Diagenesis of the Mississippian Arroyo Penasco Group, north-central New Mexico

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INTRODUCTION
The Arroyo Periasco Group of the southern Sangre de Cristo Mountains comprises the oldest Paleozoic sediments found in north-central New Mexico. The purpose of this paper is to discuss the nature and significance of the varied and spectacular diagenetic fabrics preserved within this thin Mississippian section. Eight outcrops between Taos, Las Vegas, and Santa Fe (Fig. 1) were measured, described, and sampled. Samples from five of the outcrops, Cuchilla del Ojo, Ponce de Leon, Rio Grande del Rancho, Trout Springs, and Tererro, were studied in detail utilizing standard petrographic techniques and cathodoluminescence. The carbonate members of the Arroyo Periasco Group have undergone dolomitization, dedolomitization, silicification, calcitization of evaporites, and brecciation. The complex diagenetic history of the Arroyo Periasco Group carbonates resulted from periodic episodes of exposure prior to Pennsylvanian sedimentation.

PREVIOUS WORK
Much of the previous work on the Arroyo Periasco Group in the Sangre de Cristo Mountains has concentrated on its biostratigraphic and facies relationships. A major problem surrounding the Arroyo Periasco Group has been the stratigraphic nomenclature applied to the units. Figure 2 summarizes the evolution of the stratigraphic nomenclature for these Mississippian units. Armstrong (1955) first separated the rock from the Sandia Formation and assigned a Mississippian Meramecian age on the basis of Endothyra sp. and Pectogyra sp. fauna. Baltz and Bachman (1956) and Baltz and Read (1960) disputed the Mississippian age of the units in the Sangre de Cristo and Sandia Mountains. They assigned a Devonian(?) age to the Espiritu Santo Formation on the basis of its fauna.

Baltz and Read (1960) did the first petrographic studies of the Arroyo Periasco Group, relating the rock types to several periods of transgressions and regressions across the Mississippian platform. They proposed that the Macho Member was a result of karstification during one of the regressions.

Armstrong and Holcomb (1967), in their study of the Jemez, San Pedro, and Sangre de Cristo Mountains, found a faunal assemblage that suggested an Osagean to Meramecian age. Armstrong (1967) defines three depositional cycles based on the petrography. Cycle 1 was transgressive sequence consisting of shallow-marine terrigenous clastics. The cycle-2 carbonates were a regressive sequence of intertidal to supratidal mudstones and evaporites. Cycle-3 sediments were a transgressive sequence reflecting a more open marine environment. Deposits of cycle 3 were arenaceous, echinodermal, oolitic, pelletal packstones and wackestones. Armstrong considered the brecciated Macho Member a product of dissolution and collapse of evaporite units prior to Pennsylvanian sedimentation.

Recently completed M.S. theses by Williamson (1978) and Vaught (1978) have provided information on the diagenesis of parts of the Arroyo Periasco Group, namely the Del Padre Sandstone and the Macho Member of the Tererro Formation, respectively. The current research was initiated because a comprehensive study of the diagenetic textures and their relationship to Mississippian sedimentation within the entire Arroyo Periasco Group had not been done previously.

ANALYTICAL METHODS
Standard petrographic thin sections were stained with a combination of Alizarin Red—S and potassium-ferricyanide solution for dolomite am

FIGURE 1. Location of the study area and measured sections of the Mississippian Arroyo Periasco Group. T. – Taos, L.V. – Las Vegas, S.F. – Santa Fe.
iron-rich calcite (Evamy, 1963). Slabs were etched in a 10% hydrochloric acid solution for 40 sec to aid identification of the primary sedimentary textures.

Cathodoluminescent petrography was done with a Nuclide Corp. Luminoscope model ELM-2E on a Zeiss petrographic microscope. Cathodoluminescence is the emission of light produced by stimulating certain atoms in a specimen with a wide electron beam. The use of luminescence is a qualitative tool when not used in association with the electron microprobe. Iron and manganese are the most common trace elements responsible for luminescence, but Pb⁺, Ni⁺, Cs⁺, and rare earths also effect it (Machel, 1983). The intensity of the bands or zones produced by the excitation of the sample is a function of the Mn⁺/Fe⁺ ratio, where manganese (also Pb⁺ and Cs⁺) produces and iron (also Ni⁺) quenches luminescence, especially in dolomites.

**STRATIGRAPHY**

Overlying the highly weathered, low-relief Precambrian peneplain, the Arroyo Pefiasco Group consists of the Espiritu Santo and Tererro Formations (Fig. 3). The Espiritu Santo Formation is subdivided into the lower Del Padre Sandstone and the upper carbonate member (Sutherland, 1963). Derived from Precambrian granites and schists, the sandstones were deposited during the late Osagean transgression across the platform (Armstrong and Holcomb, 1967). The Del Padre Sandstone represents a sequence of high-energy braided streams, beaches, and tidal and sabkha flats (Williamson, 1978). The Del Padre Sandstone filled the relict topography developed on the Precambrian peneplain and conformably grades upward into the crystalline limestones of the carbonate member (Fig. 4). Limestones of the carbonate member consist of algal laminated mudstones, wackestones, packstones, and gypsum horizons and nodules that were altered extensively during diagenesis. These sediments were deposited as part of a widespread supratidal to
upper-intertidal complex with sporadic flooding producing laminae of bioclasts and intraclasts.

The Macho Member of the Tererro Formation is a cemented rubble packbreccia (Morrow, 1982). The breccia blocks are composed of pelletal mudstones, pelletal and oolitic packstones, and crystalline limestones. The crystalline limestones consist of calcitized evaporites and dolomites which will be discussed in the diagenesis section. The original sediments of the breccia were deposited in supratidal to intertidal environments. Dissolution of interbedded gypsum horizons during exposure resulted in collapse and brecciation. The Macho Member is present everywhere in the field area, except in the vicinity of the Rio Pueblo section (Fig. 4).

The Turquillo, Manuelitas, and Cowles Members of the Tererro Formation were deposited following brecciation. The Turquillo and Manuelitas Members fill the topography developed on the Macho Member. The Turquillo Member, found at the Ponce de Leon, Rio Grande del Rancho, and Mora River Gap sections, consists of algally laminated mudstones and wackestones, intraformational conglomerates, and crystalline limestones. The Turquillo Member was deposited in an intertidal environment. On the basis of the foraminifers present in this unit, Armstrong and Mamet (1979) concluded that Turquillo waters were of normal marine salinities.

The Manuelitas Member of the Tererro Formation represents a sequence of normal marine, subtidal, and shoaling to intertidal deposits that is laterally equivalent to the Turquillo Member. The Manuelitas Member is composed of pellooidal, bioclastic, and oolitic packstones and grainstones. Bioclasts commonly found within the unit are pelmatozoans, bryozoans, blue-green algae, sponge spicules, brachiopods, foraminifers, ostracods, and calcispheres.

The Cowles Member, composed of sandy, pellooidal, and bioclastic packstones and calcareous sandstones, represents the final transgression and regression of the Mississippian seas in north-central New Mexico. Prior to Pennsylvanian sedimentation, erosion removed parts of the Cowles and the Manuelitas Members have been removed by the extensive downcutting associated with the development of the Taos trough (Chapin, 1981).

**DIAGENESIS**

The Arroyo Peñasco Group has been altered extensively by diagenetic processes. Carbonates of the Espiritu Santo Formation have undergone pervasive alteration which includes dolomitization, dedolomitization, calcitization of gypsum, neomorphism, silicification of gypsum, and chertification resulting in the partial to complete recrystallization and replacement of these carbonates (Fig. 5A, B). The other members of the Arroyo Peñasco Group exhibit a less severe degree of recrystallization and replacement.

**Dolomite**

Varying according to locality, the amount of dolomite preserved within the carbonates of the Arroyo Peñasco Group ranges from less than one to over 75% (Table I). Dolomite crystals range from 0.004 to 0.600 mm. The very finely crystalline, anhedral to subhedral dolomites replacing the algally laminated sediments are interpreted as formed contemporaneously under supratidal conditions by evaporative pumping analogous to that occurring today at Abu Dhabi, U.A.E. (McKenzie and others, 1980). Under the same hypersaline conditions, gypsum precipitation resulted in nodular and bedded gypsum, as well

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<td><strong>Component</strong></td>
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as scattered, euhedral gypsum (selenite) crystals within the dolomitized sediments. With increasing burial or sea-level rise, the sediments passed through the zone of hypersaline fluids to the mixing zone.

Dolomite that is limpid and euhedral is interpreted as forming in the meteoric phreatic zone. Pore space between the dolomite crystals is occluded by cosparly crystalline, poikilitic calcite spar. Euhedral dolomite crystals larger than 0.10 mm are interpreted as formed in the mixing zone, a result of co-mingling of meteoric and marine fluids (Choquette and Steinen, 1980).

The large diversity in crystal sizes and morphologies indicates dolomitization is the result of widely fluctuating pore-water salinities. Schizohaline conditions, as described by Folk and Siedlecka (1974), would produce the types of dolomites observed within the Arroyo Pefiasco Group.

Cathodoluminescent petrography of dolomite at the Ponce de Leon and Tererro sections reveals a characteristic dull-red core with a brighter red or orange second-generation dolomite. This is interpreted as reflecting a change from oxidizing meteoric fluids (dull red) found under hypersaline conditions to marine and meteoric fluids (bright) found in the mixing zone. The orangish appearance of some of the dolomites may be produced by a higher calcium concentration in the crystal lattice.

Authigenic Silica

Discrete horizons of nodular chert were found at all localities examined. Chert nodules are the most abundant within the Espiritu Santo Carbonate and Manuelitas Members. The cherts are usually banded gray to black, with the darker bands containing more clays and organics and the lighter bands more carbonates. The contact between the chert and limestone is usually sharp, but the cherts may contain remnants of carbonate such as bioclasts, dedolomites, and calcitized evaporites. The chert nodules are interpreted as formed during initial dolomitization of the carbonates because of their occurrence on bedding planes.

The Coorong Lagoon model, developed by Peterson and von der Borch (1965) for inorganic precipitation of chert, is a plausible model to apply to the cherts within the Arroyo Pefiasco Group. Periodic marine flooding and the associated bloom of organic material in ponded areas on the algal flats would raise the pH to values greater than 9.5. This would lead to dissolution of detrital quartz and the sinking of the dense, siliceous brines into the pond-floor sediments. Decay of organic material just beneath the sediment-water interface would cause the pH of the interstitial water to drop below a value of 7, triggering silica precipitation. The Arroyo Pefiasco Group includes quartz and feldspar sands which provide an abundant source of silica. Silica dissolution is manifested by the presence of embayed quartz and partially replaced feldspar grains. Corroded quartz and feldspar are found in association with the horizons that have been silicified.

Other varieties of authigenic silica within the Arroyo Pefiasco Group include euhedral megaquartz, anhedral megaquartz, chalcedonite, lutecite, and quartzine. Quartzine and lutecite are forms of length-slow chaledony which have been reported as indicative of vanished evaporites (Folk and Pitman, 1971). Euhedral megaquartz is also interpreted as formed from evaporite precursors (Friedman and Shukla, 1980). Within the carbonates of the Espiritu Santo Formation and the Macho Member, silica replacing evaporites started out initially as euhedral megaquartz, and is sometimes followed by quartzine and/or lutecite (Fig. 5B). Carbonate inclusions are locally present within the megaquartz and chaledony. Silicification of the evaporites occurred prior to the brecciation of the Macho Member, as indicated by broken clasts of megaquartz and length-slow chaledony found within the matrix.

Cribbied and Shukla (1980) described in the Silurian Lockport Formation of New York a similar occurrence of inclusion-free megaquartz, sometimes followed by length-slow chaledony. They envisioned a situation where precipitation of sulfates at shallow depths increased the pH and dissolved detrital quartz grains. With a return to more normal marine to meteoric conditions, dissolution of the gypsum would decrease the pH and lead to precipitation of quartz. Oxygen-isotope data by Miliken (1979) for Mississippian silicified evaporites from Kentucky and Tennesse supported a meteoric origin for megaquartz and a mixing-zone origin for length-slow chaledony. Within the Arroyo Pefiasco Group, late dolomitization and silicification of evaporites could proceed under the same conditions prior to brecciation and recrystallization.

The upper members of the Tererro Formation, the Turquillo, Manuelitas, and Cowles, also contain quartz after evaporites. Within these Mississippian sediments the development of fibrous silica forms pseudomorphing evaporites, is more extensive, and occurs more commonly than does euhedral megaquartz. Much of the silica is associated with nonweathering-profile paleosilcretes. Summerfield (1983) recognized this type of silcrete in the Kalahari Basin in Africa, where it occurs as laterally extensive, partially to completely silicified beds a few meters thick. A similar silcrete formed at the top of the Manuelitas Member can be traced throughout the field area. The silcrete ranges from a massive chert at the Cuchilla del Ojo, Ponce de Leon, Tererro, and Mora River Gap sections to a horizon of very large chert nodules at the Rio Pueblo section, and to a horizon of silicified evaporite nodules at the Trout Springs section. Other more areally restricted horizons of silcrete occur within the Manuelitas Member. These horizons mark episodes of rapidly fluctuating sea level during Manuelitas deposition.

Length-slow chaledony (both quartzine and lutecite) within the silcrete shows excellent zoning in both plane-polarized and reflected light. This is due to the presence of solid and fluid inclusions in the chaledony. Hematite, calcite, and saline(?) fluid inclusions are the most common (Fig. 5C). In reflected light the fluid inclusions are milky white and the hematite inclusions are red. Gypsum pseudomorphs surrounded by pseudocubic or fortification zoning (Arbey, 1980), and dolomite pseudomorphs of silica and calcite are characteristic of these units (Fig. 5D). Length-fast chaledony (chalcedonite), instead of length-slow chaledony, is found replacing some of the evaporites at the Trout Springs section. Prior calcitization of evaporites, with subsequent replacement by silica, is a probable explanation for these anomalous silica forms. The presence of relict carbonate laminae within the chaledony supports this hypothesis.

Length-slow chaledony is found replacing pelmatozoan, brachiopod, and trilobite bioclasts within the Arroyo Pefiasco Group (Fig. 4F). Miliken (1979) attributed the precipitation of length-slow chaledony to sulfate-rich siliceous pore fluids. Because conditions would favor this theory within the Mississippian units, this is the probable mode of formation.

Dedolomitization and Calcitization of Gypsum

A major period of sea-level regression and climatic change occurred after the deposition of the interbedded carbonate and evaporite units of the Macho Member. This period of exposure was responsible for the dedolomitization and calcitization of evaporites within the Espiritu Santo Carbonates and, to a lesser degree, the Macho Member. Dedolomitization is the process by which dolomite is replaced by calcite (Fig. 27, Turquillo Member).
5G). During calcitization of evaporites, calcite replaced the gypsum (or selenite) within the carbonates of the Arroyo Pefiasco Group (Figs. 5H, 6A). In the carbonates of the Espiritu Santo Formation and Macho Member, dedolomitization and calcitization of gypsum occurred penecontemporaneously. The amount of dedolomite within the sections is summarized in Table 2.

Low-relief supratidal and intertidal flats developed at this time resulted in the exposure of vast areas during minor fluctuations in sea level. Increased rainfall is thought to have accompanied an extended sea-level low, resulting in intratral solution and removal of CaSO₄ by undersaturated meteoric fluids. This led to formation collapse and brecciation which characterizes the Macho Member.

Back and others (1983), studying the Mississippian Pahasapa Limestone in the Black Hills of South Dakota and Wyoming, found dedolomitization and calcitization of evaporites to be related to a major exposure event. In their model, the presence of gypsum in the system is the major driving force of the dedolomitization process. Solution of the gypsum saturates or supersaturates the ground-water system with respect to calcium. This produces a decrease in the Mg²⁺/Ca²⁺ ratio, which in turn causes calcite precipitation. Calcite precipitation depletes the aqueous system in CO₂ and lowers the pH. As a result, dolomite dissolves to accommodate the loss of CO₂ and to increase the Me-/Ca²⁺ ratio. At low temperatures gypsum is the necessary driving component of the system, but at higher temperatures the reaction could occur without its presence.

Within the Arroyo Pefiasco Group, the fluids derived from the overlying Macho Member were enriched, but undersaturated with respect to dissolved CaSO₄. These fluids migrated downward until they intersected the water table. Once in the phreatic zone, the solutions continued to dissolve gypsum, which decreased the Mg²⁺/Ca²⁺ ratio and supersaturated the solution with calcium. Thereafter, the system followed the model of Back and others (1983) until most of the accessible gypsum was consumed.

The top of the water table is delineated by the top of the Espiritu Santo Carbonate Member. All rocks above the water table were brecciated, whereas all units below the water table were recrystallized. From the nearly uniform thickness of the Espiritu Santo Carbonates we can infer that the water table was at a very uniform depth beneath the sabkha surface and that there was very little topographic relief prior to brecciation. Fluctuations in the water table are recorded at the base of some of the breccias by the coarsely recrystallized nature of the clasts and matrix. Recrystallization of parts of the Macho Member, especially at the Trout Springs section, indicates that recrystallization continued during the transgression that deposited the Turquoise and Manuelitas Members.

The samples from the Espiritu Santo Carbonates and the Macho Member were examined under the luminoscope, as their primary diagenetic textures are no longer visible in transmitted light due to recrystallization. Luminescence revealed the presence of dedolomite and calcitized evaporites. Zoning within the pseudomorphs appears to be unrelated to surrounding calcites (Fig. 6B). If zoning was a result of cementation. Luminescence revealed the presence of dedolomite and gypsum. Recrystallization of parts of the Macho Member, especially at the Trout Springs section, indicates that recrystallization continued during the transgression that deposited the Turquoise and Manuelitas Members.

Oglesby (1976) suggested that dolomite can incorporate approximately twice as much Mn²⁺ and Fe²⁺ within its crystal lattice as can calcite. With simultaneous grain-boundary dissolution of dolomite and recrystallization of calcite, it may be possible to preserve the original trace-element composition of the dolomite within the calcite lattice (Fig. 7). The higher concentrations of Mn²⁺ and Fe²⁺ inherited during dedolomitization would produce anomalous luminescence within the dolomites (Fig. 6C). The presence of corroded zones (Fig. 6D) within the dedolomites also argues for the preservation of part of the original trace-element distribution of the dolomites.

The calcitized evaporites generally are less luminescent than the surrounding dedolomites and calcites (Fig. 6E, F). This may reflect the lack of Mn²⁺ within the evaporite lattice. Zoning present in some of the hexagonal to bladed crystals might actually reflect the chemistry of the pore fluids at the time of calcitization.

Another type of calcitized dolomite observed within the Espiritu Santo Carbonate Member is euhedral, limpid-dolomite rims surrounded by poikilitic calcite. Within some of the dolomite rims, remnants of the original, inclusion-rich dolomite core can be found forming a geopetal mound of rounded crystals. Folk and Siedlecka (1974) observed similar textures in the dolomites from Bear Island, Svalbard. Their interpretation is that the limpid dolomite formed during meteoric phreatic diagenesis and nucleated on cores of dolomite formed under hypersaline conditions. The hypersaline dolomites subsequently dissolved due to their greater solubility in meteoric phreatic environment (Fig. 8).

**Cementation**

Cementation of the packstones and grainstones of the upper members of the Tererro Formation involved early syntectial overgrowths on pelmatozoans and blocky, isopachous calcite spar. Blocky calcite spar that coarsens toward the center of pore space follows the earlier cements. These types of cements are found throughout the Manuelitas and Cowles Members and are characteristic of meteoric and marine phreatic diagenesis (Longman, 1980).

Cathodoluminescence was employed to assess the distribution of trace elements (Mn²⁺ and Fe²⁺) within these cements. The recrystallized limestone of the Espiritu Santo Formation and the Macho Member were also studied to see if their original trace-element distributions were preserved and, if so, how they compared to the upper units of the Arroyo Pefiasco Group.

The seven cement zones identified within the Arroyo Pefiasco Group are summarized in Figure 9. Nonluminescent zones–1 cements are interpreted as formed from oxidizing pore fluids of the meteoric phreatic lens having very low concentrations of Fe²⁺ and Mn²⁺ (Oglesby, 1976).

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**FIGURE 6. A – Zoned gypsum pseudomorphs (now calcitized) (scale bar = 0.606 mm, plane-polarized light, Ponce de Leon—float, probable Turquoise Member). B – Dedolomite (dd) and cement zonation under cathodoluminescence (scale bar=0.606 mm, Tererro-13b, Espiritu Santo Carbonate). C – Zoned dolomite crystals under cathodoluminescence (scale bar=0.606 mm, Trout Springs-10a, Espiritu Santo Carbonate). D – Cathodoluminescent view of corroded calcite pseudomorphs after dolomite (scale bar= 0.315 mm, Trout Springs-13, Espiritu Santo Carbonate). E – Calcitized gypsum under cathodoluminescent light (scale bar=0.253 mm, Trout Springs-13, Espiritu Santo Carbonate). F – Zoned dedolomite and euhedral gypsum pseudomorphs under cathodoluminescence (scale bar = 0.315 mm, o-porosity, Ponce de Leon, Espiritu Santo Carbonate). G – Cement stratigraphy developed in ooid, pelmatozoan grainstone. Zones 1 through 4 (scale bar=0.606 mm, Trout Springs-39, Cowles Member). H – Zones 1 through 6 cement stratigraphy (scale bar= 0.203 mm, Trout Springs-28, Manuelitas Member).**
The bright and very dull to nonluminescent bands of zone-2 cements are interpreted as reflecting abrupt changes in the ground-water system. The paleoaquifer fluctuated between oxidizing meteoric (nonluminescent) and stagnant, reducing, marine pore waters (bright).

Dull to zoned-dull cements of zone 3 are interpreted as precipitated from reducing, marine pore fluids. The paleoaquifer was not stagnant during zone-3 precipitation, as it was during precipitation of the bright cements (Grover and Read, 1983). Uplift and/or fall in sea level occurred between zone-3 and 4 cements. Nonluminescent zone-4 cements indicate a return to meteoric phreatic diagenesis within the paleoaquifer (Fig. 6G). Zone-4 and 5 cements reflect conditions similar to those that produced zone-1 and 2 cements.

The brightly luminescent zone-6 cements are interpreted as precipitated from reducing, marine pore waters in a stagnant paleoaquifer (Fig. 6H). With continued burial, the fluids became increasingly reducing as a result of restricted fluid circulation. Under these conditions, the zoned-dull cements of zone 7 were precipitated.

A complete cement stratigraphy is not seen in every slide. This is due to differential rates of calcite cementation and the timing of porosity development. Fractures within the Arroyo Pefiasco Group are filled by bright luminescing cements of zone 6 and zoned-dull cements of zone 7, reflecting their late origin.

The carbonates of the Espiritu Santo Formation and Macho Member are striking because both exhibit a cement stratigraphy that mimics the overlying packstones and grainstones of the Manuelitas and Cowles Members. These cements are found in porosity that developed prior to and during recrystallization and brecciation.

**Pyrite and Other Mineralization**

Most of the pyritization of the Arroyo Pefiasco Group occurred after fracturing, as indicated by apparent co-precipitation of both calcite and pyrite in the fractures. The reducing conditions proposed for fracture-filling cements of zones 6 and 7 were also conducive to pyrite precipitation. Minor pyrite is associated with dedolomitization and calcitization of gypsum. Most of the pyrite has been oxidized to hematite and limonite during recent weathering, pseudomorphing the original euhedral crystal form.

Minor copper and lead mineralization also is found in the Arroyo Pefiasco Group. This mineralization is interpreted as having resulted from hydrothermal activity during Laramide or more recent times. The friable sands of the Del Padre Sandstone at Cuchilla Del Ojo are cemented by a copper carbonate, giving the unit a pale-blue appearance. The Tererro and Trout Springs sections contain minor amounts of galena within the carbonates.

A second stage of Cenozoic karstification has produced caves within the Macho Member at the Trout Springs and Tererro sections. Due to its high porosity, the Macho Member acted as a conduit for migrating pore fluids, which makes it highly susceptible to dissolution.

**CONCLUSIONS**

The history of Mississippian sedimentation in northern New Mexico includes a minimum of four episodes of sea-level fluctuation. These events are accurately recorded by the dedolomites and calcitized gypsum of the Espiritu Santo carbonates, dissolution and brecciation of the Macho Member, and the paleosilcretes of the Manuelitas Member. In contrast, periods of submergence mark a return to normal sedimentation characterized by cementation, dolomitization, and chertification of the sediments (Fig. 10). The widespread correlatability of certain chronologically constrained diagenetic fabrics reinforces the presence of an extensive, low-relief depositional surface for Mississippian strata.
ACKNOWLEDGMENTS

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