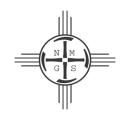
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# Diagenesis of the fanglomerate of Little Florida Mountains (Miocene), southwestern New Mexico

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# DIAGENESIS OF THE FANGLOMERATE OF LITTLE FLORIDA MOUNTAINS (MIOCENE), SOUTHWESTERN NEW MEXICO

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Abstract—The Fanglomerate of Little Florida Mountains is mainly composed of gravel-sized rhyolite clasts with arenaceous portions of the matrix classified as volcanic arenites (Q<sub>4</sub>F<sub>4</sub>RF<sub>92</sub>). The sand-sized rock fragment population is 96% volcanic and dominated by rhyolite grains (rhyolite 88%, intermediates 8%, basalt 4%). Authigenic products are diverse and primarily siliceous in composition (70% of total). Although there is overlap in the timing of some cement events, a paragenetic sequence is recognizable: (earliest) (1) limonite, (2) mixed-layer illite/smectite plus limonite, (3) megacrystalline quartz, (4) impure siliceous cements (silica ± limonite ± clay), (5) microcrystalline quartz, (6) illite, (7) opal, (8) calcite, (9) Ca-zeolite and (10) pyrite. Soil-forming processes and hydrothermal fluids may have had a major influence on cement type, amount and distribution.

#### INTRODUCTION

#### **Objectives**

Siliciclastics rich in siliceous volcanic clasts have received only modest study in terms of relating clast composition to the specifics of diagenesis. This paper concentrates on the Fanglomerate of Little Florida Mountains (Miocene), southwestern New Mexico, with the primary focus of documenting diagenetic changes characteristic of such a sedimentary rock suite (Fig. 1).

The principal objectives of the paper are: (1) to describe the framework grain and cement compositions of the fanglomerate and (2) to

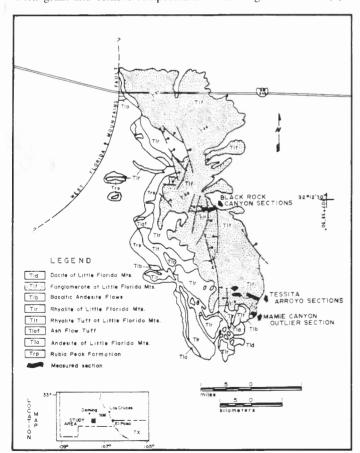


FIGURE 1. Simplified geologic and location map of the Little Florida Mountains showing areal distribution of the fanglomerate and measured section locations. Only faults of direct importance to this study are shown (adapted from Clemons, 1986).

interpret the paragenetic sequence and conditions of formation for alteration products and cements.

#### Location and geologic setting

The Little Florida Mountains make up a 9-km-long, north-northwest-trending linear range located in Luna County, New Mexico, about 10 km east-southeast of Deming (Fig. 1).

By early Miocene the study area was located within or adjacent to an extensive magmatic arc that existed along much of the flank of the southern Cordillera (Dickinson, 1981), formed by the subduction of the Farallon crustal plate beneath the western margin of the North American plate (Seager and Morgan, 1979). Regional extension in the area of the present-day Little Florida Mountains began about 29 my ago, initiating the break-up of earlier Oligocene batholiths (Chapin and Seager, 1975). The Rhyolite of Little Florida Mountains (source area for much of the fanglomerate) was emplaced as a series of domal and dike-like intrusions approximately 23.6  $\pm$  1.0 my ago (K-Ar radiometric age date by Clemons, 1982), and subsequently, the basaltic-andesite flows of the Little Florida Mountains were extruded (Fig. 2)

The Fanglomerate of Little Florida Mountains was deposited adjacent to and in response to the Basin-and-Range style uplift of the Little Florida fault block (Clemons, 1982). The basal beds of the fanglomerate lie unconformably upon the flow-banded Rhyolite of Little Florida Mountains (comprising the bulk of the presently-exposed, presumed source area), rhyolite tuffs and basaltic-andesite flows, and contain boulders derived from each suite. Overlying the basal beds are approximately 660 m of interbedded conglomerates, breccias and sandstones composed primarily of rhyolite clasts (Clemons, 1982). The fanglomerate is composed of three major facies; (1) matrix-supported breccias and conglomerates, (2) grain-support conglomerates, and (3) horizontally-laminated sandstones. These units are interpreted as interlayered debris-flow, sheetflood and channel deposits associated with alluvial fan deposition (Kiely, 1987).

Numerous late Cenozoic normal faults cut the Fanglomerate of Little Florida Mountains. These faults have a general north-northwest trend with dips of 60° to the east to vertical. Lasky (1940) measured a displacement in excess of 200 m of a mineralized vein along a normal fault in Black Rock Canyon (Fig. 1). Many of these faults are the host for calcite, fluorite, barite and extensive manganese mineral deposits (Lasky, 1940; Griswold, 1961; Clemons, 1982).

#### Previous work

The Fanglomerate of Little Florida Mountains was named by Clemons (1982) for exposures at the type locality in the Little Florida Mountains. Darton (1916) originally called the fanglomerate an "agglomerate," and Lasky (1940) observed thin sandstone beds intercalated with the conglomeratic units. He measured at least 330 m of section, and Clemons (1982) estimated approximately 660 m of the fanglomerate. Due to pervasive normal faulting of the unit, it is impossible to measure a

# Generalized Stratigraphic Section of the Little Florida Mountains

Period	Epoch	Age	Map Symbol	Unit	Thick- ness	Description of Rock Units	Columnar Section
QUATERNARY	ane - Holocene		Qs Qbf Qca Qpa Qpy Qpy			Unconsolidated dune deposits; caliche horizons.  Gravelly to clayey basinal distributary channel deposits.  Partially cemented alluvial fan deposits.	K K K
	Pleistocene-		QE E	Mimbres Formation	m16-0	Thick caliche accumulations.  Alluvial fan deposits (sandy to gravelly) with interbedded sand lenses.	William Cont.
ERTIARY	Pliocene	Pilocene pi Dacite of L. Florida Mts		Dacite of L. Florida Mts		Grayish-red, microcrystalline to glassy intrusive unit.  Spherulitic bordered, steeply-dipping to vertical flow foliation.  Extensively hydrothermally altered.	
	Miocene		Tif	Fanglomerate of Little Florida Mountains	300-650m	Interbedded breccias, conglomerates, and conglomeratic sandstones. Framework composed of rhyolitic, andesitic, and basaltic-andesite rock fragments, quartz, micas, and feldspars; matrix- to grain-supported. Cementing agents include silica (quartz, opal), clay, iron-oxide, impure siliceous cements, calcite, feldspar, and pyrite. Deposited as superimposed and juxtaposed debris flows and intercalated sheet gravel deposits in a semi-arid alluvial fan setting.	
			TIb	Basaltic-an- desite flows		Vesicular, amygdaloidal flow units; dark grayish- red to reddish-brown. Intersertal texture composed of plagioclase laths in a red cryptocrystalline glass groundmass. Extensively altered; calcite, chalcedony vug-fill.	
		23.6 ± 1.0 my	Tlr	Rhyolite of L. Florida Mts.		Elongate,irregular,domal and dike-like intrusions. Grayish-pink to dark grayish-red; flow-banded, massive, autobrecciated textures. Finely crystalline; 1-3% microphenocrysts, mostly sanidine, idiomorphic quartz, and biotite.	
1			Tit	Rhyolite Tuff L. Florida Mts.		Greenish to orangish-gray lithic tuffs and interbedded volcaniclastic units.  Black, perlitic obsidian zones on intrusion borders.	
	Oligocene	37.3 ±   Taf   Way + 100m   Taf   Ta		0-100m	Grayish-pink to pale red vent margin extrusive.  Phenocrysts comprised of plagioclase, sanidine, quartz, biotite, pumice, and lithics in a matrix of abundant axiolitic shards and glass.		
	Eocene		Tla	Andesite of L. Florida Mts.		Gray to brownish-gray intrusive and extrusive units. Plagioclase laths form a hyalopilitic, pilotax- itic textured rock with oxidized hornblende, augite, and magnetite phenocrysts (2%).	
			Тгр	Rubio Peak Formation	0-490m	Volcanic arenites and pebble conglomerates. Massive breccias and conglomeratic sandstones. Breccias composed of polylithic volcanics. Basal conglomerates with limestone, andesite, and granite clasts.	2000 000 000

FIGURE 2. Generalized stratigraphic section of the Little Florida Mountains, with descriptions of salient features of each rock unit (constructed, in part, with information from Clemons, 1982). Symbol K represents caliche accumulations.

complete, uninterrupted stratigraphic section. Clemons (1982) tentatively considered the fanglomerate to be middle Miocene, based on its stratigraphic position above the 23.6-my-old Rhyolite of Little Florida Mountains.

#### Methods and techniques

Five partial stratigraphic sections of the Fanglomerate of Little Florida Mountains were measured (Fig. 1), and detailed lithologic descriptions made. Fifty-seven samples taken from the arenaceous matrix of the conglomeratic facies (representing all five stratigraphic sections) were thin-sectioned and analyzed petrographically using a standard 300-grain point count method (Van der Plas and Tobi, 1965). Point counts were used to identify and determine the abundances of framework constituents, cements, grain replacements/alterations and porosity. Textural observerations were recorded, leading to the determination of the relative timing of diagenetic events. All samples were blue-dye impregnated to facilitate recognition of porosity, and stained for potassium and plagioclase feldspars. Two selected thin sections were polished and analyzed using reflected light microscopy for the identification of rare, opaque pore-filling minerals.

A total of eleven samples that correspond to critically important thin sections were analyzed using x-ray diffraction techniques  $(2^{\circ}-2 \theta)$  per minute). Eight of the samples were analyzed for clay content using desiccated (48 hours), glycolated (8 hours) and oven-heated (500°C for 1 hour) samples for the determination of expandable, non-expandable, and mixed-layer clays (Carroll, 1970). Three other whole-rock samples were analyzed with XRD for the identification of specific iron oxide/hydroxide and feldspar species.

#### FRAMEWORK-GRAIN COMPOSITION

The arenaceous portions of the Fanglomerate of Little Florida Mountains are rhyolitic arenites using a modification of the Folk (1974) classification scheme. Framework grain compositions were normalized and plotted on a quartz-feldspar-rock fragment ternary diagram plus volcanic-plutonic-sedimentary and rhyolite-intermediate-basalt daughter triangles. The average composition of the arenaceous portion of the fanglomerate is  $Q_4F_4RF_{92}$ ,  $Vol_{96}Plu_2Sed_2$  and  $Rhy_{88}Int_8Bas_4$  (Fig. 3).

## **Rock fragments**

Rhyolitic rock fragments are texturally diverse, including porphyritic, micro- to cryptocrystalline and tuffaceous grains. They contain less than two percent (visual estimate in thin section) microphenocrysts, mostly of euhedral quartz, sanidine and biotite, with lesser amounts of sodic plagioclase in a microcrystalline to glassy matrix. The rock microfabric is either structureless or flow banded. Aphanitic and recrystallized glassy rock fragments are the most abundant constituent of the sand-size matrix of the fanglomerate, making up an average of 46% (range 5.3 to 76.3%) of the total components. Recrystallized glass fragments reflect a variety of devitrification processes that include spherulitization and crystallization to megaquartz. Porphyritic rhyolites, consisting of a more abundant phenocryst assemblage (<5%), are less common (range 0 to 28.5%; 6.1% avg.) in the arenaceous matrix, as are rhyolite tuff fragments, which are composed mostly of tricuspate glass shards and microphenocrysts (<5%) in glassy groundmass.

Intermediate volcanic rock fragments (5.4% of the total components) commonly display an intersertal texture (pilotaxitic to trachytic) of elongate, c-twinned plagioclase laths and altered pyroxene and amphibole phenocrysts in a cryptocrystalline matrix. A portion of the intermediates contain more than 75% plagioclase. The plagioclase in approximately 50% of the intermediate rock fragments is pervasively stained with potassium cobaltinitrite, which is used for detection of K-feldspars. This may represent potassium metasomatism.

Basalt rock fragments contain plagioclase phenocrysts (<60% of each fragment) in a dark red cryptocrystalline or glassy groundmass, and comprise 2.4% of all rock constituents. Original plagioclase laths are pervasively altered (accentuated by potassium cobaltinitrite stain), and primary mafic minerals are rarely visible due to extensive oxidation. Small patches of secondary, iron-rich opaque minerals are fairly common alteration products.

Quartzofeldspathic rock fragments (0.3% of the total framework constituents) consist of individual crystals or radial aggregates of prismatic potassium feldspar and perthite in a quartz groundmass, and are probably dike or domal intrusive-related, as evidenced by their coarse crystal size and exsolution lamellae (in perthite; Hurlbut and Klein, 1977).

Epiclastic rock fragments (Fisher, 1961, 1966) consisting of fanglomerate clasts cemented with impure siliceous cements and ranging in size from 1.5 to 3.0 mm, are rare (0.6% of all components) framework grain components.

#### Mineral constituents

Optically clear, nonundulose to slightly undulose (Basu et al., 1975), subhedral to euhedral monocrystalline quartz is common throughout the arenaceous portion of the fanglomerate, and comprises up to 6.6% of some samples (avg. 2%). Grains range in size from 0.01 to 3.5 mm (long dimension), and often exhibit perlitic-like cracking. Bipyramidal, embayed grains with glass inclusions and remnant glass on their edges indicate a volcanic/hypabyssal origin for much of the quartz.

Polycrystalline quartz grains with serrate or crenulate crystalline boundries and greater than three crystal units/grain are rare (avg. 2% of framework constituents). Grains range in size from 0.25 to 2 mm in long dimension.

Euhedral to subhedral K-feldspar (up to 1.4 mm in diameter) comprises an average of 2.3% (0 to 7.8% of framework) of all components in the arenaceous fanglomerate matrix. Grains are generally inclusion-poor, and are untwinned or c-twinned. Internal cleavage planes are distinct, and perlitic cracking is not uncommon. Up to 50% of the K-feldspar in some samples has dissolved cores (avg. 10% of all samples), enhanced by blue-dye impregnation. Sanidine ± orthoclase ± adularia are common feldspar species in the unit, based on XRD analyses.

Elongate, c-twinned (>untwinned) plagioclase feldspars, predominantly albite and oligoclase, are uncommon constituents (0.5% avg.), but comprise up to five percent of some samples. Core dissolution of plagioclase is also quite common.

Biotite is present in small amounts (0.5% of all components) in most samples, and commonly exhibits evidence of alteration to iron oxide/hydroxide. These alterations are manifested as both reddish-orange halos around biotite grains and concentrations of hematite/limonite along cleavage planes. The deformation of biotite around more competent framework grains is common, as is separation of this mineral along cleavage.

The category of mafics consists of dark-reddish brown, highly altered grains with euhedral (hexagonal and octagonal) or amorphous shapes, and comprise less than one percent of the arenaceous portion of the fanglomerate. The morphology and cleavage (at nearly 90° and 60°–120° angles) of the euhedral grains suggest that they were originally pyroxenes and amphiboles, respectively. Amorphous opaques may be detrital or diagenetic, though it is difficult to ascertain which because extensive oxidation of the iron contained within the grains has produced diffuse red halos around grains, thus obliterating much of the textural evidence.

#### DIAGENETIC COMPONENTS

The sand-size matrix of the Fanglomerate of Little Florida Mountains contains several types of cement/alteration products, including: (1) impure siliceous cements; (2) microcrystalline quartz; (3) megacrystalline quartz; (4) opal; (5) limonite; (6) mixed-layer illite/smectite plus limonite; (7) illite; (8) calcite; (9) Ca-zeolite and (10) pyrite (Fig. 4). While some of the cements/alteration products are ubiquitous (e.g., impure siliceous cements), others (e.g., Ca-zeolite) are found only at specific stratigraphic sections.

#### Impure siliceous cements

The group of cements collectively termed impure siliceous cements includes mixtures (in different proportions) of micrycrystalline quartz (average crystal size  $\leq 20 \, \mu$ ), amorphous or microcrystalline iron oxide/hydroxide and a yellow, highly birefringent clay.

A predominantly microquartz-iron oxide/hydroxide-clay cement phase constitutes 7.7% (0.6 to 27.6% of framework) of the total sandstone

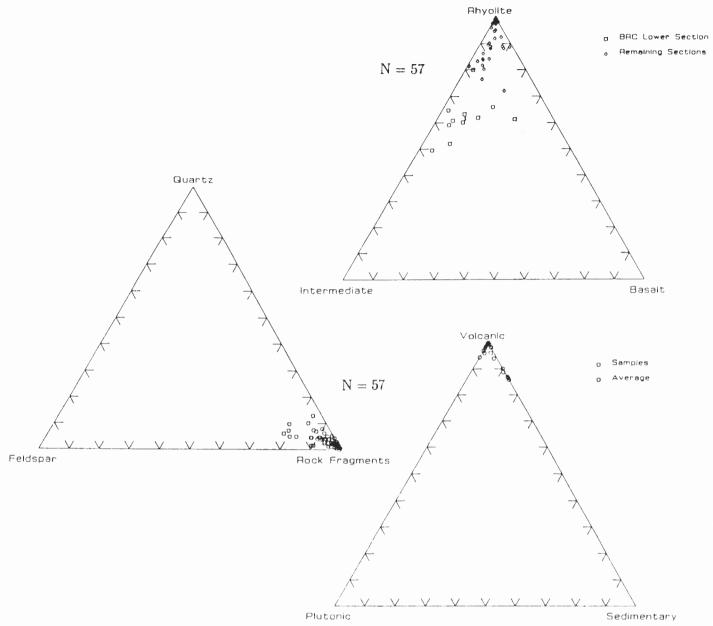


FIGURE 3. Ternary diagrams illustrating the Q-F-RF, volcanic-plutonic-sedimentary rock fragment, and rhyolite-intermediate-basalt rock fragment compositions of the arenaceous portion of the Fanglomerate of Little Florida Mountains. Q = quartz (monocrystalline + polycrystalline), F = feldspar (K-feldspar + plagioclase) and RF = total rock fragments (after Folk, 1974). Each sample point based on 300 grain point counts; 57 samples analyzed.

components (Fig. 5a). Admixed microquartz-iron oxide/hydroxide cement is also present in all samples, comprising between 0.5 and 22.9% (avg. 4.9%) of all components of the arenaceous portion of the fanglomerate. A mixture of microquartz-clay is the least volumetrically important cement of the three (<1% of all components). These three categories of impure siliceous cements together make up 44% of the cement (Fig. 4).

Cements in this group appear to be heterogeneous mixtures of intergrown crystals and/or amorphous clots. The cement patches range in size from 0.05 to 2.4 mm. The crystal size and morphology of the individual components are not easily distinguishable petrographically, because of their small grain size. The cements are generally pore-filling, and often completely support sand-sized framework grains.

#### Microcrystalline quartz

Microcrystalline quartz cement is defined as a siliceous cement intermixed with less than 10% other constituents, and with a crystal grain size of less than or equal to  $20~\mu$ . It is an uncommon (range 0 to 9.3%; avg. 1.5% of total components; avg. 6% of cements) pore-filling cement generally found as patches in impure siliceous cements. Size and shape of crystals in the cement are difficult to determine petrographically because of the fine grain size.

#### Megacrystalline quartz

Megacrystalline quartz can be differentiated from microcrystalline quartz by crystal size (>20  $\mu$ ) and by the often clearly-defined, subhedral to euhedral crystalline form of the cement in thin section. Megaquartz is a ubiquitous constituent, comprising up to 21% of the total components (avg. 5.3%) and 60% of the cement components (avg. 19%).

Cement habit and crystal size are highly variable, but the cement type can be separated into two groups: (1) coarse crystalline, bladed pore-lining cement with orientation of crystal c-axes perpendicular to grain surfaces, and (2) coarser-grained, pore-filling cement with sub-

CEMENT TYPE	NORMALIZED %	CRYSTAL HABIT/TEXTURE	PORE/GRAIN RELATIONSHIP
Impure Siliceous (Silica/Limonite/Clay)	44	Microcrystalline	Pore-filling
Megacrystalline Quartz	19	Coarse Crystalline, Bladed to Equant	Pore-filling Grain Replacement Cement Replacement
Illite/Smectite	18	Very Fine-Grained, Laminar	Pore-Lining to Pore-Filling
Limonite	9	Amorphous or Cryptocrystalline	Grain Coating Pore-Filling
Microcrystalline Quartz	6	Euhedral to Subhedral, Microcrystallinc	Pore-Filling
Pyrite	1	Aggregates of Euhedral to Subhedral Crystals	Pore-Filling
Calcite	1	Sparry, Large Crystals and Small Rhombs	Pore-Filling Grain Replacement Cement Replacement
Illite	1	Small Flakes, Laminations, Aggregated Stacks	Pore-Lining
Opal	Tr	Colloform, Growth-Banded	Pore-Lining to Pore-Filling
Ca-Zeolite	Tr	Large, Euhedral to Subhedral Crystals	Pore-Filling

FIGURE 4. Summary table of cement component of arenaceous portion of the fanglomerate. Cements are normalized to 100.

equant crystals up to 0.3 mm wide. The crystal size of quartz systematically increases toward pore centers (Fig. 5b). Individual crystals are predominantly nonundulose (Basu et al., 1975), often display 120° triple junctions and are euhedral to anhedral (mostly subhedral).

#### Opal

Opal is a rare cement (<1% of all cement components) that lines or fills pores and voids left by the dissolution of volcanic glass. Opal has a colloform habit with well-developed growth bands that closely conform to framework grain outlines, and was identified by its morphology and isotropic optical character.

#### Limonite

Iron oxide/hydroxide cement, hereafter called limonite, coats the majority of framework grains with a 5–50- $\mu$ -thick film (Fig. 5c), and occurs as incomplete pore-filling patches (up to 0.4 mm across). Deer et al. (1975) define limonite as hydrated iron oxides with poorly developed crystalline character, and of uncertain identity. In this study, all iron oxides/hydroxides have been grouped as limonite. The cement makes up an average of 2.5% (0.3 to 10%) of all constituents, and nine percent (from 1 to 25%) of the cement components. Limonite is also present as a replacement and alteration product on two percent of rhyolitic rock fragments. In association with clay, the mineraloid is found on an additional 1.8% of the rhyolitic grains.

Identification of this cement was based on its dark-reddish to orangish-brown color in reflected light. Limonite is inferred to be amorphous or to contain cryptocrystalline minerals, as it did not yield x-ray diffraction peaks characteristic of goethite and lepidocrocite (FeO(OH)), or hematite (Fe $_2O_3$ ).

#### Mixed-layer illite/smectite + limonite

An important cementing agent in the arenaceous matrix of the fanglomerate is randomly interstratified illite/smectite. The deep reddishorange, birefringent cement comprises up to 14.5% of the total components in some samples (up to 49% of the cements), and averages 5.5% overall (18% of the cements). This authigenic component is separated from the impure siliceous cements by its lack of admixed silica. The clay is primarily a pore-lining and grain-coating cement (up to 0.8 mm thick), and displays orientation of clay laminations tangential to grain surfaces (Fig. 5d). Well-developed medial sutures (Dickinson, 1970) are not uncommon.

The bright red staining of the illite/smectite component is due to the presence of intermixed iron-oxide/hydroxide, as small ( $<1~\mu$ ) red blebs that are randomly distributed in the clay. XRD analysis did not show significant amounts of crystalline hematite, geothite or lepidocrocite.

#### Illite

Illite is an uncommon cement (range 0 to 1.7%, avg. 0.5% of total components; range 0 to 7%, avg. 1% of cements) found as pore-filling aggregates of stacked crystals, as thin, tangentially-oriented flakes coating grains and as laminations intercalated with other cement phases (e.g., opal). Illite is a replacement/alteration product on 2.6% of rhyolitic rock fragments. Identification of illite was accomplished by its morphology, high birefringence and optical similarity to muscovite.

#### Calcite

Calcite is a minor cement, comprising one percent of all cement components. The majority of the cement is sparry, found as large (up to 1.5 mm), intergrown, anhedral crystals with distinct twinning lamellae, and usually fills pores and dissolution voids (Fig. 5c). Rare patches of small, subequant, rhombohedral or bladed calcite crystals act as incomplete pore fill. Less commonly, blocky calcite replaces siliceous volcanic rock fragments (<1% of all lithics).

#### Ca-zeolite

Pore-filling Ca-zeolite cement is found in small amounts in the fanglomerate (<1%), displays distinct cleavage in one direction and (mildly) takes on potassium rhodizonate stain because of the presence of calcium in the mineral structure. Crystals range in size from 0.2 to 1.1 mm (long dimension), are euhedral to subhedral and sometimes form 120° triple junctions at their intersection. General identification of this cement was accomplished with SEM-EDX analysis, which yielded strong Si<sup>4+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, and subordinate Ba<sup>2+</sup> and K<sup>+</sup> spectral peaks, and by its morphology.

#### **Pyrite**

Pyrite is an uncommon (range 0 to 3.3%, avg. 0.5% of total components; range 0 to 14%, avg. 2% of cements), incomplete pore-filling cement that forms aggregates of anhedral to subhedral crystals or individual pyritohedrons, and is opaque in transmitted light. Crystals range in size from 0.05 to 0.1 mm in long dimension.

## POROSITY

Though ubiquitous, porosity is a volumetrically minor feature of the sand-size portion of the fanglomerate, averaging only 3.8% (range 0 to 14%) of the total rock components. Three types of porosity were identified, including partial and total framework grain dissolution porosity and intergranular porosity.

Intergranular porosity (52.6% of all porosity) is both primary and secondary in origin. Primary intergranular porosity is preserved in pore centers where cementation is incomplete, most commonly in megaquartz-cemented zones. Pores are angular in shape, ranging in size from 0.09 to 2.5 mm in long dimension (avg. 0.5 mm). Secondary intergranular porosity ranges from elongate and oversize pores (up to 4.0 mm across) accompanied by "floating" grains (Schmidt and McDonald, 1979) to patches of small (5  $\mu$  to 0.2 mm), irregularly-shaped solution voids. Clay and impure siliceous cements are the most pervasively dissolved authigenic phases that yield secondary intergranular porosity.

Framework grain dissolution porosity (Siebert et al., 1984) is created by dissolution of unstable grains, such as glassy and tuffaceous rhyolites and feldspars (Mathiesen, 1984; Surdham et al., 1984). The original detrital outlines of dissolved grains are often preserved by remnant iron-oxide/hydroxide and/or clay rims. Framework grain dissolution porosity ranges in size from 0.1 to 3.7 mm (avg. 0.8 mm), and is found as (1) clusters of small (0.05 to 0.2 mm), round to angular intergranular pores, (2) larger (0.2 to 0.9 mm), irregular voids, and (3) large (>1 mm) pores whose shapes mimic the original outlines of completely dissolved framework grains.

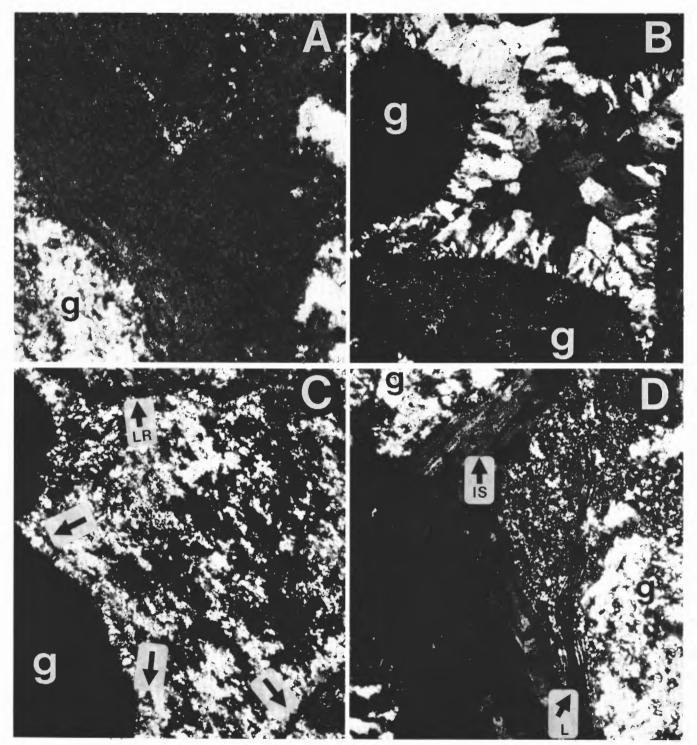


FIGURE 5. Photomicrographs of (A) Pore-filling, impure siliceous cement composed primarily of microcrystalline quartz, iron oxide/hydroxide and clay.  $\mathbf{g} =$  framework grain. Crossed nicols, horizontal dimension = 0.7 mm; (B) Coarse, subequant, subhedral to anhedral megacrystalline quartz cement as occluding cement. Notice increase in size of individual crystal units from clast surfaces toward pore center.  $\mathbf{g} =$  framework grain. Crossed nicols, horizontal dimension = 0.7 mm; (C) Late-stage pore-filling calcite cement (white, central portion) replacing earlier, pore-filling opal cement (black, central portion). Early, grain-coating limonite, and pore-lining megaquartz present on detrital grains (arrows).  $\mathbf{g} =$  framework grain. Crossed nicols, long dimension = 0.4 mm; (D) Laminar, mixed-layer illite/smectite plus limonite (IS). Notice high concentration of limonite (black) along cleavage of biotite (arrow) contained within rhyolite rock fragment, and around intermediate volcanic rock fragment (lower left).  $\mathbf{g} =$  framework grain. Crossed nicols, horizontal dimension = 0.77 mm.

#### DIAGENETIC HISTORY

# Limonite and clays

The paragenetic sequence of the authigenic products in the arenaceous portion of the fanglomerate is relatively complex (Fig. 6). Several cements overlap in timing of formation. One of the earliest diagenetic cement phases is limonite (iron-oxide/hydroxide), which pervasively coats most framework grain types. Limonite was probably formed, in part, by the dissolution/alteration of amphibole and pyroxene derived from intermediate and basaltic rock fragments, as well as biotite from all volcanic rock fragment types. Pronounced halos of reddish-orange pigment surrounding discrete amphibole, biotite and volcanic rock fragments provide petrographic evidence for such sources (Walker, 1967; Walker et al., 1978). Penetration of water along mineral cleavages enhances the dissolution of mafic silicate minerals, often resulting in the release of cations such as Mg<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup>, thus promoting the breakdown of grain structure (Huang, 1977).

Dissolution of Fe-bearing silicates, such as biotite, augite and oxides like magnetite, is enhanced by chelating agents present in soil horizons (Schalscha et al., 1967; James, 1985). Small amounts of calcium oxalate, for example, are found in interstitial waters in many soil profiles (Graustein et al., 1977; Antweiler and Drever, 1982). These ligands act to increase the solubility and mobility of such constituents as aluminum and iron by several orders of magnitude (Lind and Hem, 1975). Fe<sup>2+</sup> and Fe<sup>3+</sup> can be leached from iron-rich minerals in the A-horizon of small profiles and migrate into lower soil zones or permeable parent material as organometallic complexes. At this point, the organic molecules may degrade and release cations (Graustein, 1976). Such cations are free to form oxides and hydroxides, depending on the specific EhpH conditions. Other early cements in the fanglomerate display textures (clay skins) suggestive of the influence of near-surface, soil-related processes.

Petrographic evidence, such as infilling of dissolution voids with limonite and siliceous cements, suggests that dissolution of unstable framework grains and coeval creation of secondary porosity began relatively early in the diagenetic history of the fanglomerate. Highly dissolved grains (glass > tuff > K-feldspar and plagioclase) are preserved in part or exclusively by limonite (±clay) rims, and resultant intragranular voids filled by a variety of later cements. Grain dissolution

# Paragenesis of the Fanglomerate of Little Florida Mountains

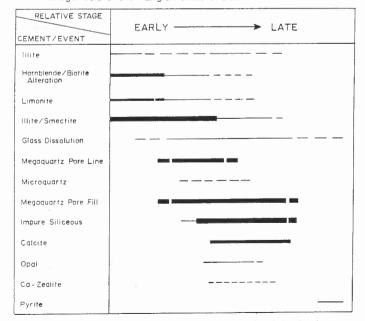


FIGURE 6. General cement and alteration paragenesis of the fanglomerate. Relative timing and abundance of each diagenetic event is indicated by length and width of bars, respectively.

probably had a major influence on the cement mineralogy by making many cations available for various chemical reactions (Surdham et al., 1984).

Iron-stained, interlayered illite/smectite forms an early cement, and displays textures (i.e., strong laminar orientation) and extinction patterns similar to clay coatings in soils (Fig. 5d; FitzPatrick, 1984). Thin layers of highly stained illite/smectite are often hard to distinguish from limonite, and the timing of formation of both cement phases was, in the relative textural sense, largely contiguous. Clay coatings can be formed by progressive deposition of clay-size particles on framework grains or pore surfaces. "Clay skins" (Walker et al., 1978) are often formed by infiltration of clay into porous deposits, such as conglomerates, in semi-arid environments where water tables are typically low (Walker and Crone, 1974; Walker et al., 1978). Yet clay coatings do not necessarily imply vertical translocation and accumulation; in situ formation of illite/smectite in terrigenous clastics is common in both soil (FitzPatrick, 1984) and non-soil (Wilson and Pittman, 1977) zones. A portion of the clay may have been incorporated into the fanglomerate during deposition. Clay clasts surrounded by other cement components may represent post-depositional infiltration residues (Wilson and Pittman, 1977), in situ fragmentation of authigenic grain coats (FitzPatrick, 1984) or syndepositional destruction and incorporation of soil clays by mass flow. The fact that clay fragments are encased in impure siliceous cements indicates that they were formed prior to silica cementation.

Red coloration of clay coatings is common in the fanglomerate as well as being typical of other coarse clastic deposits (Walker, 1967; Walker et al., 1978; Morad, 1984); the color is probably due to the presence of intermixed ferric oxides/hydroxides.

Although it can be difficult to distinguish soil from non-soil and allogenic from authigenic clay coatings, some of the characteristics outlined above, such as parallel grain orientation and medial sutures, indicate that the clay has undergone significant diagenetic organization and/or reorganization. There are several possible sources for the interlayered illite/smectite, including the alteration of hornblende, pyroxene, biotite, volcanic glass, K-feldspar and calcic plagioclase (Walker, 1967; Wilson and Pittman, 1977; Huang, 1977; Morad, 1984; Nesibtt and Young, 1984; Morad and Aldahan, 1987).

#### Siliceous cements

Formation of siliceous cements in the fanglomerate was dependent on the solubility and concentration of silica in pore fluids, which in turn was controlled by such factors as (1) temperature, (2) pH, (3) salinity, (4) type and abundance of additional silica species in solution and (5) mineralogy of the sandstone (Williams and Crerar, 1985; Porter and James, 1986). Solubility of all varieties of solid silica increases with increasing temperature (Walther and Helgeson, 1977). At higher temperatures, silica-saturated solutions contain primarily monomeric silica species, leading to the formation of coarse-crystalline quartz phases (Williams and Crerar, 1985). The deposition of pore-filling megacrystalline quartz cement in the fanglomerate may have been related to hydrothermal processes. In a study of very similar megaquartz cements, Simonson (1987) suggested that quartz cement formed from cooling hydrothermal fluids. Cooling dramatically decreases the solubility of quartz (Holland and Malinin, 1979) and saturates fluids with respect to silica, thus often resulting in quartz precipitation (Rose and Burt, 1979). Silica formation from hydrothermal waters is most effective where the temperatures drop from about 300°C to 100°C (Rimstidt and Barnes, 1980). The presence of an extensive fault system with accompanying hydrothermal mineral deposits, combined with evidence for extensive igneous activity, attest to the probable importance of hydrothermal processes in the area.

Bladed, pore-lining megaquartz is often found predating opal and probably represents precipitation from fluids undersaturated with respect to opal-A (Simonson, 1987). Ross and Chirenzelli (1985) noted the occurrence of pore-lining megaquartz in silcretes, which accumulated in thicknesses of up to 30 m on rhyolite flows, domes and volcanic conglomerates. These and other authors (Summerfield, 1983) suggest that pore-lining and -filling megaquartz cements present in silcretes are

the result of slow rates of quartz precipitation. This slow nucleation may be controlled by steadily decreasing silica concentrations, which are brought about by declining pore-fluid flow rates corresponding to permeability reduction.

Chemical environment of deposition is a major determining factor in the specific type of siliceous cement that will form. Solubility of amorphous silica sharply increases at pH values higher than about nine (Volosov et al., 1972), due to the disassociation of silicic acid, the predominant aqueous species in undersaturated silica solutions. The activity of silicic acid (H<sub>4</sub>SiO<sub>4</sub>) controls the degree of silica saturation in pore fluids (Williams et al., 1985).

A small drop in pH at higher alkalinities, temperatures or fluid volume (by evaporation, for example) can cause a silica solution to become supersaturated with respect to opal-A, thus inducing polymerization, colloid formation and precipitation of opal (Williams and Crerar, 1985). FitzPatrick (1984) documents the presence of opal pore linings in soil zones in arid and semi-arid environments. Thiry and Millot (1987) suggest that opal formation following microquartz cementation in silcrete profiles is the result of progressive concentration of silicon and other cations by downward moving solutions. As in the fanglomerate, illite is interlayered with opal in these silcretes, and may be an expression of the influx of K \* cations. The prevalence of growth-banding in opal in the arenaceous portion of the fanglomerate indicates that silica concentrations changed through time (Simonson, 1987).

Microcrystalline quartz cement is formed from fluids with silica concentrations beneath the opal-A saturation curve (Williams and Crerar, 1985). One plausible explanation for the origin of impure siliceous cements is relatively slow crystallization in the presence of other cations, which tends to limit quartz crystal size (Summerfield, 1983; Thiry and Millot, 1987). The abundance of intermixed iron-oxide and clay (illite?) in the siliceous cements lends credence to this hypothesis. Incorporation of silica during neoformation of intermixed clays, and their post-formational adsorption of silica could lower concentrations enough to facilitate microquartz crystallization (Williams et al., 1985).

There are several possible sources for the silica in the fanglomerate cements. Major externally derived sources include silica-rich hydrothermal fluids. Underlying the fanglomerate are excellent potential silica sources, including high silica (72-81 wt.%) rhyolites, andesites and microcrystalline quartz-cemented clastics (Lobo Formation). With the extensive fault system in the Little Florida Mountains acting as a fluid conduit network, subsurface waters could easily have become enriched in silica. The fault-controlled manganese, calcite, barite and fluorite deposits of the area attest to the influence of hydrothermal mineralization. The Little Florida Mountains lie within a zone of anomalously high heat flow (>2.5 HFU), perhaps related to deep crustal fractures that penetrate the mantle (Reiter et al., 1975). The source of hydrothermal fluids or heat to maintain a high geothermal gradient may have been magmatic bodies genetically related to these deep fractures. The intrusive/extrusive Rhyolite (early Miocene) and Dacite (late Miocene ?) of Little Florida Mountains show that magmatic processes were active in the study area over most of the Miocene. The latter unit intrudes an older, hydrothermally-altered vent area (Clemons, 1982).

Local sources for the silica include the dissolution and devitrification of siliceous volcanic rock fragments, features commonly observed in thin section. Dissolution is one result of early hydration reactions, which act to increase the pH of interstitial fluids and release cations into solution (Surdham and Boles, 1979; Krauskopf, 1979). A calculation of the ratio of intragranular porosity in rhyolitic rock fragments (78 wt.% SiO<sub>2</sub>) to total siliceous cements indicates that between five and 21% (avg. 13%) of these cements can be accounted for by local dissolution/reprecipitation events. This assumes that all released silica is precipitated as siliceous cement, while ignoring phase volume changes. Moreover, devitrification of volcanic glass can produce smectite cements and excess silica (Blatt et al., 1980).

Free silica was possibly provided by the dissolution of K-feldspar (or other feldspars) to produce quartz, according to the following reaction:

$$KAlSi_3O_8 + 4H^+ = 3SiO_2 + Al^{3+} + K^+ + 2H_2O$$
 Eq. 1

Morad and Aldahan (1987) calculated that the dissolution of 100 cm<sup>3</sup> of K-feldspar produces 63 cm<sup>3</sup> of quartz, leaving a 37% increase in porosity. Yet another feldspar alteration, a hydrolysis reaction (Henley et al., 1984),

$$3KA1Si_3O_8 + 2H^+ = KA1_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2K^+$$
 Eq. 2

produces subequal amounts of illite and quartz from the alteration of K-feldspar (Morad and Aldahan, 1987). Two moles of excess potassium and 15% porosity are created by this reaction.

In addition, a portion of the pore-lining illite cement was probably created by alteration of K-feldspars (Eq. 2), biotite (Morad, 1984) and volcanic glass, which together could supply many of the needed cations for clay formation (Henley et al., 1984).

### Other authigenic products

Pore-filling calcite, which formed after pore-lining megaquartz, is common in volcaniclast-rich sandstones (Galloway, 1974; Surdham and Boles, 1979; Mathisen, 1984). There are several possible calcium sources including (1) hydration and dissolution of plagioclase feldspars (Surdham and Boles, 1979), (2) infiltration of fluids rich in calcium due to the dissolution of caliche zones (FitzPatrick, 1984) and (3) release of calcium during the degradation of calcium oxalate in soils (Graustein et al., 1977). Possible sources of HCO<sub>3</sub><sup>-</sup> include the atmosphere and the decomposition of organic matter (Surdham and Boles, 1979). Formation of calcite cement after opal was probably directed by the pH and/or temperature of interstitial fluids (Blatt et al., 1980). At pH values greater than nine, opal tends to dissolve and calcite precipitate. As noted above, solubility of silica increases with temperature, but that of calcite decreases (Ellis, 1963).

Ca-zeolite is found as a pore-filling cement, often in close spatial association with calcite. Zeolites are common authigenic cements in volcaniclast-rich sandstones. They form in association with saline, alkaline pore fluids (Deffeyes, 1959; Hay, 1966; Surdham and Boles, 1979; Mathisen, 1984). A suitable chemical environment for zeolite formation can be brought about by dissolution of volcanic glass, plagioclase and K-feldspar, all of which would tend to increase silica activity and alkalinity (Hay, 1966). High pH favors precipitation of both calcite and Ca-zeolite; the  $\alpha_{CO_2}/\alpha_{H,O}$  ratio is an important control in determining which phase will precipitate (Zen, 1961).

Formation of late-stage pyrite is controlled by a variety of factors that include oxygen and sulfur activity, temperature, pH, and Eh (Ohmoto and Lasaga, 1982; Henley et al., 1984). The source of sulfur in this uncommon cement is highly speculative without isotopic data.

# **Summary discussion**

A variety of factors control the alteration of framework grains and the formation of authigenic cement phases, including temperature, pH, Eh and ion activity. The fanglomerate was subjected to a wide range of temperatures, from surface and near-surface conditions (likely including soil-related processes) to possibly greater than 200°C in hydrothermal environments.

On the basis of textural evidence, framework grain dissolution began early in the diagenesis of the fanglomerate. Dissolution is a result, in part, of hydrolysis reactions that are initiated under acidic conditions. As these reactions proceed, they tend to produce more basic fluids by utilizing H<sup>+</sup>. In soils in arid environments, hydrolysis reactions predominate over organic decay processes, thus producing alkaline, reducing conditions (Brownlow, 1979). Mixed-layer illite/smectite most likely formed under such alkaline conditions. Though limonite can form in a wide range of Eh and pH conditions (Garrels and Christ, 1965), the early formation of the phase in association with illite/smectite suggests that it was also produced in an alkaline environment.

As previously discussed, quartz precipitation can be brought about by either a decrease in pH and/or temperature. Though it is not known which of these factors exerted greater influence on opal and microquartz formation, limited fluid inclusion data suggest that the crystallization of megaquartz cement occurred at high temperatures ( $<200^{\circ}$ C), and therefore was possibly temperature dependent.

Both calcite and Ca-zeolite are late-stage cements that commonly form under alkaline conditions (pH>9), possibly indicating an increase in the pH of fluids compared to those during opal formation. If the pH is assumed to have remained relatively invariant, activities of the various ionic constituents may have been the main factor controlling cement formation.

#### **CONCLUSIONS**

- 1. Arenaceous portions of the fanglomerate are classified as rhyolite-clast volcanic-arenites. Major framework constituents of these arenites are: (a) Rock fragment components; cryptocrystalline, microcrystalline or recrystallized glassy rhyolite (70.4% of the framework), porphyritic rhyolite plus rhyolite tuff (16.4%), intermediate volcanics (7.7%), basalt (4.4%) and epiclastics (1.1%); and (b) Mineral components; monocrystalline and polycrystalline quartz (2.2 and 1.0% of the framework, respectively), potassium feldspars (2.5%), plagioclase (0.8%), opaques (Tr) and biotite (Tr).
- 2. The fanglomerate contains several diagenetic cement components, listed in paragenetic sequence: (earliest) limonite (9% of total cements), mixed-layer illite/smectite plus limonite (18%), megacrystalline quartz (19%), impure siliceous cements (silica/limonite/clay; 44%), microcrystalline quartz (6%), illite (mostly late; 1%), opal (1%), calcite (1%), Ca-zeolite (<1%) and pyrite (<1%; latest); these cements often overlap in terms of timing of formation.

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