# Rapid dissolution of calcareous nannofossils: a case study from freshly cored sediments of the south-eastern Atlantic Coastal Plain

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**Abstract** Rapid dissolution of calcareous nannofossil assemblages from freshly cored sediments is documented over a seven-month period. Examination of a series of smear-slides, made from raw material (a) on the day of coring, (b) 12 days after coring, (c) 42 days after coring, and (d) 222 days after coring, showed that dissolution had already begun to occur 12 days after coring. Complete dissolution of calcareous nannofossil assemblages occurred within seven months, in some cases, Dissolution of these assemblages resulted from the oxidation of iron sulphide, driven by the presence of oxygen, and by the production of gypsum, which occurred during natural drying in storage. Oven-drying of samples greatly increased the rate of dissolution in some samples. The presence of organic matter, such as lignite, and pyrite in sample material also significantly accelerated the rate of dissolution. Loss of calcareous nannofossils through time is obvious when comparing slides originally containing frequent or common assemblages. Abundant nannofloras underwent severe loss as well, although this is not as readily apparent in individual fields of view. By adjusting field-sampling methods, slide-making schedules and laboratory storage techniques, loss of calcareous nannofossils was minimised.

Keywords Calcareous nannofossils, dissolution, Atlantic Coastal Plain

#### 1. Introduction

Over the past several decades, dissolution of in situ calcareous microfossil assemblages has been documented, using a variety of both laboratory and field experiments. Selective dissolution of calcareous nannofossils relative to the lysocline was clearly documented by Berger (1973), who demonstrated the common occurrence of coccolith dissolution on the sea-floor. Roth & Berger (1975) showed that etching, fragmentation and differential dissolution of calcareous nannofossils occurred in surface sediments from the Pacific Ocean at depths greater than 3km. Balsam (1982) and Stuut et al. (2002) recognised that fragmentation of planktonic foraminifera shells increases with increased dissolution and that this carbonate fragmentation index can be used as a proxy for understanding deep-ocean circulation. Thierstein (1980) explored the effects of dissolution on Late Cretaceous and Danian calcareous nannofossil assemblages, by exposing samples at varying depths to corrosive deep-waters of the central North Atlantic. This study resulted in a dissolution index of fossil calcareous nannofossils that is still applicable today.

Although loss of calcareous material at the sediment/water interface due to corrosive deep-water is one of the primary causes of calcareous nannofossil dissolution, other chemical processes have been shown to affect assemblage proportions, especially in the nearshore environment. Reaves (1986) documented that oxidation of ferrous sulphide minerals in intertidal mud-flats resulted in a lowering of *in situ* pH values and consequently to undersaturation with respect to calcium carbonate. Lowered pH values led to extensive dissolution of the shells of living

Mercenaria populations in the study area. Ku et al. (1999) showed that sulphur cycling in organic-rich shelf carbonates is directly linked to carbonate dissolution. Organic matter oxidation can result in a buildup of  $\mathrm{CO}_2$ , which in turn can result in carbonate mineral undersaturation and dissolution (Canfield & Raiswell, 1991). A study by Schulte & Bard (2003), on core material located well above the lysocline, showed a direct link between variations in organic matter flux and calcite dissolution rate.

Additionally, the way in which cores and outcrop material are stored following recovery, and the manner in which they are processed following sampling, can greatly influence calcareous microfossil assemblages. Jutson (1995) noted that dissolution of nannofossils can occur in dry, raw samples stored in laboratories and Geyh et al. (1974) showed that storage of core material in cool or moist conditions can promote bacterial activity and mold growth, which can lead to bacterial sulphate reduction. Desiccation of core material can promote production of increasingly acidic interstitial waters, which in turn leads to the precipitation of gypsum. Schnitker et al. (1980) documented the rapid dissolution of benthic foraminifer faunas in conjunction with the production of 'authigenic' gypsum from cores in the Gulf of Maine. Andruleit et al. (2000) focused on the dissolution of calcareous nannofossil assemblages related to post-sampling processing methods. They observed that a variety of factors, including carbonate content and primary preservation, contribute to the long-term preservational state of calcareous nannofossil assemblages.

The purpose of this study was to document the rate of post-coring dissolution that occurred in calcareous nanno-

fossil assemblages of freshly cored marine sediments that had been stored, and resampled, over a period of seven months. The majority of micropalaeontologists are probably unaware of the rapidity with which such changes can take place, and few have noted if long-term storage has any effect on calcareous microfossil assemblages that are routinely used for biostratigraphy, palaeoecology, or surface-water reconstruction. The results of this study emphasise the need for greater awareness of potential deleterious effects when selecting, preparing and storing material for biostratigraphic and/or quantitative analyses.

# 2. Experimental procedures and materials

Two cores were examined for this study: Elizabethtown (BL-244) and Hope Plantation (BE-110), located in Bladen and Bertie Counties, North Carolina, respectively (Figure 1). Thumbnail-sized sediment samples were extracted from the central portion of core segments in order to avoid the possibility of contamination from the bentonite-based drilling mud (pH7). Slides made from coastal plain sediments typically utilise standard settling procedures as outlined in Edwards *et al.* (1999). However, smear-slides were prepared at a standard thickness for this study, in order to minimise any potential bias in the sample set that might occur during processing.

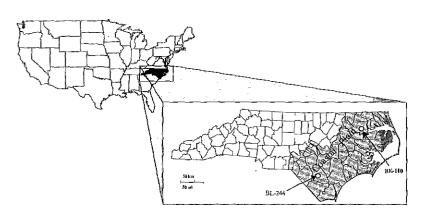


Figure 1: Map showing locations of the Hope Plantation (BE-110) and Elizabethtown (BL-244) Coreholes, North Carolina

A slide-processing schedule for the 26 fossiliferous samples was established and a set of four slides (a, b, c and d) was made from each sample. The 'a' slides were made at the drill-site the same day the sample was cored. The remaining sample material was then bagged and sent to the calcareous nannofossil laboratory, where it was stored at a constant temperature (24°C/75°F) and low humidity. The 'b' slides were made in the laboratory 12 days after the 'a' slides were prepared, the 'c' slides were made one month after the 'b' slides (42 days after coring), and the 'd' slides were produced six months after the 'c' slides (222 days after coring), all from the same, bagged sample material that was used to produce the 'a' slides at the drill-site. In all, some sediment for each sample

remained in the sample bag, unprocessed, for a total of 222 days. The slide sets were then examined for calcareous nannofossils.

All slides were examined using standard light microscope techniques on a Zeiss Photomicroscope 3. Initially, each slide was scanned at 1250x magnification to determine relative calcarcous nannofossil abundance: abundant = >10 specimens per field of view (FOV); common = 1-10 specimens per FOV; frequent = 1 specimen per 1-10 FOV; rare = 1 specimen per 11-50 FOV. Following this general scan, each slide was re-examined for 150 FOV, and counts of all identifiable nannofossils were recorded. Severely broken specimens (less than half remaining) were not included in the tally. Samples and slides are curated at the US Geological Survey calcareous nannofossil laboratory in Reston, Virginia (USA).

#### 3. Results

Nineteen samples from Hope Plantation and seven samples from Elizabethtown were examined and found to contain calcareous nannofossil assemblages. Additional samples were examined for calcareous nannofossil content, found to be barren, and were not included in this experiment.

Examination of the calcareous nannofossil data shows a clear correlation between decreasing nannofossil abun-

dance and time elapsed after coring (Tables 1, 2; Figures 2, 3). In all of the Elizabethtown samples, and 11 of the Hope Plantation samples, the number of specimens calcareous nannofossil decreased significantly from the 'a' slides, which were made on-site the day that core was extracted from the ground, to the 'b' slides, made 12 days later. In six of the Hope Plantation samples, the 'b' slides had more specimens than the 'a' slides, and this most likely represents differences in smear thickness that resulted from the preparation technique. In all but one slide examined (NJ1928), abundance of calcareous nannofossils per 150 FOV decreased from the 'a' slides to the 'd'

slides (Plate 1). Sample abundance in NJ1928 remained the same throughout the study. In some cases, the decrease in calcareous nannofossil abundance was substantial, and sediment that was catalogued as having abundant calcareous nannofossils at the drill-site was barren in seven months (e.g. sample NJ1934, Hope Plantation core; Table 1).

In the Hope Plantation core, sediment that contained abundant calcareous nannofossils when extracted on the day it was cored saw an average 55.7% reduction in abundance within seven months (Table 3). Similarly, sediment that was recorded as having common calcareous nannofossils on the day it was cored showed a 60.8% average decrease in abundance, and samples having frequent or

Sample #	Depth (m)	a slide	b slide	c slide	d slide
NJ1929	29.4	2439	3512	2068	1965
NJ1930	31.1	3409	3111	2348	2472
NJ1931	32.6	3076	3042	3289	2351
NJ1932	35.6	3308	3048	2797	2306
NJ1933	37.2	1582	1428	996	229
NJ1934	38.7	1618	1624	1471	0
NJ1935	40.4	2556	1682	1512	887
NJ1936	41.8	2373	1702	1334	141
NJ1924	197.0	84	22	15	22
NJ1925	197.1	63	59	39	26
NJ1926	197.7	6	6	0	0
NJ1928	199.2	1	1 '	1	1
NJ1941	200.1	5	6	0	0
NJ1949	206,3	33	45	1	4
NJ1950	209.2	16	0	0	0
NJ1951	212.1	12	93	20	7
NJ1952	214.0	316	167	234	170
NJ1953	217.8	292	375	200	122
NJ1954	218.7	1167	1146	818	255

Table 1: Number of calcareous nannofossils per 150 FOV per slide, Hope Plantation core

Sample #	Depth (m)	a slide	b slide	c slide	d slide
NJ1959	13.4	42	40	11	10
NJ1961	17.2	2	0	0	0
NJ1968	160.5	54	16	7	7
NJ1969	162.4	87	56	40	8
NJ1972	165.0	142	138	64	24
NJ1970	166,0	10	9	8	4
NJ1971	168.0	16	5	0	0

Table 2: Number of calcareous nannofossils per 150 FOV per slide, Elizabethtown core

Sample #	Depth (m)	% Reduction
NJ1929	29.4	19,4
NJ1930	31.1	27.5
NJ1931	32.6	23.6
NJ1932	35.6	30.3
NJ1933	37.2	85.5
NJ1934	38,7	100,0
NJ1935	40,4	65.3
NJ1936	41.8	94.0
NJ1924	197.0	73.8
NJ1925	197.1	58.7
NJ1926	197.7	100.0
NJ1928	199,2	*
NJ1941	200.1	100.0
NJ1949	206.3	87.9
NJ1950	209.2	100.0
NJ1951	212.1	41.7
NJ1952	214.0	46.2
NJ1953	217,8	58.2
NJ1954	218.7	78.1

Table 3: Percent reduction in Hope Plantation calcareous nannofossil assemblages between 'a' and 'd' slides (approximately seven months). \*Indicates no change in calcareous nannofossil abundance

Table 4: Percent reduction in Elizabethtown calcareous nannofossil assemblages between 'a' and 'd' slides (approximately seven months)

Sample #	Depth (m)	% Reduction
NJ1959	13.4	76.2
NJ1961	17.2	100.0
NJ1968	160.5	87.0
NJ1969	162.4	90.8
NJ1972	165.0	83,1
NJ1970	166.0	60.0
NJ1971	168.0	_100.0

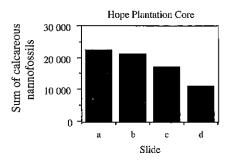
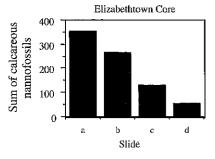


Figure 2: Histogram showing total number of calcareous nannofossil specimens tallied from 'a', 'b', 'c', and 'd' slides, Hope Plantation core. Note decreasing calcareous nannofossil numbers from 'a' slides (made on day of coring) to 'd' slides (made 222 days after coring)

Figure 3: Histogram showing total number of calcareous nannofossil specimens tallied from 'a', 'b', 'c', and 'd' slides, Elizabethtown core. Note decreasing calcareous nannofossil numbers from 'a' slides (made on day of coring) to 'd' slides (made 222 days after coring)



Sample #	Depth (m)	a slide	b slide	c slide	d slide
NJ1929	29.4	47	52	71	90
NJ1930	31.1	42	54	63	68
NJ1931	32,6	50	62	68	72
NJ1932	35.6	47	75	81	88
NJ1933	37.2	78	94	113	143
NJ1934	38.7	87	90	106	0
NJ1935	40.4	64	76	85	J <b>2</b> 1
NJ1936	41.8	85	106	135	164
NJ1924	. 197.0	141	230	321	354
NJ1925	197.1	170	206	260	278
NJ1926	197.7				
NJ1928	199.2				
NJ1941	200, L		Too sparse	for count	s
NJ1949	206.3				
NJ1950	209.2				
NJ1951	212.1	346	366	968	1431
NJ1952	214.0	158	190	204	223
NJ 1953	217.8	157	160	175	193
NJ1954	218.7	82	112	139	165

Table 5: Number of calcareous nannofossil fragments per 100 whole nannofossils per slide, Hope Plantation core

Sample #	Depth (m)	a slide	b slide	c slide	d slide	
NJ1959	13.4	344	361	549	866	
NJ1961	17.2		Too spars	e for coun	ts	
NJ1968	160.5	305	575	1017	1220	
NJ1969	162.4	195	235	328	983	
NJ1970	0.661		Ton spars	e for coun	ts	
NJ1971	0.831	Too sparse for counts				
NJ1972	165.0	135	211	323	453	

Table 6: Number of calcareous nannofossil fragments per 100 whole nannofossils per slide, Elizabethtown core

inc. diss.

150 250

Fragments per 100 whole specimens

50

50

50

50 150 250

Fragments per 100 whole specimens

350

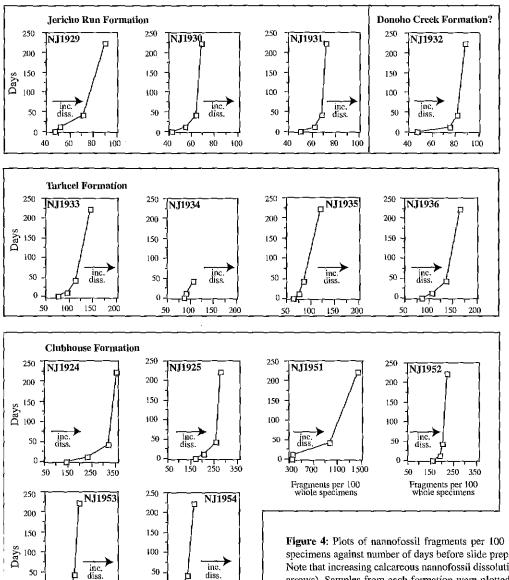


Figure 4: Plots of nannofossil fragments per 100 whole calcareous nannofossil specimens against number of days before slide preparation, Hope Plantation core. Note that increasing calcareous nannofossil dissolution is to the right (indicated by arrows). Samples from each formation were plotted at the same scale, except for NJ1951 (Clubhouse Formation), which had to be plotted at a different scale due to the excessive number of fragments recorded. Sample NJ1934 has no data point for the 'd' slide (222 days) because it was barren. See Table 1 for depth of samples in

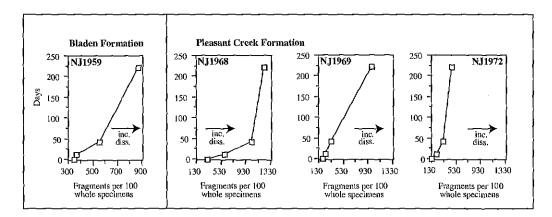


Figure 5: Plots of nannofossil fragments per 100 whole calcareous nannofossil specimens against number of days before slide preparation, Elizabethtown core. Note that increasing calcareous nannofossil dissolution is to the right (indicated by arrows). See Table 2 for depth of samples in core

rare calcareous nannofossil assemblages when freshly cored record an average 70.3% reduction in abundance. Of the 19 samples examined from Hope Plantation, four were barren and eight had calcareous nannofossil assemblages reduced by more than 50% within 222 days after coring (Table 3). The remaining seven samples experienced calcareous nannofossil assemblage reduction of between 19.4 and 46.2%. Samples from the Elizabethtown core contained only frequent or rare assemblages on the day of coring. Of the seven productive samples, two were barren and the remaining five had calcareous nannofossil assemblages reduced by 60.0% or more within 222 days after coring (Table 4). Calcareous nannofossil assemblages from Elizabethtown were reduced by an average 85.3% within seven months.

As a means of estimating dissolution and removing any bias from the specimen counts that may have been introduced during the slide-making process, calcareous nannofossil fragments per 100 whole nannofossil specimens were counted and plotted against number of days after coring (Figures 4, 5; Tables 5, 6). Several clear patterns emerge from this dataset. In the Hope Plantation core, samples that remained abundant throughout the entire 222 days experienced the most rapid dissolution within the first 42 days following coring (Figure 4; Samples NJ1929, NJ1930, NJ1931 and NJ1932), and then dissolution rates between 42 and 222 days slowed considerably. Abundant samples from different formations showed slight variations in dissolution rates. For example, Sample NJ1932, from the Donoho Creek Formation, experienced rapid dissolution in the first 12 days, which was then followed by moderate to slow dissolution rates over the next 112 days. However, Samples NJ1929, NJ1930 and NJ1931, from the Jericho Run Formation, experienced rapid to moderate dissolution for the first 42 days, and moderate to slow rates of dissolution for the remaining six months. In comparison, dissolution rates were higher in samples from marginal (Tar Heel Formation: NJ1933, NJ1934, NJ1935 and NJ1936) and shallow marine settings (Clubhouse Formation: NJ1952, NJ1953 and NJ1954), as evidenced by the increased number of fragments per 100 whole specimens counted (Figure 4). Dissolution rates from the Clubhouse Formation were high in the upper part of the formation (Figure 4; NJ1924, NJ1925, NJ1951), as evidenced by the rapid increase in fragmentation seen in Sample NJ1951, but remained slow in the basal part of the formation (NJ1952, NJ1953, NJ1954), despite the lack of any obvious lithological differences between the basal and upper parts of the sections (Weems et al., in press). This pattern is also seen in samples from the Elizabethtown core, which shows rapid dissolution rates at the top of the Pleasant Creek Formation and slow to moderate rates near the base of the section (Figure 5). Sample NJ1959 from the Bladen Formation (Elizabethtown core) has an assemblage that records very slow dissolution rates for the first 12 days, followed by rapid dissolution over the next six months. As expected, the number of fragments per 100 whole specimens increased as calcareous nannofossil abundance decreased. High fragment amounts in sediments with low initial abundances suggest that sediments with low initial calcareous nannofossil abundances most likely experienced *in situ*, natural, dissolution before coring (*e.g.* NJ1951, NJ1924; Figure 4). Overall, the rate and amount of dissolution was higher in sediments from the Elizabethtown core.

In almost every sample, dissolution rates were rapid in the days and weeks following coring, and then decreased slowly over time, usually after 42 days. Complete dissolution of calcareous nannofossils was rare. This pattern is what would be expected if conditions stayed constant during storage while the carbonate system equilibrated. If equilibrium was attained quickly, then complete loss of calcareous nannofossil assemblages was avoided. This could explain why some sample material that has been in storage for over 50 years still has nominal calcareous nannofossil assemblages (JMS-T, unpublished data).

#### 4. Discussion

Chemistry and lithology are the two most likely controlling factors in post-coring diagenesis of calcareous nannofossil assemblages in the studied suite. An understanding of the processes that occur during chemical interactions between oxygen, water, iron and calcite is necessary in order to understand the sequence of events that can lead to calcareous nannofossil dissolution.

#### 4.1 Chemistry

Dissolution of calcareous nannofossils in the studied cores is most likely occurring due to a combination of three separate processes: pyrite oxidation, gypsum production, and bacterial activity. Sediments of the southeastern Atlantic Coastal Plain were deposited in environments that ranged from fluvial to neritic, and which commonly contain terrestrially-derived material in the form of pollen and spores (Christopher & Prowell, 2002) and lignite. Total organic content in any cored interval can be as high as 30% (Self-Trail et al., 2004; Weems et al., in press). Sediments rich in organic matter commonly contain disseminated pyrite and/or pyrite and marcasite nodules. If the sediments contain pyrite or marcasite, when the core comes in contact with oxygen, pyrite oxidation can occur, as demonstrated by the chemical equations:

$$FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (1)

$$Fe^{2+} + 0.25O_2 + 2.5H_2O = Fe(OH)_3 + 2H^+$$
 (2)

These reactions generate acidity, which dissolves calcium carbonate, as demonstrated by the chemical equation:

$$CaCO_3 + H^+ \le Ca^{2+} + CO_2(g) + OH^-$$
 (3)

Dissolution will occur as long as oxygen and iron are available to drive the reaction, or until all calcium carbonate is dissolved.

In addition to pyrite oxidation, precipitation of gypsum occurred where conditions were suitable, causing further degradation of the sample material. Gypsum precipitated upon desiccation of interstitial water, which usually occurred during sample storage. In organic-rich sediments under arid conditions, gypsum has been noted to form in a matter of hours (Briskin & Schreiber, 1978). Precipitation is encouraged by both natural evaporation and forced drying in convection ovens. Free calcium (Ca<sup>2+</sup>) is supplied by the dissolution of calcareous fossils (molluses, calcareous nannofossils and foraminifera), and sulphate (SO<sub>4</sub><sup>2+</sup>) is produced from pyrite oxidation, following the equation:

$$Ca^{2+} + SO_4^{2+} + H_2O = CaSO_4.H_2O$$
 (4)

Since desiccation of samples may promote supersaturation with respect to gypsum, drying of samples could result in a greater loss of calcareous nannofossil data.

A third means of sample degradation is through bacterial activity, which can occur both in situ and immediately following coring. Bacteria can tolerate a wide range of pH conditions, most notably sulphide-oxidising bacteria, which can survive in an acidic pH range of 3.0 to 4.0 (Chapelle, 1993). Additionally, 'iron bacteria', a group of aerobic bacteria that oxidises ferrous iron as

a source of energy and that live at the interface of anaerobic and aerobic environments, become active when a constant source of oxygen is supplied. These microorganisms can be activated directly following drilling, when subsurface sediments are exposed to oxygen. If dissolved

Fe<sup>2+</sup> is present, as is often the case in inner to middle neritic and/or marginal marine sediments, then oxidation can occur, as demonstrated by Equation 2, above. Although dissolution of calcareous nannofossils has not yet been directly linked to bacterial activity, it is clear from the

experiments and observations of Chappelle (1993) that iron-oxidising bacteria exist in abundance in freshly cored sediments of the south-eastern Atlantic Coastal Plain, and it is possible that these microorganisms are contributing to the oxidation process that ultimately results in dissolution of calcareous nannofossils.

#### 4.2 Lithology

Sediment type can affect the post-coring dissolution

process to varying degrees. Examination of calcareous nannofossil samples, with regards to lithology and sedimentology, shows that several accessory components play an important role in calcareous nannofossil dissolution. Samples free of lignite or pyrite typically contain more abundant and diverse calcareous nannofossil assemblages. This is not surprising, since the oxidation process is significantly decreased in the absence of organic material and pyrite. Presence of pyrite and/or lignite is more significant than grain size, as is clearly demonstrated by samples examined from the Jericho Run and Tar Heel Formations in the Hope Plantation core (Figure 4; Table 7) and the Bladen and Pleasant Creek Formations in the Elizabethtown core (Figure 5; Table 8). The fine-silty, organic-poor sands of the Jericho Run Formation preserved calcareous nannofossil assemblages better than the clayey silts of the slightly organic Tar Heel Formation (Table 7) and the organic-rich, clayey silts and silty clays

Sample #	Depth (m)	Lithology	% Glauconite	% Pyrite	% Phosphate	% Shell material	% Organics
NJ1929	29.4	sand, f-c	0	0	10	<1	0
NJ 1930	31.1	sand, f-m	5	0	0	<i< td=""><td>0 ]</td></i<>	0 ]
NJ1931	32.6	sand, f-m	5	0	0	<1	0
NJ1932	35.6	sand, f	30	0	</td <td><li>&lt;1</li></td> <td>&lt;1</td>	<li>&lt;1</li>	<1
NJ1933	37.2	clayey silt	0	2	0	<1	2
NJ1934	38.7	clayey silt	0	2	0 1	<l< td=""><td>2</td></l<>	2
NJ 1935	40.4	clayey silt	0	2	0	i	2
NJ1936	41.8	clayey silt	0	2	0 1	1	2
NJ 1924	197.0	micrite	0	0	0	10	2
NJ1925	197.1	micrite	0	0	0	10	2
NJ1926	197.7	sand, vf	0	0	0	2	0
NJ1928	199.2	sand, vf	0	0	0	5	0
NJ1941	200.1	sand, vf	3	0	0	7	</td
NJ1949	206.3	sand, vf	0	0	0	2	<1
NJ1950	209.2	sand, vf-f	0	0	0	10	2
NJ1951	212.1	sand, vf-f	0	0	0	10	2
NJ 1952	214,0	sand, vf-f	<1	0	0	3	0
NJ1953	217.8	sand, vf-f	. <i< td=""><td>0</td><td>0</td><td>&gt;10</td><td>0 1</td></i<>	0	0	>10	0 1
NJ1954	218,7	sand, vf-f	<1	0	0	>10	0

**Table 7:** Lithology and sedimentology of samples from the Hope Plantation core. Percentages are estimates obtained from examination of core material on-site (Weems *et al.*, in press)

**Table 8:** Lithology and sedimentology of samples from the Elizabethtown core. Percentages are estimates obtained from examination of core material on-site (Self-Trail *et al.*, 2004)

Sample#	Depth (m)	Lithology	% Glauconite	% Pyrite	% Phosphate	% Shell material	% Organics
NJ1959	13.4	silt, calcareous	0	Ö	a	0	2
NJ1961	17.2	sand, f-m	0	0	D D	0	0
NJ1968	160.5	clayey silt	0	2	a	<l< td=""><td>7</td></l<>	7
NJ1969	162.4	silty clay	a	2	0	3	5
NJ1972	165,0	silty clay	0	2	0	3	4
NJ1970	166,0	silty clay	0	t t	0	· <1	2
NJ1971	168,0	sisty clay	0	0	0	3	<u> </u>

of the Bladen and Pleasant Creek Formations, which were highly destructive to calcareous nannofossil assemblages (Table 4).

The presence or absence of glauconite, phosphate and/or shell material, all common constituents in sediments representative of inner to outer neritic environments of deposition, does not appear to be significant with regard to calcareous nannofossil dissolution. Varying amounts of these constituents occur in samples with low

incidence of calcareous nannofossil dissolution, as well as high incidence of dissolution in our suite.

#### 5. Conclusions

Analysis of calcareous nannofossil assemblages from freshly cored sediments from the south-eastern Atlantic Coastal Plain over a period of seven months clearly documents their rapid dissolution. In some cases, dissolution is so rapid that biostratigraphic analyses have been compromised and samples known to contain calcareous nannofossils from temporary smear-slides made in the field are barren by the time permanent slides are made in the laboratory. The results of this study imply that samples extracted from core material that has been in storage for greater than six months could possibly contain calcareous nannofossil assemblages that have been severely compromised, especially if organic matter is present. Thus, research that relies on biostratigraphic or statistical analyses of calcareous nannofossil assemblage data from organic-rich sediments should be conducted on freshly cored samples, in order to preclude diagenetic affects from potential geochemical reactions.

Samples containing abundant calcareous nannofossils are typically assumed to be relatively free of diagenetic alteration. However, examination of Samples NJ1929-NJ1932 (Table 1) clearly shows that this is not entirely true. The nannofloras remained abundant throughout the time-frame of the experiment, yet are clearly undergoing dissolution, as evidenced by the decreased number of specimens per 150 FOV and by the increase in fragment: whole specimen ratio through time.

The observation that rapid dissolution of calcareous nannofossil assemblages from the Hope Plantation and Elizabethtown cores occurred within the first two weeks following coring is of importance to micropalaeontologists. However, by adjusting our field sampling and sample storage methods, loss of data was minimised (JMS-T, unpublished data). Recognition of factors that can contribute to the rapid dissolution of calcareous nannofossils (e.g. the presence of pyrite in sediments) can be used to dictate changes in sample storage and/or processing methods. Guidelines include: (1) prone sediment samples should be processed as quickly as possible following coring. High quality smear-slides can be produced in the field with minimal effort; (2) exposure of prone sample material to oxygen should be limited. Oxygen provides the energy needed to drive deleterious chemical and bacterial reactions. Freeze-drying or vacuum-packing samples may provide a temporary means of transporting samples from the field to the lab without the loss of additional assemblage data; (3) if samples are very wet and need to be dried before storage, use low heat (<50°C) and remove samples quickly once dry. Gypsum formation occurs naturally during air-drying, but can also be accelerated with the addition of heat; (4) recognise that core samples that have remained unprocessed for any length of time may already be compromised, even if the nannofloras are abundant and look pristine (e.g. Samples NJ1929-NJ1932). There is no way of knowing how much dissolution has occurred without first viewing a comparison smear-slide made on the day of coring.

This study represents only the first step towards understanding the effect that post-sampling dissolution has on calcareous nannofossil assemblages. Comparative studies, focusing on differing lithologies and environmental settings are needed, and both outcrop and cored sediments should be examined. Additionally, the effects of post-sampling dissolution on species diversity and assemblage composition need to be documented from a variety of environmental settings. Self-Trail and Seefelt (in prep.) are currently investigating changes in assemblage dynamics from the Hope Plantation and Elizabethtown samples.

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#### References

Andruleit, H., Kothe, A., Stager, S. & Bruns, A. 2000. Some comments concerning processing and dissolution. *Journal* of Nannoplankton Research, 22(3): 201.

Balsam, W.L. 1982. Carbonate dissolution and sedimentation on the Mid-Atlantic continental margin. Science, 217: 929-931.

Berger, W.H. 1973. Deep-sea carbonates: evidence for a coccolith lysocline. *Deep-Sea Research*, **20**: 917-921.

Briskin, M. & Schreiber, B.C. 1978. Authigenic gypsum in marine sediments. *Marine Geology*, **28**: 37-49.

Canfield, D.E. & Raiswell, R. 1991. Carbonate precipitation and dissolution: Its relevance to fossil preservation. *In*: P.A. Allison & D.E.G. Briggs (Eds). *Taphonomy: Releasing the Data Locked in the Fossil Record*, 9: 411-453.

Chapelle, F.H. 1993. Ground-water microbiology and geochemistry. John Wiley & Sons, Inc., New York: 424pp.

Christopher, R.A. & Prowell, D.C. 2002. A palynological biozonation for the Maastrichtian Stage (Upper Cretaceous) of South Carolina, USA. Cretaceous Research, 23: 639-669.

Edwards, L.E., Gohn, G.S., Self-Trail, J.M., Prowell, D.C., Bybell, L.M., Bardot, L.P., Firth, J.V., Huber, B.T., Frederiksen, N.O. & MacLeod, K.G. 1999. Physical stratigraphy, paleontology, and magnetostratigraphy of the USGS-Santee Coastal Reserve core (CHN-803), Charleston County, South Carolina. US Geological Survey Open-File Report 99-308: 1-65.

Geyh, M.A., Krumbein, W.H. & Kudrass, H.R. 1974. Unreliable <sup>14</sup>C dating of long-stored deep-sea sediments due to bacterial activity. *Marine Geology*, 17: 45-50.

Jutson, D.J. 1995. The case of the missing nannofossil or 'Now you see it, now you don't'. The 6th International

- Nannoplankton Association Conference, Copenhagen, Denmark, September 2-7, 1995, Programme and Abstracts: 64
- Ku, T.C.W., Walter, L.M., Coleman, M.L., Blake, R.E. & Martini, A.M. 1999. Coupling between sulfur recycling and syndepositional carbonate dissolution: Evidence from oxygen and sulfur isotope composition of pore water sulfate, South Florida Platform, U.S.A. Geochimica et Cosmochimica Acta, 63(17): 2529-2546.
- Reaves, C.M. 1986. Organic matter metabolizability and calcium carbonate dissolution in nearshore marine muds. *Journal of Sedimentary Petrology*, **56**(4): 486-494.
- Roth, P.H. & Berger, W.H. 1975. Distribution and dissolution of coccoliths in the south and central Pacific. In: W.V. Sliter, A.W.H. Bé & W.H. Berger (Eds). Dissolution of deep sea carbonates. Cushman Foundation for Foraminiferal Research, Special Publication, 13: 87-113.
- Schnitker, D., Mayer, L.M. & Norton, S. 1980. Loss of calcareous microfossils from sediments through gypsum formation. *Marine Geology*, 36: M35-M44.
- Schulte, S. & Bard, E. 2003. Past changes in biologically mediated dissolution of calcite above the chemical lysocline recorded in Indian Ocean sediments. Quaternary Science Reviews, 22: 1757-1770.
- Self-Trail, J.M., Wrege, B.M., Prowell, D.C., Seefelt, E.L. & Weems, R.E. 2004. Preliminary physical stratigraphy and geophysical data of the USGS Elizabethtown core (BL-244/BL-C-1-2003), Bladen County, North Carolina. US Geological Survey Open-File Report 2004-1301: 1-297.
- Stuut, J.-B.W., Prins, M.A. & Jansen, J.H.F. 2002. Fast reconnaissance of carbonate dissolution based on the size distribution of calcareous ooze on Walvis Ridge, SE Atlantic Ocean. *Marine Geology*, 190: 581-589.
- Thierstein, H.R. 1980. Selective dissolution of Late Cretaceous and earliest Tertiary calcareous nannofossils: Experimental evidence. *Cretaceous Research*, 2: 165-176.
- Weems, R.E., Wrege, B.M., Self-Trail, J.M., Prowell, D.C., McCartan-Durand, C., Seefelt, E.L., Cobbs III, E.F. & McKinney, C. In press. Preliminary physical stratigraphyand geophysical data of the USGS Hope Plantation core (BE-110-2004), Bertie County, North Carolina. US Geological Survey Open-File Report.

## Plate 1

Representative FOV pictures of an abundant (NJ1936), common (NJ1954) and frequent (NJ1969) sample: (a) on day of coring; (b) 12 days after coring; (c) 42 days after coring; and (d) 222 days after coring. Note successive decrease in calcareous nannofossil abundance from 'a' to 'd' slides in all three examples. Light microscope pictures were taken at 1250x magnification and do not represent an entire field of view

