

Magnetostratigraphy susceptibility of the Upper Ordovician Kope Formation, northern Kentucky

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Abstract

As a test of the utility of magnetic susceptibility (MS) measurements for correlation among lithified marine sequences, samples were collected from well-studied shale and limestone outcrops of the Upper Ordovician Kope Formation, northern Kentucky. The bulk (initial) low-field MS of these samples is compared among two litho- and biostratigraphically correlated sections containing the same beds. The results of this comparison demonstrated an excellent correlation among equivalent beds. Thermomagnetic susceptibility analysis supports previous XRD work indicating that illite is primary and is the main paramagnetic mineral responsible for the MS variations observed in this study. A composite of MS results for a sequence of 31 named shale–limestone couplets is used to build a composite section of Kope sequences for the area. These MS variations permit division of the various sections into a set of 28 MS cycles within the Kope Formation, covering ~ 50 m of section. These cycles suggest a systematic control by climate on the influx of detrital material that formed these sedimentary sequences, and support other work indicating Kope climate cyclicity.

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1. Introduction

Bulk (initial) low-field magnetic susceptibility (MS) has proven to be a very useful stratigraphic tool for correlating among marine sequences (e.g. Crick et al., 1997; Ellwood et al., 2000, 2001; Hansen et al., 2000). The purpose of our work was to further test the MS method in marine sediments for which the sequence, cyclicity and bio-stratigraphy is well known (Brett and Algeo, 2001b).

In addition we were interested in examining Lower Paleozoic marine sequences deposited within the North American mid-continent. Here we examine several well-defined, limestone and shale sequences from Kope Formation localities in northern Kentucky, south of Cincinnati, Ohio (Algeo and Brett, 1999).

The Kope Formation in the study area is ~ 70–75 m thick (Brett and Algeo, 2001a), and contains much of the basal Edenian Stage of the Upper Ordovician, Cincinnati Series (Weiss and Sweet, 1964). The Kope is composed primarily of 0.5 to 10 m cyclic alternations of shales/mudstones and bundles of thin (3–10 cm) beds of skeletal (brachiopod, bryozoan and crinoidal debris) packstones and grainstones (Jennette

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and Pryor, 1993; Holland et al., 1997). Those lithostratigraphic and biostratigraphic studies of the Kope that are available show detailed correlations among closely spaced sections (Tobin and Pryor, 1981; Tobin, 1982; Jennette and Pryor, 1993; Holland et al., 1997; Brett and Algeo, 2001a,b). However, long distance correlations, especially in upramp directions, are less certain because of facies changes, with consequent changes in the associated faunal assemblages. Thus, an alternative correlation approach was sought to resolve these problems. Samples were collected for this purpose from the Economy Member, Brent Submember, Southgate Member, Pioneer Valley, Snag Creek, Alexandria, and Grand View Submembers, within exposures of the Kope Formation (summarized by Brett and Algeo, 2001a).

1.1. Magnetic susceptibility: general comments

All mineral grains are “susceptible” to becoming magnetized in the presence of a magnetic field, and MS is an indicator of the strength of this transient magnetism within a material sample. MS is very different from remanent magnetism (RM), the intrinsic magnetization that accounts for the magnetic polarity of materials. MS in sediments is generally considered to be an indicator of iron-bearing minerals, ferromagnesian or clay mineral concentration, and can be quickly and easily measured on small samples. In the very low inducing magnetic fields that are generally applied, MS is largely a function of the concentration and composition (mineralogy and grain morphology) of the magnetizable material in a sample. Mathematically, MS is a tensor of the second rank (see Eq. (1) and discussion below) and therefore it has anisotropy. This means that the measured MS in a sample will be different in different directions, depending upon the mineral distributions and grain morphology. The anisotropy of magnetic susceptibility (AMS) of most rock types has been well studied (Tarling and Hrouda, 1993). However, it is somewhat time consuming to measure and requires oriented samples, as do remanent magnetic studies. Bulk (initial) measurements of MS are often performed without consideration of the AMS of samples, and for most samples the MS variation due to this anisotropy is small. The AMS effect is further reduced when samples are crushed before the MS is measured, or where friable samples are broken up during sampling. MS is typically less susceptible to remagnetization than is the remanent magnetization in rocks and can be measured on small, irregular lithic fragments and on highly friable material that is difficult to sample for either AMS or RM measurement.

Magnetizable materials in sediments include ferrimagnetic and antiferromagnetic minerals, such as the iron oxides magnetite and maghemite, and iron sulfide and sulphate minerals, including pyrrhotite and greigite, that may acquire an RM (required for reversal magnetostratigraphy), and also less magnetic paramagnetic compounds. The important paramagnetic minerals in sediments include clay, particularly chlorite, smectite and illite, ferromagnesian silicates such as biotite, pyroxene and amphiboles, iron sulfides including pyrite and marcasite, iron carbonates such as siderite and ankerite, and other iron and magnesium bearing minerals.

In addition to the ferrimagnetic and paramagnetic grains in sediments, calcite and/or quartz may also be abundant, as are organic compounds. These compounds typically acquire a very weak negative MS when placed in inducing magnetic fields, that is, their acquired MS is opposed to the low magnetic field that is applied. The presence of these diamagnetic minerals reduces the MS in a sample. Therefore factors such as changes in biological productivity of calcium carbonate or organic carbon accumulation rates may cause some variability in MS values.

Low-field magnetic susceptibility, as used in most reported studies, is defined as the ratio of the induced moment (M_i or J_i) to the strength of an applied, very low-intensity magnetic field (H_j), where

$$J_i = \chi_{ij}H_j \quad (\text{density-specific}) \quad (1)$$

or

$$M_i = k_{ij}H_j. \quad (\text{volume-specific}) \quad (2)$$

In these expressions, magnetic susceptibility in SI units is parameterized as k , indicating that the measurement is relative to a 1 cubic meter volume (m^3) and therefore is dimensionless; magnetic susceptibility parameterized as χ indicates measurement relative to a mass of 1 kg, and is given in units of m^3/kg . Both k and χ have anisotropy. Here we report the magnetic susceptibility without consideration of the AMS, and use MS to characterize this bulk (initial) low-field magnetic susceptibility.

2. Previous work

2.1. Applications and interpretations of bulk (initial) low-field magnetic susceptibility

MS variations result primarily from changes in the amount of iron oxide, clay, and ferromagnesian constituents. This variability in sedimentary sequences may be primary, produced during deposition, as well as

secondary, resulting from alteration of early deposited minerals. The primary factors include weathering, erosion and deposition rates, and biological productivity. These factors are tied to climate, tectonic and volcanic processes, availability of nutrients, and local (relative) or global sea level changes. Secondary processes include pedogenesis, diagenesis, and within-sediment redox effects driven by sulfate reducing bacteria.

2.2. Results from lithified marine sedimentary rock sequences

During diagenesis the MS of marine sediments decreases. This occurs because ferrimagnetic grains that dominate in unlithified sediments are generally converted to paramagnetic phases during burial and diagenesis, mainly by the action of sulfate reducing bacterial organisms. This process transforms most iron oxides to paramagnetic phases such as iron sulfide and carbonate minerals. In general, however, this process does not remove the iron from the system, so that total iron content is locally conserved. These new phases then contribute, along with the other paramagnetic detrital components present, such as clay, and the remaining authigenic ferrimagnetic constituents, to the MS in lithified sediments. MS values for most marine limestone, marl, shale, siltstone and sandstone range from 1×10^{-9} to 1×10^{-7} m³/kg. Shale and some marl have the highest anisotropy, but for most marine sediments it is less than 2%. Limestone, marl, siltstone and sandstone are usually less than 1%. Shale and marl samples are friable and measurement is generally on small broken and mainly randomly oriented fragments, further reducing the anisotropy effect. Therefore, the error introduced by the anisotropy of MS is minimal. A test of the MS variability in single limestone beds has demonstrated the non-varying nature of the MS over distances up to 25 km (Ellwood et al., 1999). Diagenesis also modifies some of the paramagnetic constituents that make up the terrigenous component of marine sediments. In many cases clay minerals dominate much of the detrital/eolian component, and these are generally not destroyed but may be altered. The iron is still conserved in the secondary clay, as is the paramagnetic behavior of these materials. Other common detrital components observed in marine rocks are ferromagnesian minerals, including biotite, tourmaline and other compounds (see Ellwood et al., 2000 for a discussion).

Ultimately, following diagenesis, the MS observed for most marine sedimentary rocks can be used as a proxy for physical processes responsible for delivering the detrital/eolian component of these sediments into sedimentary basins. As observed for unlithified sedi-

ments, these processes in lithified sediments are both regional and global and include climate, volcanism, tectonism, sea-level changes and eustasy.

2.3. Sea level, climate cycles, and other variations

We have observed that MS records processes that control the influx of detrital and eolian grains into the marine environment. Magnetic susceptibility variations for almost all studies of marine sedimentary rocks also show many levels of cycles. Certain cycles are interpreted to result from climatically driven processes (Ellwood et al., 2001). Other cycles are very long-term and are interpreted as resulting from transgressive–regressive (T/R) cycles associated with eustasy. As a general rule, during transgressive cycles, especially in distal marine sequences, MS is observed to decrease. This happens because detrital sediments are usually trapped near shore during transgressions. However, there are distinct MS peaks that are correlated to maximum flooding surfaces (MFS), and to sudden influxes of detrital material into sedimentary basins by turbidity currents or other sediment suspensions. Sequence stratigraphic studies have demonstrated that at times when sea level is at a maximum, producing an MFS, at the end of a transgressive cycle, there is commonly a marked reduction in carbonate sediments, accompanied by an influx of detrital material into the marine environment. There is a corresponding MS high associated with these MFSs. During regressions, when base level is lowered due to falling sea level, erosion flushes detrital sediment into ocean basins and increases the MS of basinal sediments. Thus T/R cycles play an important role in driving some cyclic MS variations.

3. Sampling

We had two main objectives for this study. First, we collected and measured the MS in overlapping sections for which the litho- and biostratigraphy was well known (Rt. 445; Fig. 2, and Truck Terminal; Fig. 3; locations 1 and 3 in Fig. 1, respectively). Our second objective was to construct a composite section from Kope exposures in the area (Fig. 1). To do this we have combined fully and partially overlapping sampled sections of the Kope Formation and present the MS data as two elements of a composite section (A and B in Figs. 4 and 5).

4. Methods

Samples were collected using a hammer and chisel at 5 cm intervals from four well-studied and well-exposed outcrops in Northern Kentucky: the KY Rt. 445 road cut

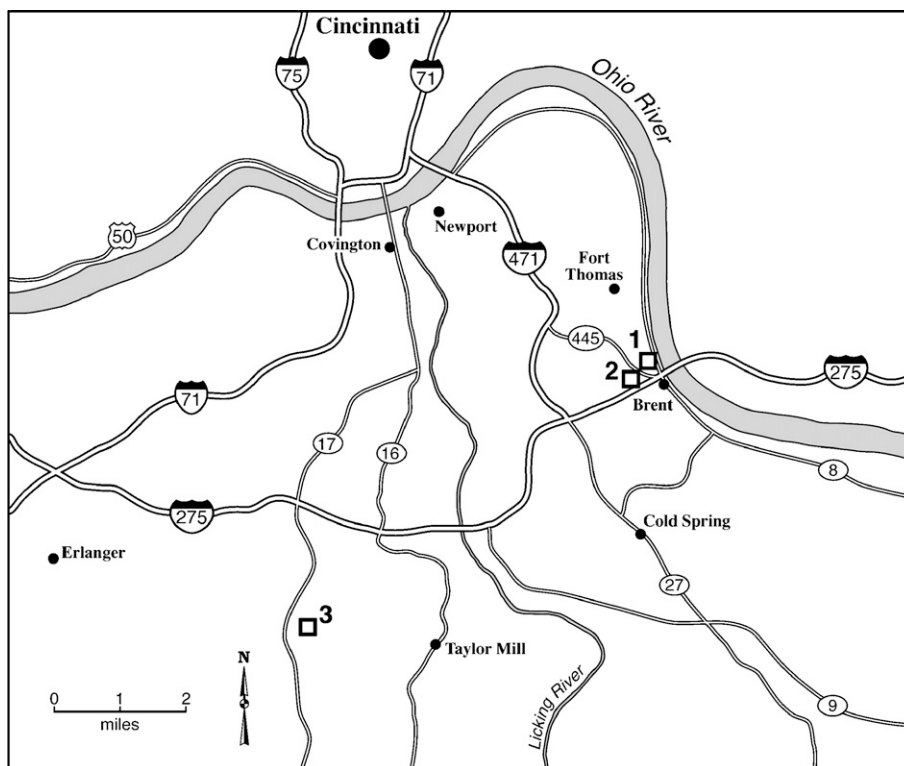


Fig. 1. Outcrop location map where the Kope was sampled in Northern Kentucky. 1—Ky Rt. 445; 2—I-275; and 3—Truck Terminal and White Castle Processing plant off KT Rt. 17 (modified from Algeo and Brett, 1999).

(Beds 1 to 13; 416 samples; 1 in Fig. 1), an outcrop located on I-275 (Beds 25 to 31; 188 samples; 2 in Fig. 1), a stream exposure behind the Truck Terminal within the Corporex Industrial Park, N end of Lake Park Drive, ~ 500 m N of the junction with Rolling Hills Drive, just to the North of the White Castle processing plant on Rt. 17 (Beds 3 to 9; 156 samples; 3 in Fig. 2), and outcrops behind the White Castle processing plant, about 1 km NW of the bridge on Rt. 17 (Madison Pike) over Banklink Creek (Beds 13 to 21; 173 samples; also 3 in Fig. 1). Our samples were collected from the Economy Member, Brent Submember, Southgate Member, Pioneer Valley, Snag Creek, Alexandria, and Grand View Submembers, of the Kope Formation (summarized by Brett and Algeo, 2001a).

All MS measurements reported in this paper were performed using the susceptibility bridge at LSU. This is a custom built bridge by Marshall Williams (University of Georgia, 1982). It is calibrated using standard salts for which values are reported in the Handbook of Physics and Chemistry and by Swartzendruber (1991). The instrument is also cross-calibrated against the KLY-3S Kappa Bridge at LSU. We report MS in terms of sample mass because it is much easier and faster to

measure with high precision than is volume. Each sample is measured three times and the mean and standard deviation of these measurements is calculated. The mean of these measurements is reported here.

4.1. Presentation of MS data from lithified sequences

For presentation purposes and inter data-set comparisons, we use the bar-log format because it emphasizes major changes in MS. In addition we present MS data in logarithmic plots due to the range of MS values often encountered. However, MS data variations in logarithmic plots for some ranges ($1-3 \times 10^x$ vs $4-9 \times 10^{-x}$) may appear to exhibit large variations that are artifacts of the presentation style. Bar-logs reduce these ambiguities. These bar-logs should be accompanied by both raw and smoothed MS data sets. Here, raw MS data (dashed line in figures) are smoothed using splines (solid line with circles indicating data point locations shown in figures). The following bar-log plot convention is used; if the MS cyclic trends increase or decrease by a factor of two or more, and if the change is represented by two or more data points, then this change is assumed to be significant and the highs and lows associated with these cycles are

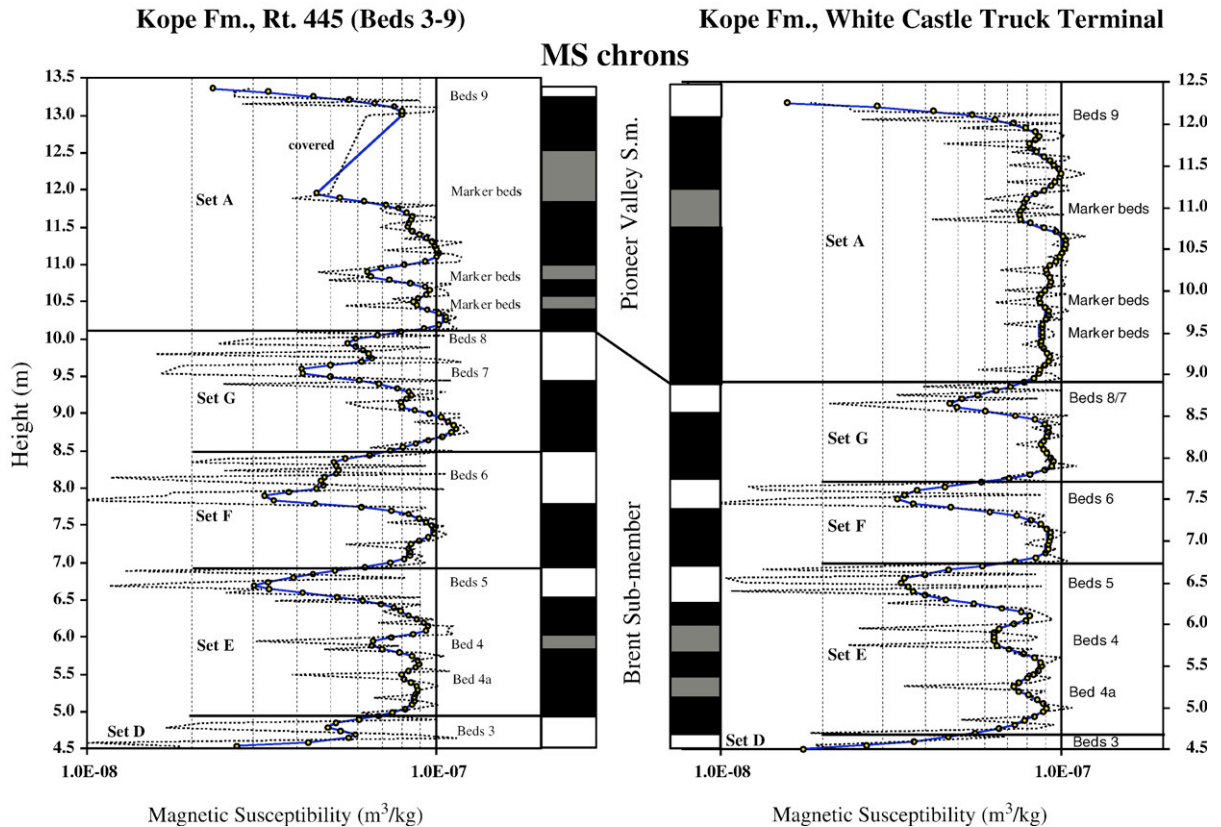


Fig. 2. Direct comparison between two sections correlated using litho- and biostratigraphic methods. Beds 3–9 are identified based on biostratigraphy and lithostratigraphy and sampled in both sections; section at Rt. 445 (1 in Fig. 1) and at the Truck Terminal on KY Rt. 17 (3 in Fig. 1). Dashed lines are raw MS data; solid lines with sample height (circles) are smoothed MS data using splines. Beds labeled 3 to 9 are packages of limestone. Sets are defined based on MS cycles; filled logs represent high MS; open logs represent low MS. Submembers are from Algeo and Brett (1999). Construction of MS bar logs is described in text.

indicated by filled (high MS values) or open (low MS values) bar-logs (shown in figures). This method is best employed when densely spaced samples are being analyzed and helps resolve variations associated with anomalous samples. Anomalous MS variations may be due to weathering effects, secondary alteration and metamorphism, longer-term trends due to factors such as plate-driven eustasy, as opposed to shorter-term climate cycles, or unique events such as impacts (Ellwood et al., 2003) and other factors. In addition, variations in detrital input between localities, or a change in detrital sediment source is resolved by developing and comparing bar logs between different localities.

5. Results

The results of our correlation work are presented in Fig. 2. Beds 3–9, mainly represent relatively thin

packages or bundles of limestone beds separated by thicker shales. Continuous samples were collected at 5 cm intervals with the exception of one covered interval just below limestone bed package 9 in the Rt. 445 outcrop. Smoothed MS data were used to build an MS chron zonation for each section and in turn to divide the data into sets that we have labeled as Series C–F within the Brent Submember, and Series A within the Pioneer Valley Submember (Fig. 2). The Marker Beds in Series A, associated with limestone bed package 9 in both sections, represent small bundles of calcisiltite/siltstone beds with relatively low MS, while in the Truck Terminal section these beds exhibit higher MS values, possibly due to the fact that they are slightly less weathered in outcrop. In addition, the section at Rt. 445 is about a meter thicker than at the Truck Terminal. This is reflected in slight condensation of the beds within the Truck Terminal section. For example, the limestone bed package containing Beds 7 and 8 is somewhat

condensed in the Truck Terminal section and therefore the MS data have a slightly different profile. This is also true for Bed 6 in the Truck Terminal section (Fig. 2).

To test the correlation between the Rt. 445 and Truck Terminal Sets, we used graphic comparison between MS chron tops and bases (Fig. 3). The agreement between the two sequences is excellent. While there is a slight amount of scatter, the Line of Correlation (LOC) fit through the MS chron graphic comparison is well constrained within the tunnel around the LOC (Fig. 3). An LOC of 45° indicates that the sediment accumulation rates between the two sections in Fig. 2 are similar. Here we have directly compared tops and bases of MS chron Sets, and compared those marker beds that are common to both sections and for which the MS and lithostratigraphy is uniquely defined.

Using the MS data, we have divided Section A into Sets A–G within the Brent Submember and Sets A–H within the Pioneer Submember (Fig. 4). Careful examination of these data indicates that Sets D and F represent

condensed intervals within the Brent Submember. In addition, Set A at the base of the Brent Submember is truncated because this set, capped by the limestone bundle collectively identified as Bed 1, was not well exposed and therefore was not sampled. Within the Pioneer Valley Submember there is some sediment accumulation rate variability between sets, but the condensation here does not appear to be as severe as in the Brent Submember. We interpret these data to indicate that the entire Pioneer Valley cyclic sequence is represented in our samples, although there is clearly some condensation. The MS data presented here are also smoothed one step more than those data presented in Fig. 2. Thus, only the distinctive calcisiltite marker beds in Set A at the base of the Pioneer Valley Submember are identified (full shaded band in Fig. 4 MS bar log). It is apparent from Fig. 4, that in Northern Kentucky where we sampled (Fig. 1), the Pioneer Valley Submember is almost double the thickness of the Brent Submember located below it.

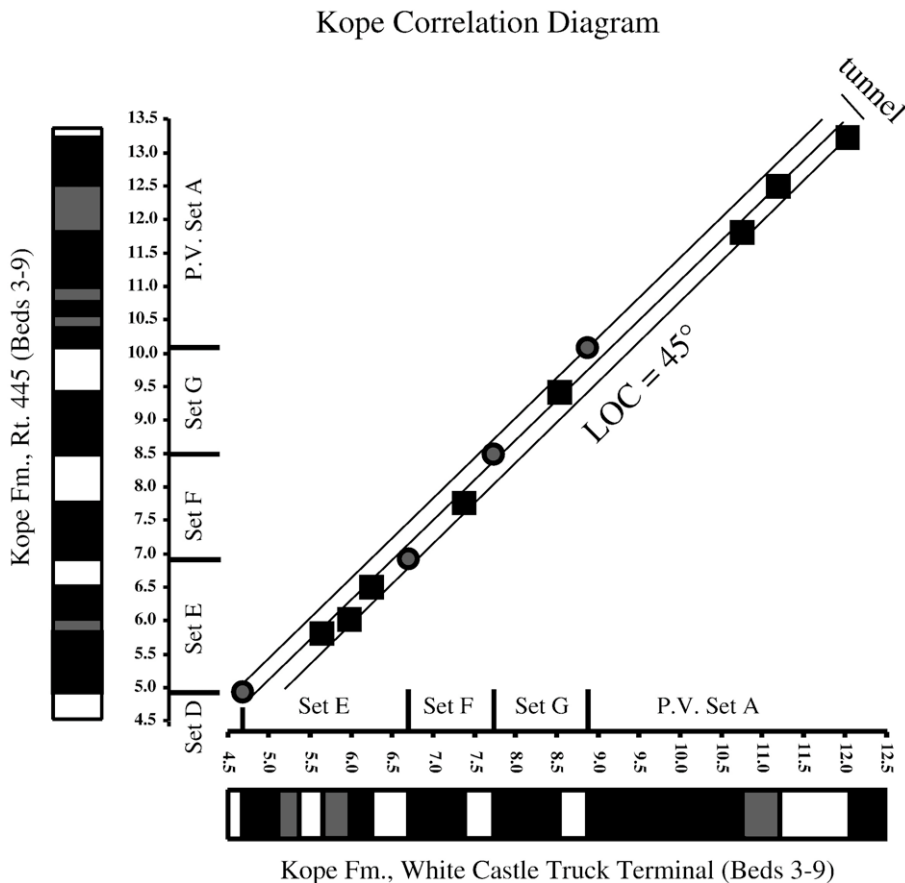


Fig. 3. Graphic comparison between the Rt. 445 and Truck Terminal MS chron data sets. Sets are compared with circles and marker beds with common MS character are compared using squares. A Line of Correlation (LOC) fit to the data is oriented at 45°. All of the data are enclosed within the delineated Tunnel.

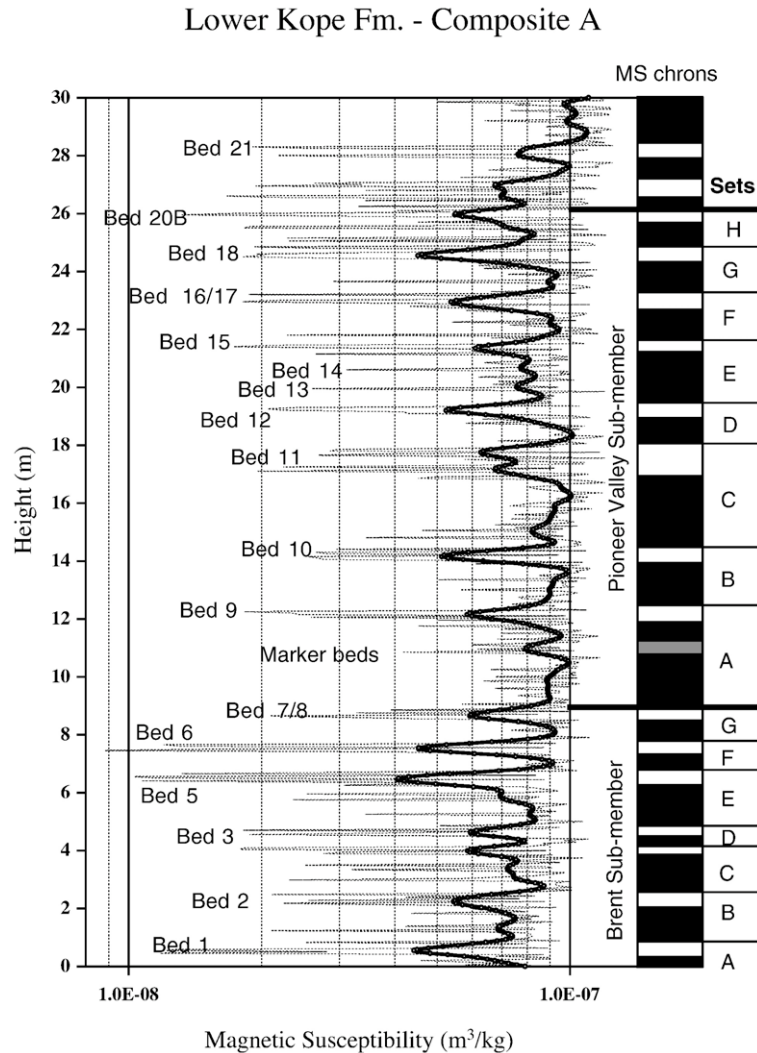


Fig. 4. Composite MS data for the lower Kope Formation beds outcropping along KY Rt. 445 (Beds 1–13) and behind the White Castle processing plant located on KY Rt. 17 (Beds 13–21). Dashed lines are the raw data; solid lines with sample height (circles) are the smoothed data using splines. Beds labeled 1 to 21 are bundles of limestone. Submembers are from [Algeo and Brett \(1999\)](#). MS bar logs (construction is described in text) are differentiated by filled (MS highs) and open (MS lows) patterns; dark shading represents calcisiltites. Sets are defined based on MS cycles.

Magnetic susceptibility data used in building Composite B ([Fig. 5](#)) includes samples from the Snag Creek and Alexandria submembers (Beds 21 to 30B), plus the lower-most Grand View Submember (Bed 31) of the Southgate Member of the Kope Formation. Above Bed 20B there is a group of limestone beds with sufficiently distinctive MS characteristics that we consider this as defining the basal set of the Snag Creek Submember, and we have labeled this interval as Set A (light filled MS bar log in [Fig. 5](#)). In addition there are five other sets defined by named limestone packages (Beds 21 to 24) and we have labeled the MS variations associated with these as Sets B to F. Two zones of distinctive calcisiltite marker beds are observed in both Set C and Set E ([Fig. 5](#)). At the

base of the Alexandria Submember, within Set A, there is also a calcisiltite marker horizon consisting of a package of these beds. The top of Set C is defined by named Bed 27A (light fill in the MS bar log, [Fig. 5](#)). This group of thin limestone beds has a higher, somewhat anomalous MS than do most of the other named limestone packages.

Stratigraphic condensation in Composite B is observed in Sets A, B and perhaps F in the Snag Creek Submember and, with the exception of Set A, within all of the Alexandria Submember series. The Snag Creek and Alexandria submembers exhibit slightly higher sediment accumulation rates than does the Brent Submember, but significantly lower rates than does the Pioneer Valley Submember.

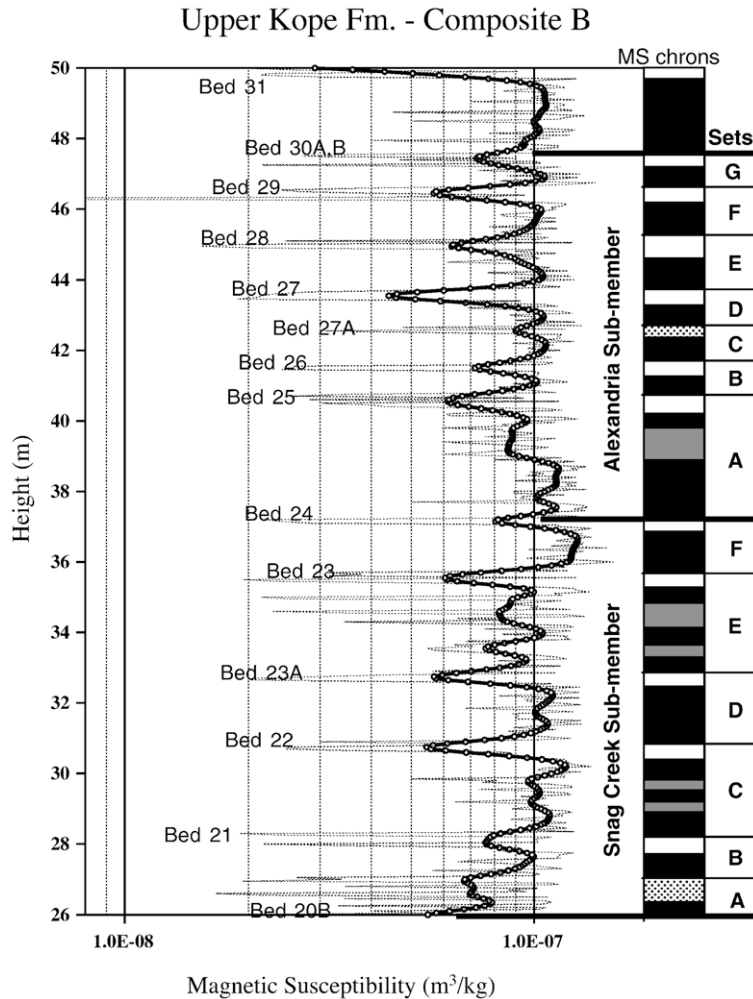


Fig. 5. Composite MS data for the upper Kope Formation beds exposed behind the White Castle processing plant located on KY Rt. 17 (3 in Fig. 1; Beds 20B to 25) and along I-275 (2 in Fig. 1; Beds 25 to 31). Dashed lines are the raw data; solid lines with sample height (circles) are the smoothed data using splines. Beds labeled 20B to 31 are bundles of limestone. Submembers are from Algeo and Brett (1999). MS bar logs (construction is described in text) are differentiated by filled (MS highs) and open (MS lows) patterns; dark shading represents calcisilities; light shading represents limestone that either is not identified as a bed set (top of Series A in the Snag Creek Submember) or has a relatively high MS (Bed 27A at the top of Set C in the Alexandria Submember). Sets are defined based on MS cycles.

5.1. Evaluation of magnetic mineralogy

We used two methods to examine the shale, mudstone and limestone samples reported here. XRD analysis showed that illite and chlorite were the abundant clay minerals in these samples. No other clay was identified. Thermomagnetic susceptibility measurements (TSM), using the KLY-3S Kappa Bridge at LSU on illite, chlorite and smectite/montmorillonite standard samples showed that the MS in illite samples dominated the paramagnetic susceptibility. This measurement involves heating a sample from room temperature to 700 °C while measuring the MS as the temperature rises. Paramagnetic

minerals show a parabolic-shaped MS decay during this process because the MS in these samples is inversely proportional to temperature of measurement (Hrouda, 1994). Ferrimagnetic minerals, on the other hand, usually show an increase in MS up to a point where the MS decays toward the Curie temperature of the minerals responsible for the MS. For magnetite this temperature is ~ 580 °C. In Kope and standard illite samples, an initial paramagnetic phase (interpreted to be illite with TSM values below 10; Fig. 6) begins to convert to a ferrimagnetic phase at temperatures near or above 400 °C. This phase is magnetite and has a ~ 580 °C Curie point (inflection at ~ 580 °C in Fig. 6a,b representing the loss at high

temperature of ferrimagnetic magnetization in magnetite). This behavior is observed in both Kope and standard illite samples (Fig. 6a,b). Standard chlorite and smectite/montmorillonite samples that we ran did not show this same behavior although the initial MS was equivalent to illite and Kope samples (Fig. 6a). There is also evidence in some samples of conversion to a second ferrimagnetic phase, maghemite, with a Curie temperature near 610 °C (e.g. limestone Bed 9 in Fig. 6b). It is probable that there are K-bentonite (thin ash now probably smectite) beds within the Kope sequences we sampled, but we were not able to identify these. This may be due to the fact that bioturbation and differential erosion and redeposition has disrupted these beds (Ver Straeten, 2004). However, even if present, the standards for smectite we have measured indicate that the effect on the MS of these K-bentonites would be minimal.

In contrast to our other work on marine rocks, MS for the Kope Formation samples seems to be lithologically dependent. That is, limestone generally has low MS values while shale/mudstone exhibit higher MS values. This effect appears to be controlled exclusively by the amount of clay (identified as illite) contained in the sample measured. Tobin and Pryor (1981) and Brett and

Algeo (2001b) have argued that the cycles in the Kope, with shale/mudstone capped by skeletal packstone and grainstone, represent fining (deepening) upward sequences, with first rapid deposition of mudstone, in part as storm deposits, followed upwards by a cap of limestone packages representing much slower deposition with possible winnowing of clay during this phase of sediment accumulation. The MS results are consistent with this hypothesis, indicating that clay deposition, responsible for the paramagnetic signature, exhibits a series of T/R cycles. We infer that the cycles observed in the Kope data sets (labeled as sets in Figs. 2, 4 and 5) are the result of climate cyclicity driving differential erosion and deposition.

6. Discussion

Variations in MS values from Kope Formation samples result from differences in the concentration of the paramagnetic clay mineral illite. These variations in marine samples can be controlled by a number of factors. Broadly these include, (1) erosion of terrigenous sediments and deposition in the marine environment, (2) erosion and redeposition within the marine environment, or (3)

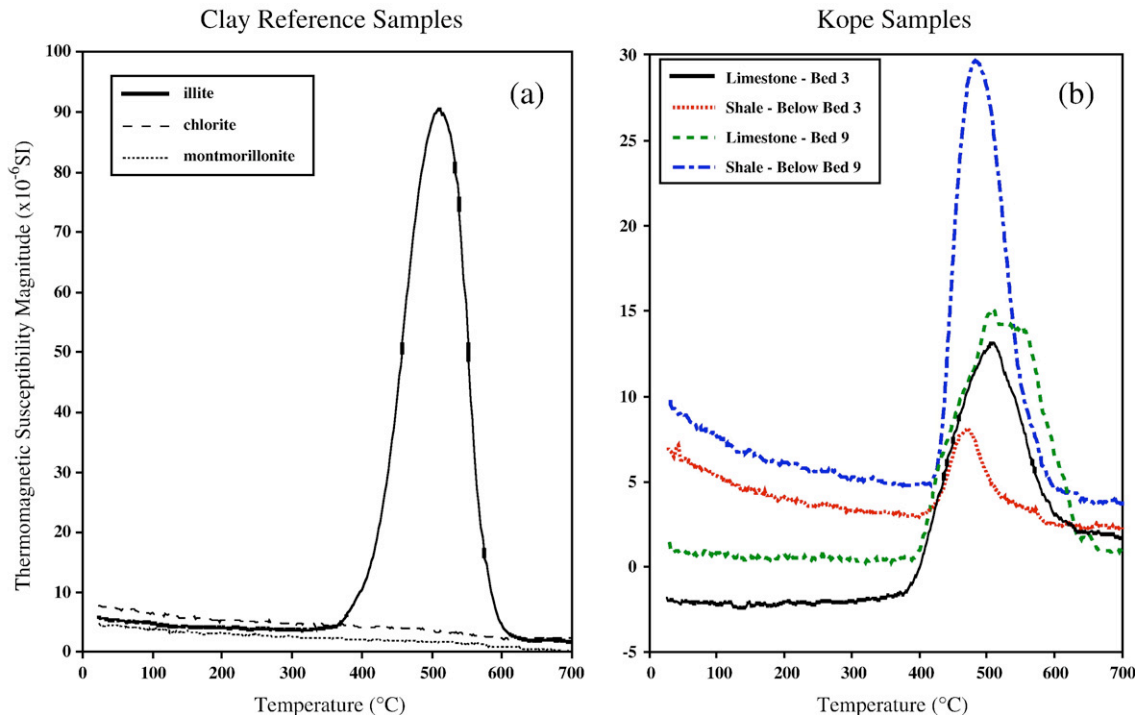


Fig. 6. Thermomagnetic susceptibility (TSM–MS vs T) results for measurements of (a) 3 typical clay reference samples, illite, chlorite and montmorillonite (smectite), and (b) limestone and shale samples from the Kope outcrop samples given in Fig. 2. At low temperatures, illite and all Kope samples exhibit the parabolic-shaped MS decay during heating typical for paramagnetic minerals (Hrouda, 1994). At higher temperatures above 350 °C in these samples, illite converts to a magnetite phase with a distinctive peak.

carbonate productivity within the marine environment, with consequent dilution of illite.

Erosion of clay minerals, primarily from Taconic orogenic sources during the Ordovician, was due mainly to physical abrasion by rainfall and runoff. Source areas in the Taconic allochthonous terrains were comprised largely of obducted/thrust basal muds, shales, and slates and these were no doubt reworked to supply clay-rich sediments to the foreland basin. Supply rates into offshore areas, however, depended not only on tectonic uplift and erosion, but also on submarine erosion, climatic rainfall-driven erosion, and base level changes.

Erosion and redeposition of fine-grained sediments within this shallow marine environment is primarily the result of large storms with wave-base erosional effects, and secondly, by density (turbidity) flows generated by storms or earthquakes. In nearshore areas, lowering of wave-base during large storms, produces seafloor erosion and winnowing of fine-grained sediments, including terrigenous muds, which would be entrained in gradient currents and moved in a net offshore direction (Aigner, 1985; Clifton, 1988).

Cyclic changes in the frequency and intensity of storms driven by climatic cycles have been invoked to explain the alternating mudstone and skeletal limestone in the Upper Ordovician, and this is especially true for the Kope Formation in the Cincinnati Arch region (Holland et al., 2001a,b). While there is no doubt that storm erosion and winnowing played an important role in sedimentation in the Kope, Brett et al. (2003) argued that this might not be the primary mechanism in generating meter-scale shale–limestone cycles. First, there is evidence for storm erosion in both mudstone and shell-rich intervals. Second, there is diagenetic evidence for sediment starvation during deposition of these skeletal rich intervals. This evidence is found in the form of concretionary layers beneath many limestone beds, and hardgrounds and phosphatic sediment within limestone beds. Moreover, while shale-dominated intervals thicken basinward, limestone beds appear to be more condensed and discrete in downramp rather than in upramp areas, in contrast to the storm-driven model. A mechanism involving storm erosion and redeposition should predict that winnowed limestone would become more diffuse and muddy downramp, probably splaying into a bundle of interbedded shale and distal graded storm beds. The traceability of thin compact skeletal limestone, and concretionary beds from shallow ramp to basinal areas (Kirchner, 2005; Kirchner and Brett, *in press*) indicates a greater degree of condensation downramp and an overall basin-wide reduction in sediment supply.

Clearly the rock and MS cycles are quite similar throughout the interval of the Kope that we have sampled (Figs. 4 and 5). This indicates changes in volume of illite-bearing terrigenous sediment, perhaps reflecting base-level changes or climatic driven cyclic erosion. Transgressive–regressive (T/R) cycles may cause variation in supply of terrigenous sediment as an indirect result of base level changes bringing additional detrital components into the marine environment. Stable to falling base level should facilitate progradation of muds into progressively more offshore areas. Conversely, rapid rises in base level may produce bays and estuaries that serve as sediment traps, reducing the supply of sediments offshore. Because progressively less detrital material is accumulating during transgressions, MS values should systematically decrease. Thus, during transgressive phases it is expected that the sequence should show a fining upwards character and a decrease in detrital influence and reduction in MS. During such times, when sediment input rates were moderate to low and conditions were favorable to benthos, limestone-forming organisms, such as crinoids, brachiopods and gastropods were abundant and dominated the accumulating sediment. Enhanced by minor winnowing during storms, the amount of illite and other detrital paramagnetic minerals making up the accumulating sediments was relatively low. Thus, productivity of diamagnetic calcium carbonate dominated over paramagnetic illite minerals within these sediments, constraining the MS at very low values.

A similar effect could be produced by climatically driven oscillations in erosion and runoff during dry-wet cycles. Shell-rich limestone would reflect drier climates with less overall input of terrigenous sediment, while shale-dominated intervals would reflect wetter climatic regimes with greater runoff of sediments to adjacent seas.

The widespread traceability of shale–limestone bundles and the cyclic character of the MS sets observed in Kope strata suggest that minor sea-level and/or climate-controlled variations in siliciclastic supply were the dominant controls on the MS signal. At present we cannot fully distinguish between base-level and climatically driven cycles, although the balance of evidence seems to slightly favor eustatic mechanisms (Brett et al., 2003, *in press*).

There is a clear MS asymmetry in most of the sets represented in Figs. 2, 4 and 5, with thin limestone bundles at the top and thicker shales below. We see clear detrital dominated accumulation in the high MS parts of cycles, as well as distinctive breaks at the base of limestone beds and rapid shifts to low detrital concentrations. There are two possible reasons for this asymmetry. It is possible that longer-term accumulation

of detrital material during still-stand to regressive events was followed by a rapid, transgressive limestone accumulation phase. Alternately, the distinction between sedimentation phases may have been enhanced by storm erosion that had the effect of sharpening the bases of skeletal hash accumulations during times of low relative sedimentation rates.

Thus, we infer that the Kope cycles started with a rapid, minor rise in base level (and/or shift to dry climate), followed by a transgressive phase with gradual accumulation of skeletal debris during times of low detrital sediment input. A maximum sediment starvation surface is represented by firmgrounds, hardgrounds, and/or thin phosphatic lags near the tops of limestone bundles. A phase of increasing influx of detrital flows may have been associated with highstand (MFS) to an early regressive phase, and/or wetter climates and enhanced runoff. Gradient and/or turbidity currents from near-shore terrigenous sedimentary accumulations clearly caused redeposition of silts in a number of sedimentary packages (sets in figures) examined here. Although the regressive phase mudstones are thicker in these sets than the transgressive phase carbonates, the amount of time represented by regression may have been equal to or even less than that represented during transgression.

6.1. Cyclicities and the time of deposition of the Kope Formation

Magnetic susceptibility cycles in the Kope Formation (Figs. 4 and 5) have been used to divide the sampled sections into a set of 28 MS chrons that cover ~ 50 m of section. This includes the Brent, Pioneer Valley, Snag Creek and Alexandria submembers, representing about two thirds of the thickness of the Kope Formation, which is estimated to be 70–75 m thick. If MS cycles represent climate cycles, and if the Edenian Stage (of which the Kope forms the majority) represents 1 to 2 million years as has been suggested elsewhere (Sadler and Cooper, 2004; Webby et al., 2004), then the MS sets outlined in Figs. 4 and 5 could represent Milankovitch obliquity cyclicities. For the Ordovician, the two major obliquity bands are ~ 30,000 and ~ 37,000 years (Berger et al., 1992). Given a total of about 40 cycles for the entire thickness of the Kope Formation (70–75 m, Brett and Algeo, 2001b), we infer that sediment deposition took from ~ 1.3 to ~ 1.6 million years. This estimate is consistent with previous estimates (Holland et al., 2001a; Holland, 2005). It is possible that there is some unrecognized condensation in the Kope composite we report here, or there may be a slight over-

or underestimation of the number of cycles represented. However, a slight change in the number of cycles (two or three) in either direction will not significantly change the time estimate for Kope deposition.

6.2. Evaluation of Kope Alteration

A concern, the post-depositional alteration of these sediments (and thus the MS) was answered using two lines of evidence. First, it has been established that the Conodont Alteration Index for this region is low, 1.0 to 1.5, indicating little post-depositional heating and alteration of Kope Formation sediments in this area (inferred from Epstein et al., 1977). Second, we performed TSM measurements on Kope limestone and shale samples and compared these to illite reference samples that are known *not* to have been altered. Alteration effects tend to change the character of the TSM curves, causing conversion to a ferrimagnetic component and increasing the overall MS for the sample from those values expected for marine samples (Ellwood et al., 2000). In the case of the Kope TSM curves, the conversion peak for illite is preserved and MS values are consistent with known, lithified marine samples. Therefore we infer that these sequences are relatively unaltered, and that alteration effects have not significantly enhanced the MS.

7. Conclusions

Our main objective for doing this work was to test if MS data from complex epicontinental sequences, like those represented by Kope sediments, could be used for correlation. To do this we sampled two litho- and biostratigraphically well-studied sections of the Upper Ordovician Kope Formation limestone and shale exposures. Separation between sites was ~ 10 km. We observe excellent MS correlations between these overlapping sequences, indicating that MS can be used for correlation in such environments. Sediment accumulation rates for the two sequences are similar, indicating that depositional processes acting at both of these sites are also similar.

Once we were able to demonstrate that correlations using MS are possible, this work was expanded to constructing an MS composite section (MS CS) from sequences where only the tops and bottoms from outcrop sections were known to overlap. The MS CS for Kope Formation sections resulted in a ~ 50 m composite that is tied to the general lithostratigraphy known for the Kope. The MS CS indicates that processes active during deposition of Kope sediments did not radically

change during the 1–2 million years during which these sediments were being deposited.

MS data reported here enhance our understanding of these marine sequences and show an excellent correlation between named beds in well studied stratigraphic sequences of mid-continent Lower Paleozoic mudstone and limestone. This work allows us to examine sections for zones of relative condensation between and among sections and to develop age estimates as floating point time scales, and demonstrates the utility of independent stratigraphic techniques in the study and correlation of marine sedimentary rocks.

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