ORIGINS AND GEOLOGIC HISTORY OF SILICEOUS METACOLLOIDAL DEPOSITS, CATHEDRAL MOUNTAIN QUADRANGLE, BREWSTER COUNTY, WEST TEXAS

BY

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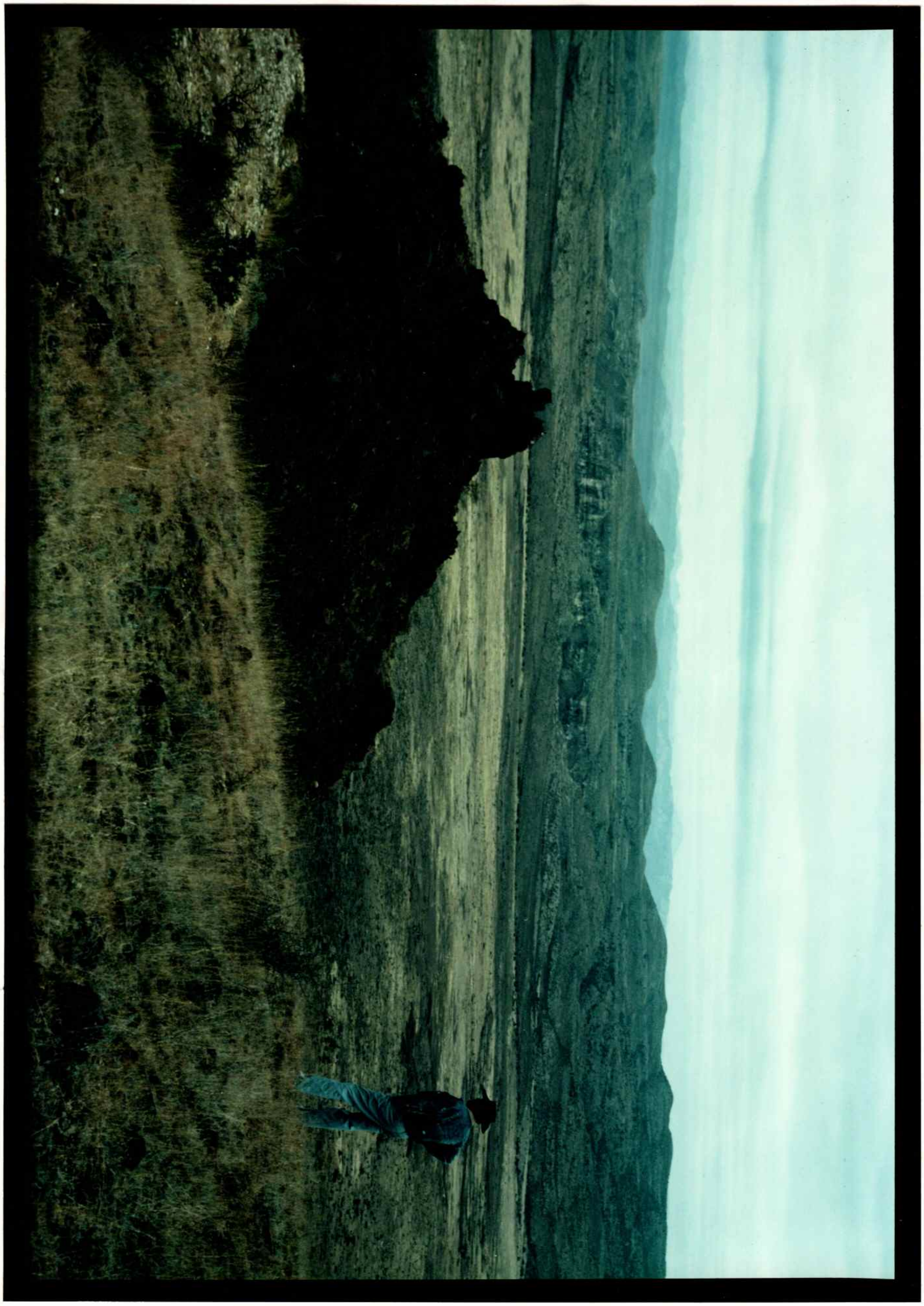

FRONTISPIECE

STRONG AND RUGGED INDIVIDUALS ARE THE KIND
OF PEOPLE IT TAKES TO CARVE OUT A GOOD LIFE
ON THE BLEAK, WEST TEXAS TERRAIN.

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INTRODUCTION

The purpose of this thesis is to determine the geology and genesis of the plume agate of the Buck Hill Volcanic Series, Cathedral Mountain Quadrangle, Trans-Pecos Texas. Seven weeks in the autumn of 1976 were spent in the field collecting agates from various rock units and searching for silica sources. Thin sections of the various agates and rock units were made. X-ray diffraction analysis proved useful for analysis of weathered tuffs.

ACKNOWLEDGMENTS

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Thanks go to Roger K. Pabian, who first suggested the problem and the area to visit; to Dr. S. B. Treves, principal advisor; to David J. Doherty, who gave helpful criticism and aid; and to the Lincoln Gem and Mineral Club for financial assistance.

Last, but not least, appreciation and thanks to Julie K. Anderson for typing the manuscript.

GEOGRAPHIC DESCRIPTION

Location

Cathedral Mountain Quadrangle lies on the southern edge of the Davis Mountains in northwestern Brewster County, West Texas (fig. 1). Alpine, the county seat, is located 6 1/2 miles north of Cathedral

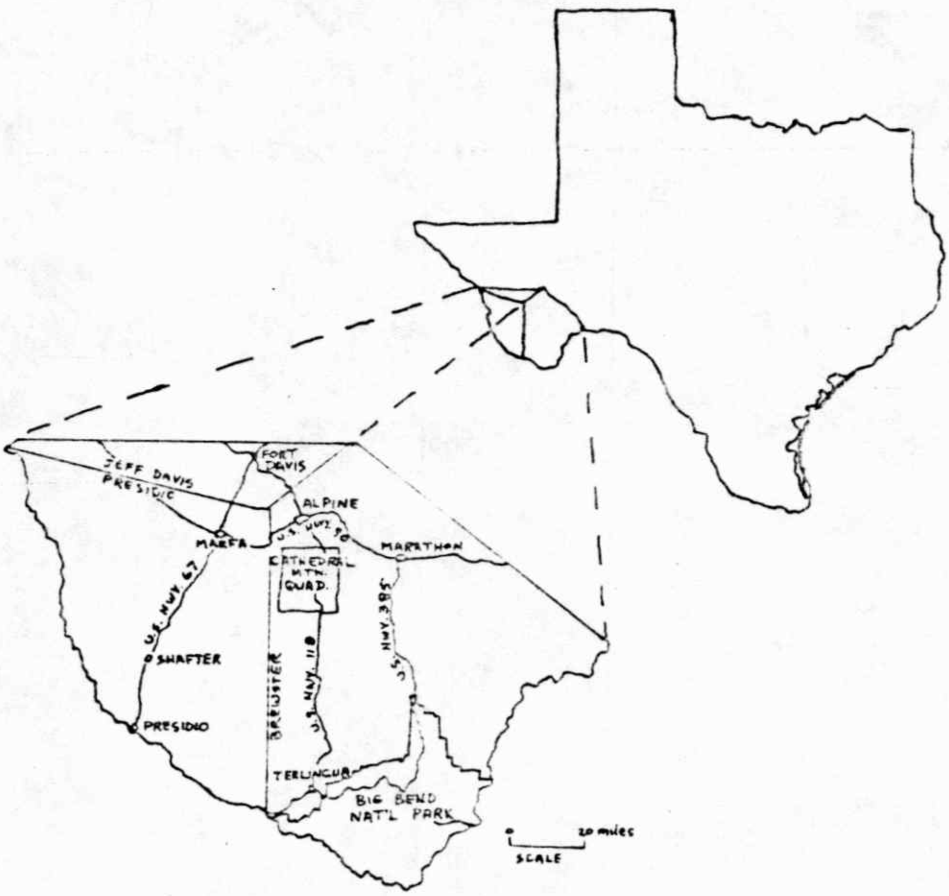

Figure 1. Location map of Cathedral Mountain Quadrangle.

Mountain Quadrangle. The north-south State Highway 118, from Alpine to Big Bend National Park, bisects the quadrangle.

Regional Setting

The southern Davis Mountains consist of a Tertiary volcanic pile characterized by a large volume of extrusive flows, punctured by intrusive masses (fig. 2). The northern and western boundaries are the Marfa and the Delaware basins, respectively. On the east, lie the Del Norte Mountains; the western-most thrust belt of the Marathon uplift. The Mexican highlands, the Basin and Range physiographic provinces, and the Appalachian and Laramide orogenic belts all intersect in this region.

Topographically, Cathedral Mountain Quadrangle contains several distinctive areas of high elevation. The most prominent is Cathedral Mountain in the northwest part of the quadrangle. An erosional remnant, uplifted by intrusive syenite, Cathedral Mountain provides the best exposures of the younger volcanic units. Haley Mountain, Elephant Mountain, and Cinega Mountain are other high areas that are capped by sills and loccolithic bodies. The topography in the area was developed by differential erosion, water being the chief agent. The region is arid. However, sporadic torrential downpours cause rapid physical erosion. Calamity Creek is the principal drainage system of the quadrangle and drains into the Rio Grande River. Minor erosion is accomplished by the wind, but due to the abundant grasses and shrubs, it is not as great an agent as water.

Vegetation in the area is principally blue gramma grass. Cacti and yuccas, wild squashes, catclaw, and lechuguilla grow in abundance. Cottonwood trees line the major drainage systems.

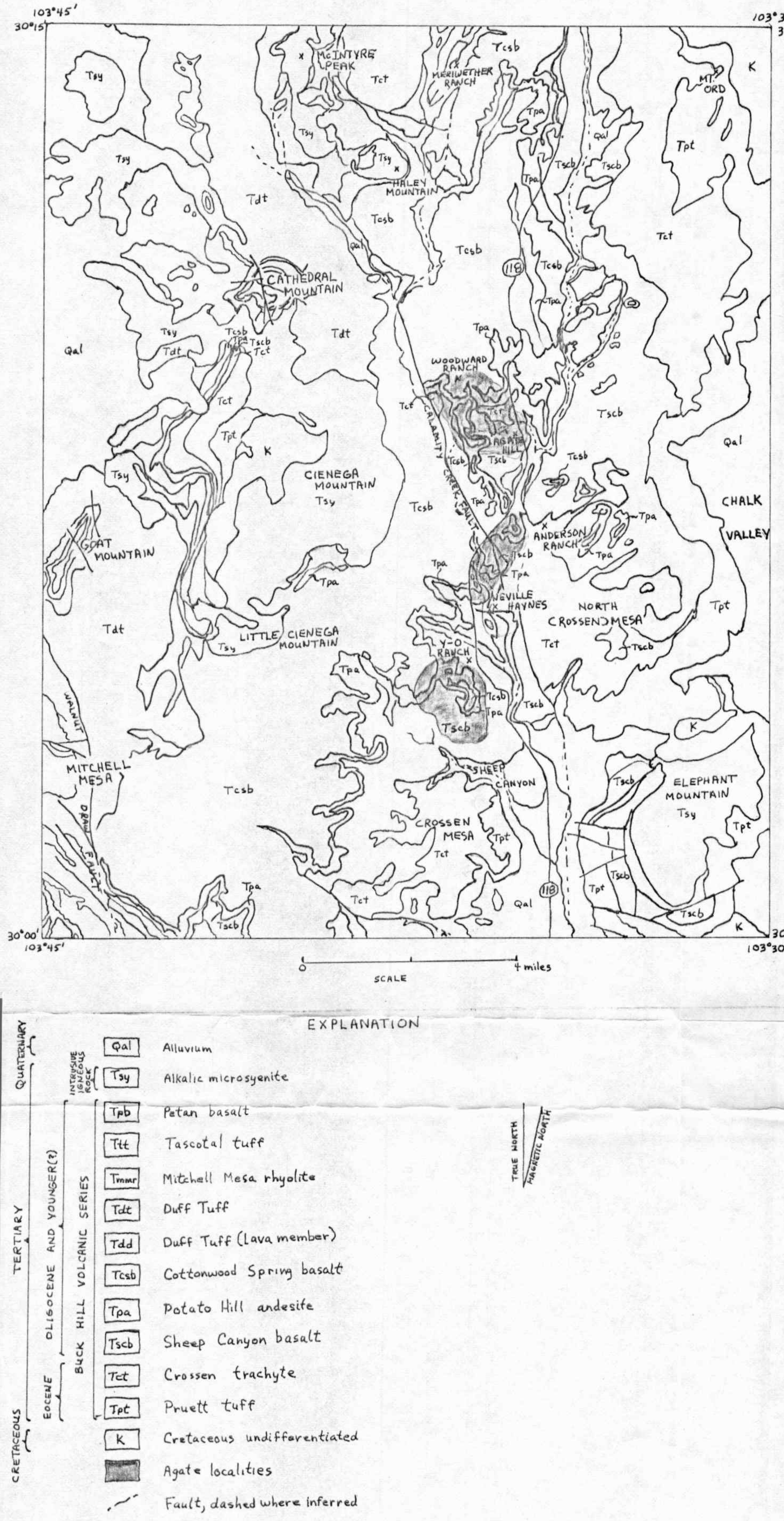

Figure 2. Geologic map of Cathedral Mountain Quadrangle, showing principal localities (McAnulty, 1955).

PREVIOUS GEOLOGIC WORK

In 1857, W. H. Emory made a military survey of the new state of Texas, which contained descriptions of the Alpine and Fort Davis areas. In 1949, Goldich and Elms did a detailed geologic study of the Buck Hill Quadrangle, a 15 minute quadrangle immediately south of the Cathedral Mountain Quadrangle. They studied and described the Oligocene volcanic rocks and named them the Buck Hill Volcanic Series.

W. N. McAnulty mapped the Cathedral Mountain Quadrangle in 1955. He described the rocks, recognized them as correlatives of the Buck Hill Volcanic Series, and revised the definition of the series. He raised the Crossen trachyte, Sheep Canyon basalt, and the Potato Hill andesite from member to formational status, because of their large extent in the Cathedral Mountain Quadrangle. Woodward (1968) provides an excellent summary of the volcanic history of the Cathedral Mountain area and its relationship to Big Bend geology.

Correlation of the rocks of the Cathedral Mountain Quadrangle to those of the Big Bend region was done by Maxwell and Dietrich (1970). Maxwell, Dietrich, Wilson, and McKnight (1972), provide a summary of the Cathedral Mountain geology in a guide book to the geology of the Big Bend area.

STRATIGRAPHY

Only those volcanic units that have been agatized are considered here. These are, from younger to older, Crossen trachyte, Sheep Canyon basalt, Potato Hill andesite, Cottonwood Spring basalt, Duff tuff, and the intrusive microsyenites (table 1).

Table 1. Composite section of Cathedral Mountain Quadrangle.

Age	Series	Formation	Thickness (feet)	Character and Distribution
Tertiary	Intrusive igneous rock	Syenite (Alkalic microsyenite) Tsy	Varies according to to type of intrusion	Light greenish gray, fine and even * textured; Weathers to a yellowish-reddish brown by exfoliation and thin sheet jointing. Occurs as sills, trap-door domes, dikes, and laccoliths. Haley Mtn., McIntyre Peak, Cathedral Mtn., Cienega Mtn., Little Cienega Mtn., Elephant Mtn.
Oligocene and younger (?)	Buck Hill Volcanic Series	Petan basalt Tpb	30-545	Very fine grained, porphrytic flows of trachybasalt with flow breccia zones. Cathedral Mtn.
		Tascotal tuff Ttt	50-462	Light gray to yellow ash flow tuff with sandstone and conglomerate beds. Cathedral Mtn.
		Mitchell Mesa rhyolite Tmmr	58-134	Pink to gray rhyolitic ash flow tuff. Cathedral Mtn.
		Duff tuff Tdt	1400-1500	Divided into 3 different rock types:* (1) lava; a yellowish brown trachyte porphry, weathers brown; A fine grained gray, pink rhyolite porphry. Haley Mtn., McIntyre Peak. (2) tuffaceous sandstone to boulder conglomerate; poor sorting, scour and fill deposits, cross bedding, and rapid facies changes, yellowish to brown to red in appearance. North and east of Cathedral Mtn., southeast side of Goat Mtn.

Table 1. Continued.

Age	Series	Formation	Thickness (feet)	Character and Distribution
		Duff tuff		(3) A white to brown gray rhyolitic ash flow tuff/air fall tuff. Goat Mtn. Predominantly southern portion of quadrangle.
		Cottonwood Spring basalt Tcsb	220-232	Purplish gray basalt. Has a speckled * shistose appearance due to feldspar laths. Many vesicular zones and amygdaloidal zones in numerous flows (at least 4). Flow breccias common. A pahoehoe lava flowing from the north and northwest. Highly dissected and eroded. Spheroidal weathering in gullies and low areas. Platy splitting on cliffs and steeper areas. Weathers to a reddish-brown color. Woodward Ranch.
		Potato Hill andesite Tpa	35-190	Fine to medium grained andesite, gray,* weathers to a reddish brown. A flow breccia on top of a thick vesicular flow, irregular vesicular hunks in the flow breccia. Weathers in thin platy sheets. Woodward Ranch, Y-O Ranch.
		Sheep Canyon basalt Tscb	0-454	Greenish black porphyritic basalt, fine* medium grained. Weathers to a greenish brown or green. At least 8 flows. Flows 1 and 3 contain hypersthene phenocrysts. Slaty and spheroidal weathering. Usually forms benches between flows. Sheep Canyon Entrant, Chalk Valley.

Table 1. Continued.

Age	Series	Formation	Thickness (feet)	Character and Distribution
Upper Eocene (Duchesne)		Crossen trachyte Tct	0-265	Porphrytic trachyte, weathers to a * reddish brown yellow. Has a pitted surface. Vesicular at top of flow; apparently only one flow. Forms steep, vertical cliffs with good vertical jointing. North Crossen Mesa, Crossen Mesa. Mt. Ord.
		Pruett tuff Tpt	474-798	Rhyolitic tuff with sandstone, conglomerate, and freshwater limestone beds. Crossen Mesa, Chalk Valley, Mt. Ord.
Cretaceous	Gulf Series	Boquillas	0-75	Marine, sedimentary rocks.

*Units described in stratigraphy section of this thesis.

Crossen trachyte

The trachyte is the oldest formation that contains agate. It occurs at Mount Ord, North Crossen Mesa, and Crossen Mesa (fig. 2). Stratigraphically it lies on the Pruett tuff and the Sheep Canyon basalt overlies it (table 1). However, the southeastern portion of the quadrangle has no trachyte between the Pruett tuff and the Sheep Canyon basalt. This has been interpreted by McAnulty (1955, p.546), as due to pre-Sheep Canyon erosion. No distinct flow units are discernable in the Crossen trachyte. There are numerous vesicular zones in well exposed sections throughout the area; with their elongation trends northwesterly to southeasterly.

The trachyte is hard and brittle with a subconchoidal fracture and is pitted where weathering has removed feldspar phenocrysts. Weathered surfaces are yellow brown to rusty brown. Occassional stubby phenocrysts of anorthoclase are enclosed in the brownish groundmass.

In thin section, a trachytic to pilotaxitic texture shows flow structures accentuated by its alignment of microlites of alkali feldspar. Orthophyric texture is also common. Phenocrysts of anorthoclase and sanidine are present (table 2). Corroded and altered to some extent, the phenocrysts show traces of carbonate, hematite, and chlorite. Altered aegerine-augite sporadically occurs as phenocrysts. Magnetite and apatite occur as accessory minerals. Primary quartz as much as fifteen percent, was reported by McAnulty (1955, p. 546) in trachyte from the Mount Ord area. In which case, the rock would be a rhyolite. Secondary quartz is abundant. In chemical analysis of this rock (table 3), the high silica content of 71 percent is explainable by introduced secondary chalcedony and quartz (McAnulty, p. 547).

The agate of Crossen trachyte is very distinctive (table 4). It is

Table 2. Modes of Buck Hill volcanic rock

	Crossen trachyte	Sheep Canyon basalt	Sheep Canyon basalt	Potato Hill andesite	Cottonwood Spring basalt	Duff tuff[2] (airfall tuff)	Intrusive syenite
	North-western portion of North Crossen Mesa, upper part of flow.	Agate Hill, top of flow.	Sheep Canyon Entrant, Middle of a flow unit.	Top of flow, Neville Haynes property.	Woodward Ranch, top of flow unit.	Eastern side of Cathedral Mountain.	Sheep Canyon Entrant.
Primary Minerals							
Orthoclase	-	-	5[3]	6	28	10	65
Anorthoclase	45	-	"	-	-	5	23
Sanidine	30	-	-	-	-	-	-
Plagioclase	-	-	65	48[1]	47	-	-
Composition			An_{55}-An_{60}	An_{55-45}	An_{55}	-	-
olivine	-	-	3	-	-	-	-
aegerine-augite	4	-	8	-	4	-	5
titano-augite	-	-	7	-	-	-	-
biotite	-	-	-	-	-	2	-

Table 2. (Con't)

	Crossen trachyte	Sheep Canyon basalt	Sheep Canyon basalt	Potato Hill andesite	Cottonwood Spring basalt	Duff tuff (airfall tuff)	Intrusive syenite
Secondary Minerals							
quartz/ chalcedony	11	20	-	15	3	-	-
chlorite	tr.	60	2	-	-	-	-
hematite	8	7	-	15	5	1	2
calcite	tr.	-	-	10	1	-	1
magnetite	1	13	7	-	3	tr.	-
ilmenite	-	-	-	-	-	-	-
apatite	tr.	-	1	-	1	-	-
antigorite	-	-	2	tr.	4	-	2[4]
iddingsite	-	-	-	tr.	2	-	"
muscovite	-	-	-	-	-	-	-
chrysotile	-	-	-	tr.	1	-	-
analcime	-	-	-	-	2	-	-
sericite	-	-	-	-	-	-	1

1. Goldich and Elms, 1949, p. 1156.
2. Rest of Duff Tuff (82 percent) consists of glass shards.
3. Combined orthoclase and anorthoclase.
4. Combined antigorite and iddingsite.

Table 3. Chemical Analyses of Buck Hill Volcanic Rocks*

	Crossen trachyte	Sheep Canyon basalt	Potato Hill andesite	Cottonwood Spring basalt	Duff tuff	Intrusive syenite
	South-eastern portion of Crossen Mesa, upper part of flow.	From porphyritic basalt in gully east side of Elephant Mtn., 100 ft. below base of syenite.	Crossen Mesa.	Potato Hill on Crossen Mesa, basal flow.	Mitchell Mesa, tuff member.	Elephant Mtn.
SiO_2	71.17	45.97	61.46	46.90	70.57	59.36
Al_2O_3	12.64	17.26	14.85	15.82	12.19	18.20
Fe_2O_3	4.28	2.84	7.23	4.18	1.29	6.19
FeO	.11	9.18	.68	7.74	.09	6.19
MgO	.13	5.63	.74	4.48	.60	.15
CaO	1.05	7.87	5.23	6.24	1.43	1.64
Na_2O	3.91	4.33	3.75	3.80	1.80	5.99
K_2O	5.05	1.00	2.58	2.32	5.09	5.28
H_2O+	.23	1.57	.22	1.93	3.36	.22
H_2O-	.12	.20	.17	1.13	2.84	1.10
CO_2	.19		.10	.02	.14	-
TiO_2	.56	2.87	1.52	2.79	.22	tr.

Table 3. (con't.)

	Crossen trachyte	Sheep Canyon basalt	Potato Hill andesite	Cottonwood Spring basalt	Duff tuff	Intrusive svenite
P_2O_5	.07	.96	1.13	1.97	.08	tr.
MnO	.14	.17	.11	.21	.01	tr.
BaO	.08	.07	.18	.23	.04	-
SrO	n.d.	.10	-	.10	n.d.	-
S	tr.		-	-	-	-
Cl	-	-	-	-	-	.31
	99.73	100.02	99.95	99.86	99.75	98.44
S.G.	2.648	2.874	2.764	2.823	2.421	

*From Goldich, S.S. and Elms, Morris A., 1949, Stratigraphy and Petrology of Buck Hill Quadrangle, Texas, Bureau of Economic Geology, The University of Texas, Austin, Texas, Report of Investigations - No.6.

Table 3. Norms of Buck Hill Volcanic Rocks*

	Crossen trachyte	Sheep Canyon basalt	Potato Hill andesite	Cottonwood Spring basalt	Intrusive syenite
Q	27.66	--	20.94	--	--
or	30.02	6.12	15.57	14.46	33.36
ab	33.01	29.87	31.96	38.25	54.49
an	1.95	25.02	15.85	15.85	--
ne	--	3.41	--	--	1.99
C	--	--	--	--	--
di	--	6.80	--	1.36	1.73
wo	--	--	--	--	0.35
hy	0.20	--	1.85	2.29	--
ol	--	15.23	--	9.74	--
mt	--	4.18	--	5.34	0.93
hm	4.32	--	7.20	--	4.80
il	0.46	5.47	1.67	5.17	0.91
tn	0.98	--	1.57	--	--
ru	--	--	--	--	--

Table 3. (con't).

	Crossen trachyte	Sheep Canyon basalt	Potato Hill andesite	Cottonwood Spring basalt	Intrusive syenite
ap	0.17	2.35	2.69	4.37	0.67
cc	0.50	--	0.20	tr.	0.70
Z	--	--	--	--	0.18

*From Goldich, S.S. and Elms, Morris A., 1949, Stratigraphy and Petrology of Buck Hill Quadrangle, Texas, Bureau of Economic Geology, The University of Texas, Austin, Texas, Report of Investigations - No. 6.

Table 4. Agate types of Buck Hill volcanic rocks.

Formation	Agate Types
Cottonwood Spring basalt	1). Plume agate; plumes black, brown, gold, and red; plumes grow horizontally along base of nodule; found in vesicles only (fig. 11). 2). Blue-gray nodules with little or no plume structure; magnesite "spots" common; with or without calcite/euhedral quartz crystals.
Potato Hill andesite	1). Diffuse red, black, lemon yellow, and clear bands; some have red plumes; originate from vesicles; "potato"-like in appearance. 2). Blue-gray nodules with little or no plume structure; magnesite "spots" common; with or without calcite/euhedral quartz crystals.
Sheep Canyon basalt	1). Microplume or "flower garden" agate; plumes of gold, red, and green color; plumes are smaller than those of Cottonwood Spring basalt; found only in layers or lenses of the basalt; plumes grow vertically (figs. 7, 8). 2). Red carnelian; purple to light red; occurs only as lenses or layers in the basalt vesicular tops. 3). Blue-gray nodules with little or no plume structure; magnesite "spots" common; with or without calcite/euhedral quartz crystals (fig. 6).
Crossen trachyte	1). Pink, with or without white bands, agate; occurs in vesicles (fig. 3).

pink; the color due to hematite (fig. 3). In thin section the hematite pervades the trachyte and appears as globules within the spherulitic chalcedony. Globules are characteristic growths from a colloidal solution (Lebedev, 1967, pp. 8-15). The hematite globules have a mean size of 20.36 $\pm$ 6.13 microns and constitute the red bands of the agates.

Fine red layers in a pink matrix are common. Cores of quartz crystals, some growing in a radial cluster fashion around a central nucleus of hematite-enriched chalcedony spherules, are present. The sequence of (1) chalcedony, (2) quartz crystals, and (3) an inner massive ball of hematite is common. Upon exposure for a long period of time, a white clayey (?) coating develops on the outer skin. Reniform aggregate structures (Lebedev, pp. 43-47) are found sparingly. Fracture lines (dessication lines ?) crisscross some agates.

Sheep Canyon basalt

This unit consists of a series of basaltic lavas, separated by thin limestone and tuff beds that overlie the Crossen trachyte. Prior to the eruption of the basalt the Crossen trachyte suffered erosion and was locally removed. The Sheep Canyon basalts flowed around Crossen trachyte hills and formed inliers. The number of flows varies from section to section. At Sheep Canyon Entrant (fig. 2), eight flows occur; at Agate Hill, three flows; and at Chalk Valley, three flows.

Vesicular tops and bottoms are common and this is one method for determining the number of flow units. The vesicular tops are a distinct green color, different from the rest of the rock. These are chloritized zones, formed during low temperature hydrothermal alteration.

The tops and bottoms of the basalt are in many cases separated by cherty, fossiliferous limestone beds or by thin tuff beds (fig. 4). The

Figure 3. Pink agate with bytroidal surface in a large vesicle of Crossen trachyte.

Figure 4. Three flows of Sheep Canyon basalt separated by freshwater limestone beds; Chalk Valley, Anderson Ranch.

tuff beds between flows are variable: one unit was strongly silicified and indurated; others were baked and very compact; one variety occurred as a white-gray weathered, friable rock. Several different localities showed a former rhyolite or ash flow. X-ray analysis showed the presence of abundant montmorillonite, α quartz, and some clinoptilolite, indication that these rocks are rhyolitic.

The basalts are rather uniform: dark green to black, fine to medium grained, and exhibits large, orange yellow phenocrysts of labradorite. Some hypersthene phenocrysts occur in the first and third flows of the Sheep Canyon basalt (McAnulty, 1955, p.547).

In thin section, the nonvesicular rocks collected from its middles of flows show an intergranular to intersertal texture. The primary mineral is labradorite (An_{55}), some are zoned with cores of An_{60} (fig. 5 and table 2). In a few sections, aegerine-augite envelops the ends of feldspar laths producing a subophitic texture. Aegerine-augite and purplish tiano-augite are the main pyroxene minerals. Olivine crystals show alteration to antigorite and chlorite. Some are completely replaced, others are merely rimmed with antigorite. Accessory minerals are magnetite, and apatite that occur as small prisms. Alkali feldspars occur interstitialy in small quantities. McAnulty (1955) found enough alkali feldspar, as high as 10 percent, to justify calling the rock a trachybasalt.

The vesicular tops show considerable alteration (table 2). Fragments of unaltered basalt are incorporated into the chloritic groundmass. Hematite and magnetite are abundant. Vesicles are filled with intergrown chalcedony and calcite. A pseudomorph of chalcedony after aragonite in one thin section showed intergrowths of calcite and chalcedony in a spherulitic crystal growth pattern.

The chemical analysis (table 3), shows a low silica content. The normative nepheline indicates that the rock is a basanitoid. The abundant TiO_2 reflects the large concentration of titano-augite in these rocks.

The agates of the Sheep Canyon basalt are both distinctive and non-distinctive. Throughout the vesicular tops of flows at Sheep Canyon entrant (fig. 2), a blue-gray agate is found (fig. 6). The southern portion of Woodward Ranch, where two flows of Sheep Canyon basalt are exposed, the same agates are found in vesicular tops of flows. On Neville Haynes' property (fig. 2), where two flows of Sheep Canyon basalt are exposed, the bottom flow or number one flow contains blue agates. These agates, fill vesicles, occasionally contain magnesite "spots", and generally lack hematite and plume structure. They show white and blue bands. The centers are occasionally filled with euhedral quartz crystals or mixtures of quartz and calcite crystals. The average size ranges from 3 to 7 cm. in length, with a mean breadth of 1-3 cm. A specimen was found that was 17 cm. in length, and 7 cm. in width.

On the topmost flow of Sheep Canyon basalt on Neville Haynes' property, plume agate occurs (fig. 7 and table 4). This variety is known as the microplume or "flower garden" agate (Woodward, personal communication, July, 1977). This agate occurs in layers or lenses within the Sheep Canyon basalt. The plumes consisting of hematite, typically grow vertically up from the bottom of the lense or layer. The vertically plumed agate is found at the top of the number two flow at Agate Hill (fig. 2), at the bottom of the second flow at Chalk Valley (fig. 8), and in the single flow surface of the basalt on Y-O Ranch. The basal plumes consist of black hematite derived from the vesicle wall.

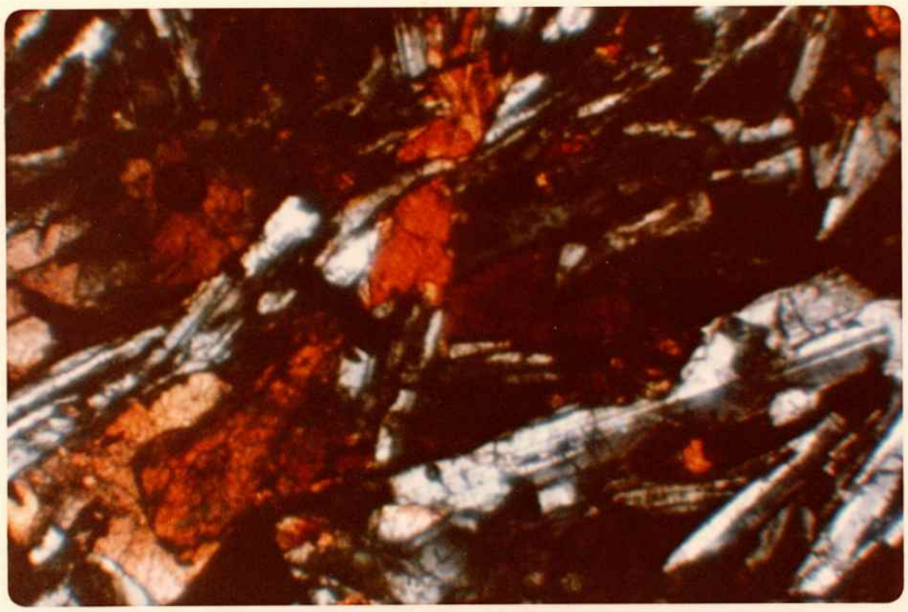

Figure 5. Labradorite laths with titano-augite and hematite from Sheep Canyon basalt, Y-O Ranch (x23).

Figure 6. Blue-gray agate nodule of vesicle filled origin from Sheep Canyon basalt.

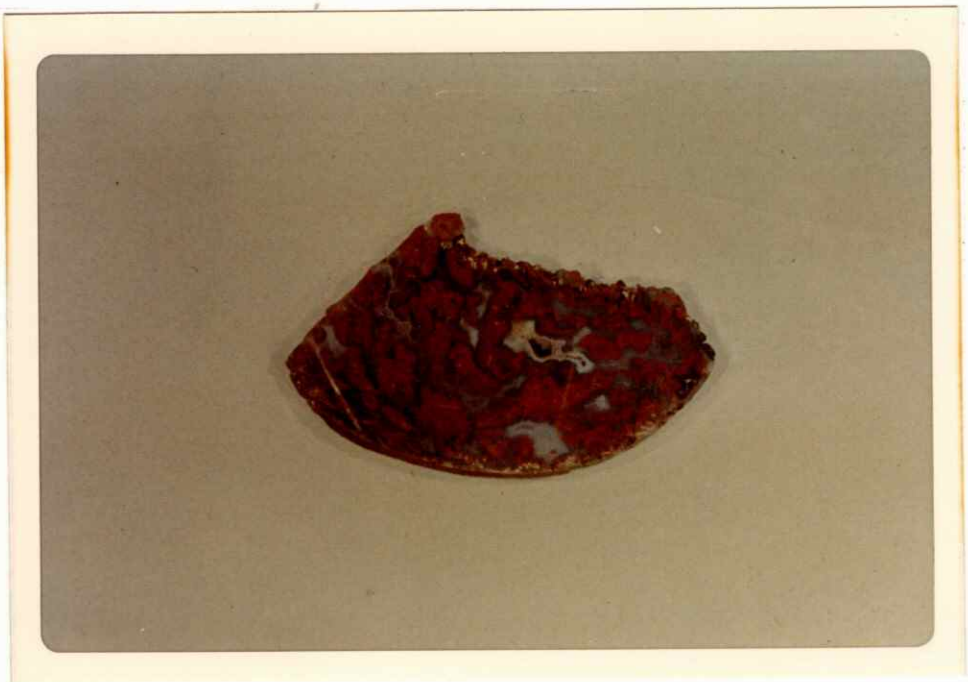

Figure 7. Flower garden agate from Sheep Canyon basalt showing vertical plume growths. Specimen measures 5.3 x 9.8 cm.

Figure 8. Flower garden agate occurrence as a lense or layer in Sheep Canyon basalt, Chalk Valley.

The color changes from black to brown to gold to red as they grow through the silica sol. The plume agate from Agate Hill has green chloritic plumes. Many of these agates have reniform aggregate and membraneous tube structures (figs. 14, 16).

Red carnelian is found at the bottom and top flows at Agate Hill (table 4). Abundant secondary minerals there include calcite of the rare basal pinacoid variety and spherulitic aragonite which is commonly replaced by agate (fig. 9). The carnelian occurs in layers and lenses in a chlorite matrix. It is red-laced. In thin section (fig. 10), globules of precipitated hematite form layers.

Potato Hill andesite

The unit consists of a distinctive aa flow that may be generally divided into an upper flow-breccia member and a lower, massive, very vesicular flow. It outcrops in the upper Sheep Canyon entrant area and at Woodward Ranch (fig. 2). The andesite overlies the Sheep Canyon basalt. A thin, well indurated tuff generally separates the units.

Weathered surfaces are a red-brown; fresh surfaces, steel gray. In the southern portion of the quadrangle, outcrops are fine grained with phenocrysts of plagioclase ranging up to 2.5 cm. in size. Toward the north, the phenocrysts gradually disappear and the rock is aphanitic.

The texture is trachytic to granular for the massive member. The andesite consists of plagioclase, some alkali feldspar, magnetite, hematite, olivine, iddingsite, antigorite, chlorite, and some clay minerals (Goldich and Elms, 1949, p. 1155) (table 2). The plagioclase occurs as small laths, but secondary hematite hinders the identification. Goldich and Elms (1949, p. 1156) identify the plagioclase as andesine (An_{55-45}). The brecciated member is similar to the massive member, but shows more

Figure 9. Pseudomorph of plume agate after aragonite from Sheep Canyon basalt.

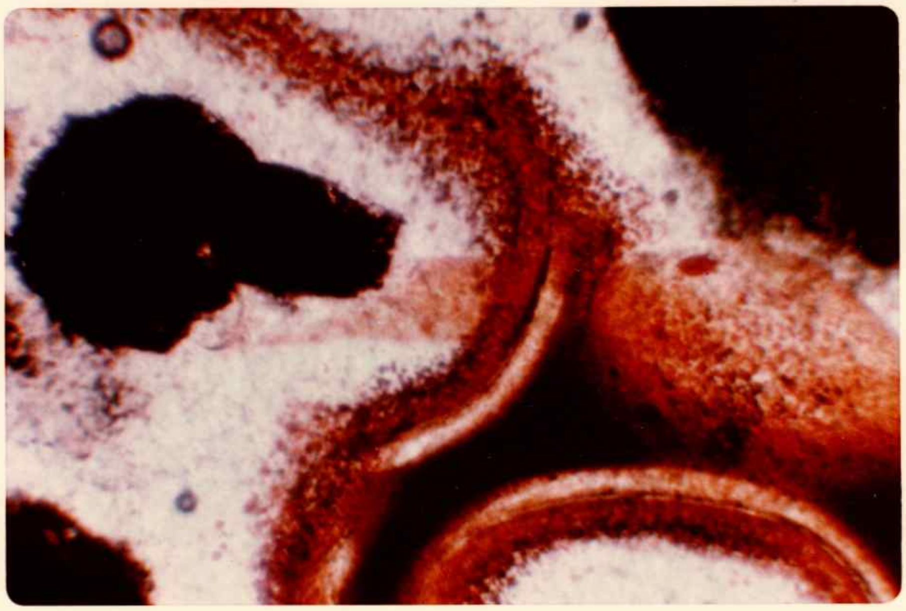

Figure 10. Globules of hematite precipitating into bands in red carnelian; from Sheep Canyon basalt, Agate Hill (x23).

oxidation. Large volumes of chalcedony and calcite cement the brecciated member.

The unusually high silica content of the andesite (table 3) is accounted for by the large amounts of introduced chalcedony and quartz. The large percentage of hematite in the norm reflects the extensive and intensive oxidation .

On Neville Haynes' property, the Potato Hill andesite yields agates from large vesicles. These agates are "potato"-like. The agates have broad, diffuse, red, black, clear, and lemon yellow bands (table 4). Some have inner cavities of drusy quartz. A red plume is found in some varieties.

Cottonwood Spring basalt

The Cottonwood Spring basalt caps many of the small hills in the area where erosion has stripped the Duff tuff away. Identification is difficult because there are numerous flows missing in the sequence due to differential erosion. The best exposures of the basalt are on the eastern sides of Cienega Mountain and Cathedral Mountain (fig. 2) where the basalt overlies Potato Hill andesite.

The rock is extremely vesicular at the tops of flows. Massive portions are fine to medium grained and red-gray. Small feldspar laths are large enough to give the rock a speckled, "schistose" appearance locally.

In thin section, the mineralogy varies slightly, from flow to flow. The texture varies from trachytic, to pilotaxitic, to subophitic. Labradorite laths (An_{55}), arranged in the direction of flow, dominate (table 2). Orthoclase mantles some of the labradorite. Alkali feldspars are sometimes as abundant as the calcic feldspars, but generally occur in smaller percentages than the calcic feldspar. Augite occurs as a light green to purplish mineral. Olivine, an abundant constituent, is altered to iddingsite, antigorite, and chyrsotile. Analcime appears between laths as interstitial clear grains or as cloudy patches replacing labradorite laths. Much of the rock is weathered and hematite obscures much of the mineralogy. Magnetite and apatite occur abundantly. Calcite and chalcedony occur as secondary minerals filling vesicles.

The agate of Cottonwood Spring basalt occurs entirely in vesicles (fig. 11) and is almost similar to the microplume agate of the Sheep Canyon basalt (table 4). The plumes grow horizontally along the length of the agate. The colors change in a pattern: from black to brown to gold to red. The plumes are probably hematite from the vesicle walls of the basalt. Many colloidal textures, as defined by Lebedev, 1967, occur within the agate, such as reniform aggregate, membraneous tubes (stalactitic), and plastic deformation. Some of the plumes are so thick that they virtually dominate the agate. Other plumes surround the outer layer of the nodule only, suggesting the plumes grew from the walls of the vesicles. Many agates consist entirely of euhedral quartz crystals, others are hollow cavities filled with drusy quartz or stalactitic growths of chalcedony. Some contain pods of the country rock.

The blue-gray agate described under the Sheep Canyon basalt section, also occur in the rocks. This variety is ubiquitous throughout the section.

Duff tuff

The Duff tuff, overlying the Cottonwood Spring basalt is found in the eastern third of the Cathedral Mountain Quadrangle (fig. 2). The Duff tuff is believed to have come from a different source than the

the previously mentioned formations (McAnulty, 1955). This source area is presumed to be Paisano Peak, a vent area seven miles north of the quadrangle, three miles west of Alpine. The lava flows, members of this unit, are thickest in the vent area and thin to the south, ending around Haley Mountain sill and Cathedral Mountain on the Meriwether Ranch. The flows, of which there are two, consist primarily of a porphrytic trachyte, weathering to a yellowish brown; and a fine grained gray, pink rhyolite porphyry (McAnulty, 1955, pp. 553-554).

Laterally the flows give way to a tuffaceous sandstone-boulder conglomerate (fig. 2). These are flood plain and stream channel deposits that are poorly sorted, show scour and fill features, cross bedding, and rapid facies changes (fig. 12).

Airfall tuffs and ash flows interfinger with the sandstone-conglomerate member at the south end of Cathedral Mountain and crop out at Goat Mountain and Mitchell Mesa (fig. 2). The interfingering airfall tuffs are crudely bedded and show some reworking. They are yellowish-white. Further south, the member is a chocolate brown, very fine-textured, ash flow tuff. Occasional feldspar and quartz phenocrysts are visible. A white coating produced by weathering gives this member a glaring appearance in the sun.

Thin sections showed progressive devitrification of the airfall tuffs. Seventy-five to ninety percent of the airfall tuff consists of glass shards which are iron stained (fig. 13). Cristobalite occurs as small crystals replacing glass shards. Phenocrysts of alkali feldspar, primarily of orthoclase and anorthoclase (table 2),predominated. Biotite phenocrysts are the main mafic mineral. A chemical analysis of this member, show it to be rich in silica (table 3) and rhyolitic.

Where the tuffs interfingered with the sandstone-conglomerate

Figure 11. Cottonwood Spring basalt with plume agate filling vesicle.

Figure 12. Outcropping of Duff tuff, sandstone-conglomerate member, showing sorting of a stream channel deposit; Meriwether Ranch.

member, more alteration and reworking is evident, the glass shard matrix is altered to clays and zeolites (?). Hematite and magnetite microcrystals are present. More reworked units contain older, basaltic clasts, and more hematite, but the feldspar remains unaltered.

The sandstone-conglomerate member consists of basaltic clasts, rounded to angular. Anorthoclase and orthoclase crystals show the same degree of reworking, but remain unaltered. Magnetite, apatite, and anastase are minor constituents. All are enclosed in a hematitic groundmass, conprising approximately 30 - 40 percent of the rock. No chalcedony or agate occurs as clasts in the conglomerate indicating that agatization is post-Duff tuff.

Intrusive Syenite

The syenites that intrude the Buck Hill Volcanic Series trend northwest to southeast throughout the quadrangle. These intrusive masses occur as sills, Haley Mountain and Elephant Mountain; domes, Elephant Mountain; laccoliths, Cienega Mountain; and plugs, McIntyre Peak and Cathedral Mountain. The syenite is light greenish gray, fine and even grained.

In thin section the rock shows a granular texture. The main minerals are alkali feldspar (table 2 and 3), which have a dusty appearance due to alteration. The feldspars seemed micro- to cryptoperthitic and weakly twinned. This rock is best described as an alkalic microsyenite (table 3). Aegerine-augite is the most abundant mafic mineral (5 - 10 percent). Olivine, 1 - 2 percent, is completely altered to serpentine and iddingsite. Apatite occurred as an accesory mineral. Secondary minerals include hematite, sericite, calcite, and clay minerals. Riebeckite characterizes the syenites of the Haley Mountain sill.

SILICA SOLUBILITIES, CRYSTAL GROWTH, AND FORMATION OF CHALCEDONY AND AGATE

Previous Work on the Solubility of Silica

The literature on silica solubility in natural waters is voluminous. The early work, 1920 to 1945, has been summarized by several authors (Roy, 1945; Kennedy, 1950; and Eitel, 1954). Hitchen (1945), makes a case for the solubility of amorphous silica and calls attention to the colloidal nature of dissolved silica.

The geologic aspects of the solubility of silica are best dealt with by Krauskopf (1956). He provides an excellent history of the chemical work. White, Brannock, and Murata (1956) give important data on the "true" solubility of silica. They discuss samples from hot springs at Steamboat Springs, Nevada, and show solubilities of silica with respect to supersaturation and the formation of chalcedony and quartz. Mackenzie and Gees (1971), under surface conditions, precipitated quartz crystals from undersaturated solutions. More recently, Oehler (1976) provides data on the nature of specific crystal growths with respect to the degree of silica saturation in solution.

Previous Work on the Nature of Chalcedony

Krauskopf (1956) defined the conditions under which chalcedony could form, e.g. near surface temperatures and pressures. This data was substantiated by White, *et al*. (1956). Carr and Fyfe (1958) and White and Corwin (1961) made chalcedony, keatite, cristobalite, and quartz in the laboratory. This was done at temperatures ranging from 100 to 300°C., simulating hydrothermal conditions. Oehler (1976), also simulating hydrothermal conditions, produced only chalcedony.

Understanding of the nature of chalcedony was advanced by the optical study of chalcedony. Previous to this work, it was believed that opal occurred between the layered bundles of fibers of chalcedony (Jones, 1952). Folk and Weaver (1952), using the electron microscope, proved that water molecules occur between the bundles of chalcedony fibers. This phenomena explains the brownish color of chalcedony under transmitted light and the differences in refractive indices of chalcedony, which range from 1.530 to 1.539. Synthetic chalcedony, produced by White and Corwin (1961), showed indices of refraction ranging from 1.48 to 1.55. Pelto (1956) heated chalcedony, and lowered the indices of refraction to 1.470. Change in the indices of refraction is obviously caused by the loss or addition of water molecules.

Formation of Metacolloidal Silica

Silicic acid and silicic gels. Silica exists as a colloid, coming from monomeric silicic acid, H_4SiO_2. Its gel state is achieved by the monomeric silicic acid atoms/molecules being attracted to the medium, in this case, water. In this sense, the gel is hydrophilic. Silicic acid molecules achieve diffusion through the water by Brownian motion.

Particles of silicic acid are very elongate, almost "fibrous" in appearance (Jirgenson and Straumanis, 1962). When a gel is formed, the particles become a combination of membraneous tube and globule types (Lebedev, 1967). Silicic acid has a very high viscosity due to its particle shape. The more elongated the particles, the more viscous the acid. As the particle shape of the silicic acid changes to globules, the solution becomes more viscous (Jirgenson and Straumanis, 1962). Thus, the gel state of a siliceous colloid is higher in viscosity than that of siliceous acid. At surface temperatures and pressures Lebedev, (1967, p. 263) observed silica gel from the Pauzhetka stream deposits and noted that the gel can easily flow.

Geologic aspects of metacolloidal silica. Chalcedony and quartz have been described in the literature as primarily hydrothermal products that occur in environments where the temperature of formation ranges from 100 to 300°C (White and Corwin, 1961, p. 118). Ingersoll (1955), using fluid inclusion thermometry, discovered the lowest temperature at which quartz crystals could form was 100-200°C.

Dissolution during weathering of natural glasses is presumed to occur at much lower temperatures, c. 25°C. Rates of dissolution and/or polymerization have been determined by Alexander et al.(1954) and summarized by Krauskopf (1956). They report that a definite solubility equilibrium was established at 25°C when the solution contains 100-140 p.p.m. SiO_2 and increased to 300-385 p.p.m. SiO_2 at 85-95°C. Krauskopf (1956, p. 24) writes:

> "The process of dissolution and polymerization of silica in dilute solution are slow. At ordinary temperatures silica gel requires several weeks to reach solubility equilibrium; opal dissolves so slowly that equilibrium probably is not reached for years. Supersaturated solutions require days or weeks to form sols and to establish equilibrium between the dissolved and colloidal fractions;.....The sluggishness of reaction means that nonequilibrium solutions -- both supersaturated solutions and solutions containing colloidal silica well below the equilibrium solubility -- may exist long enough to be of geologic interest. All of the rates are enourmously faster, of course, at temperatures near the boiling point."

Precipitation of colloidal silica (Krauskopf, 1956, p.24) may be accomplished by (1) evaporation, (2) by coprecipitation with other colloids, or (3) by a fairly concentrated solution of electrolytes.

Agate Growth and Formation

The work on agatization is scarce. The first attempt to explain agatization, the formation of concentric bands, was by Liesegang (1915). He used a simple colloidal experiment in which bichromate of potassium was mixed with a silver nitrate solution in a gel. Simple concentric bands of silver chromate were formed in the gel as the chemical reaction went to completion. The silver chromate precipitates only when the solution is saturated with silver nitrate. A layer of $AgCr_2O_4$ precipitate is formed. The silver seeks another level past the precipitate layer. When saturation occurs in this space, another precipitate layer forms. The process repeats itself; the precipitate layers (bands) forming as long as enough reactant is present to supersaturate the spaces between layers.

Farrington (1927) compared the formation of agates in nature to the phenomena described by Liesegang. No further work contributing to the understanding of the formation of agate was done until 1963, when Keith and Padden (1963, 1964) developed a general theory of spherulitic crystallization (Oehler, 1976). They note that chalcedony and agate are composed of spherulitic crystals, which require special conditions for their genesis. Primary nuclei of SiO_2 grow and eventually give rise to radially fibrous, polycrystalline aggregates in which the crystal growth is at small angles to the fiber axis, rather than along preferred crystallographic directions as in euhedral quartz crystals. Spherulitic growth (Oehler, 1976, p. 1146) occurs in, "...multicomponent systems in which component segregation occurs during crystallization and in which coefficients of diffusion in the liquid phase are small compared with crystal growth rates." The only way in which this condition can occur in a viscous material, like a colloid, is in a solution in which the concentration is well above the excess of the saturation value. Thus a saturation or viscosity "threshold" must be reached for spherulitic crystal growth or nonspherulitic crystal growth will occur (Oehler, 1976).

Silica polymorphs grow at extremely slow rates under low temperatures and pressures. As the concentration increases in the solution, the viscosity threshold is finally reached and spherulitic crystal growth will occur. The crystals will continue to grow until the colloid is consumed or diluted (Oehler, p. 1148). Conversely, in low viscosity solutions, highly diluted systems, euhedral quartz crystals or quartz overgrowths will occur (Mackenzie and Gees, 1971).

A siliceous colloid in nature will probably contain impurities. Growing spherulites would reject impurities which would be concentrated in the troughs between the spherulites and which would inhibit growth in those areas. This condition favors the growth of spherulites at their tips while the troughs between clusters of crystals are filled with impurities that now form bands.

Morphologies and textures of metacolloidal silica. From the nature of the particles in a colloidal state and crystal growth, the external morphology and texture of agates and chalcedony can reveal clues as to their origin.

Lebedev (1967, pp. 71-77) named the morphological forms plastic deformation and contraction phenomena. Contraction phenomena are shrinkage cracks caused by the drying of the gel. One of the chief arguments against the colloidal origin of chalcedony is that contraction cracks are not visible in natural chalcedony, whereas laboratory produced chalcedony and opal show shrinkage cracks. The counter-argument states that in nature chalcedony grows by the gradual accumulation of thin layers of the gel, which solidify and harden before the next layer accumulates. This process produces a large mass without dehydration cracks. This process is called the Wiegener effect, in which smaller colloidal particles accumulate around larger nuclei from dilute colloidal systems (Park and McDiarmid, 1970).

Lebedev (1967) also mentions textures common to chalcedony. The most diagnostic texture is the reniform aggregate which consists of hemispherically uneven surfaces that give rise to a botryoidal appearance (fig. 14). Other characteristic textures are globular and micro-collomorphic (fig. 15), membraneous tube (fig. 16), and spherultic crystal growth (fig. 17).

Theories of the Origins of the Silica for Agates

There are several theories as to the origins of agates and the origin of the silica source. The best known and most widely accepted explanation involve silica-rich hydrothermal fluids which agatize vesicles and cavities in the rock (Frondel, 1962). The silica-rich fluids are injected into the vesicles while the enclosing rock is still hot. The fluids are essentially a silica gel or sol which is rhythmically deposited in the cavity perhaps by periodic infusion of the gel.

The second theory concerns alteration and weathering of airfall tuffs, airfall ash, and ash flow tuffs. Meteroic waters and groundwater readily dissolve silica from ash and tuffs, producing in time, colloidal flocs or gels of silica (Krauskopf, 1956 and Surdham, 1972). The silica is deposited in vesicles and cavities of the underlying rocks. Agates, thus, are metacolloidal deposits.

The third and last theory is a variant of the second theory that involves dissolution of a silica-rich component of the rock and precip-

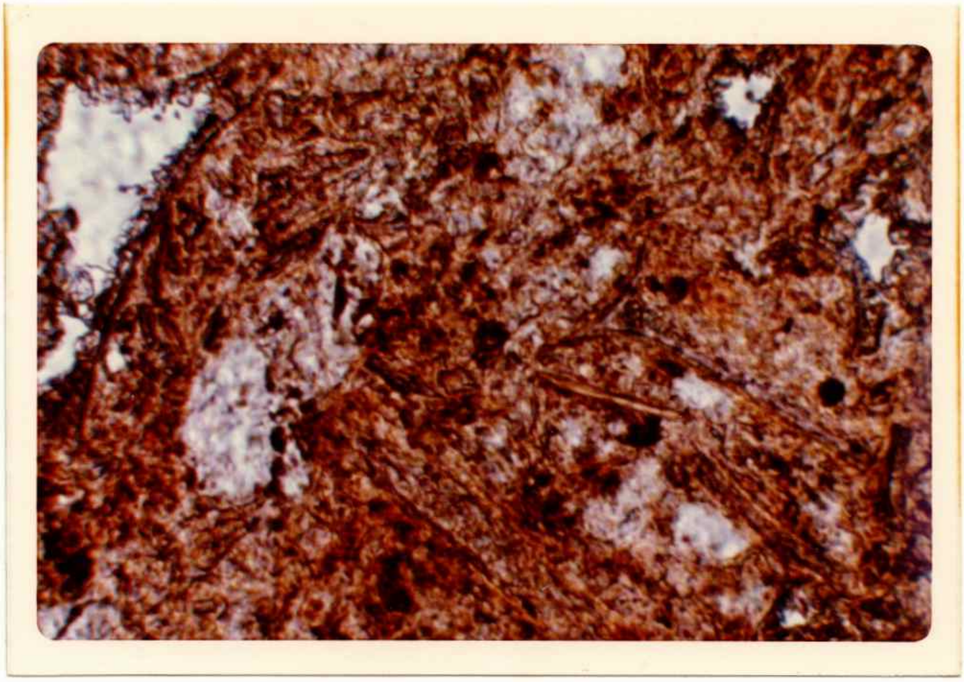

Figure 13. Duff tuff, airfall tuff member, with glass shards and alkali feldspar phenocrysts in an iron stained matrix (x60).

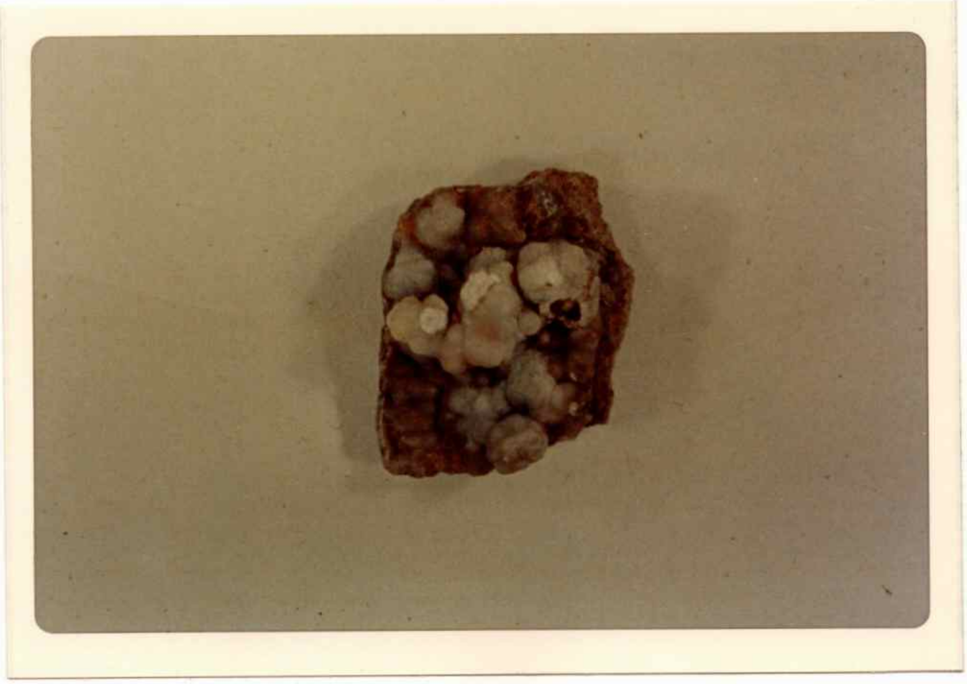

Figure 14. Reniform aggregate structure in a Sheep Canyon basalt agate.

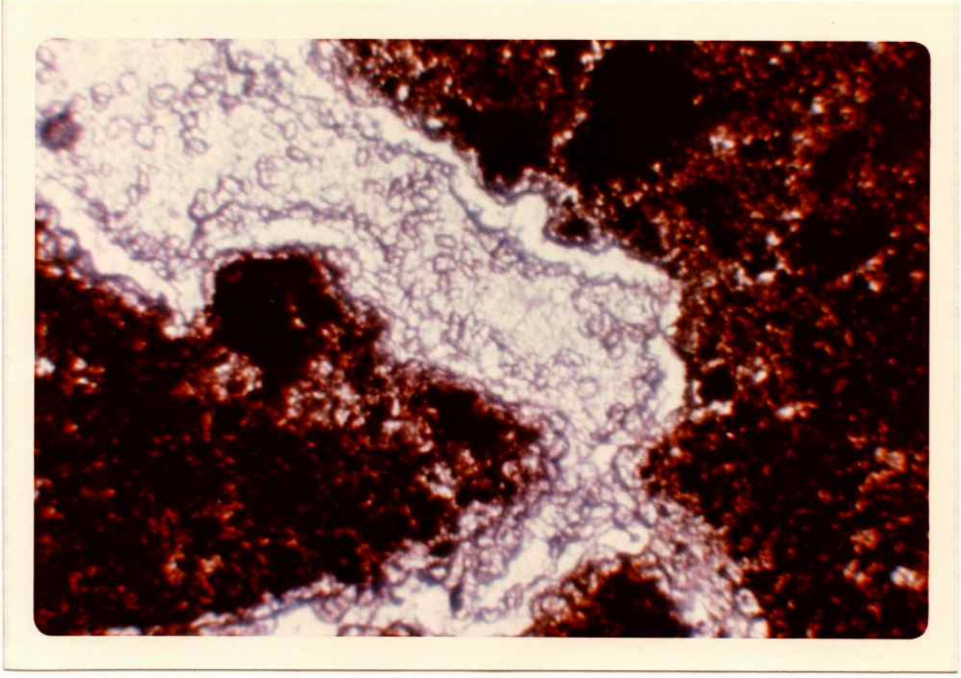

Figure 15. Microcollomorphic texture in opal from Cottonwood Spring basalt (x23).

Figure 16. Membraneous tube or stalactitic growths in agate from Sheep Canyon basalt.

Figure 17. Spherulitic growth of chalcedony, indicative of colloidal origins; from Sheep Canyon basalt, Agate Hill (x23).

itation of the silica in vesicles and cavities within the source rock.

ORIGIN OF THE AGATES IN CATHEDRAL MOUNTAIN QUADRANGLE

Plume agate is unique to the Cathedral Mountain area. Any theory of the origin of the agate in these rocks must account for these structures and,also, the remarkable abundance of agate in the area. An indication of the abundance can be gained by considering the agate content of an exposure, on the Woodward Ranch, of the Cottonwood Spring basalt. The exposure is 150 feet thick, 1,300 feet wide, 4,700 feet long, and consists of about 8 percent agate or approximately 73,320,000 cubic feet of agate. This is just one small field and does not take into account other agate-rich areas and formations (fig. 2). The large volume of agate requires a large volume of source material. The determination and investigation of the source material and its nature, the origin of the agate and the history of agatization was the purpose of this thesis.

Agate and chalcedony occur through 1,200 feet of section that ranges from the Crossen trachyte to the Cottonwood Spring basalt. The volcanic rocks came from several different source areas (Maxwell and Dietrich, 1970) and range from undersaturated basalts and syenites to rhyolites. The Pruett tuff, Crossen trachyte, Sheep Canyon basalt, Potato Hill andesite, and the Cottonwood Spring basalt are presumed to originate from an unknown source area in the Davis Mountains which has long since been covered by younger volcanic rocks (McAnulty, 1955). The Duff tuff probably comes from the Paisano Peak area (McAnulty, 1955), a few miles north of the area. The Mitchell Mesa rhyolite, Tascotal tuff, and Petan basalt come from the southern source area, the Chinati

Mountains (Maxwell and Dietrich, 1970).

Study is also complicated by the lava amount. Much of the volcanic rock is gone (fig. 2). Weathering has released much agate from the rocks and much of it has been transported downslope.

Despite these problems, it is possible to evaluate the various possibilities for the origin of the agate in light of field observations and laboratory work and to suggest a geologic history for these rocks that include the history of agatization.

The theory of the hydrothermal origin of the agates must involve the production of hydrothermal solutions during the period of volcanivity or intrusive igneous activity. Such solutions, silica-rich or silica-poor would pass through the rocks, silica-poor solutions might leach silica from the rocks, and deposit it as agate in vesicles and other openings in the rock.

The field evidence, analytical data, and laboratory work do not support or indicate a history of hydrothermal activity.

Secondary mineralization is confined to the tops of flows in the Sheep Canyon basalt where chloritization has also occurred. The alteration is spotty and resembles that usually ascribed to late stage deuteric alteration. Most of the flow units have not been altered. The feldspars are not sericitized and the mafic minerals are not altered.

The Crossen trachyte, Potato Hill andesite, and Cottonwood Spring basalt all have suffered extensive erosion, weathering, and oxidation. The Potato Hill andesite is not much more than a residual soil in some areas.

The agatization is spotty. Many of the vesicles and joints are not filled with agate and the mineralization does not seem to be related to any alteration that might indicate the activity of hydrothermal solutions.

The intrusive, alkali microsyenite in this area is undersaturated with respect to silica and thus not a likely candidate for a source of hydrothermal silica. Contacts of lavas and pyroclastics with the sills, laccoliths, and plugs showed no hydrothermal alteration and no silicification. If these bodies had produced large volumes of hydrothermal solutions there should be some evidence of hydrothermal alteration at contacts with other units. There are none.

It seems reasonable to expect hydrothermal solutions to be produced in the vicinity of vents. The source area of these rocks in in the Davis Mountains, 10 to 12 miles away from the agatized rocks. On the other hand, such alteration is evident by the Duff tuff in the Paisano Peak area, where it shows alteration to nontronite (?).

The most likely source for the silica required to form the agates of the area is probably the tuffaceous units that occur in and on the agatized volcanic rocks (table 2). The field evidence, experimental data, and laboratory analysis support this hypothesis.

The Duff tuff is silica-rich (table 3). Tuffaceous sandstones-boulder conglomerates occur between the lava member and the airfall tuff member of the Duff tuff. The sandstone-conglomerate member shows scour and fill structures, poorly sorted beds, rapid facies changes, and crossbedding that indicate these are stream and floodplain deposits (fig. 12). Thin section analysis of the sandstones shows unaltered feldspars typical of the devitrified ash flow member of the Duff tuff, and basaltic and rhyolitic clasts in a hematitic groundmass. No agate or chalcedony is found in the sandstones or conglomerates indicating agatization must be post-Duff tuff and hence, could not be attributable to any pre-Duff tuff igneous activity.

Ash flow tuffs that occur between the Sheep Canyon basalt flows and the Potato Hill andesite are differentially hornfelsized. Other tuffs are weathered. X-ray analysis of the weathered tuffs indicate the presence of montmorillonite, clinoptilolite, quartz, various opaque heavies, and zircons. The quartz, at least some of the heavy minerals and zircons are probably primary minerals. The montmorillonite and clinoptilolite are secondary products of the weathering.

The tuff may be altered by meteoric waters, in an open system, as defined by Surdham (1972), with the water cutting, frequently, across stratigraphic boundaries. In an open system, weathering of ash and airfall tuffs produces a siliceous gel and montmorillonite depending on whether the pH is greater or less than 8 (Surdham, 1972). Little clinoptilolite, the next mineral phase, is formed as silica is now controlled by the solid phase, e.g. agates. The ion product of sodium, silicic acid, and aluminate necessary to form clinoptilolite is very rarely exceeded in this case (Walton, 1975). Simply stated, weathering of siliceous units like the interflow ashes and tuffs and the Duff tuff may yield colloidal silica in abundance as indicated below:

ash flow/airfall tuff + devitrification + $H_2O \longrightarrow$
siliceous gel + montmorillonite $\longrightarrow$ agates $\pm$
clinoptilolite

The silica-rich solution thus produced infiltrates the underlying volcanic rocks, accumulating in vesicles, cracks, and fissures and permeates the rock. Permeation by silica is shown by the chemical analysis (table 3) of Crossen trachyte and Potato Hill andesite, which have an abnormally high percentage of silica for a trachyte and andesite, respectively, due to the introduced chalcedony (Goldich and Elms, 1949, p. 1152). The silica-rich solutions, however, did not permeate every vesicle and crack and hence, the agatization is spotty (fig. 2).

Precipitation of the colloidal silica was accomplished by evaporation and/or electrolytes (Krauskopf, 1956, p. 24). The Fe_2O_3, that constitutes the plumes and color the agate, must have been in solution with the silica or was introduced from the vesicle walls of the rock. The gel has considerable electrical charge and may attract iron salts (Krauskopf, 1956, p. 24). Once in the vesicle, the filling probably expands as silica particles changed from elongate to globular, a feature which also inhibits escape from the vesicle (Woodward, personal communication, August, 1977).

The colloidal textures, reniform aggregate (fig. 14), globular and microcollomorphic (fig. 15), membraneous tube (fig. 16), and spherulitic crystal growth (fig. 17) shown in the agates are further evidence of growth from colloidal solutions of silica (Lebedev, 1967).

CONCLUSION AND HISTORY OF AGATIZATION

That the agates of the Cathedral Mountain Quadrangle are not hydrothermal in origin is indicated by the lack of the hydrothermal alteration of the rocks that contain the agate and, since the local flow units or intrusive rocks seem unlikely sources of hydrothermal solutions, obvious or reasonable source of any hydrothermal solutions is lacking.

On the other hand, the geologic evidence does show that the agates are precipitated from colloidal solution (Lebedev, 1967 and Oehler, 1976), who proved that chalcedony could be produced at 20 to 30 ^{o} C.

The stratigraphic evidence indicates that the agatization is post-Duff tuff. Silica-rich solutions were probably produced as soon after post-Duff tuff times as weathering could occur. Thus, agatization of these rocks probably dates from mid-Miocene times. The climate (Woodward, 1968) since that time has been cyclical, ranging from humid to dry. Much erosion has taken place. Erosion exposed tuffs to meteoric waters and, therefore, has been an important factor in the production of the silica-rich, agatizing solutions. Exposure of mineralized rocks may also have hastened syneresis, the dehydration and hardening of the gel.

Field work indicates that the various varieties of plume agate are reliable indicators of stratigraphic units (table 4), but that the blue-gray agates occur throughout the volcanic pile. No evidence of any age differential of the agates has been detected. The cyclic diffusion and concentration of impurities within the silica gel to produce layered structures like those of the blue-gray agates is well understood (Lebedev, 1967). The mechanism of growth of the plumes is not understood, but might reflect a point source of contamination of pure silica-gels after the gel enters the vesicle or cavity. Experiments with silica gels would probably help explain the process of plume growth. The varieties of plume agate and their occurrence and confinement to single stratigraphic horizons are probably related to the chemistry of the rocks in which the agates occur.

The occurrence of the plume agate and the blue-gray, banded agates may reflect two major periods of weathering and erosion or a change in rate of weathering and erosion or in the chemistry of the silica-bearing solutions during agatizations. The field work, laboratory analysis of the rocks and agates of this area, and a thorough review of the subject of dissolution of silica and its precipitation have revealed no evidence that may be used to evaluate this aspect of the problem.

BIBLIOGRAPHY

Alexander, G. B., Heston, W. M., and Iler, H. K., 1954, The solubility of amorphous silica in water: Journal of Physical Chemistry, volume 58, p. 453-455.

Carr, R. M., and Fyfe, W. S., 1958, Some observations of the crystallization of amorphous silica: American Mineralogist, volume 43, p. 908-916.

Dake, H. C., Fleener, Frank L., and Wilson, Ben Hur, 1938, Quartz family minerals: McGraw-Hill Book Co., New York, 304 p.

Eitel, W., 1954, Physical chemistry of the silicates: University of Chicago Press, Chicago.

Emory, W. H., 1857, United States and Mexican boundary survey: U.S. 34th Cong., 1st session, Ex. Doc., No. 135, volume 1, pt. 1, p. 74-92.

Farrington, O. C., 1927, Agate-physical properties and origins: Field Museum of Natural History, Chicago, Geology Leaflet 8, 36 p.

Folk, Robert L., and Weaver, Charles Edward, 1952, A study of the texture of composition of chert: American Journal of Science, volume 250, p. 498-510.

Frondel, Clifford, 1962, The system of mineralogy (Dana's), Volume III, Silica Minerals, seventh ed.: John Wiley and Sons, Inc., New York.

Goldich, Samuel S., and Elms, Morris A., 1949, Stratigraphy and petrology of Buck Hill Quadrangle, Texas: Geol. Soc. America, volume 60, no. 7, p. 1133-1182.

Goldschmidt, V. M., 1954, Geochemistry, ed. Alex Muir: Clarendon Press, Oxford, 730 p.

Hitchen, C. S., 1945, The "solubility" of silica: Econ. Geol., volume 40, p. 361-365.

Ingerson, Earl, 1955, Geologic thermometry : Special Paper 62, Geol. Soc. America, p. 465-488.

-----1955, Methods and problems in geologic thermometry: Econ. Geol., Fiftieth Anniversary Volume, p. 341-410.

Jirgensons, J., and Straumanis, A., 1962, A short textbook of colloid chemistry, second ed.: McGraw-Hill, New York.

Jones, Francis T., 1952, Iris agate: American Mineralogist, volume 37, p. 578-587.

Kennedy, G. C., 1950, A portion of the system silica-water: Econ. Geol., volume 45, p. 629-653.

Krauskopf, Konrad B., 1956, Dissolution and precipitation of silica at low temperatures: Geochimica et Cosmochimica Acta, volume 10, p. 1-26.

-----1959, The geochemistry of silica in sedimentary environments: Silica in Sediments, S.E.P.M. Special Publication, No. 7, p. 4-19.

-----1967, Introduction to geochemistry: McGraw-Hill Book Co., New York.

Lebedev, Lev. M., 1967, Metacolloids in endogenic deposits: Plenum Press, New York, 298 p.

Liesegang, R. E., 1915, Die achate: Dresden and Leipzig.

Mackenzie, F. T., and Gees, R., 1971, Quartz: synthesis at earth surface conditions: Science, volume 173, p. 533-535.

Maxwell, Ross A., and Dietrich, John W., 1970, Correlation of Tertiary rock units, West Texas: Report of Investigations-No. 70, Bureau of Economic Geology, Univ. of Texas at Austin, Austin, Texas.

Maxwell, Ross A., Dietrich, J. W., Wilson, J. A., and McKnight, J. F., 1972, Geology of the Big Bend Area, Texas: West Texas Geological Society Field Trip Guidebook, Midland, Texas, 233 p.

McAnulty, W. N., 1955, Geology of Cathedral Mountain Quadrangle, Brewster County, Texas: Bull. Geol. Soc. of America, volume 66, p. 531-588.

Oehler, John H., 1976, Hydrothermal crystallization of silica gel: Geol. Soc. of America Bull., volume 87, p. 1143-1152.

Pabian, Roger K., 1977, Inclusions in agates from the late precambrian Keweenawan basalts of the Lake Superior region, Minnesota and Michigan [abs.]: Proceedings the Nebraska Academy of Sciences and Affiliated Societies, 87th Annual Meeting, p. 42-43.

Park, Charles F., Jr., and MacDiarmid, Roy A., 1970, Ore deposits: W. H. Freeman and Co., San Francisco,

Pelto, Chester R., 1956, A study of chalcedony: American Journal of Science, volume 254, p. 32-50.

Ratliff, L. F., and Allen, B. L., 1970, The mineralogy and genesis of two soils from Trans-Pecos Texas: Soil Science, volume 110, no. 8, p. 268-277.

Roy, C. J., 1945, Silica in natural waters: American Journal of Science, volume 243, p. 393-403.

Sinkankas, John, 1961, What do we really know about the formation of agate and chalcedony?: Agates of North America, Arts and Crafts Press, San Diego, p. 6-10.

Surdam, Ronald C., and Parker, Ronald D., 1972, Authigenic alumino-silicate minerals in the tuffaceous rocks of the Green River Formation, Wyoming: Geol. Soc. of America Bull., volume 83, p. 689-700.

Walton, Anthony W., 1975, Zeolitic diagenesis in Oligocene volcanic sediments, Trans-Pecos Texas: G. S. A. Bull., volume 86, p. 615-624.

White, Donald E., Brannock, W. W., and Murata, K. J., 1956, Silica in hot-spring waters: Geochimica et Cosmochimica Acta, volume 10, p. 27-59.

White, J. F., and Corwin, J. F., 1961, Synthesis and origin of chalcedony: The American Mineralogist, volume 46, p. 112-119.

Woodward, Frank J., Jr., 1968, A summary of the Tertiary geology in Trans-Pecos Texas and its relation to rocks and mineral deposits in the Gulf Coast Plain: Unpublished manuscript.

Zarins, Andrejs, 1977, Origins and geologic history of siliceous metacolloidal deposits, Cathedral Mountain Quadrangle, Brewster County, Texas [abs.]: Proceedings the Nebraska Academy of Sciences and Affiliated Societies, 87th Annual Meeting, p. 46.