Int. Assoc. Sedimentol. Spec. Publ. (2012) **45**, 257–270

Geochemical evidence for meteoric diagenesis and cryptic surfaces of subaerial exposure in Upper Ordovician peritidal carbonates from the Nashville Dome, central Tennessee, USA

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ABSTRACT

This paper uses a geochemical approach to evaluate possible surfaces of subaerial exposure in three intervals within a limestone section previously studied using a sequence stratigraphic approach. Specifically, geochemical results suggest that meteoric diagenesis occurred at surfaces of subaerial exposure at the top of a 3rd order Type I sequence, at the top of a subtidal parasequence and within a subtidal parasequence in Mohawkian (Upper Ordovician) carbonate strata of the Nashville Dome in the eastern United States. Minima in $\delta^{13}C$ and in Sr concentration exist below all three of these surfaces, and minima in $\delta^{18}O$ are present below two of them. The results confirm that these geochemical measures can be used to recognize surfaces of subaerial exposure in carbonate strata at least as old as the Early Mohawkian, and they suggest that a photosynthesizing biological community was present on the land surface at this locality in the Early Mohawkian. Most significantly, with regard to stratigraphy, the recognition of cryptic surfaces of subaerial exposure at the top of and within subtidal parasequences implies that subaerial exposure may be more common than expected in shallow-water carbonate strata. The results further emphasize the importance of combining geochemistry and sequence stratigraphy in recognizing surfaces of subaerial exposure and thus in understanding sea-level change.

Within these data, multiple samples along individual horizons yield large ranges and variances. For example, the range of $\delta^{13}C$ values among seven stratigraphically and lithologically indistinguishable samples is 1.5‰. The large variances in the data, combined with other recent work, indicate that multiple samples along individual horizons are necessary for geochemical characterization of strata near surfaces of subaerial exposure.

INTRODUCTION

Understanding the history of sea-level change has been a major goal of the earth sciences. One indicator of sea-level change in the stratigraphic record is the presence of surfaces of subaerial exposure in marine strata. Sequence stratigraphy has provided a useful model for integrating sedimentological observations into interpretations of sea-level change and subaerial exposure (e.g. Vail *et al.*, 1977; Hallam, 1984; Vail, 1992; Coe, 2003), and geochemistry has provided a useful complementary tool in recognizing subaerial exposure through its diagenetic effects in limestones (e.g. Beier, 1987; Goldstein, 1991; Algeo, 1996; Fouke *et al.*, 1996; Railsback *et al.*, 2003; Theiling *et al.*, 2007). In an example of this complementary relationship, this paper examines geochemical diagenetic evidence for cryptic surfaces of subaerial exposure in limestones for which a sequence-stratigraphic interpretation had already been developed.

Subaerial exposure, sequence stratigraphy and geochemistry

Sequence stratigraphy predicts subaerial exposure in marine carbonates in two stratigraphic settings. Firstly, subaerial exposure and meteoric diagenesis should occur at any peritidally-capped parasequence (i.e. a cycle that is bounded by flooding surfaces and that commonly displays upward shallowing, *sensu* Van Wagoner *et al.*, 1990). Secondly, subaerial exposure and meteoric diagenesis could also be expected at any sequence boundary at which an unconformity is developed. This would include any Type I sequence boundary (*sensu* Van Wagoner *et al.*, 1990), particularly above which the lowstand systems tract is missing and at which the transgressive surface is therefore merged with the sequence boundary. The absence of this lowstand systems tract would imply subaerial exposure during the time of the lowstand. This latter scenario is commonly developed in settings with relatively low subsidence rates, such as the updip portions of passive margins and in cratonic basins. In contrast, Type II sequence boundaries (*sensu* Van Wagoner *et al.*, 1990) and Type I sequence boundaries overlain by the lowstand systems tract would not necessarily be expected to have subaerial exposure or a record of meteoric diagenesis in most carbonate systems. Although the terms parasequence and sequence have been used in a wide variety of senses, the usage here stresses the nature of the bounding surfaces, not the thickness or duration of the cycle. Hence, many cycles described as parasequences on the basis of other criteria, such as thickness or estimated duration, would be considered as high-frequency sequences (c.f. Mitchum & Van Wagoner, 1991) in the sense used here, that is, if they were bounded by subaerial exposure surfaces. In short, evidence of subaerial exposure that does not coincide with peritidally-capped parasequences or with combined sequence boundaries/transgressive surfaces would not be predictable from an understanding of sequence stratigraphic architecture alone.

The most widely used geochemical method to detect surfaces of subaerial exposure in carbonate sediments involves stable isotopes of C and, to a lesser extent, O (e.g. Allan & Matthews, 1982). In the case of carbon, photosynthesizing organisms produce organic matter depleted in ^{13}C relative to the pool of inorganic C on which they act. Respiration by bacteria and roots of plants and decay of dead bacterial and plant matter therefore adds ^{13}C-depleted CO_2 to soil gas, and subsequent shallow meteoric cementation thus produces carbonate cements with $\delta^{13}C$ values lower than those of unaltered marine carbonate. Researchers either microsample such cements (e.g., Meyers & Lohmann, 1985), sample rock components susceptible to early diagenesis, such as micrite (e.g., Railsback *et al.*, 2003) or use whole-rock samples (e.g., Allan & Matthews, 1982). Allan & Matthews showed that low $\delta^{13}C$ values occur predictably beneath known surfaces of extensive subaerial exposure, and this approach has been used in subsequent work to identify or confirm surfaces of subaerial exposure (e.g. Beier, 1987; Algeo, 1996; Goldstein, 1991; Fouke *et al.*, 1996).

O isotopes have also been used to recognize surfaces of subaerial exposure, albeit with less certain application. For example, Allan and Matthews (1982) concluded that elevated $\delta^{18}O$ values beneath surfaces were indicative of subaerial exposure, and they attributed those elevated values to evaporation that depleted ^{16}O from meteoric waters. On the other hand, Lohmann (1982, 1988) concluded that early meteoric cements were characterized by $\delta^{18}O$ values less than those of the marine sediment being cemented because of the generally ^{18}O-depleted nature of shallow meteoric waters. In addition, Land (1995) has questioned whether O isotope compositions of ancient calcites reflect the conditions under which such calcites formed. His arguments would suggest that O isotope data collected in these studies might have little to do with early meteoric diagenesis and more to do with subsequent burial conditions.

A third geochemical tool that has been used to recognize surfaces of subaerial exposure in ancient carbonates is Sr concentration. The distribution coefficient for incorporation of Sr^{2+} in aragonite is much greater than that for incorporation in calcite, so that Sr^{2+} in marine carbonates is more abundant in aragonite, the less stable of the two polymorphs (Railsback, 1999). Railsback *et al.* (2003) argued that subaerial exposure should therefore result in early preferential dissolution of aragonite and thus in depletion of Sr below exposure surfaces. They therefore used low Sr concentrations as part of two of their three ranked criteria for recognizing surfaces of subaerial exposure.

This research

The main goal of this research was to test the hypothesis that cryptic surfaces of subaerial exposure can be detected geochemically within or at the top of parasequences that have been interpreted by sequence stratigraphic methods to have been deposited in subtidal, rather than peritidal to supratidal, conditions. 'Cryptic' as used here means 'not evident from visual field or petrographic evidence'. As the strata used for this test are Upper Ordovician and thus predate the oldest known vascular land plants (Wellman & Gray, 2000), we first tested the hypothesis that subaerial exposure can be recognized just below a previously recognized sequence boundary (i.e. a known surface of subaerial exposure).

This analysis largely uses the methods of Railsback *et al.* (2003) in combining C and O isotope data and Sr concentration data to discern surfaces of subaerial exposure. However, in tests within subtidal carbonates, the analysis also utilizes the approach of Theiling *et al.* (2007) by making statistical comparisons of multiple samples grouped above and below hypothesized surfaces of subaerial exposure. This approach allows a more objective evaluation of the data than that provided by the arbitrary criteria employed by Railsback *et al.* (2003), and it better incorporates the variance of data along individual horizons. This is the first research to use the multiple-sample approach beyond the work of Theiling *et al.* (2007) itself.

STRATIGRAPHIC CONTEXT

Holland and Patzkowsky (1997, 1998) described eleven third-order depositional sequences, each spanning one to three million years, in Upper Ordovician strata in the Nashville Dome (Fig. 1). Sequences in the Mohawkian Series are numbered M1 to M6 and those in the Cincinnatian Series are numbered C1 to C6, although the C6 is not preserved in the Nashville Dome. Each sequence consists of a retrogradational set of parasequences, forming the transgressive systems tract (TST) and an overlying progradational set of parasequences, forming the highstand systems tract (HST). Some of the sequence boundaries display evidence of

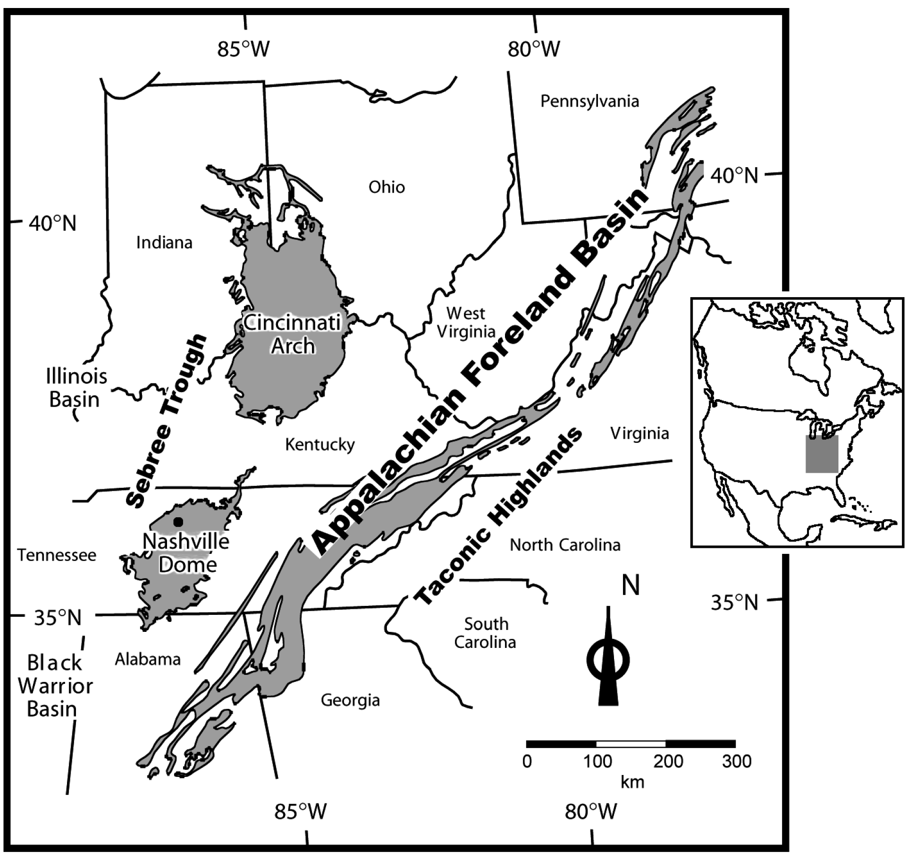

Fig. 1. Map of the eastern United States with the Ordovician outcrop area shaded. The Central Valley site in the northern Nashville Dome used in this study is shown with a filled circle.

regional truncation (M5, C5, Ordovician-Silurian boundary), chertification (M2, M3, M4, M5) and diagenetic mottling (M5, C1, C2). Minor palaeokarst features have been recognized at some outcrops of the M4, M5, M6 and C5 sequence boundaries, as well as the Ordovician-Silurian boundary, in the form of teepee-like deformation, scalloped and overhanging surfaces and 1 cm-wide fissures. Each of these sequence boundaries was later modified as a transgressive surface and thus commonly displays features associated with sediment starvation during transgression, such as borings, hardgrounds, pyritization, phosphatization and skeletal and intraclastic lags.

Upper Ordovician rocks in the Nashville Dome consist mainly of carbonates, with varying proportions of thin intervals, beds and partings of siliciclastic mudstone. The M1 through M4 sequences are characterized by tropical-type carbonates that contain abundant micrite, a wide diversity of allochems (including abundant peloids and uncommon ooids), common hardgrounds and a warm-water fossil assemblage (Holland & Patzkowsky, 1997; Patzkowsky & Holland, 1999). These tropical-type carbonates are consonant with the Nashville Dome's position at approximately 20° S throughout the Late Ordovician. Backstripping analysis reveals long-term accommodation rates of 18 m Myr^{-1} during the M2 through M6 sequences (Holland & Patzkowsky, 1998).

This paper reports results from the Type I sequence boundary between the Lower Mohawkian M1 and M2 sequences. That sequence boundary is also the contact between the Murfreesboro Limestone and the overlying Pierce Limestone (Figs. 2–5). The paper also reports results from two other intervals in the M2 sequence (i.e. within the Ridley Limestone), one at the top of a subtidal parasequence and one within a subtidal parasequence. The parasequence top studied here, which is 21.20 m above the base of the section (Fig. 2), can be recognized in the field on the basis of a change from lighter-coloured skeletal packstones below to darker-coloured skeletal and peloidal mudstones, wackestones and packstones above (Figs. 3 and 6). It provides no lithological evidence of subaerial exposure, but preliminary isotopic and trace elemental data collected by Heim *et al.* (2004) suggested a possible surface of subaerial exposure there. The second horizon studied is located 26.53 m above the base of the section and 0.27 m below a parasequence top and thus within a parasequence (Fig. 2). It lies within skeletal and peloidal packstones and has no distinguishing characteristics (Figs. 3 and 7). It therefore has no lithological evidence of subaerial exposure and was only suspected as a possible surface of subaerial exposure on the basis of preliminary isotopic and trace elemental data collected by Heim *et al.* (2004).

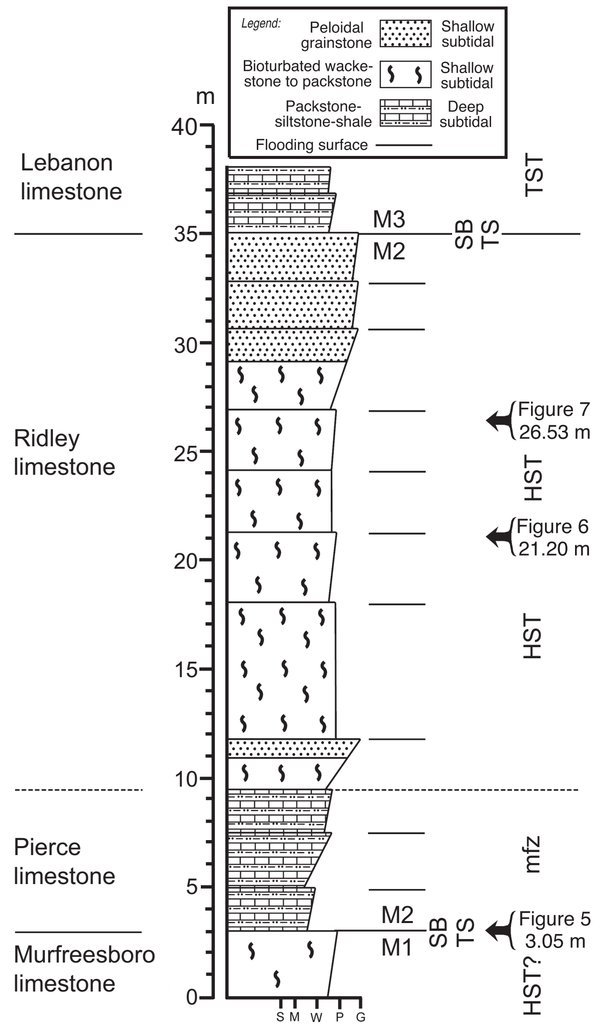

Fig. 2. Stratigraphic column of the Central Valley section sampled in this study. Column is from Figure 8 of Holland and Patzkowsky (1998), lithologies in legend are from Figure 7 of that paper, and water depths in legend are from Tables 2 and 4 of that paper. Arrows at right point to intervals sampled and indicate figures in this paper showing data from those intervals. SB = sequence boundary, TS = transgressive surface, HST = highstand systems tract, mfz = maximum flooding zone and TST = transgressive systems tract. At base, S = shale, M = lime mudstone, W = wackestone, P = packstone and G = grainstone.

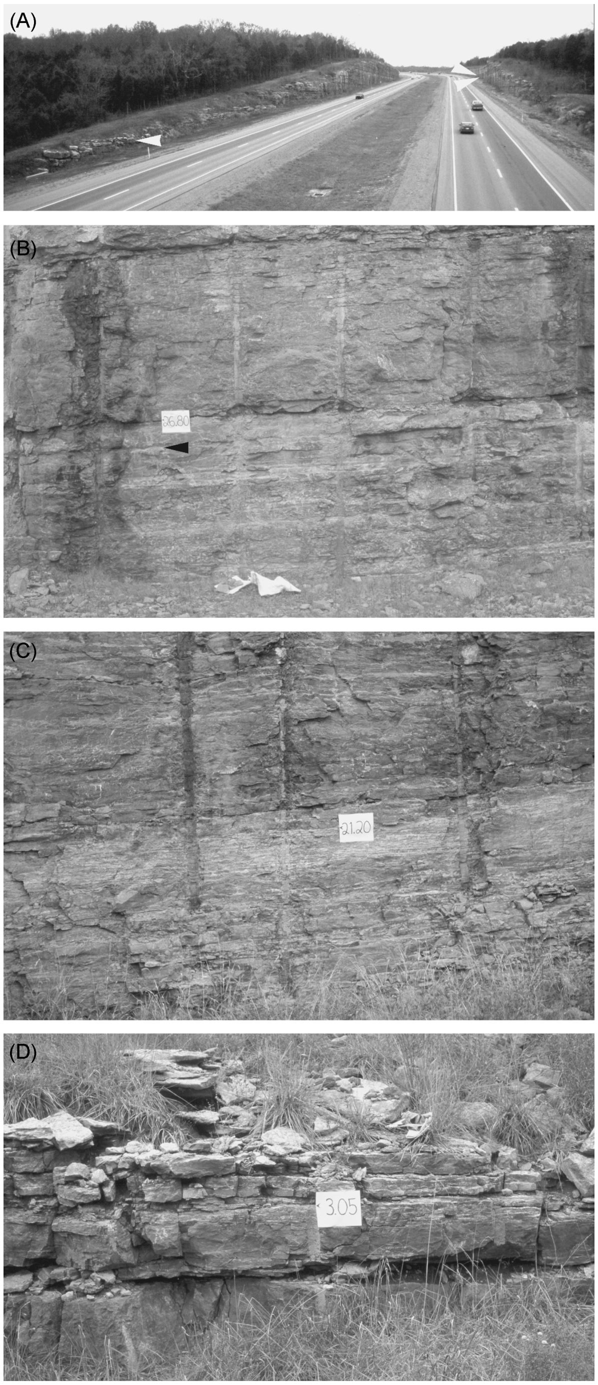

Fig. 3. Field photographs of roadcuts along Tennessee Highway 840 in Rutherford County, Tennessee. (A) View looking south from bridge for Central Valley Road. White pointer at left indicates sequence boundary 3.05 m above base of section; white pointers at right indicate parasequence tops 21.20 m and 26.80 m above base of section. (B), (C) and (D) Photographs of roadcut at sequence boundary and parasequence tops marked in (A). In B), black pointer indicates level, at 26.53 m above base of section, at which subaerial exposure is inferred within parasequence. In (B), (C) and (D), labelled pieces of paper hanging from rock are 21.60 cm in height.

METHODS

Hand samples were collected from a recent road cut in the M1 and M2 sequences in the Central Valley section of Holland and Patzkowsky (1998). The section is located along Tennessee Highway 840 just south of Central Valley Road and the East Fork of the Stones River in Rutherford County, Tennessee (35° 58′ 13″ N; 86° 27′ 01″ W) (Figs. 1 and 3). Samples were taken in the interval from ~1.0 m below to 0.5 m above each hypothesized surface of subaerial exposure. Vertical distances between samples were typically a few centimetres to at most 40 cm. Where multiple samples were collected along one horizon, bedding-parallel distances between adjacent samples ranged from 5 cm to 2.3 m. Single samples were not collected at commonly used vertical spacings of more than 1 m through the entire section because the results of Theiling *et al.* (2007), as well as the results of this paper itself, call into question the usefulness of such a sampling strategy, as discussed further below.

The samples were sectioned and the cut surfaces were polished. Powdered subsamples of micrite or micrite-rich material were obtained from these samples using a dental drill (Fig. 4). Bioclasts, cements, areas of microspar and anything other than micrite were avoided in the drilling. Slow drilling speeds were used to minimize possible recrystallization and isotopic fractionation.

CO_2 was extracted from samples for isotopic analysis using the phosphoric acid method of McCrea (1950) and was analysed using the dual inlet of either a Finnegan Delta E or Finnegan MAT 252 mass spectrometer in the Stable Isotope Laboratory of the Department of Geology of the University of Georgia. Two laboratory carbonate standards that have been calibrated with NBS-19 and NBS-18 were prepared and analysed with each batch of samples. Isotopic results were normalized to those standards using a two-point scale, and thus all $\delta^{13}C$ and $\delta^{18}O$ data are reported here relative to VPDB. Precision is better than ±0.1‰ for both $\delta^{13}C$ and $\delta^{18}O$. Isotopic data are therefore reported to one decimal place, whereas means of data are reported to two decimal places.

Subsamples of the same powders were reacted with HCl and analysed in solution using a Thermo Jarrell-Ash 965 inductively coupled argon plasma (ICP) spectrometer in the University of Georgia Chemical Analysis Laboratory. Elemental

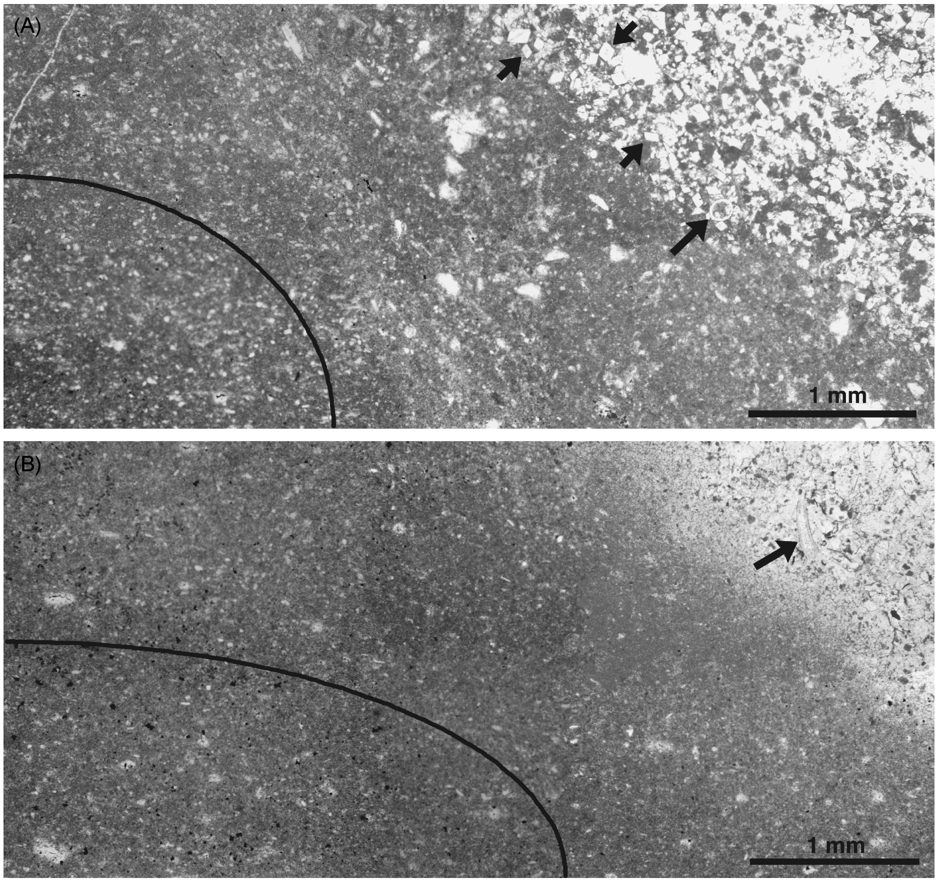

Fig. 4. Mosaics of photomicrographs of samples, with areas micro-sampled for geochemical analysis. (A) Sample from 26.10 m above base of section. (B) A further sample from 21.60 m above base of section. Long arrows point to skeletal grains and shorter arrows point to dolomite in burrows at upper right of each image. Arcs at lower left of each image enclose micrite-rich areas from which parts of powders were drilled for geochemical analysis. White line at upper left of (A) is an artefact of thin-section preparation, not a fracture in the rock.

concentrations of Sr in calcite are reported here using Sr/Ca ratios and assuming 40.0 wt% Ca in Mg-free calcite or proportionately lower Ca concentrations in Mg-bearing calcites. The Thermo Jarrell-Ash 965 ICP results have standard errors of 0.46% for Ca, 0.30% for Mg and 0.48% for Sr, which yields a standard error of 1%, or 0.0004 wt% Sr. Previous replicate analyses yielded differences in Sr concentration of 0.001 wt% Sr (Railsback *et al.*, 2003).

Mol % $MgCO_3$ was calculated as the concentration of Mg divided by the sum of the concentrations of Ca, Mg and Fe. Samples with Mg concentrations greater than 3.4 mol % $MgCO_3$ were excluded from the data set because they presumably contain significant dolomite. The value of 3.4 mol % $MgCO_3$ was selected because isotopic compositions and/or Sr concentrations of samples with Mg contents above that value were commonly extreme outliers relative to other samples from the same horizons. This procedure eliminated six of 64 original samples.

RESULTS

Test of a sequence boundary

Values of $\delta^{13}C$ from samples near the sequence boundary between the M1 and M2 sequences, which is 3.05 m above the base of the section, range from −1.0‰ to −0.3‰ relative to VPDB, and $\delta^{18}O$ values range from −5.0‰ to −4.1‰ vs. VPDB (Fig. 5; Table 1). Sr concentrations near that boundary range from 0.030 wt % to 0.042 wt % (Fig. 5). The lowest values of all three parameters are found 10 cm to 90 cm below the sequence boundary, as would be expected as a result of subaerial exposure and meteoric diagenesis in

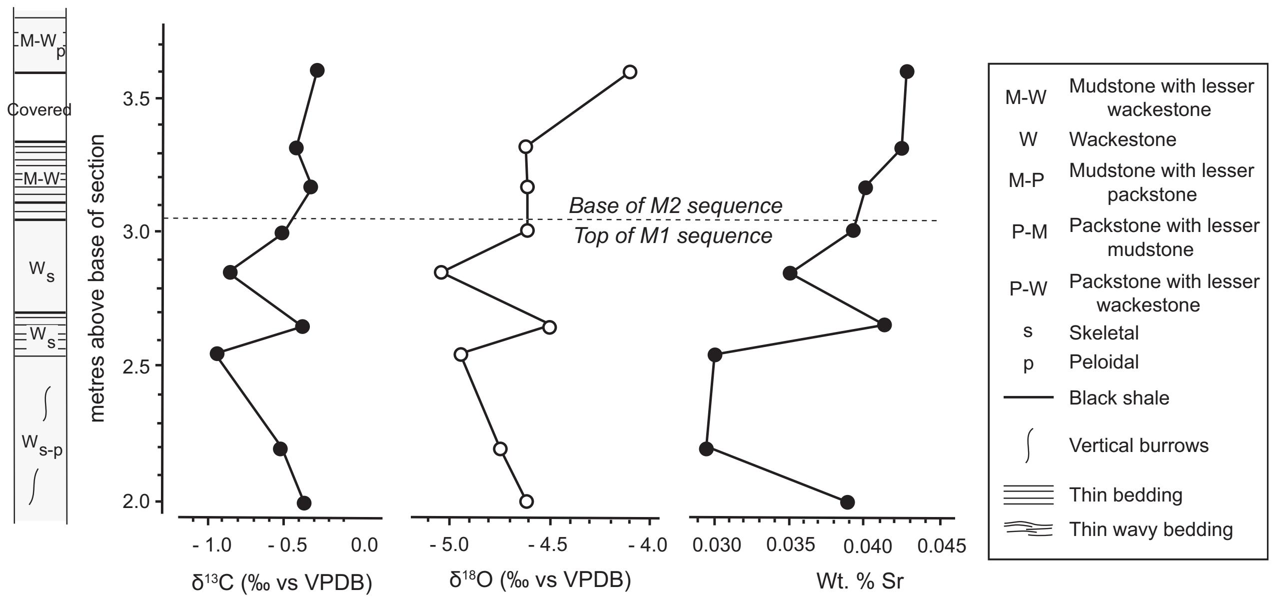

Fig. 5. Lithologic log and plots of $\delta^{13}C$, $\delta^{18}O$ and Sr concentration (weight %) in micrite above and below the Type I sequence boundary between the M1 and M2 sequences at 3.05 metres above the base of the Central Valley locality. Lows in $\delta^{13}C$ and Sr concentration and either a high or a low in $\delta^{18}O$, are expected below a surface of subaerial exposure.

Ordovician limestones (Figure 6 and Table 1 of Railsback *et al.*, 2003). The lowest values of $\delta^{13}C$ are about 0.5‰ less than the background or baseline values of roughly −0.4‰ vs. VPDB, again consistent the depletions observed at surfaces of subaerial exposure and meteoric diagenesis in Ordovician limestones (Figures 7 to 12 and Table 1 of Railsback *et al.*, 2003).

The low values of $\delta^{13}C$, $\delta^{18}O$ and Sr concentration below the parasequence top are in

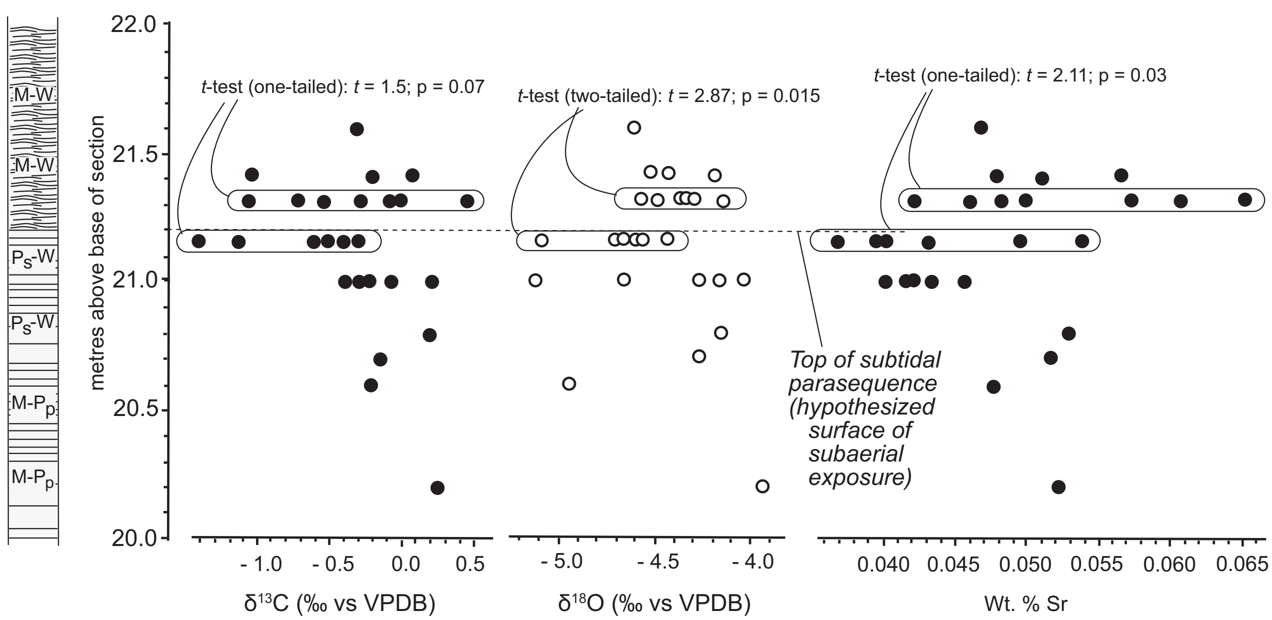

Fig. 6. Lithological log and plots of $\delta^{13}C$, $\delta^{18}O$ and Sr concentration in micrite above and below the top of a subtidal parasequence in the M2 sequence at 21.20 metres above the base of the Central Valley locality. Lows in $\delta^{13}C$ and Sr concentration, and either a high or a low in $\delta^{18}O$, are expected below a surface of subaerial exposure. Legend for lithological log is shown in Fig. 5. Also shown are results from t-tests applied to samples circled in the figure.

Table 1. Stable isotope and Sr concentration data.

Stratigraphic position (metres)	$\delta^{13}C$ (‰ vs. VPDB)	$\delta^{18}O$ (‰ vs. VPDB)	wt % Sr
27.10	−0.2	−5.1	0.0327
26.90	−0.2	−5.0	0.0327
26.75	−0.4	−4.5	0.0315
26.68	0.1	−4.3	0.0335
26.67	0.3	−4.2	0.0302
26.65	−0.2	−4.5	0.0349
26.65	0.4	−4.2	0.0317
26.64	−0.3	−4.5	0.0322
26.64	0.0	−4.6	0.0325
26.59	0.2	−4.2	0.0326
26.56	0.2	−4.4	0.0341
26.56	0.8	−4.3	0.0343
26.50	−0.3	−4.6	0.0317
26.50	−0.5	−4.0	0.0319
26.50	−1.1	−4.7	0.0322
26.43	−0.7	−4.4	0.0319
26.43	−0.6	−4.1	0.0297
26.41	−0.9	−4.8	0.0289
26.41	−0.4	−4.1	0.0299
26.40	−0.8	−4.1	0.0317
26.38	0.0	−4.0	0.0321
26.23	0.2	−4.1	0.0340
26.10	1.1	−3.4	0.0303
21.60	−0.3	−4.6	0.0468
21.42	0.1	−4.5	0.0566
21.42	−1.0	−4.4	0.0480
21.41	−0.2	−4.2	0.0511
21.32	0.0	−4.6	0.0482
21.32	−0.7	−4.5	0.0423
21.32	−1.1	−4.3	0.0461
21.32	0.5	−4.1	0.0573
21.32	−0.1	−4.3	0.0607
21.32	−0.5	−4.5	0.0501
21.32	−0.3	−4.4	0.0653
21.16	−0.5	−4.7	0.0368
21.16	−0.6	−4.4	0.0495
21.16	−0.3	−5.1	0.0539
21.16	−0.4	−4.6	0.0433
21.16	−1.4	−4.6	0.0405
21.16	−1.1	−4.7	0.0396
21.00	−0.1	−4.0	0.0416
21.00	−0.2	−4.7	0.0457
21.00	−0.3	−4.2	0.0401
21.00	0.2	−4.3	0.0434
21.00	−0.4	−5.1	0.0418
20.80	0.2	−4.2	0.0531
20.70	−0.1	−4.3	0.0517
20.60	−0.2	−4.9	0.0478
20.20	0.2	−3.9	0.0523
3.60	−0.3	−4.1	0.0428
3.32	−0.4	−4.6	0.0424
3.17	−0.3	−4.6	0.0401
3.00	−0.5	−4.6	0.0392
2.85	−0.9	−5.0	0.0351
2.65	−0.4	−4.5	0.0412
2.55	−0.9	−4.9	0.0300
2.20	−0.5	−4.7	0.0295
2.00	−0.4	−4.6	0.0389

wackestones with no petrographic characteristics distinguishing them from wackestones above and below, which have values of $\delta^{13}C$, $\delta^{18}O$ and Sr concentration typical of the entire 1.7 m interval.

Test of a subtidal parasequence top

Values of $\delta^{13}C$ from samples near a parasequence top at 21.20 m above the base of the section range from −1.4‰ to +0.5‰ relative to VPDB (Fig. 6; Table 1). The two lowest values are just below the parasequence boundary, and the greatest value is just above the boundary. The mean $\delta^{13}C$ of samples just below the boundary is −0.73, whereas the mean $\delta^{13}C$ of samples just above the boundary is −0.32‰ vs VPDB, although the difference is not statistically significant using a t-test at $\alpha = 0.05$ ($t = 1.5$; $n_1 = 6$, $n_2 = 7$; $p = 0.07$).

Values of $\delta^{18}O$ from samples near this parasequence top range from −5.1‰ to −3.9‰ vs VPDB (Fig. 6; Table 1). One of the two lowest values is just below the parasequence boundary. The mean $\delta^{18}O$ of samples just below the boundary is −4.67, whereas the mean $\delta^{18}O$ of samples just above the boundary is −4.38‰ vs. VPDB, and the difference is statistically significant using a t-test at $\alpha = 0.05$ ($t = 2.87$; $n_1 = 6$, $n_2 = 7$; $p = 0.015$).

Sr concentrations of these samples range from 0.037 wt. % to 0.065 wt. % (Fig. 6; Table 1). The two lowest values are just below the parasequence boundary, and the three greatest values are just above the parasequence boundary. The mean Sr concentration of samples just below the boundary is 0.0439 wt %, whereas the mean Sr concentration of samples just above the boundary is 0.0529 wt %, and the difference is statistically significant using a t-test at $\alpha = 0.05$ ($t = 2.11$; $n_1 = 6$, $n_2 = 7$; $p = 0.03$).

The low values of $\delta^{13}C$, $\delta^{18}O$ and Sr concentration below the parasequence top are in skeletal packstones and wackestones with no petrographic characteristics distinguishing them from skeletal packstones and wackestones below, which have values of $\delta^{13}C$, $\delta^{18}O$ and Sr concentrations typical of the entire two-metre interval.

Test of a surface within a subtidal parasequence

Values of $\delta^{13}C$ from samples near 26.53 m above the base of the section and 0.27 m below a parasequence top range from −1.1‰ to +1.2‰ relative to VPDB (Fig. 7; Table 1). The seven lowest values are just below the hypothesized surface, and the

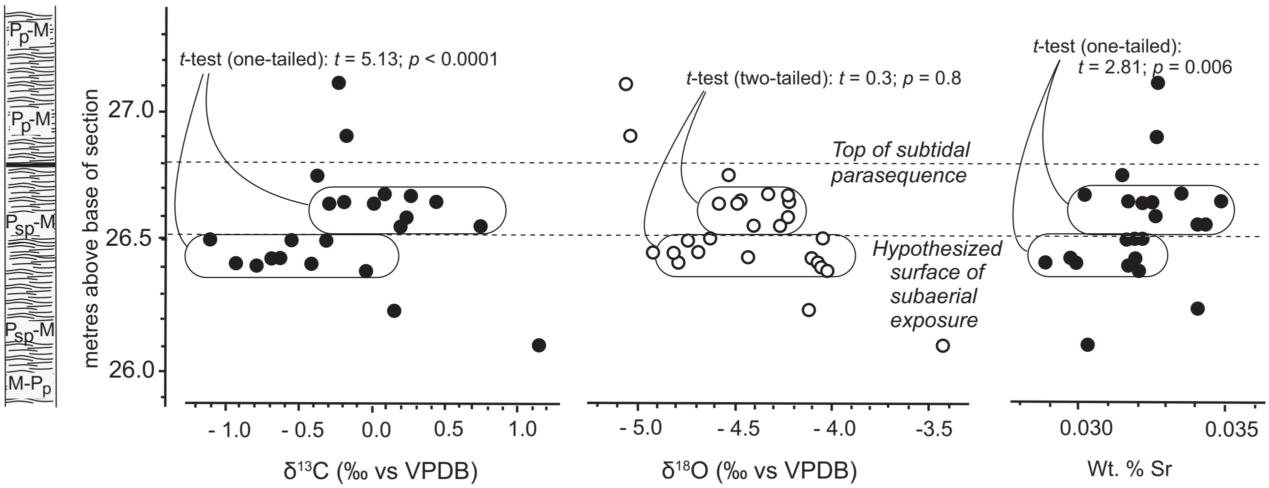

Fig. 7. Lithologic log and plots of $\delta^{13}C$, $\delta^{18}O$ and Sr concentration in micrite above and below a hypothesized surface of subaerial exposure in a subtidal parasequence in the M2 sequence at metre 26.53 of the Central Valley locality. Lows in $\delta^{13}C$ and Sr concentration and either a high or a low in $\delta^{18}O$, are expected below a surface of subaerial exposure. Legend for lithological log is shown in Fig. 5. Also shown are results from t-tests applied to samples circled in the figure.

second-greatest to sixth-greatest values are just above the surface. The mean $\delta^{13}C$ of samples just below the surface is -0.60, whereas the mean $\delta^{13}C$ of samples just above the surface is $+0.17$‰ vs VPDB, and the difference is statistically significant ($t = 5.13$; $n_1 = 9$, $n_2 = 9$; $p < 0.0001$).

Values of $\delta^{18}O$ from samples near this surface range from -5.1‰ to -3.4‰ vs VPDB (Fig. 7; Table 1). Values generally decrease upward. The mean $\delta^{18}O$ of samples just below the surface is -4.32, whereas the mean $\delta^{18}O$ of samples just above the surface is almost identical at -4.35‰ vs VPDB. This minor difference is not statistically significant ($t = 0.3$; $n_1 = 9$, $n_2 = 9$; $p = 0.8$).

Sr concentrations of these samples range from 0.029 to 0.034 wt % (Fig. 7; Table 1). The three lowest values are just below the hypothesized surface and the three greatest values are just above that surface. The mean Sr concentration of samples just below the boundary is 0.0311 wt %, whereas the mean Sr concentration of samples just above the boundary is 0.0329 wt %, and the difference is statistically significant ($t = 2.81$; $n_1 = 9$, $n_2 = 9$; $p = 0.006$).

The low values of $\delta^{13}C$ and Sr concentration are in skeletal-peloidal packstones to mudstones with no petrographic characteristics distinguishing them from skeletal-peloidal packstones to mudstones above or below, which have values of $\delta^{13}C$ and Sr concentration typical of the entire 1.2 m interval.

DISCUSSION

Sequence boundary between M1 and M2 sequences

The presence of samples with low $\delta^{13}C$, low $\delta^{18}O$ and low Sr concentration below the surface previously interpreted as a Type I sequence boundary (Fig. 5) supports the contention that surfaces of subaerial exposure and meteoric diagenesis can be recognized in carbonates at least as old as the Early Mohawkian (early Late Ordovician). Low $\delta^{13}C$ and $\delta^{18}O$ values below the sequence boundary presumably resulted from input of ^{12}C-rich carbon and ^{18}O-depleted oxygen in cements precipitated by meteoric waters percolating downward from the exposure surface (Allan & Matthews, 1982), whereas low Sr concentrations probably resulted from dissolution of aragonite by incoming meteoric water during subaerial diagenesis (Railsback *et al.*, 2003). Input of ^{12}C-rich carbon implies that there was a photosynthesizing biological community on the land surface at this locality in the Early Mohawkian, slightly earlier than a similar inference in Late Mohawkian to Cincinnatian strata by Railsback *et al.* (2003). The Early Mohawkian predates the first reported evidence of vascular land plants in the Silurian but not the earliest plant microfossils, such as spores that may have been produced by bryophytes (Wellman & Gray, 2000). The evidence of photosynthesis on the

Early Mohawkian land surface reported here is also compatible with the interpretation by Panchuk *et al.* (2005) that modelling of variation in $\delta^{13}C_{CO3CO3}$ across the Mohawkian epeiric sea requires a flux of C into that sea from a bryophyte-dominated terrestrial ecosystem, rather than a barren land surface.

Surfaces within and at the top of subtidal parasequences

Cryptic surfaces of subaerial exposure?

Lower values of $\delta^{13}C$ and lower Sr concentrations below hypothesized surfaces of subaerial exposure at the top of a subtidal parasequence (at 21.20 metres above base of section) and within a subtidal parasequence (at 26.53 metres above base of section) are consistent with the hypothesis that meteoric diagenesis occurred below surfaces of subaerial exposure there soon after deposition. O isotope data further support the hypothesis of subaerial exposure at the parasequence top at 21.20 metres but fail to support that hypothesis at the intra-parasequence surface at 26.53 metres. However, that failure is hardly surprising, given the variety of O isotope trends possible below surfaces of subaerial exposure, as discussed above.

Geochemical evidence of subaerial exposure at the top of a subtidal parasequence and within a subtidal parasequence suggests that subaerial exposure is potentially more common than expected in shallow-water carbonate strata based on sequence-stratigraphic principles alone. Facies in these parasequences provide no suggestion of shallowing to subaerial environments. This lack of facies change suggests short-term relative falls in sea-level at a rate faster than tidal-flat progradation (Read *et al.*, 1986). Subaerial exposure at tops of parasequences suggests that metre-scale cycles commonly interpreted as parasequences may actually represent higher-order sequences (e.g. Mitchum & Van Wagoner, 1991).

Evidence of subaerial exposure within a subtidal parasequence suggests that subaerial exposure occurred more frequently than one would expect from the conventional placement of sequence and parasequence boundaries. This represents a type of 'missed beat' in which high-frequency relative changes in sea-level occurred but are not expressed by changes in facies (e.g. Koerschner & Read, 1989; Goldhammer *et al.*, 1993).

Other possible interpretations

In addition to the interpretation above, other scenarios might account for the observed trends within the data. For example, maximum flooding surfaces, hardground surfaces, early marine cemented horizons and periods of possible anoxia might cause similar patterns. However, the intervals discussed above do not coincide with any of the major flooding surfaces identified by Holland and Patzkowsky (1997, 1998) and, although the parasequence top at 21.20 metres lies beneath a minor flooding surface, the horizon at 26.53 m within a parasequence shows no evidence of association with a flooding surface. Hardgrounds have been recognized within the Ordovician strata of the Nashville Dome (Holland & Patzkowsky, 1997, 1998) but the two surfaces in question lack both the pyritized and phosphatized character of those hardgrounds. As only micrites were sampled for this project, large proportions of early marine cement cannot have been incorporated in the material used for stable isotope analysis and there is no evidence of preferential cementation within any particular horizon of micrites sampled. Finally, neither increased proportions of organic carbon, increases in the abundance of pyrite, nor changes in the fauna suggest that the horizons in question were deposited under anoxic conditions. In short, although thoroughness requires that these alternate interpretations be considered, the available evidence provides no particular support for any of them.

Variance of geochemical parameters

One of the most striking features of the data reported in this paper is the large variance in $\delta^{13}C$, $\delta^{18}O$ and Sr concentration along single horizons (Fig. 6) or within very small (<20 cm) stratigraphic intervals (Fig. 7). For example, the range of $\delta^{13}C$ values at 21.32 m above the base of the section, among seven stratigraphically and lithologically indistinguishable samples, is 1.5‰. That equals the $\pm 1\sigma$ variation of all Upper Ordovician $\delta^{13}C$ data from around the world reported by Veizer *et al.* (1999) in their Figure 10.

Theiling *et al.* (2007) have demonstrated that these large variances along stratigraphic horizons may be common. Theiling *et al.* (2007) took 10 replicate samples along each of 25 stratigraphic horizons in Ordovician strata younger than those described in this paper. Along each of the 25 horizons, there was no apparent variation in mineralogy, in lithology, in depositional or diagenetic fabric, or in colour: each horizon yielded 10 seemingly uniform samples. Individual horizons nonetheless had ranges of $\delta^{13}C$ as great as 2.4‰ and ranges of $\delta^{18}O$ as great as 2.8‰, and Sr concentrations varied by as much as a factor of four within single horizons. Even the smallest ranges observed from any one stratigraphic horizon were 0.2 ‰ in $\delta^{13}C$ and 0.3 ‰ in $\delta^{18}O$, greater than the analytical error of 0.1‰.

Examination of replicate samples along depositional horizons has likewise shown large ranges and variances in other kinds of data. For example, Webber (2005) took replicate samples along stratigraphic horizons and found considerable variation in fossil assemblages within bedsets. Bennington (2003) similarly found large variations in species abundance in replicate samples within single outcrops of one bed. These palaeontological data obviously differ in character from geochemical data in many ways, but they support the general notion of variation, rather than complete uniformity, along stratigraphic horizons.

The large ranges and variances in the geochemical data reported in this paper might nonetheless lead a sceptic to question whether such data are of any use in interpreting subaerial exposure or other depositional or diagenetic events. With such large ranges and variances of the data measured from different parcels of micrite in any one horizon, what is the $\delta^{13}C$ of that horizon and how can we be sure whether or not it is different from the $\delta^{13}C$ of the horizon above or below? As an answer, our sceptic might consider the simple example of the heights of two forests. If one were to measure the heights of some trees in what seems to be an old-growth rainforest, one would find a range of heights and no two trees of exactly the same height. One would thus not be able to speak of one number, nor of the height of any one tree, as the 'height of the old forest'. Instead, one could only speak of the mean and variance of the heights of the trees measured. One would nonetheless have a quantitative characterization of the heights in the trees in that forest. One could also measure the heights of trees in a seemingly young forest and one would likewise find a range of heights with no two exactly the same. One would thus not be able to speak of one number as the 'height of the young forest', but only of the mean and variance of the heights of the trees measured therein. As with the old-growth forest one would nonetheless have a quantitative characterization of the heights in the trees in the young forest. Some of the taller trees in the young forest might be taller than the shorter trees of the old forest and thus the two distributions might overlap. A *t*-test could nonetheless then determine the probability that the two samples of heights, one sample from trees considered by us to be an old-growth forest and one sample from the trees considered by us to be a young forest, could have been drawn from one unimodal distribution.

The same logic applies to stratigraphic horizons: the geochemical data presented here, the geochemical data of Theiling *et al.* (2007) and the analogous palaeontological data of Webber (2005) and Bennington (2003) discussed above illustrate that variation along depositional horizons is probably the rule rather than the exception. The cause of geochemical variation along stratigraphic horizons is probably patchiness in the depositional surfaces or land surfaces that those horizons represent: cracks, burrows, borings, ponding of water and clustering of organisms all generate environmental diversity that can lead to geochemical diversity. As a result, no one piece of rock can yield a single $\delta^{13}C$ value that is uniquely 'good data' providing the '$\delta^{13}C$ of the horizon', in contrast to other values of $\delta^{13}C$ from seemingly identical pieces of rock along the same horizon - just as the height of no one tree defines the 'height of a forest' to the exclusion of other trees in that forest. Single rock samples therefore cannot be expected to characterize stratigraphic horizons, and use of single samples to do so ignores the possibility, if not probability, that the one sample collected differs from the mean for the entire horizon. Instead, use of multiple samples acknowledging the existence of natural variation along horizons, determination of mean and variance, and use of statistical tests to determine the probability that two sample sets are drawn from the same unimodal population seems the only way that we can aspire to use geochemical data in distinguishing between stratigraphic horizons that have undergone different depositional or diagenetic processes.

CONCLUSIONS

1. Low $\delta^{13}C$ values, $\delta^{18}O$ values and Sr concentrations below a previously recognized Type I sequence boundary at the top of the M1 sequence indicate that these geochemical parameters can be used to recognize surfaces

of subaerial exposure in carbonate strata at least as old as the Early Mohawkian (Early Caradoc), Late Ordovician. This result is significant because it demonstrates that these geochemical parameters can be used to recognize surfaces of subaerial exposure in carbonate strata that predate the appearance of vascular land plants at that time. Furthermore, the results suggest that a photosynthesizing biological community of some sort was present on the land surface at this locality in the Early Mohawkian.
2. $\delta^{13}C$, $\delta^{18}O$ and Sr concentration data combine to suggest that a cryptic surface of subaerial exposure is present at the top of a subtidal parasequence. This conclusion is significant because it suggests that surfaces of subaerial exposure may be present at parasequence tops where the sequence stratigraphic method yields no indication of subaerial exposure.
3. $\delta^{13}C$ and Sr concentration data combine to suggest that a cryptic surface of subaerial exposure is present within a subtidal parasequence. This conclusion is significant because it suggests that surfaces of subaerial exposure may be present within parasequences where the sequence stratigraphic method yields no indication of subaerial exposure.
4. Conclusions 2 and 3 together suggest that subaerial exposure may be more common in shallow-water carbonate strata than is apparent from conventional sequence stratigraphy and/or from conventional geochemical sampling involving single samples spaced at vertical distances of 0.5 metres to 5 metres. Instead, replicate geochemical sampling at smaller vertical intervals may be necessary to obtain a more complete record of subaerial exposure and thus of sea-level change.
5. Where multiple samples were taken along individual horizons, the data yield large ranges and variances in geochemical measures. These large variances in the data, combined with the work of Theiling et al. (2007), indicate that multiple samples along individual horizons are necessary for geochemical characterization of strata near surfaces of subaerial exposure.

ACKNOWLEDGEMENTS

We thank Dr. Bethany Theiling for her advice regarding sampling for this project. We thank Dr. Andrew Horbury of Cambridge Carbonates and Dr Ana M. Alonso-Zarza of the Universidad Complutense de Madrid for reviews that improved the manuscript. We also thank the Department of Geology of the University of Georgia for financial support of field and analytical work.

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