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THE RELATIONSHIP BETWEEN HYDROCARBON MIGRATION AND AUTHIGENIC MAGNETITE: TESTING THE HYPOTHESIS

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RELATIONSHIP BETWEEN HYDROCARBON MIGRATION AND AUTHIGENIC MAGNETITE: TESTING THE HYPOTHESIS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter II

Chapter III

THE RELATIONSHIP BETWEEN HYDROCARBON MIGRATION AND AUTHIGENIC MAGNETITE: TESTING THE HYPOTHESIS

CHAPTER 1

INTRODUCTION

Authigenic magnetic minerals such as magnetite have been reported from several sedimentary units and their presence has been tentatively linked to migration of hydrocarbons or related brines. If the hypothesis that hydrocarbons can cause the formation of authigenic magnetite is correct, there are several potential applications. For example, aeromagnetic surveys performed in search of anomalous concentrations of magnetic minerals might help locate petroleum accumulations, and paleomagnetic analyses might be used to date the formation of magnetite and, hence, the migration of hydrocarbons. Testing the hypothesis is also important because additional results may lead to a better understanding of the origin of secondary magnetizations that reside in magnetite. The hydrocarbon/magnetite hypothesis has, however, not been adequately tested.

The objectives of this study are 1) to test the hypothesis that hydrocarbon migration can cause the formation of authigenic magnetite, and 2) to date the acquisition of remanence in the magnetic phases found. In order to accomplish these objectives, an integrated approach incorporating paleomagnetic, rock magnetic, petrographic, and organic geochemical methods was employed.

The following chapters describe the investigations of the lower Ordovician Upper Arbuckle Group in southern Oklahoma. Chapter 2 describes the examination of limestones containing Liesegang bands in the Kindblade Formation in the Arbuckle Mountains (south central Oklahoma). Chapter 3 describes the examination of hydrocarbon-containing exposures of the Kindblade and McKenzie Hill Formations of the Upper Arbuckle Group in the Limestone (Slick) Hills of southwestern Oklahoma. Upper Arbuckle Group carbonates in the two locations are similar lithologically, yet they differ magnetically. Magnetization in the Liesegang bands resides in hematite, while the dominant magnetic mineral in Limestone Hills specimens appears to be magnetite.

CHAPTER 2

PALEOMAGNETIC DATING OF LIESEGANG BANDS

ABSTRACT

Paleomagnetic analysis, in conjunction with petrographic studies, is used in this study to date the formation of hematite Liesegang bands in the Ordovician Upper Arbuckle Group in southern Oklahoma. The hematite bands form symmetrical patterns on both sides of calcite-filled fractures in dolomitic beds. The bands decrease in abundance and become more diffuse away from the fractures.

Samples from distinctly banded dolomite near the fractures contain a relatively strong chemical remanent magnetization (CRM) with a southeasterly declination and shallow inclination. Samples farther from the fractures that are less distinctively banded or have no bands contain a weaker and less stable CRM. Samples were collected from both flanks of the Arbuckle anticline (late Pennsylvanian folding), and a fold test indicates that the CRM is post-folding. The pole position for the CRM corresponds to the Early Permian (280 Ma) part of the Apparent Polar Wander Path for stable North America. Petrographic evidence, stable demagnetization to above 600^{o}C, and rock magnetic

experiments indicate that the CRM resides in hematite. These results suggest that the Liesegang bands formed in the Early Permian, probably by precipitation of hematite from fluids that emanated from the fractures. The fluids also apparently caused dedolomitization and precipitation of calcite in intercrystalline pore spaces. These fluids were probably the source of iron in the bands, although iron released from dedolomitization and from oxidation of pyrite may have been local sources of iron.

INTRODUCTION

Paleomagnetic analysis is an approach that can provide information on the timing of diagenetic events in sedimentary rocks. Paleomagnetic dating is based on the premise that magnetic minerals acquire a stable magnetization aligned with the field in which they form. If this magnetization can be isolated, then the magnetic direction may be compared to the Apparent Polar Wander Path for stable North America (e.g. Irving and Irving, 1982), and the time at which the magnetic mineral formed may be ascertained. This approach is particularly powerful if it is combined with fold tests (Graham, 1949) which constrain the timing of remanence acquisition, assuming that the time of folding is known. For example, if specimens from opposite flanks of a fold group better after correcting for field orientation, then the magnetization was acquired before folding, but if specimens group better using <u>in situ</u> orientations, then the magnetization was acquired after folding.

Recent studies have used the paleomagnetic approach to date dedolomitization (Elmore et al., 1985; Loucks and Elmore, in press) and mineralization associated with uranium deposits (Reynolds et al., 1985). In this paper, results are reported which deal with the origin and timing of formation of Liesegang bands in the Upper Arbuckle Group in southern Oklahoma.

Liesegang banding, as used here, refers to long (up to 50 cm), narrow bands of red iron oxide minerals parallel to calcite-filled fractures which are roughly perpendicular to bedding (Figure 1). The bands are situated symmetrically on both sides of the fractures. Bands are most common in "ribbon rock" (Tenney, 1984), i.e. beds which consist of light gray, ripple cross laminated, peloidal grainstones that alternate with tan to red dolomitic layers. The red bands are restricted to tan, dolomitic regions and are not found in grey limestone (Figure 1). Liesegang bands, first reported by Liesegang (1913), have been reported in soils, with their origin attributed to water level fluctuations due to seasonal or intermittent perched water table (Brewer, 1964). Other previous studies of Liesegang bands include those of Ortoleva (1983) and co-workers, whose work involves, in part, mathematical models of band formation.

GEOLOGIC SETTING AND PREVIOUS WORK

The Liesegang bands investigated in this study are found in the West Spring Creek and Kindblade Formations of the Ordovician Upper Arbuckle Group. The Upper Arbuckle Group is comprised of shallow water carbonates deposited within the southern Oklahoma aulacogen (Wickham, 1978). Deposition was largely in intertidal to subtidal settings with facies representative of both normal and episodic sedimentation (Tenney, 1984). Uplift and folding of the Paleozoic sediments, forming the Arbuckle Mountains,

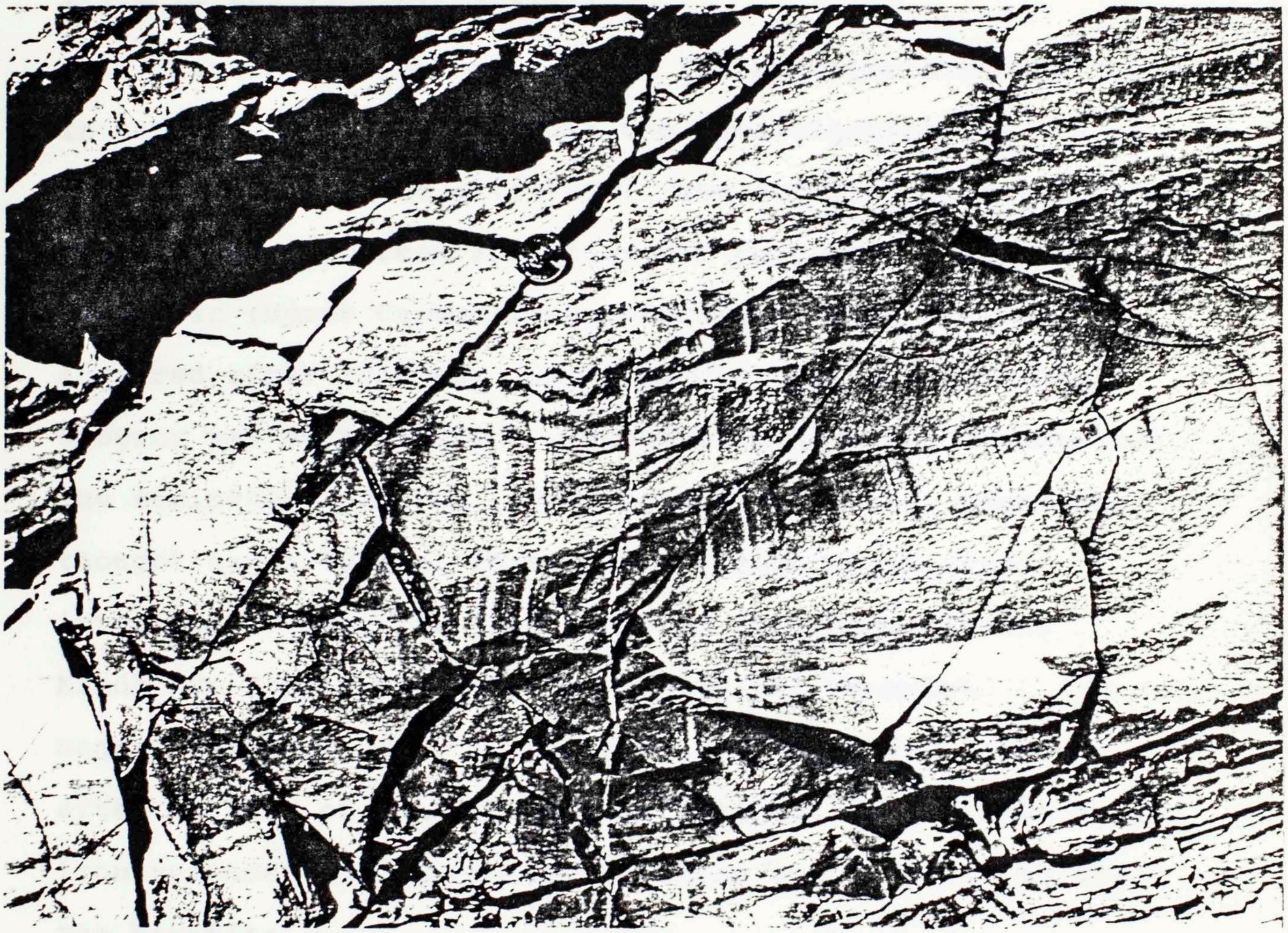


Figure 1. Liesegang banding in the Kindblade Formation from the south flank of the Arbuckle Anticline. Note symmetrical arrangement of hematite bands on both sides of calcite-filled fracture. Banding is localized in tan dolomitized rock, whereas gray limestone rock is not stained by hematite. (Penny for scale.)

occurred during the late Paleozoic in the Virgilian epoch, i.e. late Pennsylvanian (Ham, 1978). Upper Arbuckle Group carbonates are exposed in outcrop with dips of approximately 50 degrees on the south flank and 70 degrees on the north flank of the Arbuckle Anticline.

Previous paleomagnetic work in the Upper Arbuckle Group in southern Oklahoma includes the investigations of Steiner (1973) and Elmore et al.(1985). Steiner (1973) investigated the West Spring Creek Formation and reported a late Paleozoic (upper Carboniferous-Permian) magnetization acquired after folding. She proposed that the Arbuckle orogeny was of sufficient intensity to heat and remagnetize the sediments involved. The magnetization was, therefore, thought to be thermal in origin. Elmore et al.(1985) investigated hematite that is found in burrows in the Kindblade Formation and found a chemical remanent magnetization (CRM) acquired some 280 Ma before present, after folding of the Arbuckle anticline. They proposed that iron released during dedolomitization was oxidized to form the hematite.

SAMPLING AND LABORATORY TECHNIQUES

Paleomagnetic and Rock Magnetic

Approximately 60 samples were collected with a portable coring apparatus and oriented _in situ_ with a clinometer and Brunton compass. Sampling sites are located in roadcut outcrops along Interstate 35 in southern Oklahoma (Figure

2). Samples were collected from two sites on the south flank and two on the north flank of the Arbuckle anticline so that a fold test could be performed. Specimens (cylinders of 2.2 cm length, 2.5 cm diameter) were cut from the samples and measured in a United Scientific Three Axis cryogenic magnetometer. Thermal techniques proved most successful in demagnetization and were used for all specimens. Specimens were heated using a Schonstedt TSD-1 unit in a stepwise manner from 50^{O}C to approximately 680^{O}C (in 100^{O} steps up to 400^{O}C, in 50^{O} steps to 500^{O}C, and subsequently by 25^{O} steps). During each heating step, specimens were held at a constant temperature for 30 minutes and then cooled in a field of no more than 5 nT before being measured. Results for each specimen were plotted on orthogonal projections (Zijderfeld, 1967), consisting of a vertical and a horizontal projection of the vector endpoints of each demagnetization step. The direction and magnitude of components in the specimens were determined by visual inspection of the orthogonal projections followed by vector subtraction. Line segments chosen consisted of at least three colinear points. Site means were calculated using the specimen directions, and mean directions for the components were calculated, giving equal weight to each specimen (Table 1).

Representative specimens were chosen for isothermal remanent magnetization (IRM) acquisition and decay experiments to aid in the identification of magnetic

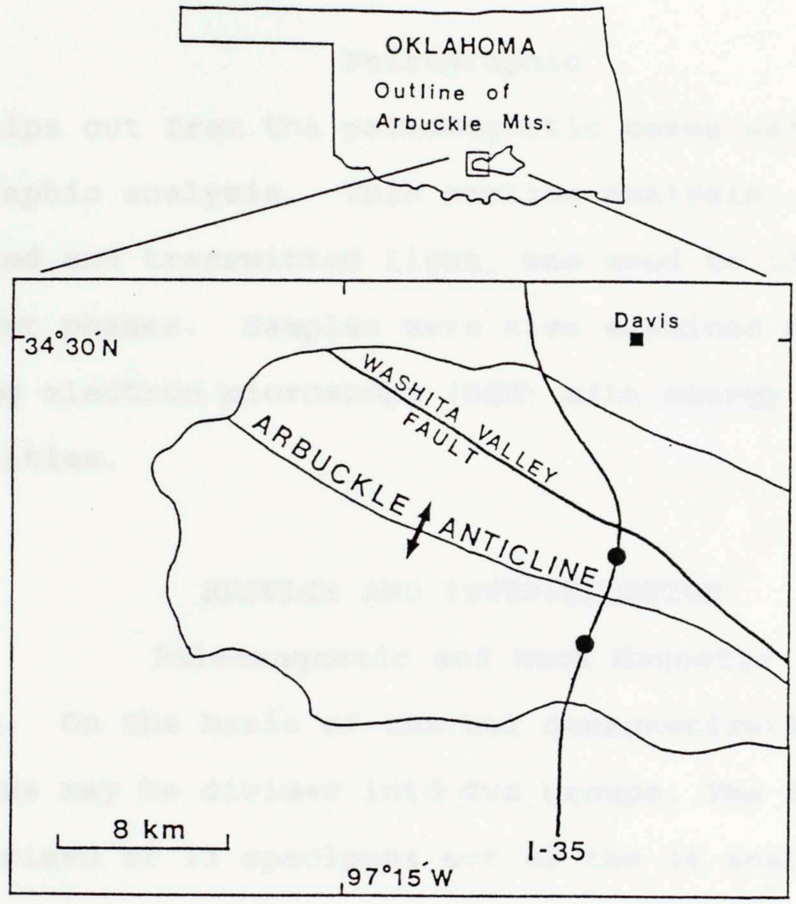


Figure 2. Location map with dots showing sampling sites on the north and south flanks of the Arbuckle Anticline in southern Oklahoma.

mineralogy. Acquisition of IRM was accomplished with a water-cooled electromagnet at field strengths of .02, .04, .07, 0.1, 0.15, 0.3, 0.5, and 0.7 (or 0.8) Tesla. Decay of IRM was conducted in 50 degree steps to 700 degrees C.

Petrographic

Chips cut from the paleomagnetic cores were used for petrographic analysis. Thin section analysis, using both reflected and transmitted light, was used to identify the different phases. Samples were also examined using a scanning electron microscope (SEM) with energy dispersive capabilities.

RESULTS AND INTERPRETATION

Paleomagnetic and Rock Magnetic

Group I. On the basis of thermal demagnetization results, specimens may be divided into two groups. The first group(I) is comprised of 33 specimens out of the 54 analyzed. Specimens in this group displayed the most distinct banding pattern in outcrop. Natural remanent magnetization (NRM) intensities were found to decrease in samples with increasing distance from the calcite-filled fracture (Figure 3), and samples with the highest NRM intensities were those which exhibited the maximum red staining.

In most of the specimens in this group, stable, consistent decay in a southeasterly and shallow direction was removed during thermal demagnetization (Figure 4a,b).

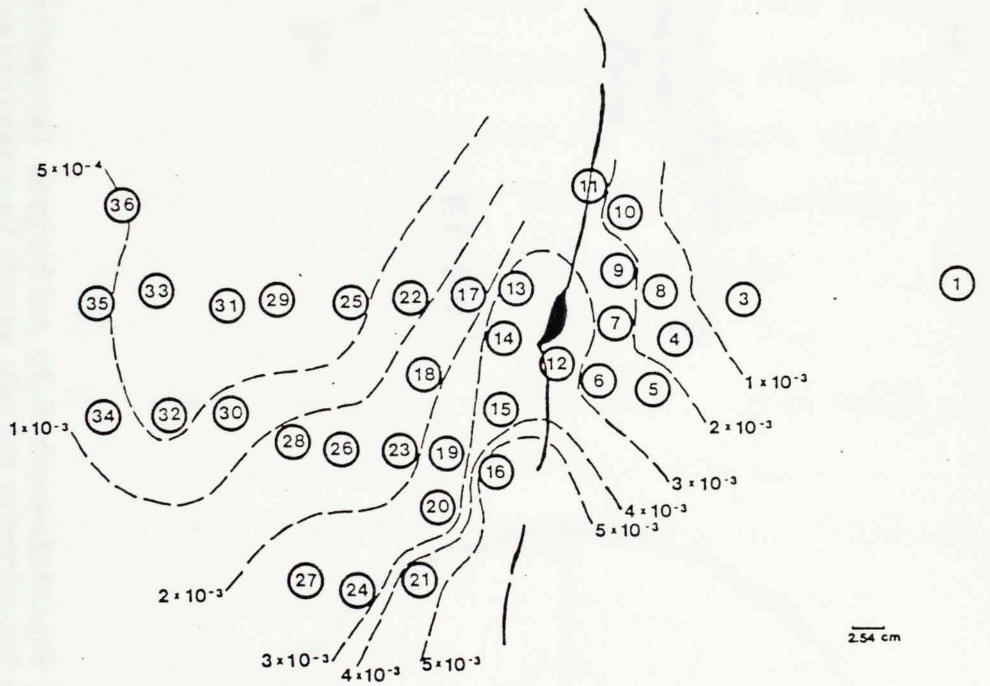


Figure 3. Natural remanent magnetization (in A/m) intensities decrease away from calcite-filled fracture at site "KF". Highest magnitudes correspond to areas of maximum staining by hematite. Circled numbers correspond to specimen drill hole locations (drill holes are 2.5 cm in diameter).

Figure 4a. Figure 4b.

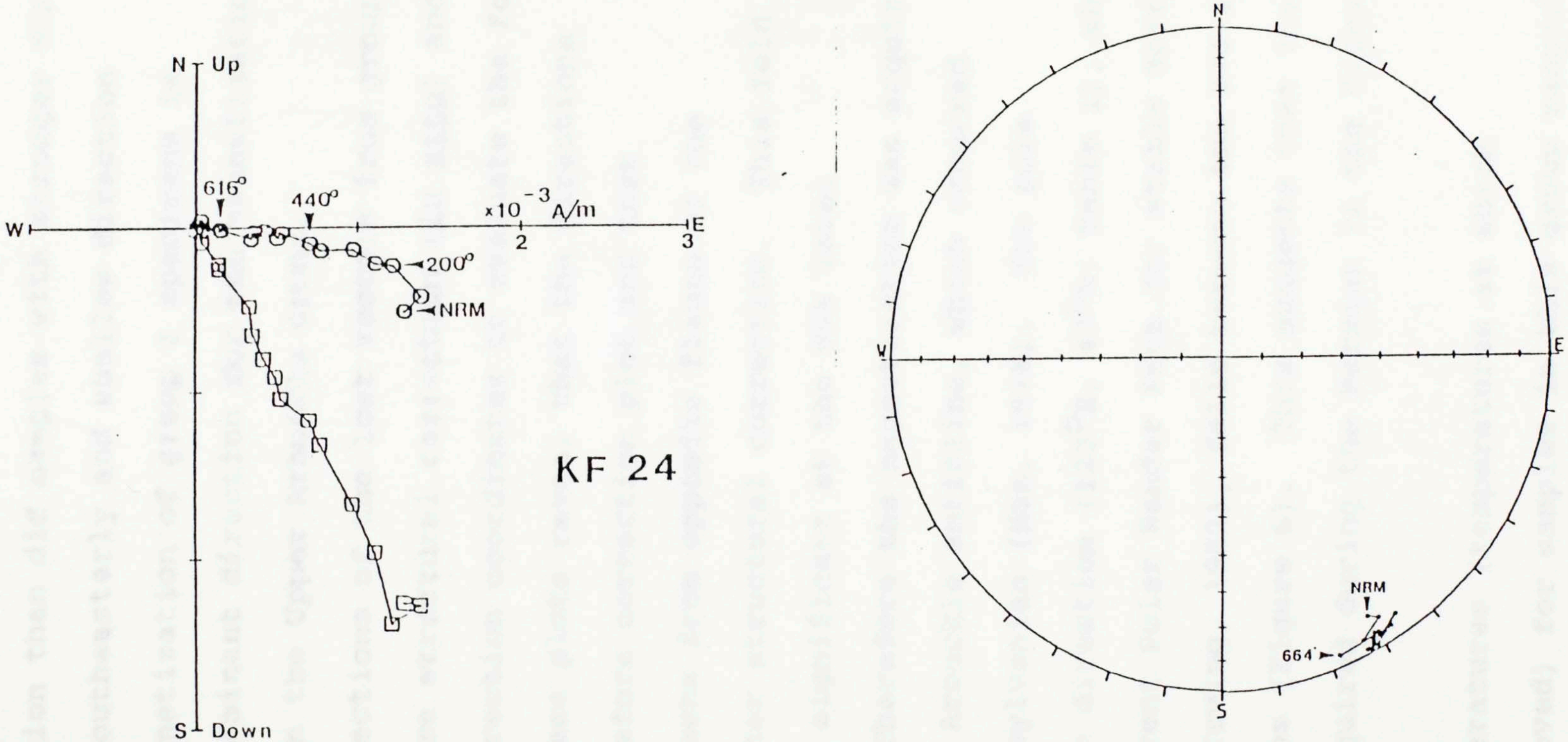


Figure 4. a) Orthogonal projection of a representative specimen from site "KF" illustrating consistency of decay during progressive thermal demagnetization. Squares and circles indicate that the direction of magnetization removed is southeasterly in declination and shallow in inclination, respectively. Intensities decrease toward origin with increasing temperature. Projection plotted in bedding (before structural correction) coordinates. b) Equal area stereographic projection of the demagnetization behavior of specimen KF24 (bedding coordinates). Closed symbols show positive inclination; open symbols show negative inclination.

Specimens with NRM intensities less than 5 x 10^{-4} amperes/meter (A/m) displayed more erratic behavior during thermal demagnetization than did samples with stronger NRM intensities. This southeasterly and shallow direction removed during demagnetization of group I specimens is interpreted as the dominant direction for the magnetization in Liesegang bands in the Upper Arbuckle Group.

Equal area projections of the lost vectors from group I were plotted in before structural correction (in situ) and after structural correction coordinates to evaluate the fold test (Figure 5). These plots reveal that the directions group well for the before correction plot and that directions for specimens from opposite flanks of the anticline diverge after structural correction. This fold test is positive and significant at the 99% level (McElhinny, 1964). Therefore the magnetization was acquired after folding of the Arbuckle anticline, which occurred during the late Pennsylvanian (Ham, 1978). The pole position for the mean direction (123^{O}E, 47^{O}N; Table 1), when compared to the Apparent Polar Wander Path for stable North America (Irving and Irving, 1982), falls between the 270 and 280 million year poles (Figure 6). This suggests that the magnetization was acquired during the Permian in the Kiaman interval.

Unblocking temperatures (temperatures at which magnetization is removed) for samples in this group ranged up to 675^{O}C. Because some of the magnetization remains

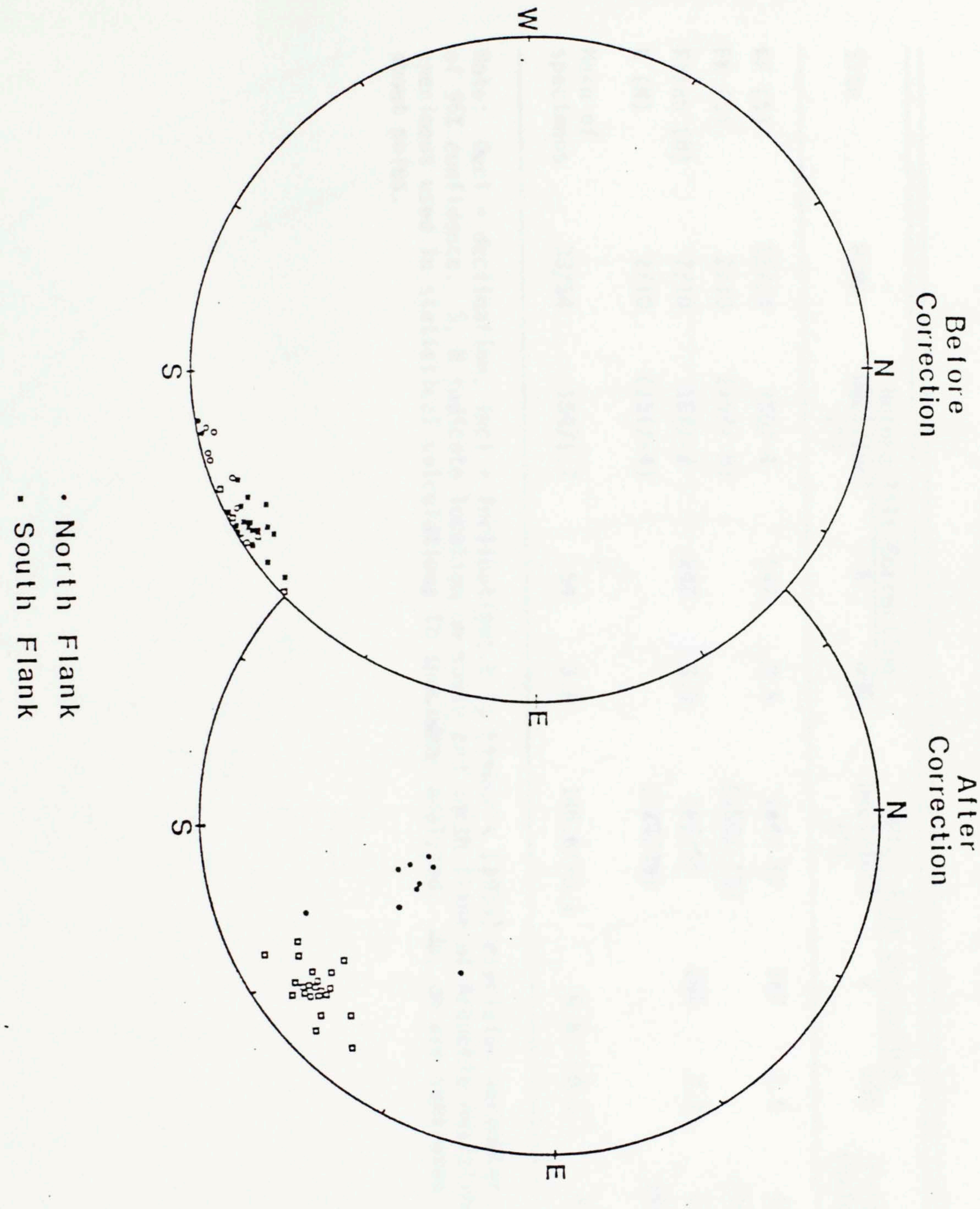


Figure 5. Equal area projection of specimen directions. Specimen directions group well for in situ (before correction) plot, diverge after structural correction. Open symbols show negative inclination; closed symbols show positive inclination.

Table 1 - Summary of Paleomagnetic Results

Site	N/No	Before Tilt Correction Decl/Incl (°)	k	α95	After Tilt Correction Decl/Incl (°)	k	α95	Pole Position (before correction	dp	dm
KF (S)	22/24	150/ 4	147	2.5	144/-17	147	2.5	44°N, 126°E	1.3	2.6
FK (S)	2/10	(152/ 8)			(150/-13)			(44°N, 123°E)		
KSlab (N)	7/10	167/-2	242	3.9	157/55	242	3.9	54°N, 106°E	1.9	3.9
K (N)	2/10	(151/-4)			(124/49)			(48°N, 129°E)		
Mean of specimens	33/54	154/1.7	54	3.4	146.6/-0.1	6.6	10.5	47°N, 123°E	1.7	3.4

Note: Decl = declination, incl = inclination; k is Fisher's (1953) precision parameter; α95 is radius of cone of 95% confidence. S, N indicate location on south and north flank of Arbuckle Anticline. N/No is ratio of specimens used in statistical calculations to specimens analyzed. dp, dm are semi-axes of oval of 95% confidence about poles.

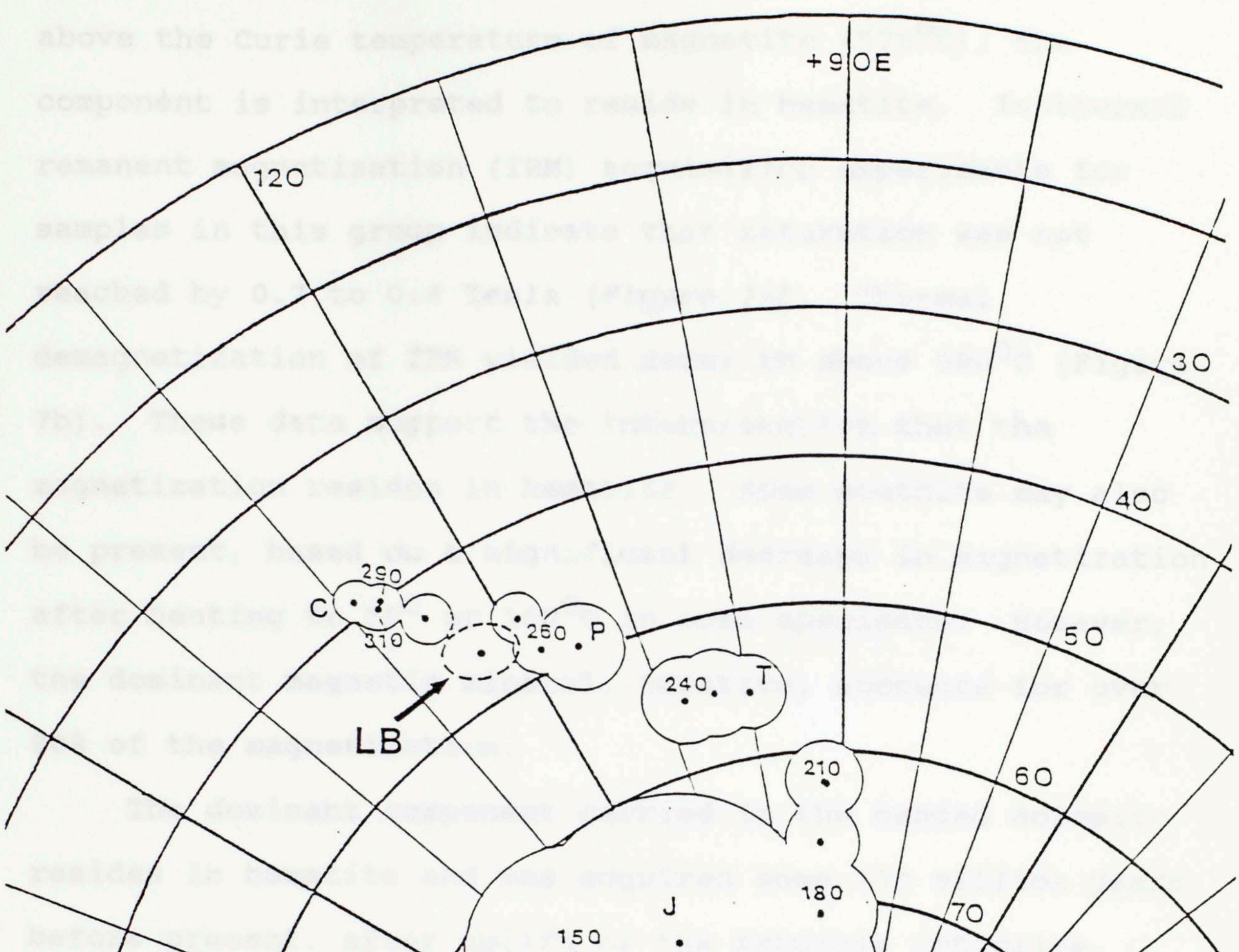


Figure 6. Apparent Polar Wander Path for Stable North America showing pole position (LB) for Liesegang bands in Upper Arbuckle Group with dashed oval of 95% confidence (dp,dm). Late Paleozoic to Recent path after Irving and Irving (1982). Error envelopes around Late Paleozoic-Recent poles correspond to standard errors.

above the Curie temperature of magnetite (578^{O}C), the component is interpreted to reside in hematite. Isothermal remanent magnetization (IRM) acquisition experiments for samples in this group indicate that saturation was not reached by 0.7 to 0.8 Tesla (Figure 7a). Thermal demagnetization of IRM yielded decay to above 580^{O}C (Figure 7b). These data support the interpretation that the magnetization resides in hematite. Some goethite may also be present, based on a significant decrease in magnetization after heating to 50^{O} or 100^{O}C in some specimens. However, the dominant magnetic mineral, hematite, accounts for over 80% of the magnetization.

The dominant component carried in the banded dolomite resides in hematite and was acquired some 280 million years before present, after uplift of the Arbuckle anticline. Steiner (1973) interprets the magnetization in the West Spring Creek Formation as a viscous partial remanent magnetization (VpTRM). On the basis of conodont color alteration index, burial temperatures in the Arbuckle Group were probably never above 100^{O}C (Elmore et al., 1985). Based on theoretical relaxation time-blocking temperature relations for hematite (Pullaiah et al., 1975), and assuming a burial time of 300 million years and a burial temperature of 100^{O}C, the indicated maximum theoretical laboratory blocking temperature is about 400^{O}C. Because the magnetizations in all specimens in this group have unblocking temperatures in excess of 500^{O}C, and in most

Figure 7a.

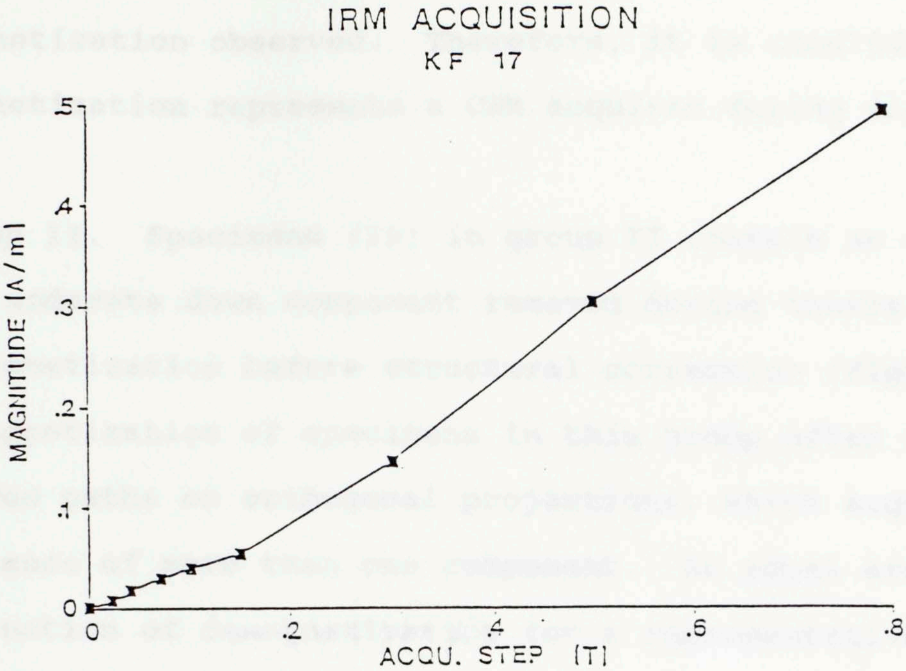


Figure 7b.

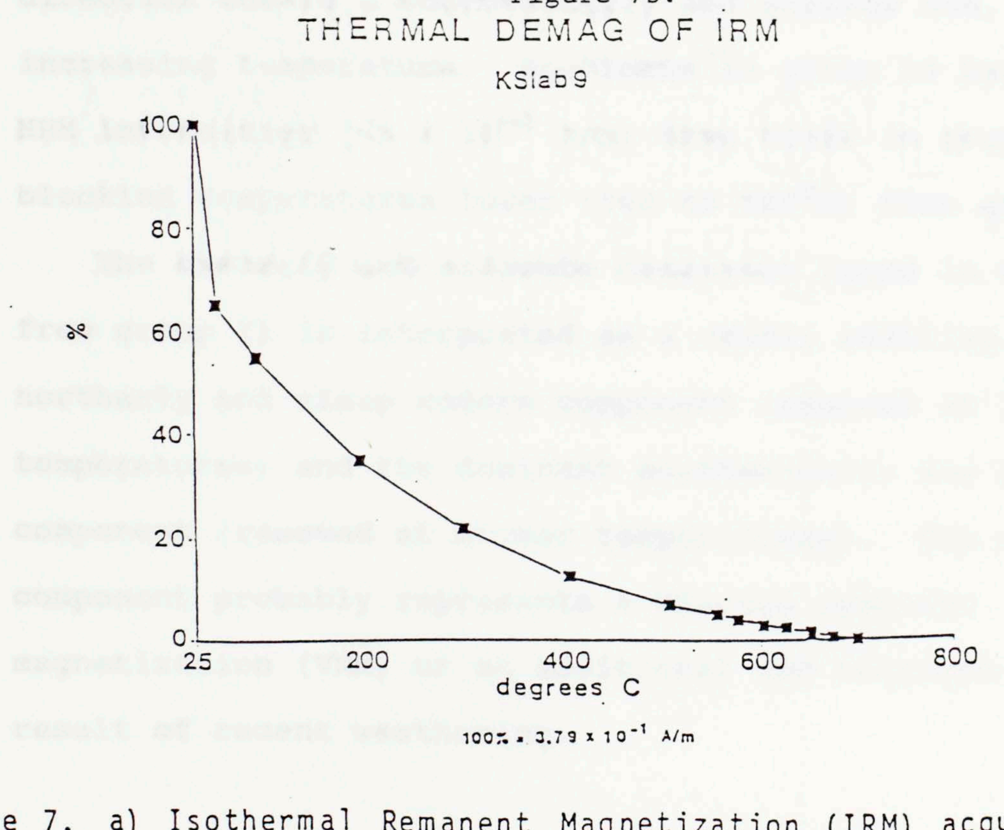


Figure 7. a) Isothermal Remanent Magnetization (IRM) acquisition plot. Saturation is not reached by 0.7 Tesla, suggesting that the magnetization resides in a high coercivity mineral such as hematite. If the magnetization resided in magnetite, saturation would probably have been reached by 0.3 T. b) IRM decay plot, illustrating decay to above 580^{o}C.

cases over 600^{o}C, a VpTRM could not account for the magnetization observed. Therefore, it is concluded that the magnetization represents a CRM acquired during diagenesis.

Group II. Specimens (19) in group II contain an easterly and moderate down component removed during thermal demagnetization before structural correction (Figure 8a). Demagnetization of specimens in this group often result in curved paths on orthogonal projections, which suggests the presence of more than one component. An equal area projection of demagnetization for a representative specimen (Figure 9b) illustrates a streaked path away from the modern direction toward a southeasterly and shallow one, with increasing temperature. Specimens in group II had weaker NRM intensities ($<8 \times 10^{-4}$ A/m) than those in group I, and blocking temperatures lower (500 to 525^{o}C) than group I.

The easterly and moderate component found in specimens from group II is interpreted as a vector addition of a northerly and steep modern component (removed at low temperatures) and the dominant southeasterly and shallow component (removed at higher temperatures). The modern component probably represents a viscous remanent magnetization (VRM) or an additional CRM acquired as a result of recent weathering.

Other. Two specimens out of 54 analyzed did not fall into either of the previously described groups. In one of

Figure 8a. Figure 8b.

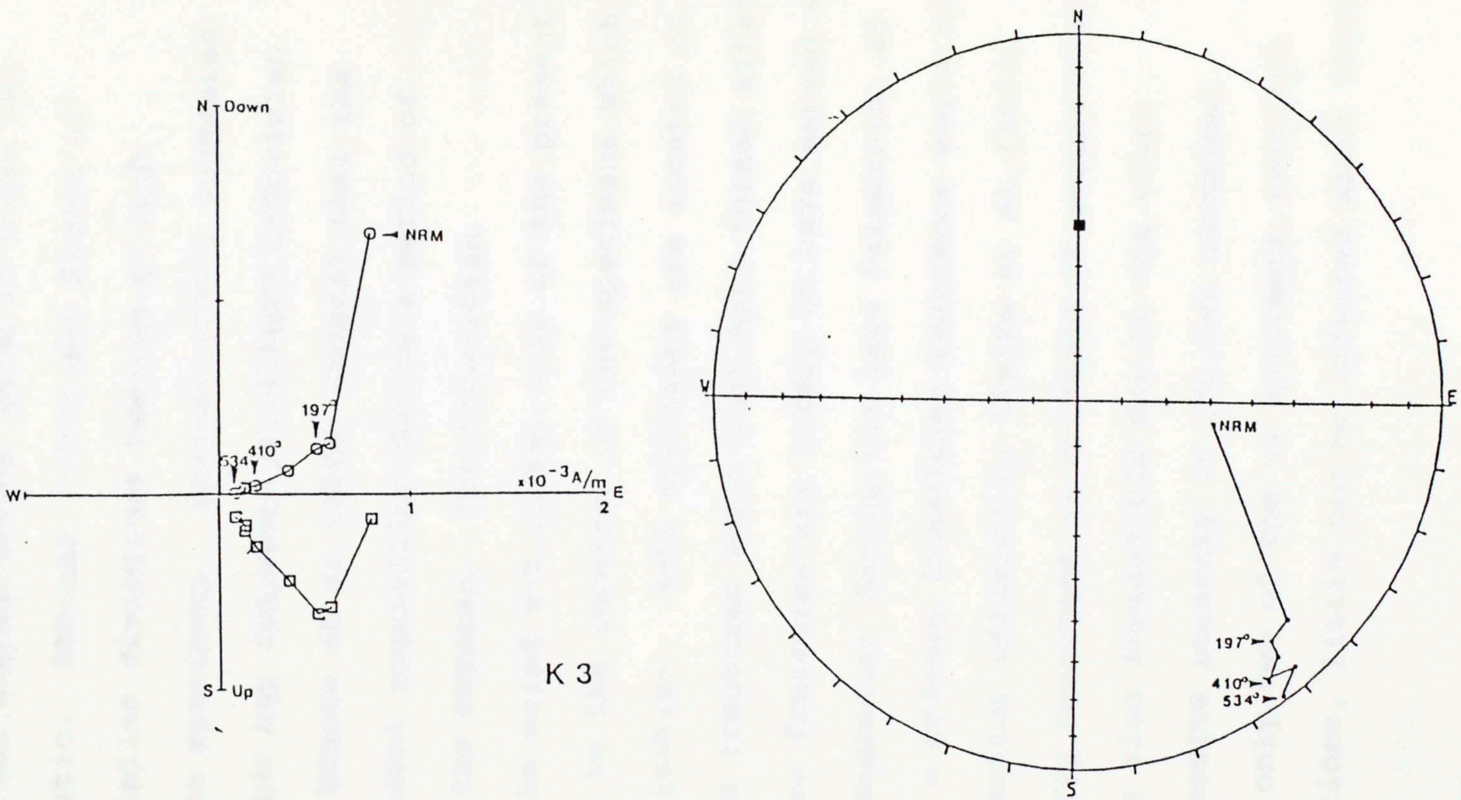


Figure 8. Results from Group II. a) Orthogonal projection (before correction) of thermal demagnetization of NRM from specimen "K3", one of the group II specimens. Note easterly and steep component removed at low temperatures, with southeasterly and shallow direction removed at higher temperatures, producing a generally curved path. b) Stereographic projection of demagnetization behavior of specimen "K3", illustrating movement from easterly and steep direction to southeasterly and shallow endpoint. Square corresponds to the modern field direction (axial geocentric dipole model) for the study area.

these specimens, a northwesterly and steep negative direction (before correction) was removed, and in the other specimen, a northwesterly and steep positive direction (before correction) was removed during demagnetization.

The origin of the magnetization found in these two specimens is enigmatic. Steiner (1973) and Elmore et al.(1985) report similar directions removed at high temperatures in some specimens. Steiner (1973) suggested that these directions may represent a primary Ordovician remanence, whereas Elmore et al.(1985) suggest that the direction may represent acquisition during a period of normal polarity in the Permian. The Ordovician interpretation may be ruled out in the case of the present study, however, due to the location of the specimens which exhibit this magnetization. Both specimens are located on major calcite-filled fractures which must have formed after lithification. These fractures are likely to have served as conduits for fluid migration during the late Paleozoic, so it is unlikely that a primary Ordovician remanence would be present. The explanation offerred by Elmore et al.(1985) that the northwesterly component is evidence of acquisition during a reversal is also implausible due to the steep inclinations and opposite polarity of the two anomalous specimens. Because only two of the 54 specimens examined exhibit these directions, little can be inferred about their origin.

Petrography

As previously mentioned, the Liesegang bands are found in beds which consist of dolomitic layers that alternate with ripple cross laminated grainstones (Figure 1). The dolomitic layers are 1-3 cm thick and drape the underlying grainstones. The hematite bands are found only in the dolomitic layers and are not present in the undolomitized rocks. In addition, bands are frequently concentrated in shaly, clay-rich laminae in the carbonates. The samples investigated contained a variable clastic content, including quartz and minor feldspars, both of which were found with and without overgrowths. Clastic grains are commonly restricted to discreet laminae but also occur dispersed in the carbonate.

The fracture fillings are composed largely of calcite (Figure 9a). Pyrite, partly replaced by hematite is also found in one of the calcite-filled fractures (Figure 9b). Authigenic pyrite is also found disseminated in carbonate that does not contain Liesegang bands. Samples of banded carbonate away from the fractures are primarily composed of dolomite and calcite. Most calcite occurs as cement filling intercrystalline porosity, but some dedolomite is also present (Figure 9c). The amount of calcite cement markedly decreases away from the fractures. Dedolomite also apparently decreases away from the fractures, although the trend is not as clear as for calcite cement. The dedolomite

Figure 9a. Photomicrograph of main fracture and surrounding dolomite. Calcite is stained with Alizarin red solution. Fracture and interstitial spaces largely calcite. Dedolomite and detrital quartz are also present. (Scale bar = 300 µm; plane light)

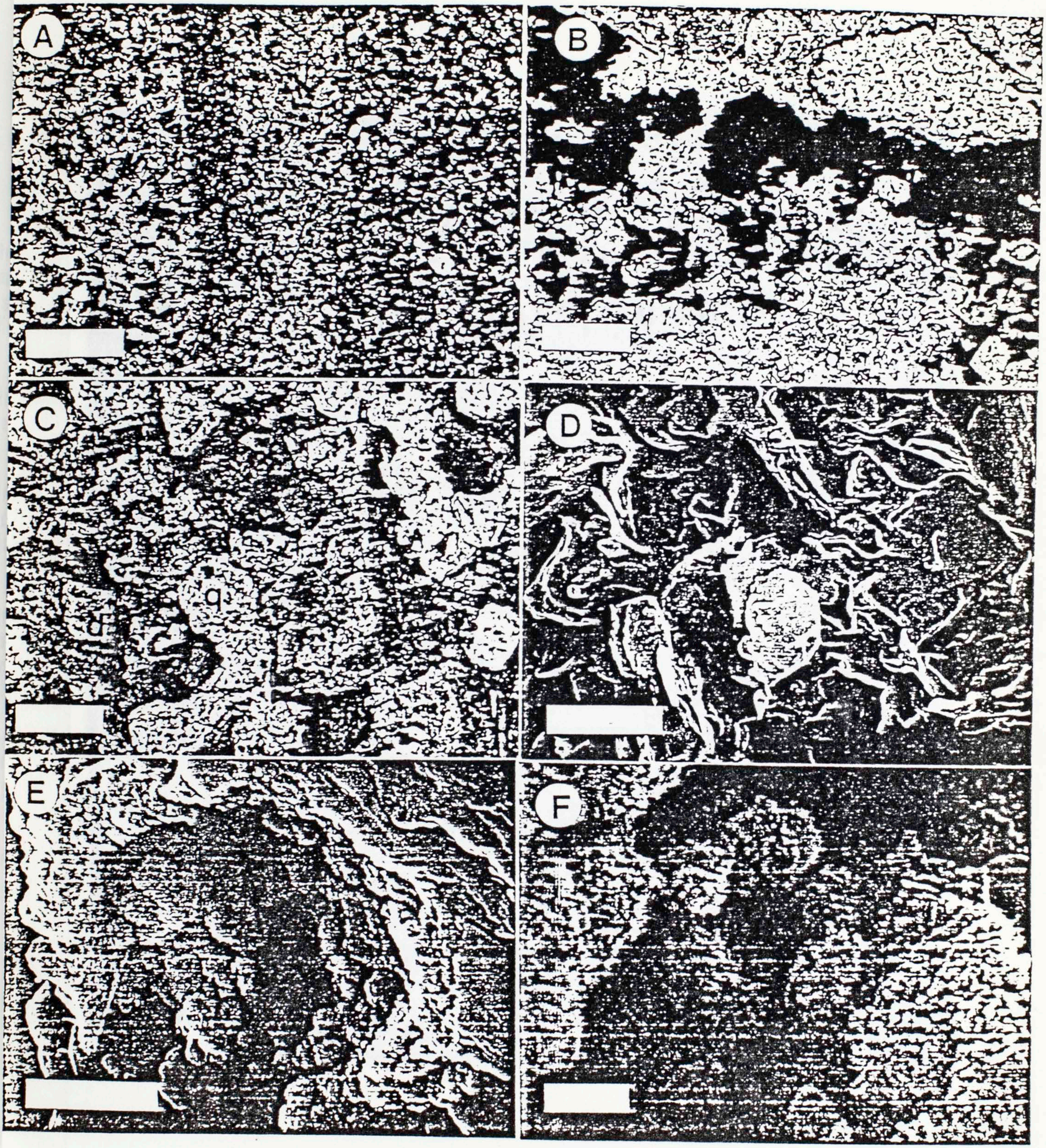
Figure 9b. Photomicrograph illustrating pyrite in fracture. Pyrite is partly altered to hematite. (Scale bar = 100 µm, plane light)

Figure 9c. Photomicrograph illustrating dolomite (d) partially replaced by calcite (c) (dedolomite). Calcite is stained with Alizarin red solution. Note quartz (q) grains with overgrowths. (Scale bar = 100 µm; plane light)

Figure 9d. SEM photomicrograph illustrating authigenic clay minerals. Fine grained (<1 micron) hematite is frequently associated with these clays. Energy dispersive analysis indicates these clays have an illitic composition. Scale bar = 3 µm.

Figure 9e. SEM photomicrograph of very fine grained hematite (as indicated by energy dispersive analysis). Scale bar = 3 µm.

Figure 9f. Close up of hematite in 9e. Scale bar = .5 µm.


A
B
C
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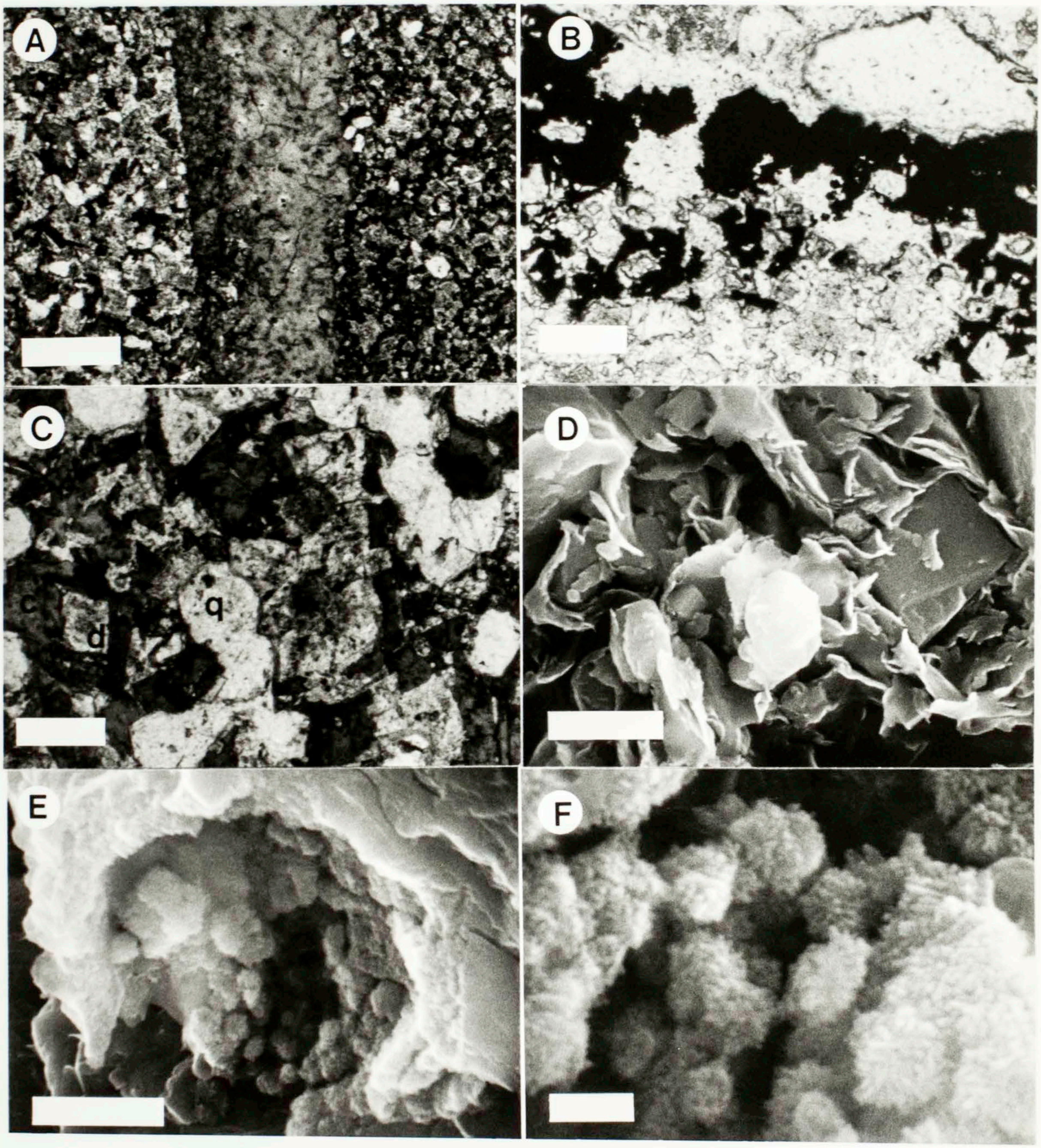
A
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q
D
E
F

consists of calcite filling rhombohedral zones within dolomite crystals. In contrast to some other reports of dedolomite (e.g. Frank, 1981), iron oxides are not directly associated with the dedolomite.

Scanning electron microscopy (SEM) and energy dispersive analysis revealed the presence of dolomite, dedolomite, and clays with an illitic composition (Figure 9d). Very fine grained crystals (<1 micron in diameter) were also identified (Figures 9e, 9f). Energy dispersive analysis indicates that the crystals are composed of iron, and they are interpreted to be hematite. The delicacy and euhedral morphology of the hematite found suggests an authigenic origin. The petrographic investigation thus supports the conclusion of rock magnetic analysis, i.e. that hematite is the dominant magnetic mineral.

DISCUSSION

Hematite carries the magnetization in Liesegang bands in the Upper Arbuckle Group in southern Oklahoma. It is proposed that fractures, which presumably formed during uplift of the Arbuckle Mountains, served as conduits for fluids rich in calcium and iron. These fluids migrated out from fractures into beds which had been dolomitized. These dolomitized beds presumably provided ample porosity and permeability for fluid migration, whereas limestones which had not been dolomitized lacked sufficient porosity and permeability for the outward migration of fluids. As these fluids migrated into dolomite beds, several diagenetic changes took place: dolomite was replaced by calcite (dedolomitization), and hematite bands and calcite cement precipitated. Authigenic clays may also have precipitated, but the textural relationships between the other phases and the clays are not clear.

Sargent (1969), in a petrographic and geochemical study of the Arbuckle Group in southern Oklahoma, proposed that dedolomitization probably occurred under near surface conditions. He states that dedolomitized rocks (in the Arbuckle Anticline) are high in ferric iron, and therefore that the possibility exists that the original rocks were ferroan dolomite. He further proposed that the ferroan dolomites were tectonic in origin, i.e. related to fractures, based upon their field occurrences. Sargent (1969) also suggested that "highly localized fluids" moving along faults during a late tectonic or post-tectonic episode apparently were responsible for this dedolomitization, which is in agreement with the conclusions from this study.

The results of this study are also similar to those found by Elmore et al.(1985) in their investigation of hematite in burrows in the Kindblade Formation. The pole position they report (43^{O}N, 129^{O}E) is similar to the pole position obtained for Liesegang bands (47^{O}N, 127^{O}E). The hematite in these burrows is associated with dedolomite and was interpreted as having formed by direct precipitation when ferrous iron was released from ferroan dolomite and oxidized. Similar fluids, i.e. rich in calcium and iron, may have been responsible for the precipitation of hematite in the burrows and in the Liesegang bands in this carbonate unit.

There are several possible sources of the iron contained in the hematite Liesegang bands. Some of the iron in the hematite was probably carried in the fluids, although the original source is open to question. The iron may have been liberated during the smectite to illite transformation at depth (e.g. Walker and Runnels, 1984). This iron may then have been mobilized during or after uplift. Local release of iron from ferroan dolomite during dedolomitization may have contributed some iron, but dedolomite is not common, and the amount present in the samples investigated does not appear to be great enough to account for all of the iron present in hematite. Furthermore, no distinct trend in dedolomitization is observed with distance from the calcite-filled fracture. Such a trend might be expected, given the decrease in intensity of NRM away from the fracture. One other source of iron may be the oxidation of pyrite. Sargent (1969) noted that sulfide mineralization is commonly associated with epigenetic dolomitization in the Arbuckle Group, and, as previously mentioned, pyrite, partially altered to hematite, is found in at least one fracture.

A possible diagenetic history for the rock containing the Liesegang bands might include dolomitization sometime after uplift (or during uplift), perhaps with dolomitizing fluids emanating from the fractures. Pyrite may have precipitated in these fractures after the flow of dolomitizing fluids had subsided. Then, at a later time, perhaps due to late tectonic activity, calcium- and iron-rich fluids flowed through these fractures. The fluids probably carried some iron. Dissolution and oxidation of iron in pyrite and oxidation of iron released during dedolomitization were probably local sources for the iron.

The exact cause of the formation of the intricate banding in Liesegang bands is unknown. Liesegang bands can form as a result of a propagating redox front (Ortoleva, 1983). A possible explanation for the intricate banding could be that fluid movement was rhythmic due to a fluctuating water table, causing discrete areas to be sites of hematite precipitation. This situation would be analagous to the method of formation of bands in soils proposed by Brewer (1964).

Late Paleozoic or Kiaman secondary magnetizations similar to that reported in this study have been reported from many early and middle Paleozoic units all over the world (e.g. McCabe et al., 1983; Irving and Pullaiah, 1976). The magnetizations are dominantly reversed in polarity and reside in both magnetite and hematite. Although the numerous reports of Kiaman remagnetization might suggest global or regional events, these hypotheses are difficult to evaluate and test. The results from the Liesegang band-containing carbonates suggest that remagnetization in the Upper Arbuckle Group is at least partially related to tectonic deformation.

CONCLUSIONS

1) Liesegang bands in the Ordovician Kindblade Formation in southern Oklahoma contain diagenetic hematite in symmetrically banded patterns around calcite-filled fractures.

2) The hematite carries a Chemical Remanent Magnetization (CRM) which was acquired some 280 m.y. before present, after uplift of the Arbuckle Mountains during Late Pennsylvanian-Permian.

3) Migration of calcium- and iron-rich fluids from fractures through dolomite beds may have been responsible for dedolomitization and precipitation of hematite.

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CHAPTER 3

ORIGIN OF MAGNETIZATION IN UPPER ARBUCKLE GROUP: LIMESTONE HILLS, SOUTHWESTERN OKLAHOMA

ABSTRACT

Rock magnetic, paleomagnetic, petrographic, and organic geochemical studies of the Upper Arbuckle Group in southern Oklahoma were undertaken to test for a relationship between hydrocarbons and authigenic magnetite.

Results from hydrocarbon-containing carbonates from the Limestone Hills indicate a secondary magnetization that is dominated by a low coercivity phase. The magnetization is apparently synfolding and is interpreted as a Chemical Remanent Magnetization (CRM) acquired during the Pennsylvanian. Rock magnetic results suggest that magnetite is the primary magnetic phase, although pyrrhotite may also be present in some specimens. Petrographic results suggest the presence of magnetite as spherules and as needles.

These results from the relatively hydrocarbon-rich Limestone Hills carbonates are in contrast with previous work on the relatively hydrocarbon-poor carbonates in the Arbuckle Mountains that indicates a Permian CRM residing in hematite. The results of these preliminary studies suggest

that the presence of hydrocarbons may provide conditions required for formation of authigenic magnetite and associated magnetizations.

INTRODUCTION

Authigenic magnetic minerals such as magnetite have been reported from several sedimentary units and their presence has been linked to migration of hydrocarbons or related brines (e.g. Donovan, 1974). If a relationship between hydrocarbons and the formation of authigenic magnetite can be established, then there are several potential applications. For example, aeromagnetic surveys performed in search of anomalous concentrations of magnetic minerals might help locate petroleum accumulations (Donovan et al., 1979), and paleomagnetic analyses might be used to date the formation of magnetite and, hence, the migration of hydrocarbons. Testing the hypothesis is also important because additional results may lead to a better understanding of the origin of secondary magnetizations that reside in magnetite. The hydrocarbon/magnetite hypothesis has, however, not been adequately tested. The objective of this investigation is to test the hypothesis by determining the magnetic mineralogy in hydrocarbon-impregnated limestones of the Arbuckle Group and comparing the results with previous work on unimpregnated limestones from the same unit in which hematite is the dominant magnetic mineral (Chapter 2; Elmore et al., 1985). A secondary objective is to date the formation of the magnetic phases observed.

In order to accomplish these objectives, a combination of paleomagnetic, rock magnetic, petrographic, and organic geochemical techniques is employed. Paleomagnetic dating is based on the premise that authigenic magnetic minerals commonly acquire a stable magnetization aligned with the magnetic field in which they form. If this magnetization can be isolated, then the corresponding pole position can be compared to the Apparent Polar Wander Path for stable North America (e.g. Irving and Irving, 1982), and the time at which the magnetic mineral formed may be ascertained. This approach is particularly successful if it is combined with fold tests (Graham, 1949) which constrain the timing of remanence acquisition, assuming that the time of folding is known. Rock magnetic and petrographic studies are undertaken to identify the magnetic mineralogies present. The results of the geochemical studies quantify and characterize the hydrocarbons in the samples.

GEOLOGIC SETTING AND PREVIOUS WORK

Samples were collected for this study from outcrops in the Limestone (Slick) Hills of southwestern Oklahoma (Figure 1). The area is bordered to the southwest by the Wichita Mountains and to the north by the Anadarko Basin. The exposures investigated are from the McKenzie Hill and Kindblade Formations of the Ordovician Upper Arbuckle Group. Facies found in the Upper Arbuckle Group in the Limestone Hills are similar to those observed in the Arbuckle Mountains, i.e. deposited in subtidal to intertidal settings (Tenney, 1984) within the southern Oklahoma aulacogen

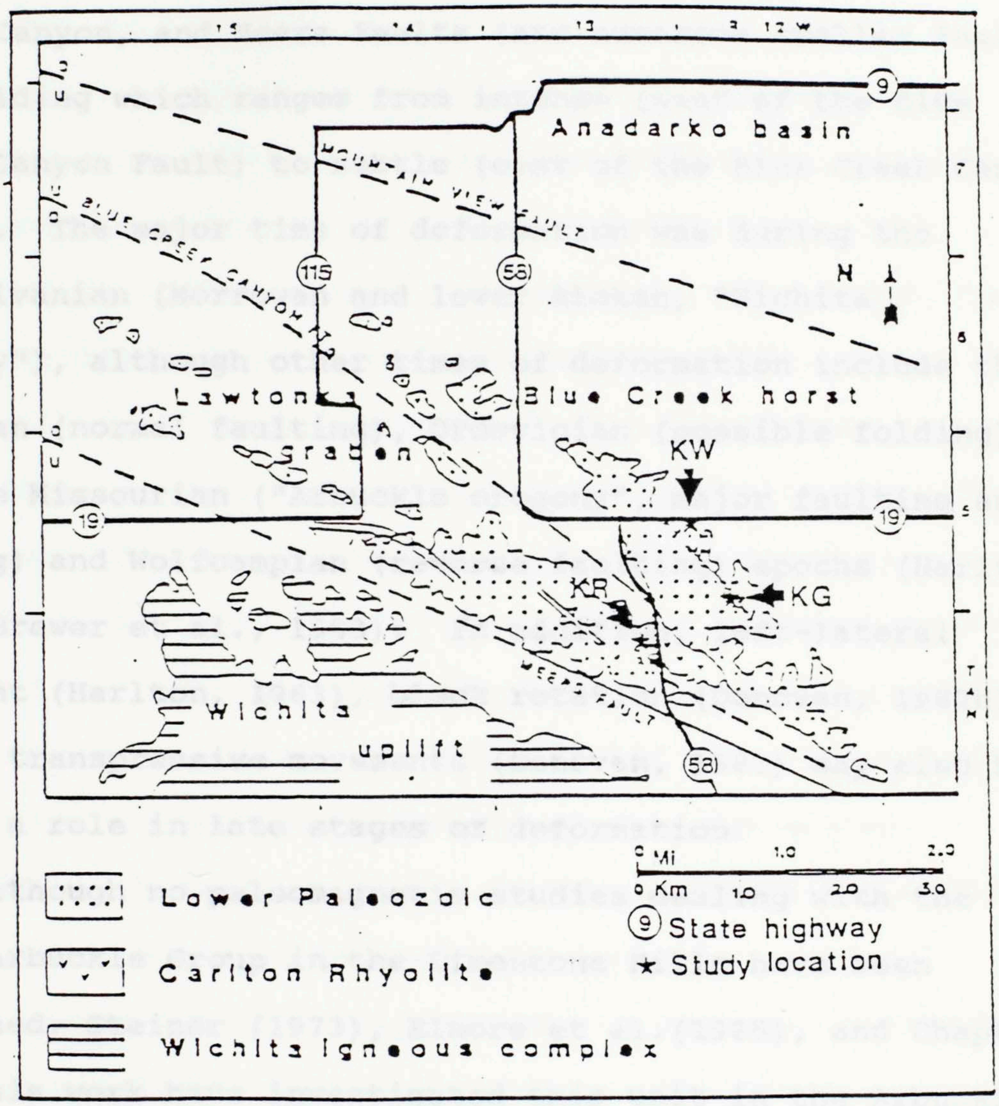


Figure 1. Location map for Limestone Hills study area showing major tectonic elements (after Donovan, 1983). Sampling locations (KR, KW, and KG) indicated with stars.

(Wickham, 1978). Major deformation in the area is evidenced by a complex fault system, including the Mountain View, Blue Creek Canyon, and Meers Faults (and numerous smaller faults) and folding which ranges from intense (west of the Blue Creek Canyon Fault) to subtle (east of the Blue Creek Canyon Fault). The major time of deformation was during the Pennsylvanian (Morrowan and lower Atokan, "Wichita orogeny"), although other times of deformation include the Cambrian (normal faulting), Ordovician (possible folding), and the Missourian ("Arbuckle orogeny", major faulting and folding) and Wolfcampian (reverse faulting) epochs (Harlton, 1963; Brewer et al., 1983). In addition, left-lateral movement (Harlton, 1963), block rotation (Donovan, 1982b), and/or transpressive movements (Donovan, 1983) may also have played a role in late stages of deformation.

Although no paleomagnetic studies dealing with the Upper Arbuckle Group in the Limestone Hills have been published, Steiner (1973), Elmore et al.(1985), and Chapter 2 of this work have investigated this unit in the Arbuckle Mountains. In these studies, late Pennsylvanian-Permian magnetizations were reported.

BACKGROUND

Perhaps the earliest report of authigenic magnetite was by Friedman (1954), but interest in the hydrocarbon/authigenic magnetite problem has heightened since the suggestion by Donovan that hydrocarbon migration may cause the formation of authigenic magnetite (1974). Zuhair et al. (1985) reported mineralogic alteration, termed a Hydrocarbon-Induced Diagenetic Aureole (HIDA), above the Cement oil field which included pyrite, marcasite, pyrrhotite, galena, and sphalerite in crestal rocks. The occurrence of magnetite was, however, not reported. Reynolds et al.(1984) report the presence of ferrimagnetic pyrrhotite at this location and suggest that it is related to hydrocarbons. Reynolds et al. (1985) also suggest that the magnetite reported by Donovan et al. (1979) may represent contamination from drilling equipment. Boardman (1985), in a study of aeromagnetic anomalies over oil fields, suggested that this phenomenon may also represent a drilling equipment-related feature and not one related to the presence of diagenetic magnetite.

McCabe et al.(1983) reported diagenetic magnetite in the Lower Devonian Helderberg carbonates and interpreted the magnetization as a Chemical Remanent Magnetization (CRM) which formed in the late Carboniferous to early Permian. They suggested that this CRM might be associated with hydrocarbons or oil-related brines. Magnetite isolated by magnetic extraction from the Helderberg and other units (McCabe et al., 1983, 1984) exhibited spheroidal and botryoidal forms with compositions (i.e. iron as the only detectable cation) consistent with a diagenetic origin. Wisnioweicki et al. (1983) report a similar late Paleozoic CRM residing in diagenetic magnetite in the late Cambrian Bonneterre Formation in southeastern Missouri. In these studies, a thermal origin (viscous partial thermoremanent magnetization, or VpTRM) was ruled out on the basis of relatively low burial temperatures calculated from conodont alteration indices and use of the remagnetization curves for magnetite of Pullaiah et al.(1975). Recently, however, Kent (1985) has suggested that some of the magnetizations reported by McCabe et al.(1983) may be thermoviscous in origin. Thus, the origin of magnetizations (CRM, VpTRM?) residing in diagenetic magnetite is controversial.

Previous work on the hydrocarbon/authigenic magnetite problem has failed to resolve the issue. Questions regarding mineralogic changes associated with the presence of hydrocarbons and those regarding the origin of magnetizations will be addressed in this paper.

SAMPLING AND LABORATORY TECHNIQUES

Paleomagnetic and Rock Magnetic

Approximately 110 samples were collected with a portable coring apparatus and oriented <u>in situ</u> with a clinometer and Brunton compass. Three locations were sampled (Figure 1). One location (KR or Kimbell Ranch) is to the southwest of the Blue Creek Canyon Fault. This location includes 6 sites. Two of the sites are on the northeast flank, one is on the crest, and three are on the southwest flank of the Paradox anticline. Location KW is on a roadcut on Highway 19, northeast of the Blue Creek Canyon Fault. Six sites of varying lithology were sampled in the shallowly dipping carbonates at this location. The third location, northeast of the Blue Creek Canyon Fault, is the Mission Creek Anticline. Two sites from the east flank and two from the west flank were sampled at location KG (Gilbreath Ranch) in an attempt to perform a second fold test in the area.

Specimens (cylinders of 2.2 cm in length and 2.5 cm in diameter) were cut from the samples, and their Natural Remanent Magnetizations (NRM) were measured in a United Scientific Three Axis cryogenic magnetometer. Seventy specimens were demagnetized using Alternating Field (AF) demagnetization techniques. Using this method, specimens were demagnetized (and subsequently remanence measured) at steps of 50, 100, 200, 300, 400, 500, 600, 750, 900, and 1250 gauss in a shielded 2 axis tumbling unit. Seventeen specimens were demagnetized with thermal demagnetization techniques. These specimens were heated using a Schonstedt TSD-1 unit in a stepwise manner for 30 minutes at each temperature (some specimens at 100, 200, 250, 300, 325, 350, 400, 450, 500, 550, 600, 650, 675^{O}C and others at 100^{O}C intervals to 400^{o}C, in 50^{o}C steps to 500^{o}C and subsequently by 25^{o}C steps to 675^{o}C). Specimens cooled in a field of no more than 5 nT before being measured after each heating. Three specimens were demagnetized by AF techniques and then further demagnetized using thermal techniques with methods similar to those described above. Directional and intensity results were plotted on orthogonal projections (Zijderveld, 1967) consisting of a vertical and horizontal projection of the vector endpoints of each demagnetization step. The direction and magnitude of components removed during demagnetization were obtained through visual inspection followed by vector subtraction. Line segments chosen consisted of at least three colinear points. Mean directions of components were calculated giving equal weight to each specimen.

Representative specimens were chosen for isothermal remanent magnetization (IRM) acquisition and decay experiments to aid in the identification of the magnetic mineralogy. Acquisition of IRM was accomplished with a water-cooled electromagnet at field strengths of 0.02, 0.04, 0.07, 0.1, 0.15, 0.3, 0.5, and 0.8 Tesla. Thermal decay of IRM was conducted in 50^{o}C steps to 700^{o}C.

Petrography

Chips cut from the paleomagnetic cores and outcrop samples were used for petrographic analysis. Thin section analysis, using both reflected and transmitted light, was used to identify different mineralogies and lithologies. Extraction of magnetic phases was achieved by dissolving the limestone samples (one from each location) in 1.5 M glacial acetic acid buffered to pH=4 with sodium acetate. The magnetic minerals were extracted from the insoluble residue in a slurry apparatus and examined with a scanning electron microscope (SEM) with energy dispersive capabilities.

Organic Geochemistry

Ten samples from the Upper Arbuckle Group were analysed using geochemical techniques. All geochemical analyses were performed at Cities Service Technology Center, Tulsa, Oklahoma. Four samples were from different sites at location KR, four were from location KW, and one was from location KG. One sample was from a location (KF) in the Arbuckle Mountains (see Chapter 2). This sample, which did not exhibit any odor of hydrocarbons in the field, was used for comparison with samples from the Limestone Hills which did exhibit hydrocarbon odor in the field. All samples (except that from KG) used in geochemical analysis were fresh outcrop samples. Fresh samples are preferred over paleomagnetic cores in that the latter may be contaminated with oil used to lubricate the coring apparatus. In the case of KG, however, paleomagnetic cores had to be used.

Samples used in geochemical analyses were first crushed to a diameter of several centimeters. Chips of this size were used for the analysis of light hydrocarbons. For other analyses, however, chips were ground to 200 mesh size.

The first geochemical analysis performed in an effort to quantify the amount of organic matter present in the samples was the determination of total organic carbon (TOC). For this procedure, approximately 15 grams of each ground rock sample were dissolved in 10% hydrochloric acid and then rinsed with distilled water. Approximately 0.1 grams of the acid insoluble residue was then combusted in the Leco instrument. The amount of carbon dioxide produced during this combustion is proportional to the amount of organic carbon present in the sample.

Rock-Eval pyrolysis was also performed on all samples. This technique provides an estimate of the amount of hydrocarbons present in samples as free hydrocarbons and the amount released as a result of pyrolysis. For this procedure, 0.1 grams of ground rock sample were pyrolysed in the Rock-Eval instrument with the temperature program commonly used in the laboratory (oven temperature held at $300^{O}C$ for 3 minutes, ramped at $25^{O}C$/minute, and held at $550^{O}C$ for 1 minute).

Gas chromatography was used to quantify and characterize the light (C_1 - C_{6+}) hydrocarbons. For this analysis, 2.5 grams of crushed rock sample were ground in an air-tight container for 5 minutes and then heated for 5 minutes in a $90^{O}C$ hot water bath. Then 1cc of the headspace gas was collected and manually injected into a Hewlett

Packard 5830A gas chromatograph for analysis, under specifications normally used in the laboratory (6' n-Octane on Poracil C 100/120 mesh, dual flame ionization detectors, He carrier gas; injection temperature 200^{O}C, FID temperature 300^{O}C, GC oven temperature held at 50^{O}C for 2 minutes, ramped at 10^{O}C/minute to 95^{O}C).

One sample from location KR was chosen for gas chromatography of the C_{15+} saturate fraction. This sample was chosen because it had the highest TOC and Rock-Eval values of all Kindblade samples analysed. For this analysis, approximately 100 grams of ground rock sample were extracted (Soxhlet extraction) for 24 hours in chloroform:methanol (90:10). Asphaltenes were precipitated out with pentane. The deasphalted extract was then separated into saturate, aromatic, and NSO fractions on a silica-alumina column with pentane, toluene, and chloroform:methanol (90:10), respectively. The saturate fraction was diluted 100:1 with heptane, and the dilute saturate fraction was injected into a Hewlett Packard gas chromatograph for analysis, using specifications commonly used in the Cities Service laboratory (for details of this procedure, the reader is referred to Rohrback, 1983).

RESULTS AND INTERPRETATION

Paleomagnetic and Rock Magnetic

Location KR. Specimens from this location are from the McKenzie Hill Formation of the Upper Arbuckle Group. Strata at this location exhibit the strongest folding of the three locations studied. Dips on both limbs were approximately 60^{o}, and the anticline plunges 25^{o} in a N54^{o}W direction. The NRM intensities (Table 1) for specimens on the north flank (sites KR 1 and KR 2) were as much as an order of magnitude higher than those from the crest of the anticline (site KR 3) or the south flank (sites KR 4, KR 5, and KR 6).

In most of the specimens from this location, stable, consistent decay in a southeasterly and moderate to shallow direction was removed during AF and thermal demagnetization (Figure 2). In specimens with the strongest NRM intensities (KR 1 and KR 2), this southeasterly and shallow direction appeared to be the only direction removed during demagnetization after the NRM step. In specimens from other sites, however, a northerly to northeasterly and steep down component was removed at low field strengths (Figure 3). In some instances, the presence of this second component produced a curved demagnetization path on the orthogonal projections.

Equal area projections of the dominant specimen directions from location KR were plotted for before structural correction (in situ) and after structural correction (Figure 4a). These plots reveal that the directions group well for the before correction plot and that directions from opposite flanks cross and diverge after structural correction. Because this anticline plunges 25^{o} in a N54^{o}W direction, a plunge correction was also applied

Table 1. Summary of geochemical results with NRM average intensities.

Sample	Average NRM Intensity (A/m)	Total Light Hydrocarbons (ppm)	TOC (%)	S_1	S_2
KF	0.6×10^{-3}	15,727	0.04	.0.0	.0 0
KG1	0.772×10^{-3}	46,462	0.04	.0.0	.0.0
KR1	6.62×10^{-3}	466,800	0.12	.0 2	.0 4
KR2	10.40×10^{-3}	540,937	0.14	.0.3	.0 6
KR3	0.728×10^{-3}	198,413	0.05	.0.0	.0.1
KR4	1.37×10^{-3}	167,197	0.04	.0 1	.0 0
KW2	0.351×10^{-3}	44,041	0.03	.0 0	.0 0
KW3	0.922×10^{-3}	7,948	0.03	.0 1	.0 0
KW4	0.488×10^{-3}	39,918	0.02	.0 1	.0 0
KW5	0.217×10^{-3}	63,182	0.05	.0 1	.0 0

Note: Total light hydrocarbons from gas chromatography. S1 and S2 are peaks obtained in Rock-Eval pyrolysis. S1 indicates amount of free hydrocarbons present; S2 indicates amount produced upon pyrolysis. A/m is Amperes/meter.

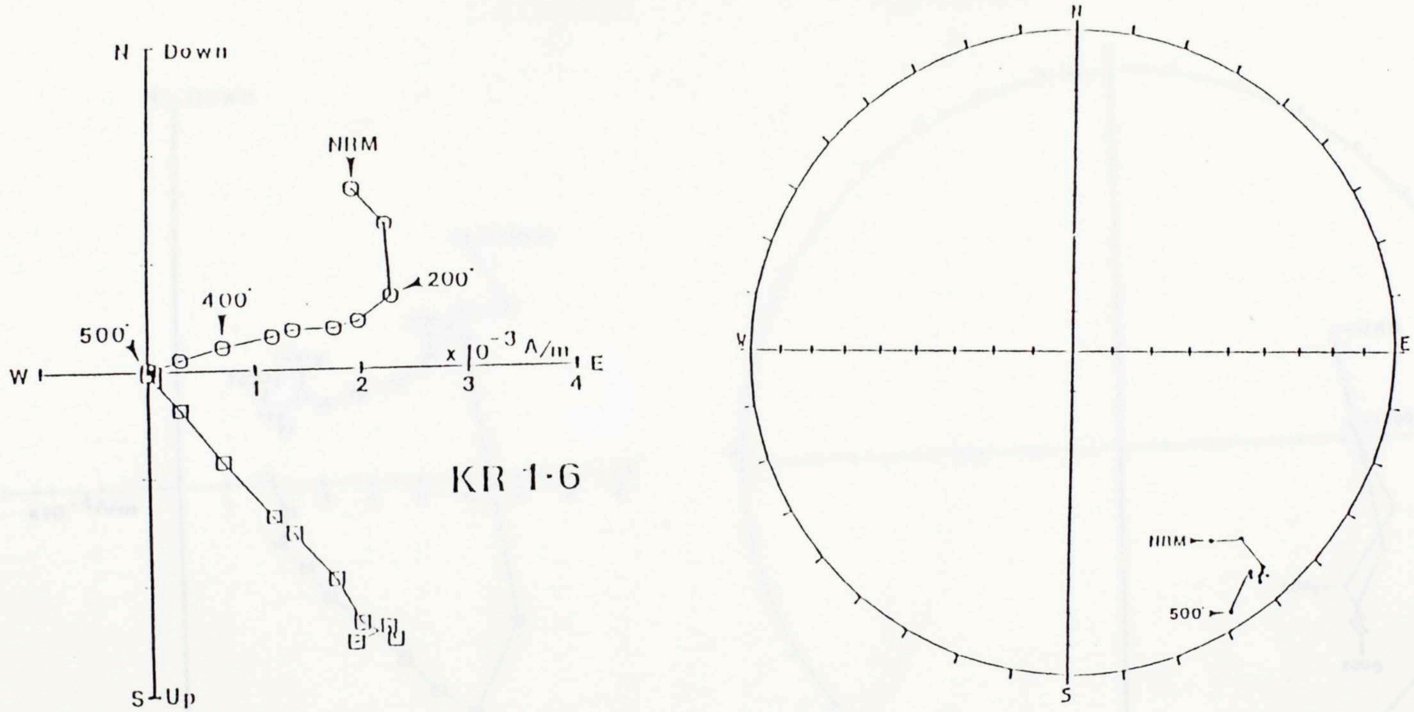


Figure 2. a) Example of an orthogonal projection of AF demagnetization of specimen KR 1-6. Specimens from this site typically exhibited consistent decay during demagnetization. Squares and circles indicate that the direction of magnetization removed is southeasterly in declination and shallow in inclination, respectively. Intensities decrease toward origin with increasing field strength. b) Schmidt equal area projection of the demagnetization behavior of specimen KR 1-6. Closed symbols show positive inclination; open symbols show negative inclination.

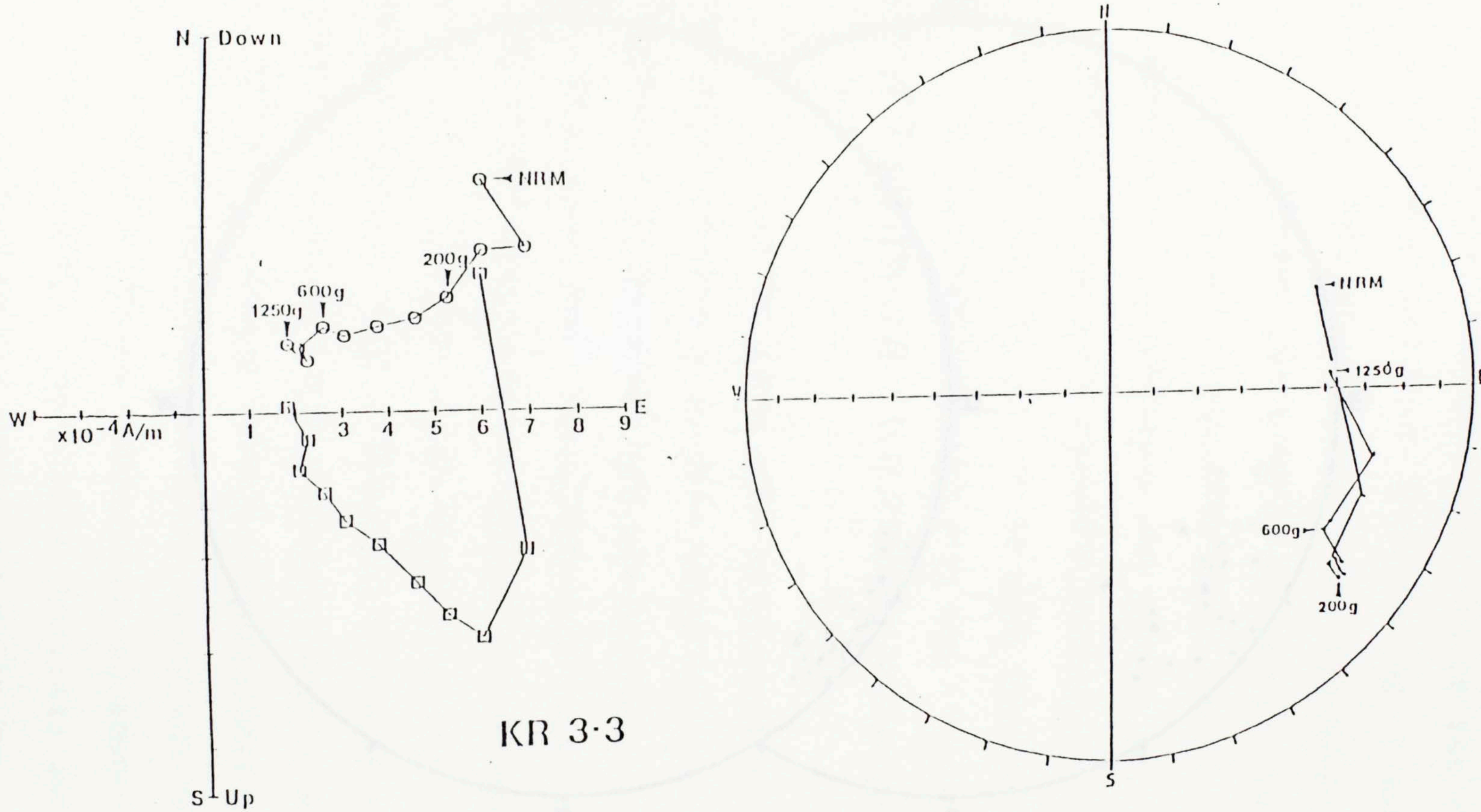


Figure 3. a) Example of orthogonal projection of AF demagnetization of specimen KR 3-3. Specimens from this site typically exhibited decay in a northerly and steep direction at low field strengths and subsequently in a southeasterly and moderate direction. b) Schmidt equal area projection of the demagnetization behavior of specimen KR 3-3.

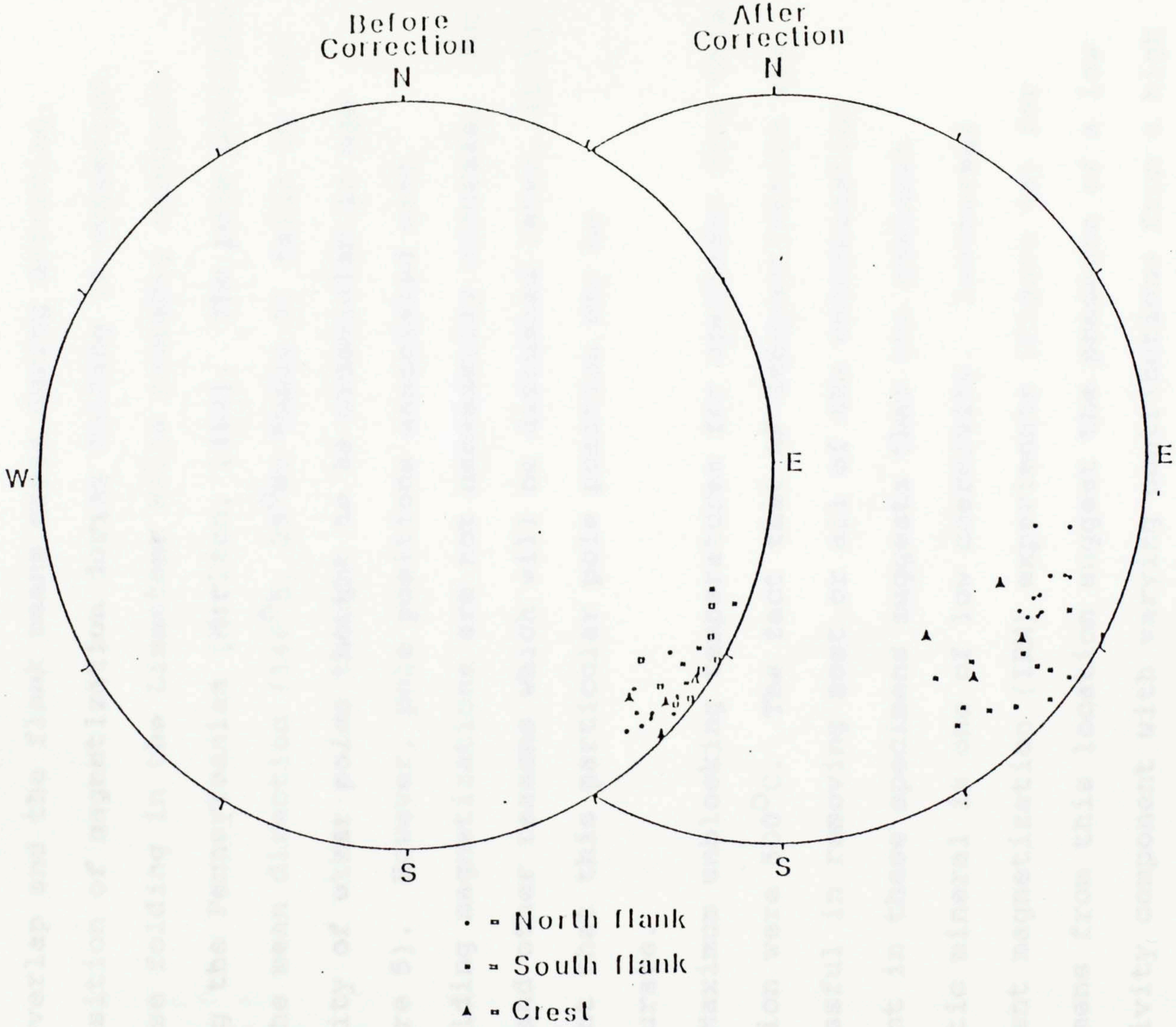


Figure 4a. Equal area projection of specimen directions. Specimens group well for <u>in situ</u> (before structural correction) plot, diverge after structural correction. Open symbols show negative inclination; closed symbols show positive inclination.

(Norman, 1960). After correction for the plunge, mean directions for the north and south flanks diverge more distinctly after crossing (Figure 4b). Because alpha 95 ovals of confidence for the before correction flank means do not overlap and the flank means cross during unfolding, acquisition of magnetization during folding is suggested. Intense folding in the Limestone Hills probably occurred during the Pennsylvanian (Harlton, 1963). The pole position for the mean direction (146^{O}E, 29^{O}N; Table 2) falls in the vicinity of other poles thought to be Ordovician in age (Figure 5). However, pole positions associated with synfolding magnetizations are not necessarily accurate. For this and other reasons which will be discussed later, it is thought that this particular pole position may be inaccurate.

Maximum unblocking temperatures for specimens from this location were 500^{O}C. The fact that AF demagnetization was successful in removing most or all of the magnetization present in these specimens suggests that the dominant magnetic mineral is one of low coercivity. Isothermal remanent magnetization (IRM) experiments (Figure 6a) for specimens from this location suggest the presence of a low coercivity component with varying contributions from a high coercivity mineral. For example, in a specimen from site KR 2 (KR 2-6), over 95% of the magnetization induced by 0.8 Tesla was acquired by 0.3T. This suggests that the magnetization probably resides in a low coercivity mineral

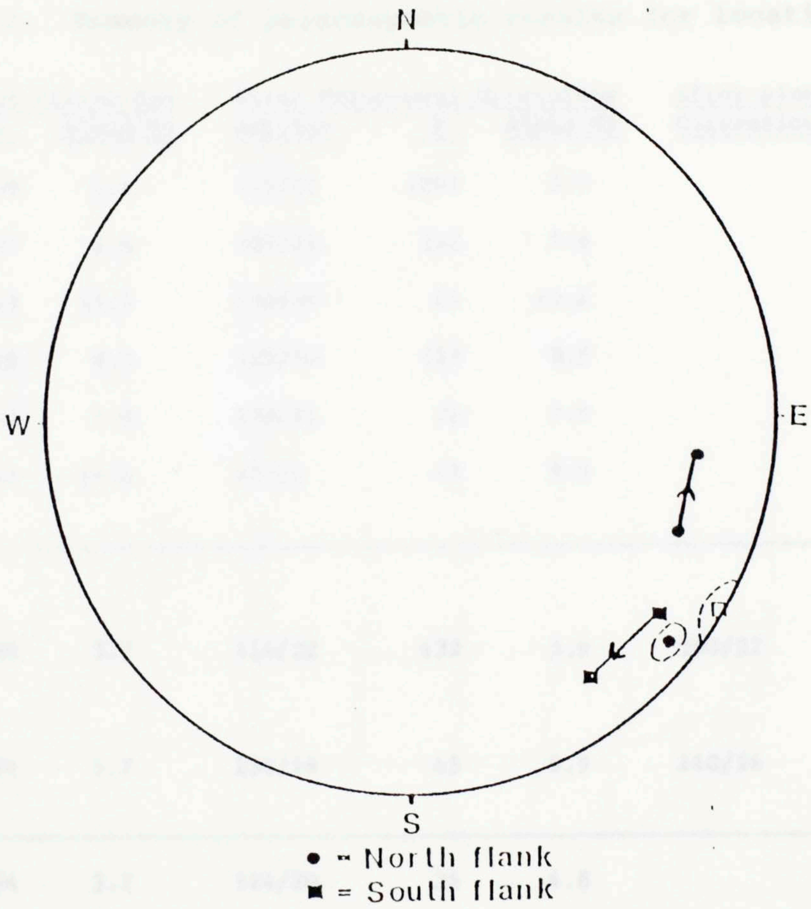


Figure 4b. Equal area projection of flank means, with dots representing mean of north flank specimens, squares representing mean of south flank specimens. Before structural correction, alpha 95's for flank means do not overlap; flank means cross and diverge during structural correction. Arrows indicate change in "after structural correction" means after correcting for plunge.

Table 2. Summary of paleomagnetic results for location KR.

Site	N/No	Before Structural Correction Dec/Inc	k	Alpha 95	After Structural Correction Dec/Inc	k	Alpha 95	After plunge Correction	Before Correction Pole	dp	dm
KR1	5/6	136/8	1008	2.4	119/22	1007	2.4		137/33.5	1.2	2.3
KR2	6/6	128/8	142	5.6	109/22	142	5.6		144/28	2.8	5.7
KR3	4/5	132/4.5	69	11.2	130/30	47	13.6		143/31.5	5.6	11.2
KR4	4/4	122/-5	116	8.5	125/10	117	8.5		154/27.5	4.3	8.6
KR5	6/6	120/4	73	7.9	138/21	72	7.9		152/23	3.9	7.9
KR6	3/6	129/-8	41	19.6	127/6	41	9.9		151/33	9.9	19.7
North Flank Mean (KR1 and KR2)	11/12	132/8	150	3.7	114/22	132	3.9	100/22	141/30.5	1.9	3.8
South Flank Mean (KR4, KR5, KR6)	13/16	123/-1	54	5.7	131/14	45	5.9	148/16	152/27	2.8	5.7
All specimens	28/33	128/3	54	3.7	124/20	34	4.8		146/29	1.9	3.8

Note: Dec = declination, inc = inclination. k is Fisher's (1953) precision parameter; alpha 95 is radius of cone of 95% confidence. N/No is ratio of specimens used in statistical calculations to specimens analyzed; dp, dm are semi-axes of oval of 95% confidence about poles.

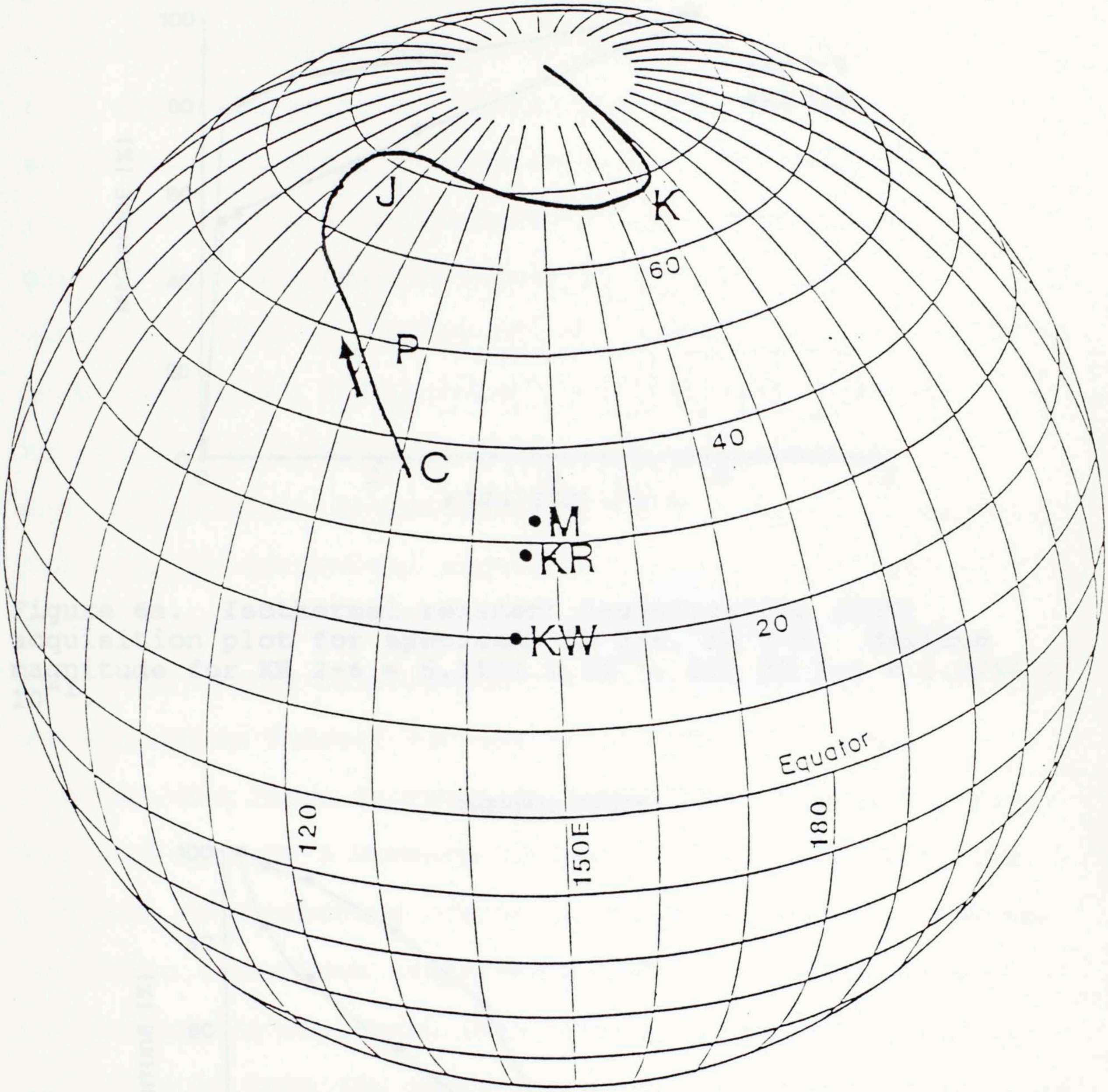


Figure 5. Apparent polar wander path for stable North America from Carboniferous to Recent showing pole positions for locations KR and KW. Late Paleozoic to Recent path after Irving and Irving, 1982. Ordovician pole (M) shown for reference (after Watts and Van der Voo, 1979).

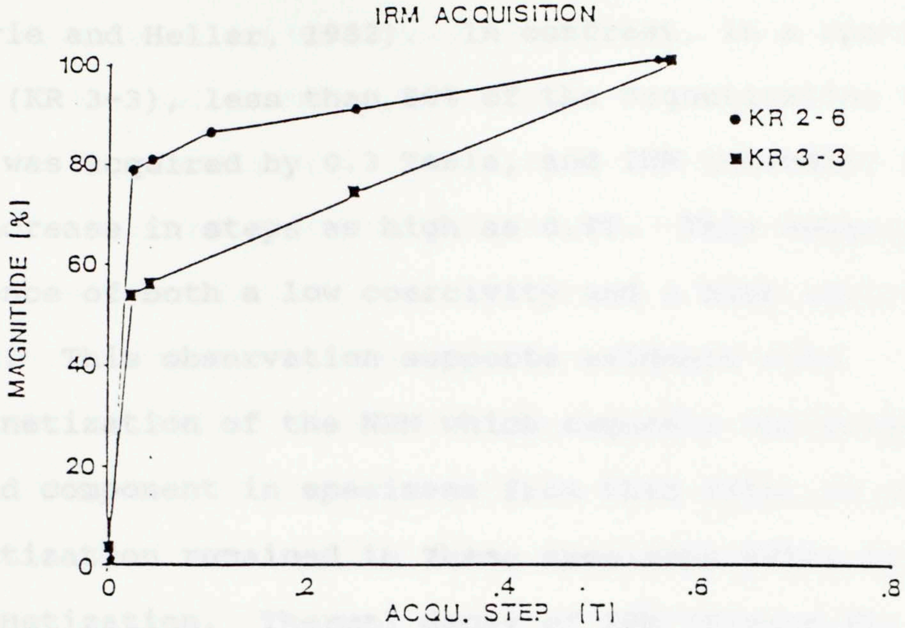


Figure 6a. Isothermal remanent magnetization (IRM) acquisition plot for specimens KR 2-6, KR 3-3. Maximum magnitude for KR 2-6 = 5.1178 x 10^{-1}, for KR 3-3 = 1.2788 x 10^{-1}.

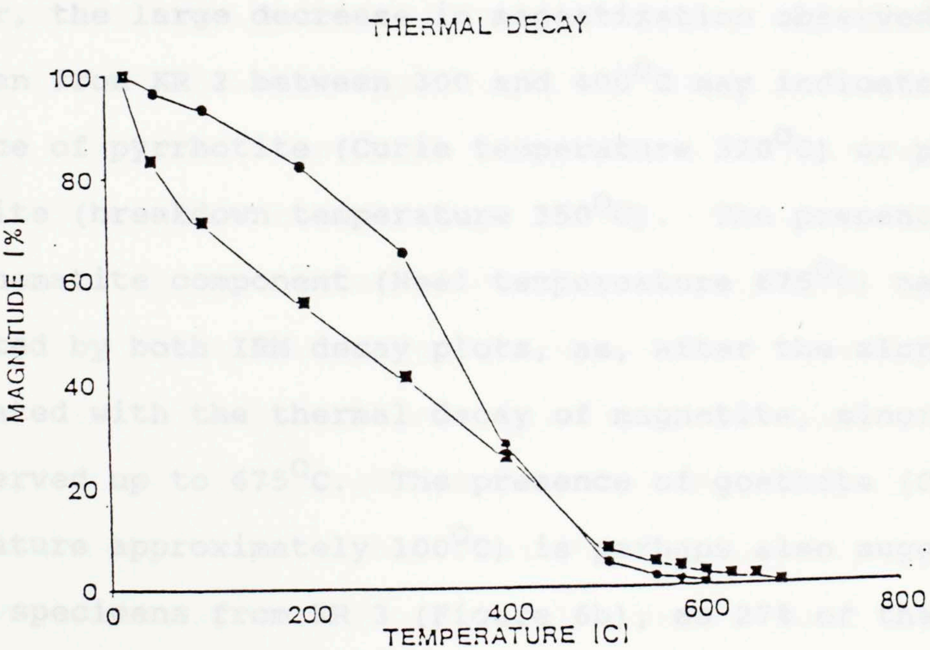


Figure 6b. IRM decay plot for specimens KR 2-6, KR 3-3.

(Lowrie and Heller, 1982). In contrast, in a specimen from KR 3 (KR 3-3), less than 80% of the magnetization induced by 0.8T was acquired by 0.3 Tesla, and IRM intensity continued to increase in steps as high as 0.8T. This suggests the presence of both a low coercivity and a high coercivity phase. This observation supports evidence from demagnetization of the NRM which suggests the presence of a second component in specimens from this site, as some magnetization remained in these specimens after AF demagnetization. Thermal decay of IRM (Figure 6b) suggests the presence of several magnetic minerals. The dominant magnetic mineral in both examples shown appears to be magnetite (Curie temperature 578^{O}C), as less than 5% of the magnetization induced remains after the 575^{O}C step. However, the large decrease in magnetization observed in a specimen from KR 2 between 300 and 400^{O}C may indicate the presence of pyrrhotite (Curie temperature 320^{O}C) or perhaps maghemite (breakdown temperature 350^{O}C). The presence of a minor hematite component (Neel tempereature 675^{O}C) may be suggested by both IRM decay plots, as, after the slope break associated with the thermal decay of magnetite, minor decay is observed up to 675^{O}C. The presence of goethite (Curie temperature approximately 100^{O}C) is perhaps also suggested in the specimens from KR 3 (Figure 6b), as 27% of the magnetization induced is removed by the 100^{O}C step. Although several magnetic minerals may be present in the McKenzie Hill limestones investigated, the dominant magnetic mineral appears to be magnetite, based on the IRM acquisition and decay experiments.

Having determined that magnetite is the dominant magnetic mineral (with varying contributions from pyrrhotite or maghemite, hematite, and goethite), the origin of the magnetization must be addressed; i.e. is the magnetization thermal, detrital, or chemical in origin? A thermoviscous origin may be eliminated for the magnetization observed at location KR. The maximum laboratory unblocking temperature for KR specimens investigated was 500^{O}C. In order to have blocking temperatures of this magnitude, burial temperatures of 250^{O}C would be required, using the theoretical relaxation time-blocking temperature curves of Middleton and Schmidt (1982) for burial times of 300 million years. Burial histories for this portion of the southern Oklahoma aulacogen indicate that Upper Arbuckle Group sediments were probably not buried more than three to four kilometers, which would produce burial temperatures of less than 120^{O}C, according to the estimates of Cardott and Lambert (1985), thus falling short of the 250^{O}C temperature predicted as necessary for a thermoviscous magnetization. Because unblocking temperatures of all Limestone Hills specimens were similar to those of location KR, the possibility of a thermoviscous origin of magnetization may be confidently eliminated for this and all other sites. The synfolding remanence acquisition rules out the possibility of a Detrital Remanent Magnetization (DRM). The origin of the dominant component of the magnetization is therefore probably a chemical remanent magnetization (CRM). This CRM resides in magnetite, the dominant magnetic mineral, and possibly pyrrhotite. The goethite, hematite, and maghemite, whose presence is suggested by IRM results, are probably the result of recent weathering. They may represent a second CRM resulting from the oxidation of magnetite or pyrrhotite. The northerly to northeasterly and steep down component is probably a modern viscous remanent magnetization (VRM) that resides in magnetite or pyrrhotite.

Although the magnetization is most likely chemical in origin, the possibility exists that a detrital component may be present as well. This detrital component may have been masked by the presence of the CRM. If coercivity and blocking temperature spectra completely overlapped, the original DRM and the secondary CRM may be indistinguishable. A vector addition of an Ordovician DRM and a younger CRM (probably Pennsylvanian) might account for the results observed, including the fold test results and the pole position for the magnetization. The relative contributions of the two types of magnetization (CRM and DRM) are impossible to estimate, so this theory is untestable.

Location KW. Specimens from this location were collected in the Kindblade Formation. At this location, the Kindblade carbonates have a monoclinal dip of approximately 8^{O}, and Permian Post Oak conglomerates overlie the exposed

Ordovician rocks. Lithologies sampled include oosparites, pelsparites, and dolomites, some with black bands on either side of a fracture (Liesegang band-like features?), and a pinkish yellow carbonate fracture-fill deposit. This fracture filling has been interpreted as a karst feature which was probably exposed to the Permian land surface (Donovan, 1982a). The NRM intensities for specimens from location KW were generally an order of magnitude less than those from location KR (Table 1).

In most specimens from this location, a southeasterly and moderate to shallow direction was removed during demagnetization. In some specimens a northerly to northeasterly and steep down component was removed at low temperatures or field strengths, which resulted in curved paths on orthogonal projections (Figure 7). These directions removed during demagnetization are very similar to those observed in KR specimens, and the southeasterly and moderate to shallow direction is interpreted as the dominant magnetization in these specimens as well (Table 3). Although a pole position calculated for specimens from this location (before structural correction: 20^{O}N, 145^{O}E; after structural correction, 20^{O}N, 148^{O}E) falls near Ordovician poles, it is thought that the magnetization at this location was acquired at the same time as that at location KR, i.e. during the Pennsylvanian with some contribution from a Recent component. Evidence for this interpretation will be discussed later.

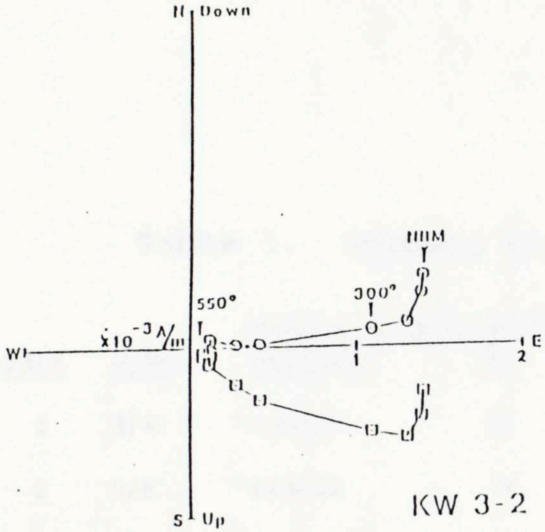


Figure 7a.

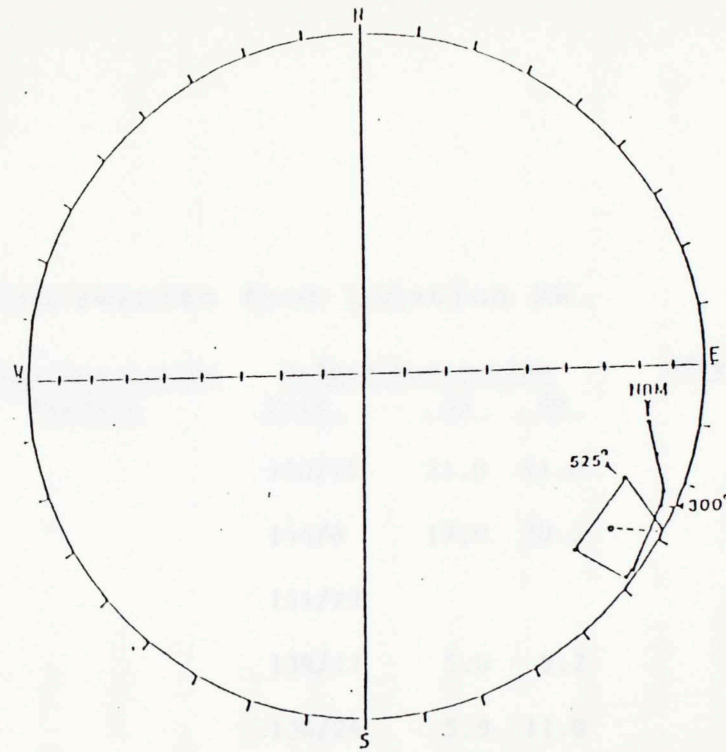


Figure 7b.

Figure 7. a) Example of orthogonal projection of thermal demagnetization of specimen KW 3-2. b) Schmidt equal area projection of the demagnetization behavior of specimen KW 3-2.

Table 3. Summary of paleomagnetic results from location KW.

Site	N/No	Before Structural Correction Dec/Inc	k	Alpha 95	After Correction Dec/Inc	Before Correction Pole	dp	dm	After Correction Pole
1	3/4	130/16	11	40.0		140/26	21.0	41.0	
2	5/8	113/32	9	27.0		144/8	17.0	30.5	
3	2/3	125/-3				151/29			
4	7/8	123/27	52	8.4		139/17	5.0	9.2	
5	3/5	131/23	140	10.5		136/24	5.9	11.0	
6	8/8	102/35	24	11.7		149/-2	7.7	13.4	
Mean of all sites		121/16	25	13.5	120/13	145/17	7.5	14.0	148/20

Note: See Table 2 for symbol explanations.

Unblocking temperatures for 9 specimens from this location ranged from 500 to 575°C; one specimen decayed by 450°C. Specimens from all sites exhibited some decay with AF demagnetization, suggesting the presence of a low coercivity phase. However, specimens from several sites had magnetization remaining after AF demagnetization (e.g. Figure 7); in these specimens, the presence of a higher coercivity phase such as hematite is also suggested. IRM acquisition experiments (Figure 8a) indicate the presence of a low coercivity phase in all specimens examined, as an abrupt rise in acquisition by 0.3 Tesla is observed. A specimen from the fracture filling (KW 3-1) exhibits contributions from both low and high coercivity minerals, as an abrupt rise in IRM is observed up to 0.3T, and a gradual rise is observed through the 0.8T step. IRM decay experiments (Figure 8b) suggest the presence of magnetite, with more than 98% of the induced magnetization removed by 575°C in most specimens examined. However, hematite is suggested as a minor component in most specimens (e.g. Figure 8b), and as a more significant contributor in specimens from site 3 (fracture fill). The presence of pyrrhotite or maghemite is also suggested in at least one specimen (KW 6-1), as an abrupt decrease in intensity occurs between the 300 and 400°C steps in thermal demagnetization of IRM. In more detailed thermal decay of IRM of some specimens, it appears that the major decrease in intensity occurs during heating to 350°C which may suggest that, at

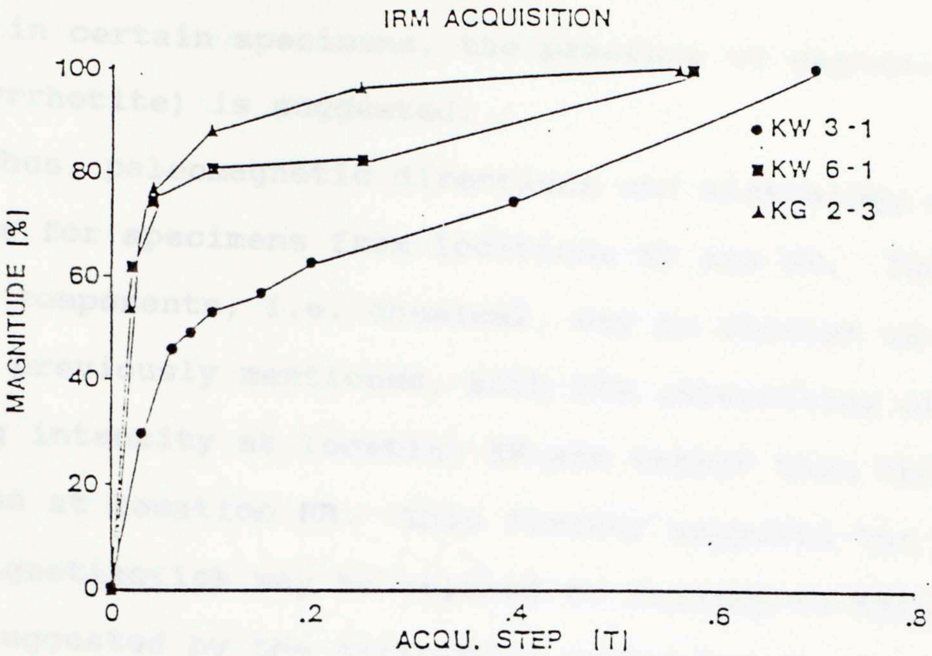


Figure 8a. IRM acquisition plot for specimens KW 3-1, KW 6-1, and KG 2-3. Maximum magnitude for KW 3-1 = 6.0273 x 10^{-2}, for KW 6-1 = 4.6449 x 10^{-2}, and for KG 2-3 = 7.821 x 10^{-2}.

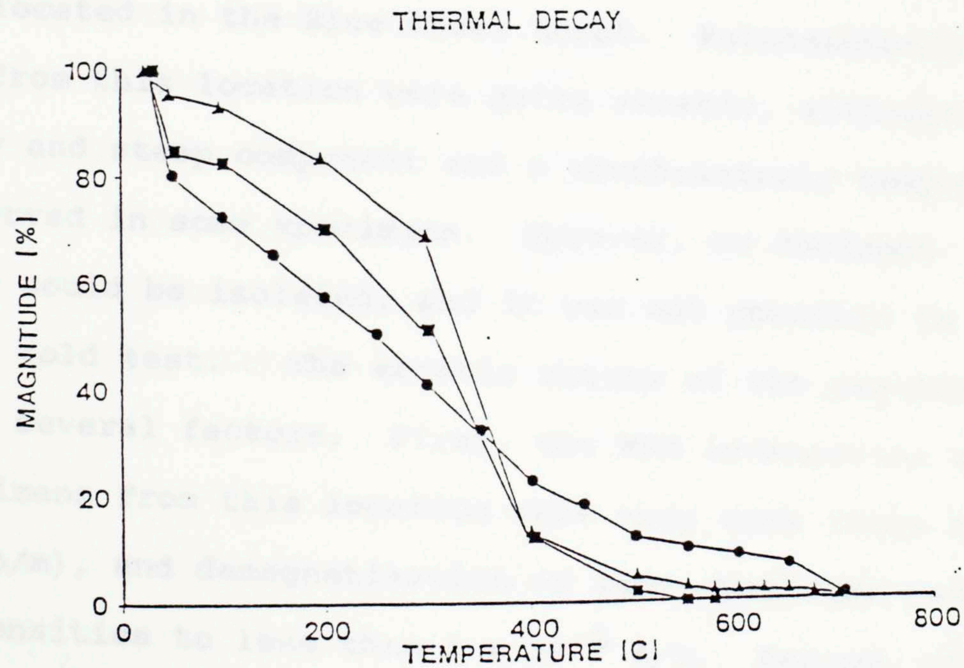


Figure 8b. IRM decay plot for specimens KW 3-1, KW 6-1, and KG 2-3.

least in certain specimens, the presence of maghemite (and not pyrrhotite) is suggested.

Thus, paleomagnetic directions and mineralogy are quite similar for specimens from locations KR and KW. The origin of the components, i.e. chemical, may be similar as well. As was previously mentioned, both NRM intensities and folding intensity at location KW are weaker than those observed at location KR. This further supports the premise that magnetization may be related to folding in this area, as is suggested by the synfolding magnetization of KR.

Location KG. Specimens from this location are from the Kindblade Formation. NRM intensities were found to be similar to those found in specimens from location KW, which is also located in the Blue Creek Horst. Paleomagnetic results from this location were quite erratic, although a northerly and steep component and a southeasterly component were observed in some specimens. However, no dominant direction could be isolated, and it was not possible to perform a fold test. The erratic nature of the results may be due to several factors. First, the NRM intensities of some specimens from this location were very weak (less than 2×10^{-4} A/m), and demagnetization of many specimens reduced their intensities to less than 5×10^{-5} A/m. Second, the presence of multiple mineralogies may have caused demagnetization results to appear erratic. Isothermal Remanent Magnetization acquisition experiments (Figure 8a) suggest the presence of a low coercivity component and, in a few specimens, a higher coercivity component is also present. During the decay of IRM, a decrease of 50% of the magnetization between 300 and 400^{O}C steps (Figure 8b) suggests a major contribution by pyrrhotite or maghemite. The magnetic properties of pyrrhotite are not well known, and there is some evidence that pyrrhotite carries an unstable magnetization (Sheriff and Shive, 1982). This could cause the erratic demagnetization results that were observed. Unblocking temperatures of 550 to 575^{O}C for the NRM and a break in slope in decay of IRM at 550 to 575^{O}C suggest that magnetite may also be present.

The magnetization in specimens from location KG probably represents one or more CRMs. However, due to the erratic behavior of these specimens during demagnetization, no reliable direction could be isolated, and it was not possible to apply a fold test. A frequently observed northerly and steep component, removed at low temperatures and field strengths, may represent a modern CRM or a modern viscous component (VRM) in magnetite or pyrrhotite.

Petrography

Transmitted and reflected light microscopy of a representative suite of specimens reveals the presence of several opaque phases, including magnetite, hematite, and pyrite. The distribution of pyrite in many specimens (especially those from location KW) was interesting. For example, pyrite was observed replacing ooids, with the radial fabric preserved. Additionally, pyrite was found to form the banded features investigated. Hematite pseudomorphed after pyrite was also observed in some specimens. Opaque minerals were frequently found in association with fossils in the thin sections studied. Also, opaque minerals were found in and around fractures in these carbonates. One specimen contained opaque minerals (magnetite partly altered to hematite) in a fracture which bisected a trilobite (Figure 9a). Abundant opaque minerals (<1 micron in diameter) were also observed in circular, sometimes concentric, forms in thin section (Figures 9b). Based upon the characteristics of these grains in reflected light, they are probably not magnetite. They may, however, be composed of maghemite or hematite which has formed as a result of weathering of magnetite. The uniform circular nature of the grains suggests an authigenic origin.

Scanning electron microscopy (SEM) of the magnetic extracts from each location revealed the presence of spheres (Figures 10a,b,c) consisting entirely of iron, based on energy dispersive analysis. These spheres, which are often observed in clusters, may be related to circular forms observed in thin sections. Close examination of these spheres revealed the presence of asssociated small needle-or plate-shaped forms, tentatively interpreted as magnetite or hematite (Figure 10a,c,d). SEM investigation also revealed the presence of iron minerals in cubic forms. This is

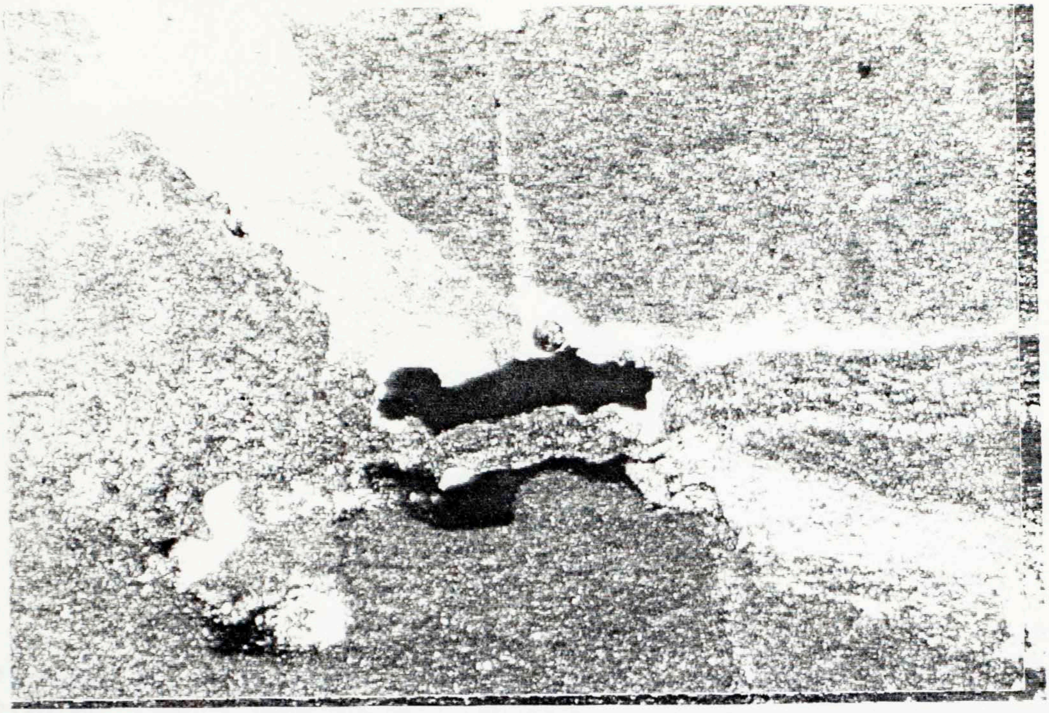


Figure 9a. Thin section photomicrograph from a specimen from site KG3 of trilobite cut by a fracture. Fracture contains authigenic magnetite, hematite after magnetite, and pyrite.

Figure 9b. Circular opaque minerals, as clusters and single grains from site KR 2.

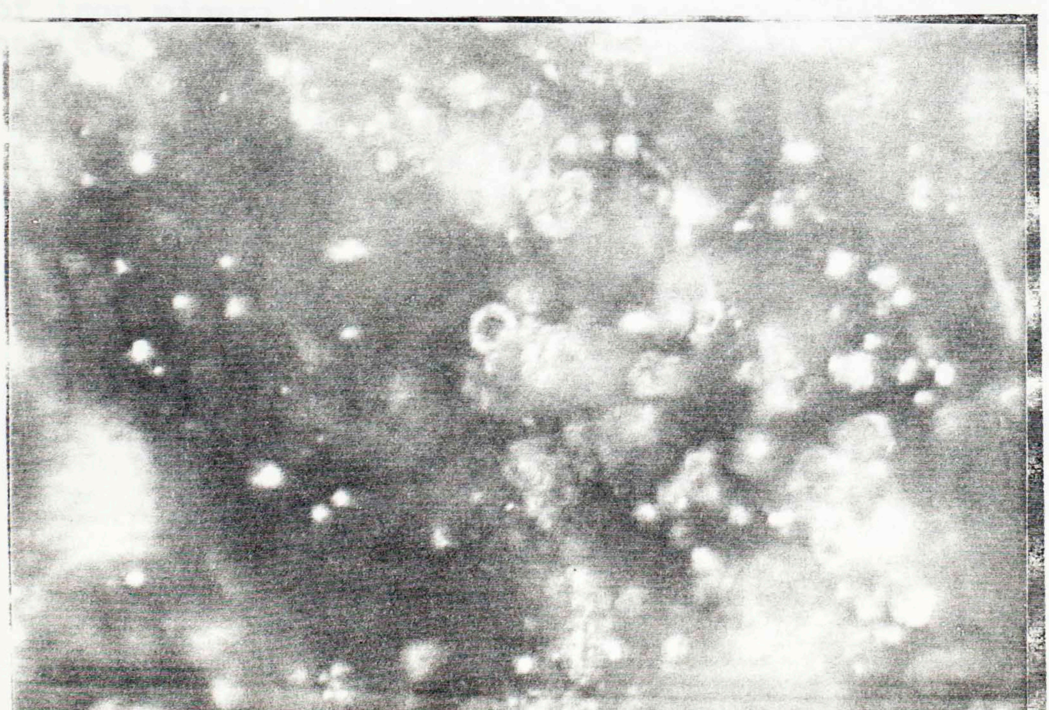
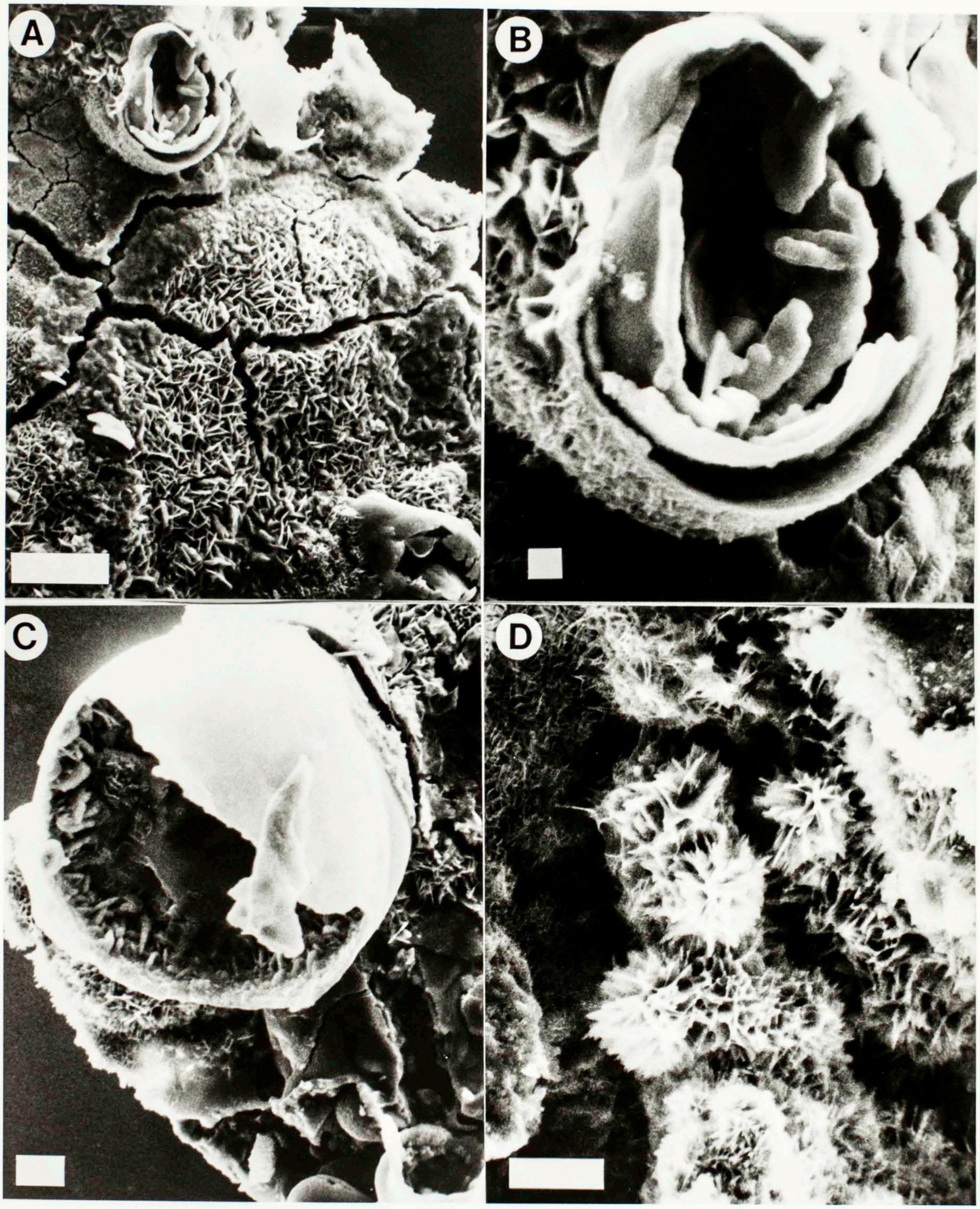


Figure 10. All scale bars equal 10 microns.
Figure 10a. SEM photomicrograph from sample from site KR 2 illustrating two forms in which iron minerals occur: concentric spheres and needles.
Figure 10b. Enlargement of concentric spheres observed in 10a, interpreted as magnetite, based upon EDA and form.
Figure 10c. SEM photomicrograph of another iron containing phase. Plate- or needle-like phases (hematite?) apparently line the spherical iron mineral, interpreted to be magnetite.
Figure 10d. SEM photomicrograph from sample from site KR 2 of iron mineral interpreted as hemetite, based upon EDA and habit.


A
B
C
D

tentatively interpreted as hematite which has replaced pyrite, based upon observations from transmitted and reflected microscopy.

Organic Geochemistry

An attempt was made to correlate geochemical parameters investigated with NRM intensity of the samples (Table 1). (For this correlation, an average of NRM intensities from all specimens in a site was used.) The result of the comparison of the geochemical analyses with NRM intensities was a roughly positive correlation (Figure 11). That is, the two samples which had the highest NRM intensities (KR 1 and KR 2) also had the highest organic content. (Results from light hydrocarbon concentrations plotted against NRM intensities produced a graph which was almost identical to that shown for TOC versus NRM intensity). The two samples which contained the lowest organic content (as measured by light hydrocarbon content) also contained the most highly oxidized magnetic phases. One of these organically lean samples was the fracture filling from location KW, in which both magnetite and hematite components were identified based on the rock magnetic results. The other lean sample was the sample from the Arbuckle Mountains in which hematite in Liesegang bands is the only magnetic phase observed. The use of NRM intensities for this comparison may not be the most informative choice as these intensities include magnetization residing in hematite as well as magnetite.

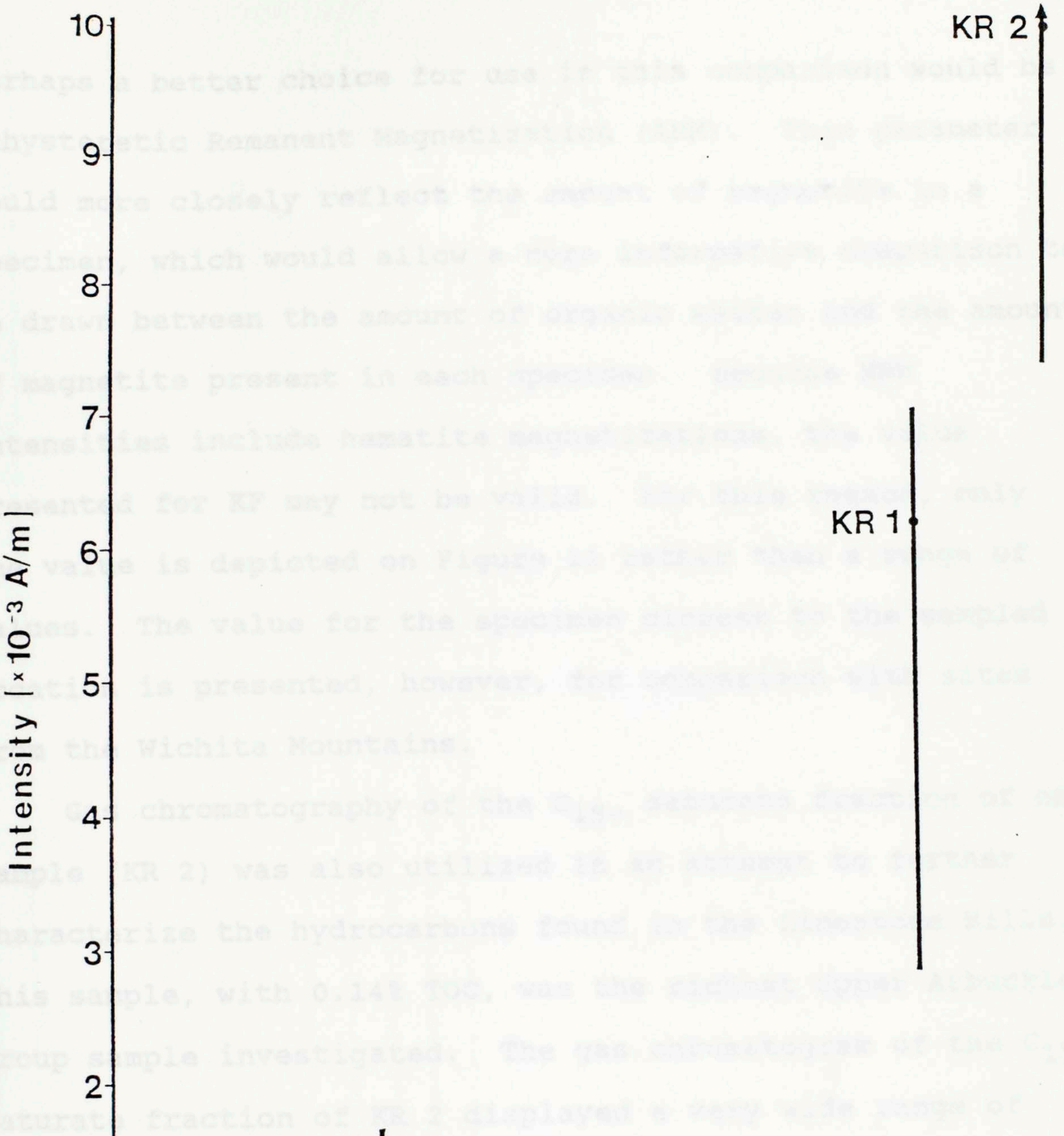


Figure 11. Plot of total organic carbon against NRM intensity. Intensities are represented by a range of values and an average (indicated by dot) of all specimens analyzed from particular site. Note roughly positive correlation.

Perhaps a better choice for use in this comparison would be Anhysteretic Remanent Magnetization (ARM). This parameter would more closely reflect the amount of magnetite in a specimen, which would allow a more informative comparison to be drawn between the amount of organic matter and the amount of magnetite present in each specimen. Because NRM intensities include hematite magnetizations, the value presented for KF may not be valid. For this reason, only one value is depicted on Figure 11 rather than a range of values. The value for the specimen closest to the sampled location is presented, however, for comparison with sites from the Wichita Mountains.

Gas chromatography of the C_{15+} saturate fraction of one sample (KR 2) was also utilized in an attempt to further characterize the hydrocarbons found in the Limestone Hills. This sample, with 0.14% TOC, was the richest Upper Arbuckle Group sample investigated. The gas chromatogram of the C_{15+} saturate fraction of KR 2 displayed a very wide range of carbon number compounds, from C_{15} to C_{38} (Figure 12). A pristane/phytane ratio of 0.9 suggests that the hydrocarbons present probably formed under highly reducing conditions (e.g. Tissot and Welte, 1984), which may be consistent with the formation of magnetite. The abundance of higher molecular weight compounds might suggest some terrestrial input (e.g. Tissot and Welte, 1984). Since the Arbuckle Group was deposited during the Ordovician, before the evolution of land plants, this might indicate that the

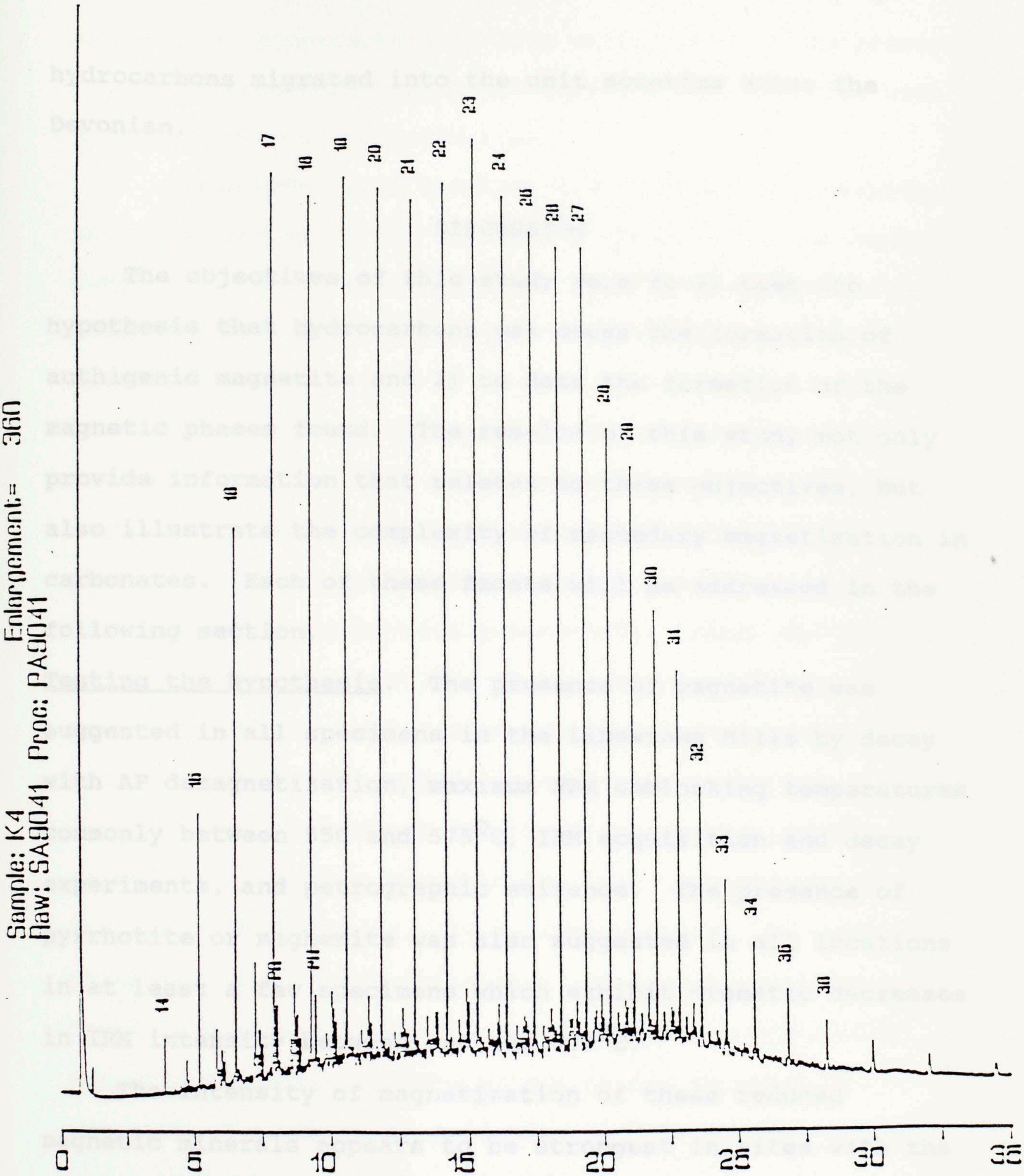


Figure 12. Gas chromatogram of C_{15+} saturate fraction of sample K4 (from site KR 2). See text for interpretation and column conditions.

hydrocarbons migrated into the unit sometime after the Devonian.

DISCUSSION

The objectives of this study were to 1) test the hypothesis that hydrocarbons can cause the formation of authigenic magnetite and 2) to date the formation of the magnetic phases found. The results of this study not only provide information that relates to these objectives, but also illustrate the complexity of secondary magnetization in carbonates. Each of these facets will be addressed in the following section.

Testing the hypothesis. The presence of magnetite was suggested in all specimens in the Limestone Hills by decay with AF demagnetization, maximum NRM unblocking temperatures commonly between 550 and 575^{O}C, IRM acquisition and decay experiments, and petrographic evidence. The presence of pyrrhotite or maghemite was also suggested in all locations in at least a few specimens which exhibit dramatic decreases in IRM intensity between 300 and 400^{O}C.

The intensity of magnetization of these reduced magnetic minerals appears to be strongest in sites with the highest organic content and strongest folding. The fact that high magnetic intensity, consistent decay, high organic content, and intense folding are present in one location (KR) suggests that a cause and effect relationship exists between them. Perhaps the intense folding caused the trapping of hydrocarbons at this anticline, and the presence of the hydrocarbons caused the formation of magnetite with a high intensity of magnetization.

Minor amounts of oxidized magnetic phases, goethite, hematite, and maghemite may also be present in some samples. Samples which contain the lowest amounts of hydrocarbons exhibited the largest contribution from these more oxidized magnetic phases.

Thus, the results of this study do provide at least empirical evidence that where hydrocarbons are present, magnetite (and possibly pyrrhotite) will predominate, whereas in locations where hydrocarbons are less prevalent, hematite and goethite will predominate. Thus, the presence of hydrocarbons may provide conditions required for the formation and/or preservation of authigenic magnetite (and possibly pyrrhotite) and associated magnetizations.

Supporting evidence for the hydrocarbon/magnetite relationship is also found in the Upper Arbuckle Group in the Arbuckle Mountains. In an active quarry, deposits of gilsonite (black asphaltite with conchoidal fracture) were found in vugs and fractures in the Kindblade carbonates. Magnetic extraction of the gilsonite has revealed the presence of magnetic grains which include magnetite and pyrrhotite, based on SEM and XRD data (Elmore et al., 1986). Also, a gas chromatogram of the saturate fraction of this gilsonite indicates that biodegradation has affected these hydrocarbons. The presence of these magnetic minerals in these hydrocarbons strongly suggests that a relationship does exist between hydrocarbons and the formation of authigenic magnetite and/or pyrrhotite.

Geochemical models for the formation of authigenic magnetite are not well developed. Berner (1964) showed that formation of diagenetic magnetite is thermodynamically possible for several reactions (e.g. pyrite-magnetite). Magnetite may also form during the oxidation of Fe (II) from solution in interstitial marine sediments during early diagenesis (Murray, 1979). Biodegradation of hydrocarbons may result in precipitation of some authigenic mineral phases, including pyrite and pyrrhotite (Sassen, 1980; Tarling, 1983), although magnetite has not been specifically mentioned.

One possible source for iron in magnetite in the Arbuckle Group would be other iron containing minerals. For example, alteration of pyrite by oil field brines with an Eh of -0.2 (Gautier et al., 1985), with varying concentrations of sulfur might produce either magnetite or pyrrhotite (Garrels and Christ, 1965). Perhaps a chain of diagenetic reactions might result in a transition from pyrite to pyrrhotite to magnetite, producing the combinations observed in this study. Another potential source of the iron in magnetite might be other iron oxides such as hematite, as was suggested by Donovan et al. (1979).

A second potential source of iron for the formation of authigenic magnetite might be from organic-rich shales. The suggestion has been made (Walker and Runnels, 1985) that when organic matter is absent, the smectite to illite transformation produces Fe^{+3} and that when organic matter is present, the transformation produces Fe^{+2}. In this case, Fe^{+2} might be carried with hydrocarbons or with oil-related brines and then precipitated out as magnetite in the reservoir. Wanli (1985) notes that the iron content of oils decreases as migration distance increases. These factors might suggest that iron from oil-producing shales may play a role in the formation of authigenic magnetite.

Age of remanence acquisition. The pole positions calculated for locations KR and KW fall near middle to late Ordovician poles from North America. However, the fold test at location KR indicated that the magnetization was acquired during folding, and most authors suggest that the most intense deformation in this region occurred during the Pennsylvanian, although some authors have suggested that folding may have occurred during the Ordovician. Therefore, two potential times (i.e. late Paleozoic if the folding occurred during the Pennsylvanian, or Ordovician, if folding occurred during the Ordovician) might be suggested for the acquisition of the CRM residing in magnetite.

The preferred interpretation for the magnetization in these samples is that it represents a CRM acquired in the late Paleozoic, or, more specifically, during the Pennsylvanian to Permian. Fold test results indicate that the magnetization is synfolding in origin. Intense folding such as that found in the Lawtonka Graben (e.g. the Paradox Anticline of location KR) probably formed during the Wichita orogeny (i.e. Morrowan to Atokan). Another factor supporting a late Paleozoic age of diagenesis is the similarity of results for the fracture filling (site KW 3) to the results from other sites in KW and KR (Figure 7). If this fracture filling formed in the late Paleozoic (Donovan, 1982a), then the magnetization should be no older than late Paleozoic (unless clasts contained in the fracture contained randomly oriented magnetizations, which does not appear to be the case). Thus, this site in particular lends support to the late Paleozoic age of remanence acquisition.

If the magnetization was acquired during the late Paleozoic, several factors may provide explanations for a pole position which does not coincide with other late Paleozoic poles. First, the structural complexity of the region may have produced anomalous paleomagnetic results. As previously mentioned, several periods of deformation have affected the area, causing intense folding. Also, structural rotations have been suggested for the region (Donovan, 1982b), and transpressive left-lateral shear (Donovan, 1983) may have tightened and/or rotated previously formed structures. A magnetization may have formed during one folding event (causing the synfolding fold test results), and then the fold may have been rotated by later deformation periods. If left-lateral wrench movement has occurred in the area, then a counterclockwise external rotation (Wilcox et al., 1973; Williams, 1986) may have caused the direction of magnetization to appear more easterly than would be expected for Kiaman magnetization. Such a rotation, i.e. counterclockwise, may have affected the Paradox Anticline (near the sampling location KR) as it approaches the Blue Creek Canyon Fault (D.W. Stearns, personal communication, 1986). As depicted in Figure 13, the trend of the Anticline changes from N12^{O}W to N55^{O}W near the fault. It is beyond the scope of this work to unravel such structural complications. Perhaps further work in the area may help to better constrain the role which structure may play in the paleomagnetic results obtained in the region.

Second, there is a distinct possibility for the existence of several magnetic components in the investigated strata. Although the magnetization is interpreted as a CRM, a detrital component may also be present, as was previously discussed. A detrital component with a varying degree of contribution from a CRM acquired during the late Paleozoic may explain why the most intensely folded, most organically rich, most intensely magnetized specimens (from sites KR 1 and KR 2) have pole positions which plot closest to the late Paleozoic portion of the APWP while those less affected by folding and organic matter fall closer to the Ordovician portion. In addition, a viscous modern component in magnetite or pyrrhotite and/or a second CRM in hematite, goethite, or maghemite resulting from recent weathering may

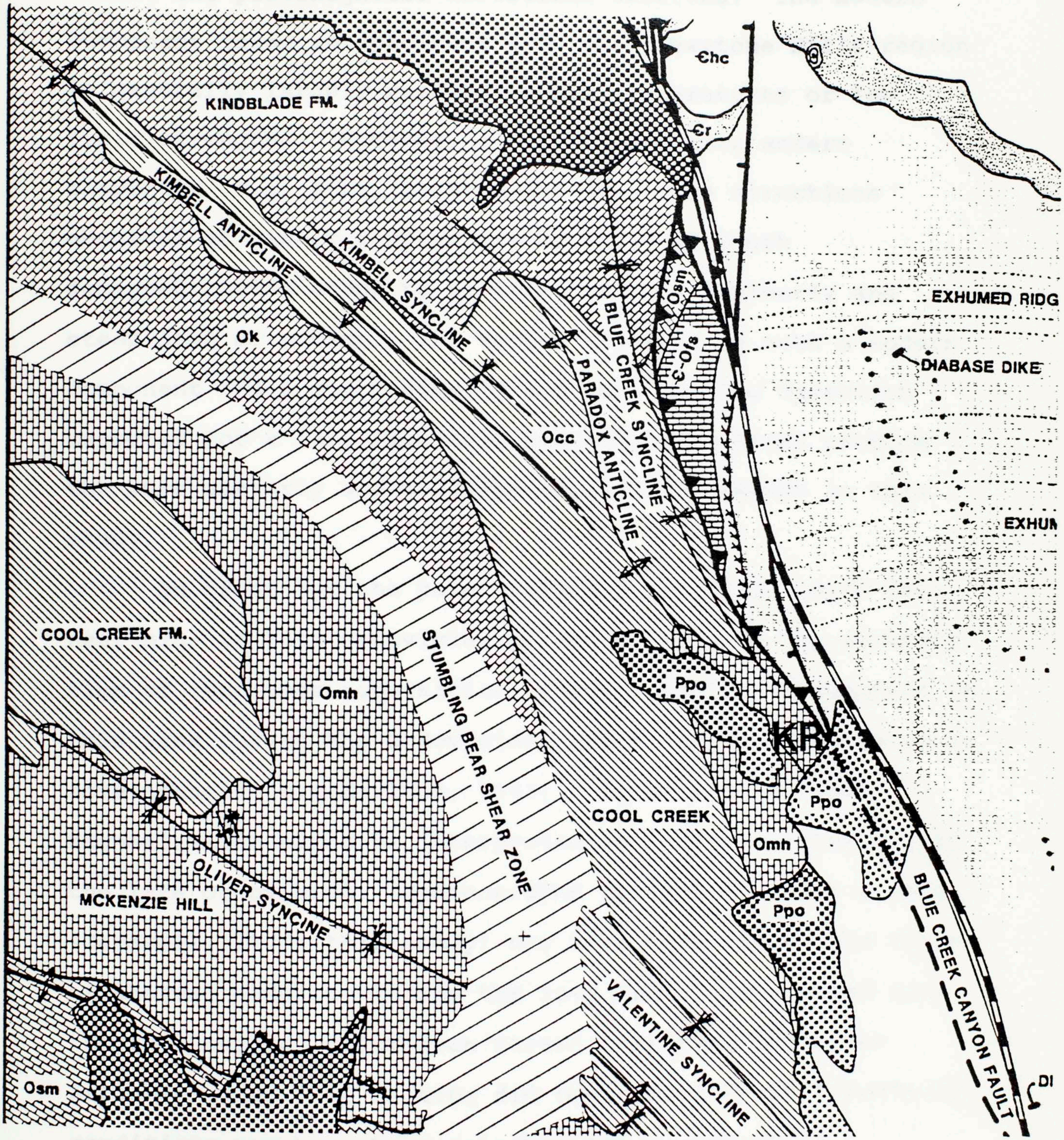


Figure 13. Map illustrating change in orientation in a counterclockwise direction of Paradox Anticline as it approaches Blue Creek Canyon Fault (after Donovan, 1983). Approximate sampling area for location KR indicated (KR).

affect the paleomagnetic directions observed. The modern component found in specimens from the Limestone Hills region is generally largely removed at low temperatures or low field strengths. However, a "tail" of a hard modern component (e.g. Kent, 1985) might cause the directions observed at higher temperature or field strength demagnetization steps to be affected by a northerly and steep down direction. The vector addition of such a modern component and a southeasterly and very shallow direction expected for a late Paleozoic magnetization might produce the more easterly and moderate direction observed in this study.

In order for the pole positions obtained, which fall near mid- to late Ordovician poles, to reflect the accurate time of remanence acquisition, folding must have occurred in this area during the Ordovician, which has been suggested by some authors (e.g.Harlton, 1963). In this case, the magnetization might be interpreted as a CRM acquired during the late Ordovician. Hydrocarbons present in these strata (Cardwell, 1977; this study) may have been within the range of thermal maturity during the late Ordovician, based upon the thickness of Ordovician strata overlying the Upper Arbuckle Group. If folding did occur during the Ordovician, conditions may have been suitable for formation of authigenic magnetite.

Although a case might be made for late Ordovician magnetization, the bulk of the geologic evidence points to the late Paleozoic deformation for these strata; thus, the Pennsylvanian age of formation of magnetite is preferred since the fold test indicates acquisition of magnetization during folding. Oliver (1986) suggests that fluid (e.g. hydrocarbon) migration may be associated with convergent margin tectonics, and that this phenomenon might explain paleomagnetic results which suggest synfolding magnetizations (e.g.McCabe et al., 1983). The results of this study and the tectonics associated with the deformation of the southern Oklahoma aulacogen during the late Paleozoic may be consistent with Oliver's (1986) hypothesis.

Complexity of magnetization. This study of the Upper Arbuckle Group in southern Oklahoma has illustrated the complexity of magnetization which may be found in one unit sampled in different regions. In areas such as the Arbuckle Mountains, the magnetization may be relatively straightforward. The magnetization in Liesegang bands in the Arbuckle Mountains represents a CRM residing in hematite which formed in the late Paleozoic. However, the magnetization may also be very complex, as in the case of the Upper Arbuckle Group in the Limestone Hills. These hydrocarbon-impregnated carbonates appear to have a magnetization which represents a CRM residing in diagenetic magnetite. Other magnetic phases such as pyrrhotite, maghemite, hematite, and goethite complicate the magnetic story, and an absolute date may not be confidently assigned to magnetizations residing in these phases.

Several factors may contribute to the complexity of magnetization of one unit in different areas. One factor is the role of depositional mineralogy. Perhaps the presence of detrital magnetite or pyrite may determine the diagenetic changes which may later occur as a result of hydrocarbon migration into a unit or the maturation of hydrocarbons within the unit. Perhaps fluids which migrate through a unit, either oxidizing as in the Arbuckle Mountains or reducing as in the Wichita Mountains, are the major controlling factors which determine magnetization. The role of other diagenetic alterations (i.e. silica replacement, dolomitization, or dedolomitization) which alter porosity and permeability must also be considered, especially if fluid flow is the dominant factor controlling magnetization.

The study has illustrated the complexity of the hydrocarbon/authigenic magnetite issue, and future investigation of the problem is needed to provide further evidence in support of the hypothesis that hydrocarbons can cause the formation of authigenic magnetite. However, this study has shown that an empirical relationship between hydrocarbons and magnetite may be suggested in the Upper Arbuckle Group in southern Oklahoma. In locations where hydrocarbons are abundant, magnetite is the dominant magnetic phase present. In locations where hydrocarbons are present in smaller amounts, other magnetic minerals may play more important roles in the magnetization.

CONCLUSIONS

1. Hydrocarbon-impregnated limestones of the Upper Arbuckle Group in the Limestone Hills contain a magnetization residing primarily in magnetite (with some contribution from pyrrhotite or maghemite and minor hematite and goethite).

2. Fold test results indicate that the magnetization was acquired during folding. The age of remanence acquisition is concluded to be Pennsylvanian.

3. The results of this study support the hypothesis that there is a relationship between hydrocarbons and authigenic magnetite.

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