of diagenetic changes has occurred in each tuff unit, involving early dissolution of glass grain surfaces and precipitation of grain-coating montmorillonite, followed by precipitation of erionite in pore spaces. A chemical environment of increasing alkalinity above an initial pH >9 is suggested.

The age and stratigraphic relations of Killdeer Mountain strata remain unknown. Several materials from Killdeer tuff units may provide useful radiometric or fission-track ages. Chemical correlation techniques can be applied using these tuffs and other volcanically derived units of Oligocene or younger age in the northern Great Plains region.

INTRODUCTION

The Killdeer Mountains is the name given to a prominent mesa in west-central Dunn County, North Dakota, about ten miles northwest of the town of Killdeer (fig. 1). A divide separates the northern portion of the mesa from a much larger southern portion. The entire elevated region is roughly nine miles long and six miles wide, and rises 700 feet above the surrounding plains. The vertical cliffs that occur along the flanks of much of the mesa expose rock that is nearly everywhere else covered by grassy soil or trees.

General Geology

The Killdeer Mountains are made up of essentially flat-lying limestones, dolostones, sandstones, and tuffites that are locally exposed primarily along slump scarps and other vertical faces irregularly located around the perimeter of the mountains. The abundance of slump structures along the flanks of the mountains hinders the local correlation of beds, but Delimata (1975), using data from 43 measured sections, determined that Killdeer rocks "are generally characterized by poor lateral and/or vertical continuity." A widespread and lithologically distinct burrowed unit serves as a marker bed over a large portion of the mountains. Delimata noted a variety of bedding structures in Killdeer rocks, including, from most to least common: planar bedding, small-scale ripple cross-stratification, and very rare large-scale trough cross-stratification. He also observed intraformational breccias, mudcracks, and structures he considered to be pellets and oolites.

Limestone and dolostone are the most common rock types in exposed sections of the Killdeer Mountains. Delimata (1975) considered most of the remaining, poorly indurated rocks to be tuffites, based on his observation of abundant "volcanic clasts" in the silt size range. Stone (1973) reported abundant glass shards in the "main, ledge-forming concretionary sandstone of the Killdeer Mountains" (burrowed marker unit of this report). Portions of Killdeer carbonates and tuffites have been locally silicified, forming impure cherts (Delimata, 1975). Mudstones or clayey units are absent except for reported

thin deposits near the base of the mountains (discussed below).

Delimata (1975) has interpreted Killdeer rocks as representing primarily lacustrine environments, with local fluvial deposition suggested by large-scale cross strata and coarse sediments. He judged limestone to have formed as a primary precipitate in shallow lake water, dolomite to have formed as an early replacement of limestone, and silicification of sediments to have occurred as a result of highly alkaline brines percolating downward and becoming silica-enriched as they encountered tuffaceous sediments. Delimata interpreted the Killdeer Mountains to represent an inverted lake basin, preserved where a silicified carbonate core has withstood the physical and chemical weathering that has removed less resistant flanking sediments.

Stratigraphy

The most current stratigraphic interpretation of the Killdeer Mountains uses a modified version of the informal terminology of Stone (1972). Stone informally proposed that the rock units comprising the Killdeer Mountains be assigned to the Killdeer Formation as a lithologically distinct correlative of the Arikaree Group of South Dakota and Nebraska. The term Killdeer is retained for informal use in this study because rocks of the Killdeer Mountains are lithologically distinct from other Middle Cenozoic units in the region. However, lateral stratigraphic relations of Killdeer rocks remain unclear (fig. 2); they may be referable (in age) to Arikaree Group strata or they may be correlative with nearby and younger White River Group units. The lower contact of the units comprising the Killdeer Mountains has been observed by earlier workers at a few localities near the base of the mountains (Quirke, 1913, 1918; Stone, 1972, 1973). Quirke (1913) reported that thin exposures of pale-green and white clayey rocks unconformably overlie Fort Union Formation rocks at three locations near the base of the mountains. Rocks below the unconformity are now recognized as part of the Eocene Golden Valley Formation. Quirke recognized the similarity between the clayey rocks at the base of Mountains and Oligocene White River Formation rocks exposed farther south in North Dakota. Using this evidence, he

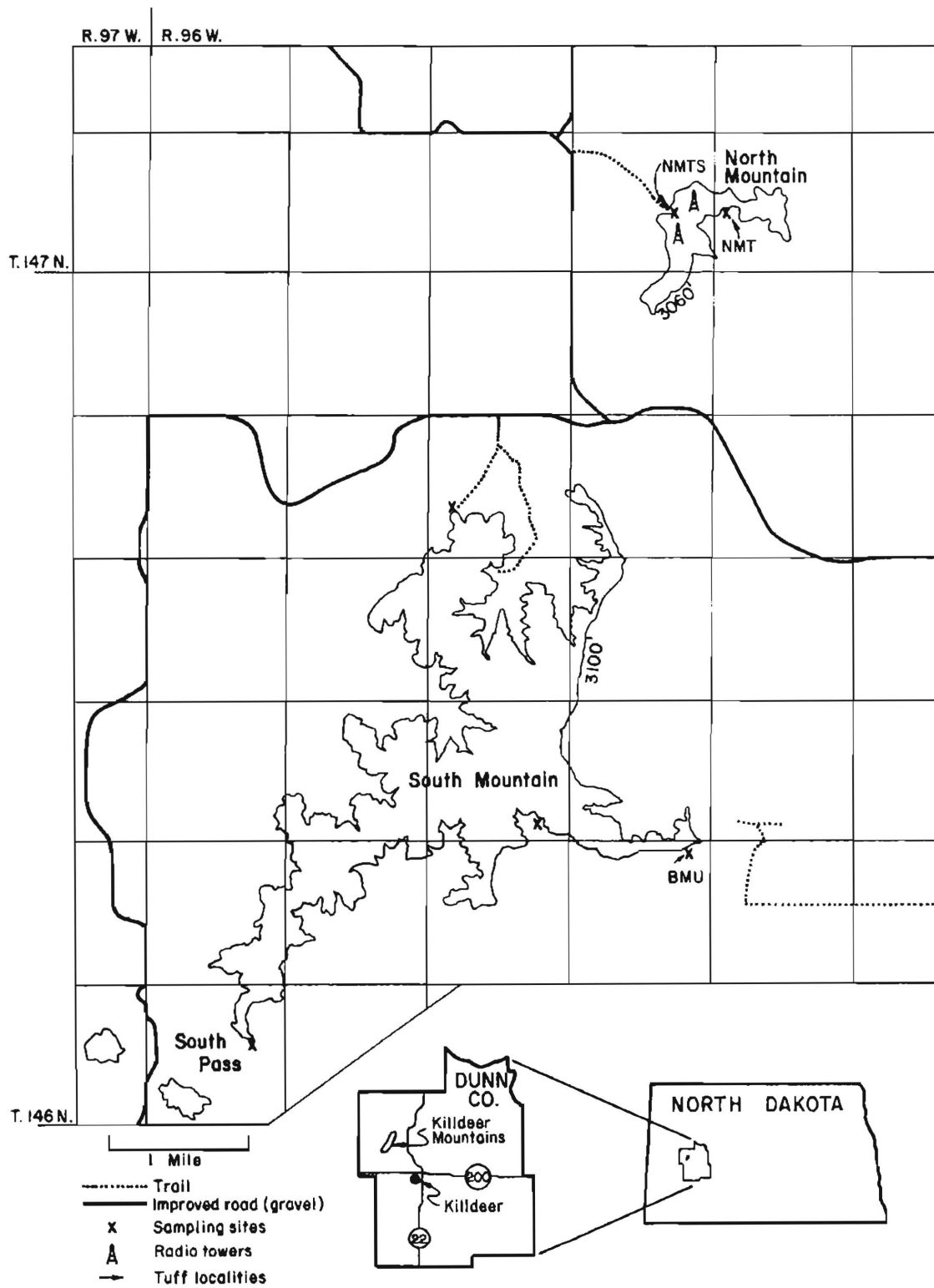


Figure 1. Location map of Killdeer Mountains in Dunn County, North Dakota, showing sampling localities and locations of tuffs. BMU=burrowed marker unit, NMT=North Mountain tuff, NMTS=North Mountain tuffaceous sandstone.

SERIES	ROCK UNIT	
MIocene	ARIKAREE GROUP (South Dakota, Nebraska)	
? OLIGOCENE ? ? MIocene ?	KILLDEER MOUNTAINS STRATA	
OLIGOCENE	WHITE RIVER GROUP	BRULE FORMATION
		CHADRON FORMATION
Eocene	GOLDEN VALLEY FORMATION	CAMELS BUTTE MEMBER
PALEOCENE		BEAR DEN MEMBER
	FORT UNION GROUP	SENTINEL BUTTE FORMATION

Figure 2. Generalized stratigraphic column representing current understanding of stratigraphic relations between Killdeer Mountain strata and other formal Cenozoic rock units of the northern Great Plains region.

referred Killdeer Mountain strata to the Oligocene series. Stone (1973), using this same evidence, suggested that only the clayey rocks near the base of the mountains are Oligocene, and that the greater part of the clay-free units comprising the mountains are Miocene. The actual age and stratigraphic affinities of Killdeer rocks remain unknown. It can be said with confidence only that they are Oligocene or younger. Fossil evidence that might lead to more precise age assignments for Killdeer rocks have not been reported despite the efforts of several workers.

Purpose of Study

This study was undertaken to determine if any Killdeer rocks might actually be volcanic tuffs with only minor detrital admixture. A specific intent was to search for friable or

only weakly cemented tuff units that might, through laboratory characterization, be determined to be sufficiently preserved so as to be suitable for dating and/or petrologic correlation with other units. This study is intended as an early stage of a longer term effort to document a time-stratigraphic framework for Tertiary rocks of the northern Great Plains region.

Methods

Grab samples of all friable and weakly cemented units were taken from exposures at five different localities within the Killdeer Mountains (fig. 1). In the laboratory, initial qualitative determinations of volcanic glass, phenocryst, and authigenic zeolite content of each sample were made by optical microscopy using grain mounts prepared by brushing grains directly from samples into Caedex. Grain mounts used for point counting were prepared using grains cleaned of alteration products by treatment in an ultrasonic water bath. Whole-rock thin sections were prepared of most samples using epoxy impregnation. Detection of minor constituents in samples was aided by concentrating minerals according to their magnetic susceptibilities using a magnetic separator. Chemical data were obtained by microprobe analysis, using a JEOL 35C scanning electron microscope fitted with a KEVEX energy dispersive detector and a Tracor Northern TN-2000 X-ray analyzer. Microprobe data were processed using a Tracor Northern XML fitting program and the matrix correction program of Bence and Albee (1968). Minerals were identified using polarized light microscopy, X-ray diffraction, and SEM/microprobe techniques.

RESULTS

Nearly all units sampled contain various amounts of explosively derived volcanic materials. A complete gradation from slightly to highly tuffaceous sediments to tuffs occurs in Killdeer strata. That some Killdeer units can be properly considered as tuffs is based on their percentage of known and probable pyroclastic constituents. According to Fisher and Schmincke (1984) (following Schmid, 1981), tuff is composed of at least 75 percent pyroclastic constituents of either juvenile,

cognate, or accidental origin. Not every unit discussed in this report has been clearly documented to contain over 75 percent pyroclastic materials. However, descriptive nomenclature recommendations aside, three Killdeer units have been found to contain sufficient quantities of pyroclastic material to justify their study as deposits of potential value for dating and/or petrologic correlation with other units.

Results of point counts of the Killdeer deposits found to contain abundant pyroclastic components are provided in table 1. Volcanic glass grains are the dominant constituents of each sample. Most opaque grains are thought to be titanium-rich magnetite, a probable phenocryst, based on microprobe analysis of opaque grains concentrated by magnetic separation. The presence of glass crusts on some feldspar grains indicates that some undetermined number of feldspar grains are phenocrysts. Because nearly all Killdeer samples examined contain glass shards, and therefore reworked phenocrysts, it has not proven possible to use comparisons of feldspar species between tuffs and non-tuffs to confidently distinguish detritally admixed and phenocryst feldspar grains in these samples. Each tuff sample contains both potassic feldspar and calcic and intermediate plagioclase grains. It has not been possible to isolate glass-encrusted grains for exact feldspar identification of verifiable phenocrysts. Elongate, subhedral to euhedral green grains occur in each sample and have been identified as hornblende using optical properties and microprobe analysis. Glass crusts seen on some of these grains are clear indicators of a volcanic origin. A strongly pleochroic, roughly equant, orange-colored orthopyroxene is also present in minor amounts in each tuff sample. Volcanic rock fragments are common in each tuff sample; some are easily recognized by the typical presence of phenocryst or xenocryst crystals set in a glassy or altered-glass groundmass, while others appear as nearly opaque grains because of either strong groundmass alteration or abundant iron-rich inclusions. The abundance of volcanic glass grains together with minerals and rock fragments of known and probable pyroclastic derivation leads to the interpretation that at least two Killdeer units (BMU and NMT of table 1) should be considered volcanic tuffs. A third Killdeer

unit (NMTS) was found to contain a highly variable amount of known pyroclastic material. This unit must be classified as a highly tuffaceous sandstone using the terminology recommended by Schmid (1981), but is included in this report because of its potential value for dating and stratigraphic correlation.

The Killdeer units determined to be tuffs include: 1) the burrowed marker unit (described below), and 2) a two- to three-foot-thick, partially lithified to friable, light-gray unit between a grass-covered slope and an overlying, indurated, cliff-rimming ledge east of the very top of the trail leading to the radio towers on North Mountain. The highly tuffaceous sandstone is a thick (~12 feet), light-gray, crossbedded unit exposed along the east wall of a roadcut nearing the top of the trail to the radio towers on North Mountain. The sites at which each of these units were sampled are shown in figure 1. A chalky-white five-foot-thick unit capping a vertical section near South Pass, near the southwestern end of the Killdeer Mountains, has been called a tuff by Delimata (1975); however, no evidence for a volcanic origin of this unit has been detected in this study.

The name "burrowed marker unit" is informally applied to a conspicuous unit with abundant, prominently exposed, ichnofaunal trace fossil burrows. This is the "wormy marker unit" of Delimata (1975) and the "main, ledge-forming concretionary sandstone" of Stone (1972). This unit occurs low in the sequence of Killdeer strata, and is widespread in the Killdeer Mountains although not everywhere easily recognized. Close examination of the burrowed interval of this unit reveals it to consist of a repeating sequence of strongly indurated burrowed horizons separated by recessed friable units which contain comparatively few, and commonly no, burrows. Plane bed laminations and ripple bedding commonly are preserved within the friable layers. Petrographic examination reveals both indurated and friable portions of this unit to be mineralogically similar (table 1) except for pervasive calcite cement that has replaced most glass shards in the indurated layers, leaving glass ghosts visible in thin sections viewed under medium magnification using the condenser lens. The indurated portions of this unit can be considered limestones in a strictly descriptive sense, but clearly must be

Table 1. Results of 200-Grain Point Counts of Killdeer Glass-Rich Samples.

Sample	Glass	VRF	Feld	Q/F	Opaque	Horn	Pyrox	URF
NMT (upper)	76	5	4	12	< 1	< 1	< 1	2
NMT (lower)	77	8	3	8	1	< 1	< 1	4
BMU #4*	61	10	8	13	< 1	< 1	< 1	8
BMU #3	53	5	17	11	1	2	< 1	12
BMU #1	61	6	9	19	< 1	< 1	< 1	4
NMTS #9	60	4	11	7	1	< 1	< 1	8
NMTS #8	62	4	11	14	3	1	< 1	5
NMTS #6	65	6	14	9	< 1	1	< 1	5
NMTS #5	50	4	18	16	1	2	< 1	9
NMTS #4	50	9	12	20	2	2	< 1	5
NMTS #3	22	5	33	27	1	1	< 1	10
NMTS #1	56	1	20	13	< 1	1	1	9

Data in percent. Abbreviations: VRF=volcanic rock fragments, Feld=feldspar, Q/F=indistinguished quartz and feldspar, Horn=hornblende, Pyrox=pyroxene, URF=rock fragments of unknown origin, NMT=North Mountain tuff, NMTS=North Mountain tuffaceous sandstone, BMU=burrowed marker unit.

*BMU #4 is from an indurated (calcite-cemented) portion of the burrowed marker unit. Glass ghosts were counted as glass. BMU #1 and #3 are from friable portions. Point count data is from sand-size grains (>63 μm) from each sample.

called calcite-replaced tuffs in the more meaningful petrogenetic sense. The thickness of the prominently burrowed interval of the burrowed marker unit averages about eight feet (Delimata, 1975). Material exposed and sampled ten and more feet below the lowest uncovered portion of clearly recognizable burrowed marker unit is petrographically similar to the friable portions of that unit. These exposures may be the result of slumping, which is common in the Killdeer Mountains, or may be evidence that the original tuff accumulation(s) comprising the burrowed marker unit was(were), at least locally, perhaps tens of feet thick. The apparent great thickness of tuff comprising the burrowed marker unit and other units reported in this study is not thought to represent accumulation from airfall during single very large-scale eruption events. It is far more likely that Killdeer tuff units accumulated in low areas (e.g., lakes, valley bottoms) through the transport by wind and running water of more widespread but thinner ash mantles. Although variations in point count data between portions of the burrowed marker unit suggest that some detrital input of epiclastic material has occurred, the unit is, overall, highly tuffaceous and probably contains portions accumulated directly from airfall with little or no sedimentary reworking.

The second tuff exposure, below a cliff-rimming ledge and above a grass-covered slope east of the radio towers on North Mountain, consists of an upper moderately lithified portion, and a lower friable portion. The entire unit is two to three feet thick. Calcite in the form of small pore-filling crystals and crystal aggregates is the cementing agent in the upper portion. This is the most glass-rich unit of those examined in this study.

The roadcut exposure of tuffaceous sandstone on North Mountain extends up to 12 feet in thickness and is overlain by a grass-covered slope. Both horizontally laminated and ripple-bedded intervals occur vertically throughout the sequence of friable sandstone interrupted by thin (few inches), inconspicuous, indurated lenses. The indurated lenses are, for the most part, cemented by calcite that has replaced many of the glass shards present. Local thin zones seen in some thin sections, sandwiched between areas of calcite cementation, are cemented by a low-birefringence form of silica with broadly

sweeping extinction. This silica is interpreted to be a form of chalcedony lacking the more common fibrous or feathery texture. A parallel arrangement of fine linear structures is seen locally within this cement. These characteristics are suggestive of a calcite-replacement origin for this silica (Williams et al., 1982, p. 399).

Glass Grains

The dominant component of each tuff sample is volcanic glass in the form of bubble-wall shards and pumice fragments (fig. 3a,c,e). The glass is rhyolitic in composition, as determined by microprobe analysis of individual shards (table 2). Among the minor pumice fragments present, not much variety exists in the type of vesicle morphologies seen. Roughly straight, tube-like vesicles occur in some grains, but more commonly, up to several large, roughly spherical vesicles occur, especially in the larger, sand-size pumice fragments. Lunate or Y-shaped bubble junction shards are common, but the great majority of grains occur as angular, featureless curved plates or roughly equant grains with one or more raised ribs. Most shards are colorless, although brown- or green-colored glass grains are occasionally seen. Weak to moderate birefringence is seen along the edges and commonly on the surface of virtually all glass grains. Glass grains range in size from fine silt to medium sand with a very small number of grains as large as 600 μm present in each sample. The modal size range of each sample is from 63 to 88 μm (very fine sand).

Diagenetic Products

Using scanning electron microscopy and microprobe analysis, all glass grains were determined to be uniformly coated by a substance of smectite composition, giving the surface of each grain an irregular, or roughened, rather than smooth appearance, and being the source of the birefringence mentioned above (fig. 3a). High resolution images revealed this coating material to have a crenulated morphology typical of authigenic smectites, although only poorly to moderately developed (fig. 3b). Rare opportunities for profile views across the glass/smectite boundary revealed glass surfaces to be pitted by

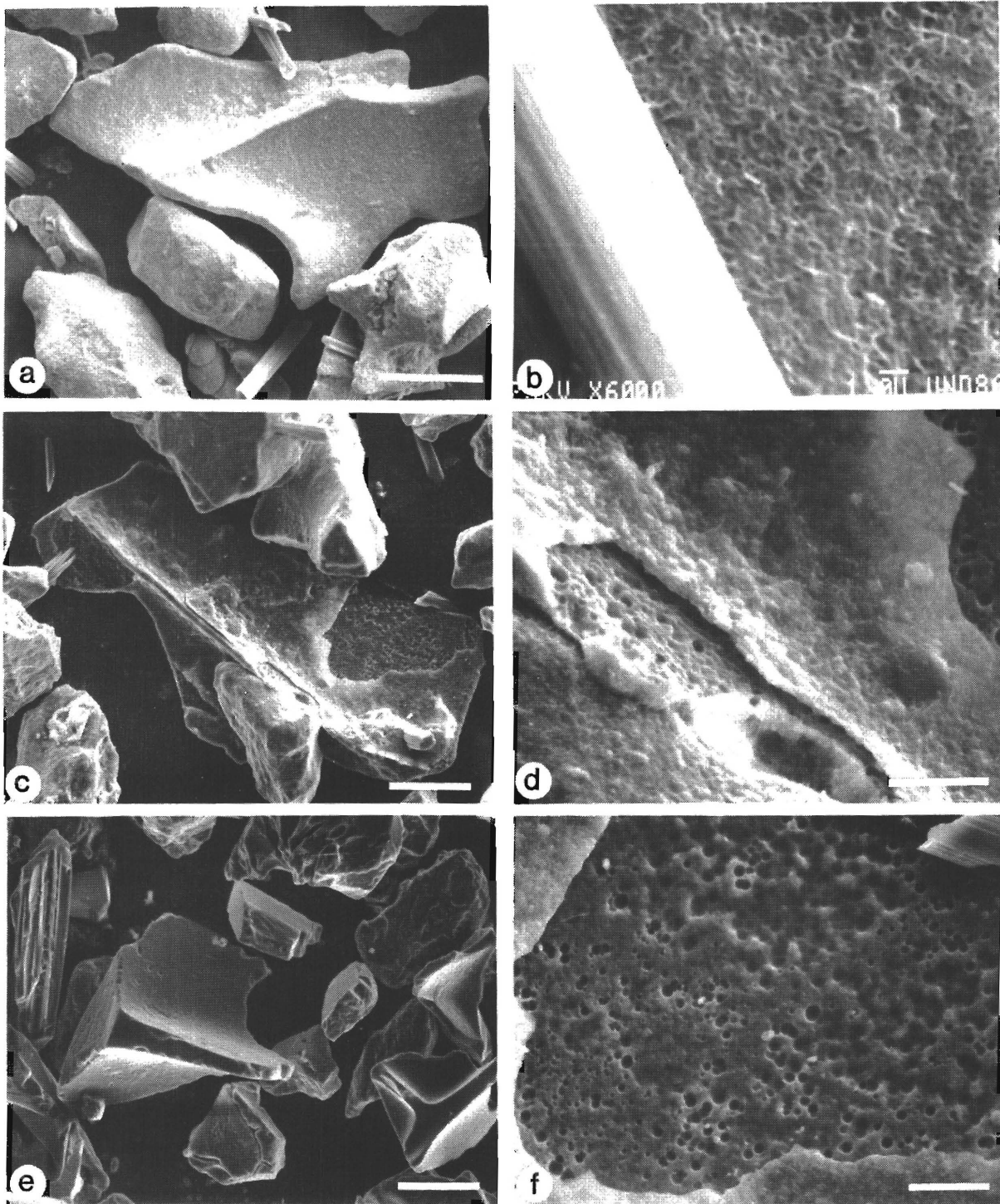


Figure 3. SEM photographs of glass grains and alteration features/products. a) A bubble-wall glass shard and other grains coated by authigenic montmorillonite, giving the surface of each grain a roughened appearance. Note the authigenic erionite rods projecting from a clay-coated grain in top center of photo (odd feature beneath erionite rod in lower center of photo is probably algal fruiting body--personal communication, Ed Steadman). Bar=50 μm . b) Close-up view of clay coating revealing crenulated morphology of authigenic smectite. Bar=1 μm . c) Glass grain with clay-free areas revealing glass surface. Bar=50 μm . d) Close-up view of (c) showing physical relationship between etched glass surface and precipitated clay coating. Bar=10 μm . e) Glass and other grains from which clay coatings have been removed by ultrasonic bathing. Bar=50 μm . f) Close-up view of (c) showing individual bowl-shaped, and coalesced etch features on glass grain surface. Bar=10 μm .

Table 2. Microprobe Analyses of Glass Grains and Authigenic Products

	<u>BMU</u>			<u>NMT</u>			<u>NMTS</u>		
	Glass*	Clay	Zeolite	Glass*	Clay	Zeolite	Glass*	Clay	Zeolite
SiO ₂	78.49	70.37	72.22	78.86	71.75	73.78	78.68	72.73	71.08
Al ₂ O ₃	12.69	14.25	17.09	12.65	14.18	17.85	12.85	12.09	18.12
FeO	0.98	5.06	0.32	1.04	3.87	0.00	1.25	3.63	0.00
MgO	0.00	1.95	2.06	0.00	4.10	2.20	0.00	2.89	2.49
CaO	0.44	1.88	4.39	0.60	0.75	3.52	0.68	0.39	2.75
Na ₂ O	1.37	1.33	0.00	1.79	0.46	0.00	1.81	0.00	0.93
K ₂ O	5.22	4.07	3.64	4.73	4.48	2.32	4.73	7.84	4.63
TiO ₂	0.13	0.73	0.00	0.20	0.41	0.00	0.00	0.43	0.00
MnO	0.00	0.19	0.14	0.00	0.00	0.33	0.00	0.00	0.00
SO ₃	0.00	0.17	0.14	0.13	0.00	0.00	0.00	0.00	0.00

Note: *Mean values given for 10 glass specimens. Total iron as FeO. Calculated H₂O-free. Normalized to 100%.

small, bowl-shaped depressions, as if etched (fig. 3c,d). These same views revealed that clay rests upon the glass, but is not firmly anchored to it. Further investigation revealed that all mineral grains present in addition to glass, except for zeolites (discussed below) and fragments of calcite cement, were also coated by smectite. The smectite coatings can be removed from glass and mineral grain surfaces by ultrasonication in a water bath (fig. 3e). A few drops from clay slurries obtained in this manner were sedimented onto glass disks and determined by standard X-ray diffraction methods to consist of 17 Å montmorillonite.

The surfaces of some, but not all, of the glass and feldspar grains freed of smectite coatings were found to be etched in a manner consistent with chemical dissolution. Etch pits on glass grains are shallow, bowl-shaped features that are individually discernable even though they are nearly continuous, often coalescing over the glass grain surface (fig.

3f). This is consistent with the idea that glass dissolution should be nearly congruent, and not strongly ordered by atomic networks. Feldspar etch pits are commonly rectangular and only locally positioned within grain surfaces; a result of surface-reaction controlled dissolution along dislocations (Berner and Holdren, 1979). Apart from the features produced by surface dissolution, glass grains freed from clay coatings appear completely isotropic and not devitrified.

The zeolite minerals, found to be abundant in Killdeer tuffs and virtually all other Killdeer samples examined, project outward at various angles from glass and mineral grains, using the smectite coatings as a substrate (fig. 3a,c). This is clear evidence that the zeolites do not replace glass shards, and post-date the development of the smectite coatings. The primary zeolite present has been identified as erionite (fig. 4), using both standard powder X-ray diffraction techniques and microprobe analysis of individual crystals

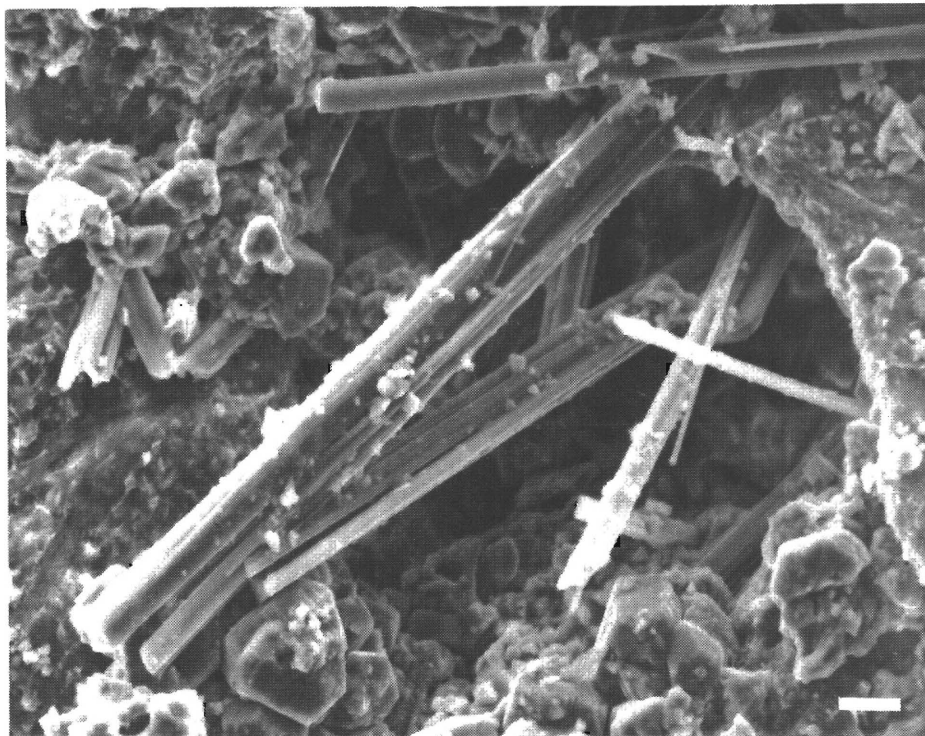


Figure 4. SEM photograph of authigenic erionite rods and calcite crystal aggregates in pore space of an indurated sample from the NITS. Bar=10 μm .

(table 2). A very small number of rectangular clinoptilolite crystals have also been seen. Delimata (1975) reported chabazite to be present in Killdeer samples, but this mineral has not been detected in this study. Erionite crystals vary in size between Killdeer rock samples, with some samples containing large numbers of very small ($\sim 30 \mu\text{m}$) needle-shaped crystals and other samples containing crystals commonly $160 \mu\text{m}$ in length. This study has not succeeded in quantifying the amount of zeolite present in Killdeer samples. Zeolite content varies greatly even between samples from the same tuff deposit. Considering the pore-filling mode of origin of zeolites in Killdeer samples, even though large numbers of erionite crystals are present in most samples, the total percentage volume of a sample that is occupied by erionite is certainly less than the original porosity of that sample.

Authigenic calcite occurs in the friable portions of some tuff samples as aggregates of $\sim 5 \mu\text{m}$ crystals overlying the smectite coatings. Edge and corner terminations normally are not well developed among these crystals.

This calcite probably post-dates the development of zeolite in most samples. As in the burrowed marker unit, indurated portions of Killdeer tuffs are normally strongly cemented by pore-filling and glass-grain-replacing calcite.

DISCUSSION

Diagenesis

The physical evidence reported above leads to a generalized interpretation of the chemical conditions following the deposition of Killdeer tuffs. Initially alkaline pore water conditions promoted dissolution of glass and saturation of pore waters with respect to colloidal smectite constituents. Precipitation of colloidal smectite then changed pore water chemistry to that favoring erionite crystallization. A more detailed explanation of chemical changes leading to the observed glass and authigenic mineral relationships is suggested by the apparent patterns observed in literature accounts of glass/solution/clay+zeolite interactions in both the field and laboratory (for

a review, see Hay, 1966, and Fisher and Schmincke, 1984). That glass dissolution and mineral precipitation reactions were the dominant processes regulating early pore solution chemistries in the Killdeer tuffs is supported by the fact that a glass → clay → zeolite sequence appears to be a general rule among zeolitized silicic vitric tuffs (Hay, 1966).

The presence of rhyolitic glass, and both authigenic montmorillonite and erionite in the Killdeer tuffs fits well with an interpretation of an initially intermediate to alkaline environment, modified in stages by the growth of new minerals. Chemical data for glass grains and authigenic products are presented in table 2 as a basis for the following discussion. Dissolution of rhyolitic glass shards serves to raise the pH and alkalinity of pore solutions through hydrolysis of the glass and an early release of alkali ions to solution. Commonly, the earliest authigenic mineral to form in tuffs under these conditions of increasing alkalinity is montmorillonite, which in the case of Killdeer tuffs has formed through precipitation, possibly as a colloidal gel, upon glass and all other framework grain surfaces. Silicon and alkali ions are lost to solution during the development of montmorillonite from glass. The $\text{Na}^+ + \text{K}^+ : \text{H}^+$ activity ratio should also increase; this has been discussed by Sheppard and Gude (1968) and by Boles and Surdam (1979) as providing an environment more suitable for the formation of zeolites than of additional montmorillonite. Zeolite formation from solutions also is favored by a high pH and high silica activity (Hay, 1966). That erionite is the zeolite species formed in the Killdeer tuffs suggests the pH was >9 and that the activity of alumina had increased beyond the values that would have favored zeolites of higher Si:Al ratios, such as mordenite or clinoptilolite, to form (Mariner and Surdam, 1970).

It is perhaps important to note that, once the montmorillonite coatings were removed by ultrasonication, not all glass grains appeared chemically etched to the same degree by early reactions with pore solutions; while a small number of grains appeared deeply etched, most grains appeared only slightly to moderately etched, and a great many glass grains were seen to have entirely smooth, unetched surfaces. If this is interpreted as evidence that most glass dissolution ceased following

montmorillonite formation, then conditions for mobilizing alumina (for later erionite formation) may have been present before montmorillonite formation. Alumina solubility is relatively low below a pH of 9, suggesting pore solutions present during glass dissolution had a pH of 9 or greater.

The appearance of calcite as a late cement in portions of Killdeer tuff units, both as local pore-occupying minute-calcite aggregates and as pervasive pore-filling and glass-grain-replacing cement, is evidence of a continued alkaline solution, undersaturated in silica. That calcite formed late is suggested by the evidence mentioned above that the pH was >9 (under atmospheric pCO_2 conditions, calcite is relatively insoluble at pH 9 or greater). If suitable concentrations of calcium ion were present during early diagenesis, it seems calcite should have formed. It is true that, where small irregular crystals and crystal aggregates of calcite lie atop montmorillonite coatings together with erionite, it is difficult to determine whether calcite development post-dated or was contemporaneous with zeolite formation. The presence of pervasive calcite cement within the burrowed intervals of the burrowed marker unit and within thin indurated portions of the roadcut tuffaceous sandstone exposure on North Mountain is evidence that calcium-saturated waters did pass through these units at some time. That calcite was not an early diagenetic product somehow curiously localized within the indurated portions of the units is evidenced by the presence of montmorillonite coatings on remaining framework grains reclaimed as an insoluble residue following disaggregation of well-indurated samples in dilute HCL. The source of calcium for calcite development was presumably either the limestone units so common in the Killdeer Mountains or the alkaline lake water (Delimata, 1975) thought to have formed those limestones.

In the case of the burrowed marker unit, it remains unclear why calcite cementation should be restricted to obviously burrowed intervals that occur in vertical repetition between uncemented and commonly non-burrowed layers. Perhaps burrowed intervals provided permeable flow paths for the fluids causing cementation, or perhaps biochemical processes of the burrowing organisms somehow led to increased concentration of calcium ions or carbonate molecules. Burrowing organisms

may have left their burrows during periods of rapid ash influx to migrate upwards and take up residence at the new sediment-water interface. This is a possible explanation for the vertical repetition of burrowed and non-burrowed levels in the wormy marker unit. Alternatively, rapid ash influx may have led to the death of burrowing organisms, with the new sediment-water interface only later repopulated by new individuals.

Silicified portions of the otherwise calcite-cemented lenses within the tuffaceous sandstone on North Mountain presumably formed late through replacement of calcite as a result of more acid pore solution conditions perhaps caused by fresh water influx.

Value for Dating

Units recognizable as volcanic tuffs are useful for assessing the age of enclosing sedimentary rocks because the primary constituents of volcanic ashes are formed, and have their radiometric clocks set, essentially at the time of eruption. The principle technique applied in the radiometric dating of Tertiary volcanic tuffs is the K-Ar method. Individual mineral analyses are used rather than whole-rock analyses because of the possibility of contamination of the ash by older materials through sedimentary reworking or by incorporation of accidental country-rock fragments into the ash cloud during eruption. Minerals normally used include feldspars (especially sanidine), biotite, amphiboles, and pyroxenes. Biotite is nearly totally absent in Killdeer tuffs and other sediments. The difficulties in determining which feldspar crystals are phenocrysts and not detrital contaminants in Killdeer tuffs have been mentioned above. Hornblende is known to be a phenocryst in Killdeer tuff samples because of the glass crusts seen on several hornblende crystals. Older hornblende grains may have been added to Killdeer tuffs by sedimentary reworking, so a K-Ar age for this mineral should be considered a maximum age. Volcanic glass can provide useful K-Ar ages under certain conditions. Killdeer tuff glass grains have certainly lost some potassium through surface dissolution, but this dissolution is thought to have occurred early. The remaining glass may still contain most of its original potassium, because there is no evidence that a devitrification front has

proceeded beyond the etched surfaces of glass grains. The loss of radiogenic Argon by diffusion from glass grains can occur at relatively high temperatures, but may not be a problem in the case of only shallowly buried Killdeer tuffs. If potassium decay and argon accumulation in Killdeer tuff glass grains has occurred without interference following only an early period of glass dissolution, the K-Ar dating of a glass separate may provide a valid age determination for Killdeer tuffs.

Glass or other grains from Killdeer tuffs might also be dated by the fission-track method. The accuracy of glass ages determined by this method would depend largely on the appropriate application of corrections for the potentially large amounts of track annealing anticipated for glasses of Middle Cenozoic age.

An additional material that could possibly be dated as an alternative to, or as a check of, dating glass and/or hornblende includes the authigenic montmorillonite that coats all framework grains in Killdeer tuffs (and other sediments). Because the clay coatings are thought to have formed early after an initial period of glass grain surface dissolution, the K-Ar age of this clay would provide a minimum age for Killdeer samples. This clay can be easily concentrated by washing samples in an ultrasonic bath, centrifuging the liquid to sink zeolites, and drying the remaining clay suspension.

Petrologic Correlation

Volcanic tuffs commonly serve as ideal stratigraphic markers because they are normally deposited over broad regions during an instant of geologic time. Correlation of tuffs over a distance requires that they be identifiable in isolated occurrences and also distinguishable from any other tuffs with which they may be associated. Careful petrographic and chemical methods must be utilized to make final identifications of individual tuffs. The three deposits discussed in this report should have chemical fingerprints distinct from one another if they represent different eruption events, but sufficiently detailed sampling and laboratory effort might reveal that one or more of these deposits individually may also have formed by the successive accumulation of ash from more

than one eruption event. The actual determination of individually distinct genetic units or their absence within the larger Killdeer tuffs of this report would be important should other tuffs, or even bentonites from other regions, be proposed as candidates for correlation with Killdeer rocks.

Summary

At least two units in the Killdeer Mountains are volcanic tuffs, with a third unit also consisting dominantly of glass shards, phenocrysts, and accessory or accidental volcanic rock fragments. Killdeer tuffs probably accumulated in low areas through both direct airfall contribution and the reworking of more widespread ash mantles. Single tuff deposits might actually consist of successive accumulations of ash from more than one eruption event. The burrowed marker unit is actually an accumulation of successive layers of volcanic ash resulting from either separate eruption events, changes in the rate of rinsing of an ash mantle into low-lying areas, or both. Following deposition, the Killdeer tuffs have undergone a series of chemical changes involving the early dissolution of glass grain surfaces and precipitation of grain-coating montmorillonite, followed by erionite growth in pore spaces. A chemical environment of increasing alkalinity is suggested to explain the observed mineralogic changes. Calcite cementation occurred later in portions of the tuff units, commonly replacing glass shards, leaving glass ghosts visible within a calcite matrix.

Materials from Killdeer tuffs seem sufficiently well preserved to be suitable for radiometric or fission-track dating to obtain a minimum age for Killdeer strata. Petrologic fingerprints of Killdeer tuffs may eventually be used to correlate Killdeer strata with other stratigraphic units in the northern Great Plains region.

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