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An improved sample preparation technique for calcareous nannofossils in organic-rich mudstones

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Abstract Calcareous nannofossils have been routinely applied as a biostratigraphic tool in the oil industry for many decades. Industrial samples are traditionally prepared using a slurry-smear technique, which is relatively fast, simple and uses no chemicals. Recent increases in unconventional resource plays in the oil industry have resulted in a significant number of nannofossil biostratigraphy projects derived from organic-rich source-rocks. While slurry-smear slides are satisfactory for nannofossil samples in most lithologies, this preparation technique has proved insufficient for such samples. Shale-gas source-rocks are often rich in clays, silts, opaque minerals and organic components. In addition, amorphous organic material in the sediment can bond grains together, trapping nannofossil specimens and impeding identification. We propose a modified method of sample preparation for calcareous nannofossils that minimises these issues and increases the number of identifiable specimens. This relatively simple method is modeled after foraminifera cleaning techniques for palaeothermometry, which focus on minimising adulteration of fossil specimens. The proposed technique for calcareous nannofossils uses sodium hypochlorite to lighten the organic matter and to aid in the dissociation of nannofossils from background sediments. Semi-quantitative analysis shows significant reduction in organic matter, and increases in relative abundance and species richness. The technique was applied to samples from the Upper Cretaceous Eagle Ford and La Luna Formations and the Upper Jurassic-Lower Cretaceous Haynesville Formation. Overall, the method is relatively quick, and minor increases in sample preparation time are offset by improved data quality and potential for higher-resolution biostratigraphy in unconventional resource plays.

Keywords calcareous nannofossils, sample preparation, sample processing, organic-rich mudstones, unconventional hydrocarbon resources

1. Introduction

Calcareous nannofossils are the remains of coccolithophores (photosynthetic, unicellular algae of Division Haptophyta), which are generally high in abundance and diversity in open-marine settings. The biostratigraphic utility of these microfossils has been significant in both industry and academia since the 1960s, and they continue to be a key component in biostratigraphic analysis. Industrial calcareous nannofossil samples (usually in the form of cuttings) are commonly prepared as slurry-smear slides (following Watkins & Bergen, 2003). This method is relatively fast and simple, and uses only dilute (10%) hydrochloric acid (HCl) for cleaning glassware between samples, yielding excellent results in most lithologies (Plate 1).

Recently, the hydrocarbon industry has developed assets in unconventional resources, such as shale-gas plays (Holditch, 2003; Boughal, 2008; Stevens & Kuushraa, 2009; Toon, 2011; Leimkuhler & Leveille, 2012). Lithologies from shale-gas plays tend to be high in clays, opaque minerals, such as pyrite and marine-derived amorphous organic matter (AOM), with intermittent terrestrial organics. When prepared using the slurry-smear method, these components significantly obscure individual nannofossil specimens and can cause aggregations of nannofossils and background sediments (Plate 1). This impedes species-level identification of nannofossil specimens and can skew abundance and diversity data. With an increasing number of industry-based biostratigraphy projects derived from shale-gas assets, we address the need for a modified nannofossil sample preparation technique that both lightens organic matter and dissociates specimens from AOM and clays, without the dissolution of carbonate or the mechanical degradation of nannofossil specimens.

2. Methodology

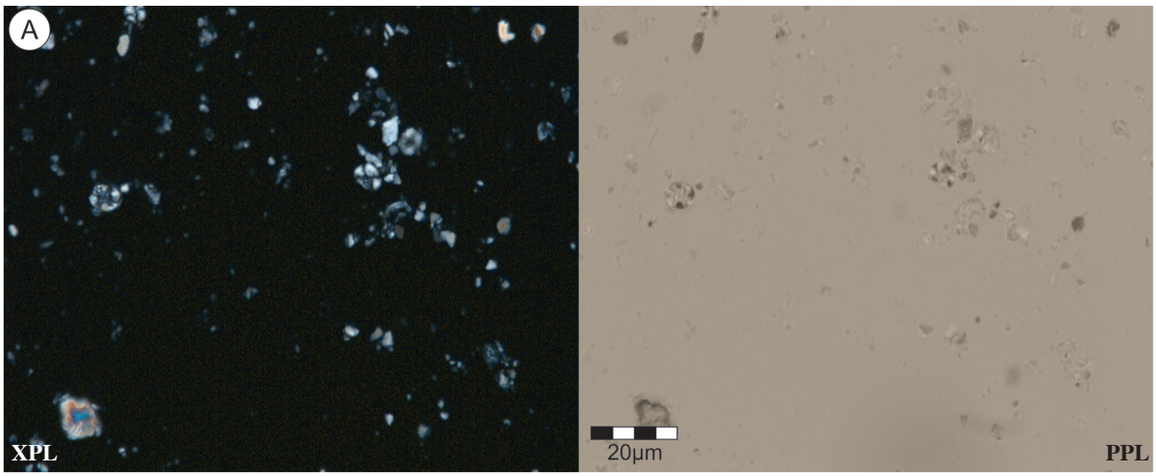
2.1 Experimentation

The sample preparation method presented here is based on foraminifera cleaning procedures for palaeothermometry, which are designed to remove clays and organic material without altering either morphology or isotopic ratios. Such procedures are often of extended duration (Bice & Norris, 2005; Blanco-Ameijeiras *et al*., 2012), going to great lengths to ensure that dissolution of fossil carbonate is minimised. The goal of this study was to modify such preparation procedures for the needs of nannofossil identification using basic light microscopy at ~1000–1250x magnification.

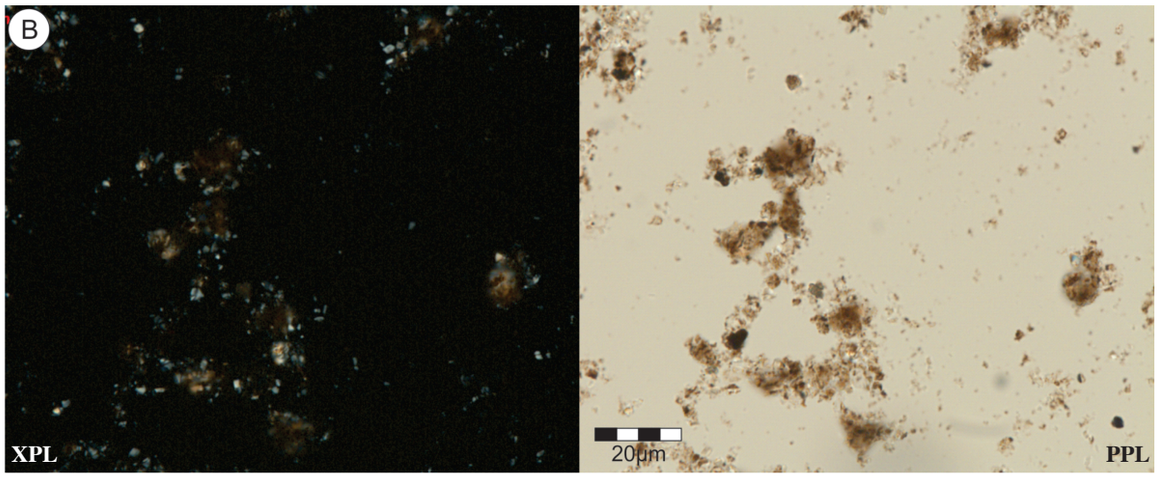
Several cleaning procedures were compared (Ander-

Plate 1

Comparison of slurry-smear slide preparations of (**A**) carbonate-dominated *vs*. (**B**) organic-rich lithologies
Organic matter particularly evident in Eagle Ford Fm in PPL (lower right)
Photomicrographs taken at 630x magnification for wider FOV



open-marine chalk, Swanage, southern England



restricted-marine organic-rich mudstone, Eagle Ford Formation, Texas, USA

son, 1961; Clark, 1973; Hodgkinson, 1991; Martin & Lea, 2002; Barker *et al*., 2003; Bice & Norris, 2005; Weldeab *et al*., 2006; Krause-Nehring *et al*., 2011; Blanco-Ameijeiras *et al*., 2012) and were considered for both the base procedure and potential modifications. Our final procedure uses sodium hypochlorite (NaClO - bleach), as it was noted for its superior cleaning ability and relatively low potential for reactivity (Anderson, 1961; Hodgkinson, 1991; Gaffey & Bronnimann, 1993; Pingitore *et al*., 1993; Bice & Norris, 2005). We eliminated a buffered hydrogen peroxide (H_2O_2) solution as the primary reagent, because of its potential for reaction with organic matter and production of formic acid, which can dissolve carbonate fossils (Anderson, 1961; Hodgkinson, 1991; Gaffey & Bronnimann, 1993). In addition, some studies have shown hydrogen peroxide to be less effective than bleach in the lightening of organic matter (Hodgkinson, 1991; Bice & Norris, 2005).

The basic cleaning procedure was tested at 9.0, 9.5 and ~12.0pH (pure household bleach). For each pH level, samples were exposed to one, two or three iterations of the cleaning procedure. Although initial trials showed a notable reduction of organic matter at 9.0 and 9.5pH, significant amounts remained in the final slide preparations. Bice & Norris (2005) achieved exceptional results using pure bleach (5.25-6.0% NaClO by volume), so this more aggressive approach was included in later trials. Though initial readings of pure bleach are notably basic (~11.5-12.0pH), the pH decays rapidly through the reaction with

organic matter at elevated temperatures, stabilising between 9.0-9.5pH.

In addition to variations in pH and number of cleaning iterations, samples were compared with and without the use of an ultrasonic bath. It is suspected that ultrasonic pressure may damage microfossils (Hodgkinson, 1991). Research by Clark (1973) detailed such effects, but also identified an ideal time/pressure relationship for such cleaning procedures. This requires an ultrasonic bath capable of changes in frequency. While we acknowledge the potential for ultrasonic cleaning in nannofossil preparation, particularly in more lithified samples, we saw no significant difference in our samples prepared with and without an ultrasonic bath. We conclude that ideal results can be achieved without this process.

The final procedure (detailed below) is a modification of Bice & Norris (2005) and Anderson (1961). A primary goal was to identify maximum effectiveness with minimal processing, and to decrease potential damage to fossil specimens and subsequent data. Optimum results were achieved with two iterations of the bleach-cleaning/bicarbonate-washing procedure and no ultrasonic bath. The best results were achieved using pure bleach. *Clorox*-brand bleach is recommended, as it has the highest NaClO by volume (6%) and, therefore, stronger cleaning potential. Duration of washing is based on Anderson (1961). The bleaching is followed by washing with a bicarbonate solution to disperse the sample. Thorough washing with deionised water is critical after applying the bicarbonate solution, as detailed in Step 3, below. We found that insufficient washing results in residual bicarbonate ions, which recrystallise on drying, obscuring a significant proportion of the coverslip. With batch-processing, this should not inhibit preparation efficiency. Finally, use of the centrifuge separates the sample into two distinct layers. We prepared slides from both layers, as well as from mixed samples. We consistently found optimum nannofossil concentrations in the lower (darker) layer, while the upper (lighter) layer is dominated by clays. Until further investigation, we suggest preparation of two slides, one from each layer, to minimise potential issues with size fractionation.

2.2 Resultant procedure

Preparation: Place ~0.1g of sample into a 15ml glass centrifuge tube. Fill a beaker with ~5-6cm of water and place on a hot-plate. Steps 1-3 must be conducted under a fume hood.

Step 1 - NaClO wash: Add 3ml pure bleach to the sample, then place the centrifuge tube on a Vortex mixer at medium speed for 3-5 seconds to ensure good contact between sediment and reagent. Boil the sample in a water-bath for 15 minutes. Centrifuge the sample at 1000rpm for 7 minutes, then decant the supernatant. Repeat Step 1.

Step 2 - $NaHCO_3$ wash: Add ~5ml of 9.5pH sodium bicarbonate solution to the sample, then place the centrifuge tube on a Vortex mixer at medium speed for 3-5 seconds. Boil the sample in a water-bath for 15 minutes. Centrifuge at 1000rpm for 7 minutes, then decant the supernatant. Repeat Step 2, but *instead*, centrifuge the sample at 2500rpm for 10 minutes.

Step 3 - H_2O wash: Add 5 ml deionised water to the sample, then place the centrifuge tube on a Vortex mixer at medium speed for 5-10 seconds. Centrifuge the sample at 2000rpm for 4 minutes, then decant the supernatant. Repeat this process for a total of 3 iterations. After the final (third) decanting, add 5ml of deionised water and place the centrifuge tube on a Vortex mixer at low speed to mix overnight, if possible, or for a minimum of 4 hours. Centrifuge at 2000rpm for 10 minutes, then decant the supernatant.

Step 4 - slide preparation: After the final centrifugation, the sample will be separated into two layers. Prepare a slide from each layer, using the method of Watkins & Bergen (2003). If dispersion of sediment across the coverslip is sufficient on initial application, a double-slurry preparation may not be necessary. Take care not to overload the coverslip with sediment. Optimum thickness can often be judged by placing the coverslip on a sheet of white paper; ideally, the coverslip should look very slightly dusty, though it should be noted that sediment colour can vary.

Most centrifuge and Vortex machines can hold six or more samples, which allows for batch processing. Using two six-tube centrifuge machines and a 12-tube Vortex attachment, we were able to process two 12-sample batches a day (24 samples, 48 slides) using the above procedure.

3. Results

Samples were selected from three well-known, unconventional-resource formations: 1) the Cretaceous Eagle Ford Formation (Fm), 2) the Cretaceous La Luna Fm and 3) the Jurassic-Lower Cretaceous Haynesville Fm (Figure 1). In general, the depositional settings for these formations

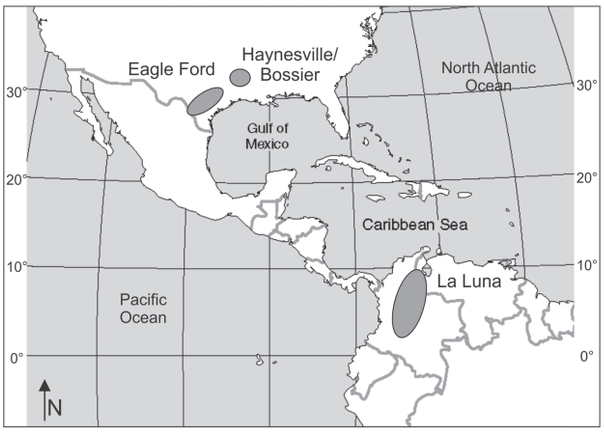


Figure 1: Map of North and South America, illustrating generalised distributions of Jurassic Haynesville and Cretaceous Eagle Ford and La Luna Formations

provide for both a shelf/platform carbonate component, as well as a fluvial/deltaic siliciclastic component (Rangel *et al*., 2000; Hammes *et al*., 2011; Driskill *et al*., 2012). As a result, these formations show varying proportions of carbonate and siliciclastic material, as well as variations in terrestrial and marine organic matter. The palaeotopography provided a restricted to semi-restricted marine setting, with water-column stratification and dysoxic to anoxic bottom-water conditions (Rangel *et al*., 2000; Hammes *et al*., 2011; Driskill *et al*., 2012). These conditions promoted the preservation of organic material, as well as the frequent formation of pyrite. Total organic carbon (TOC) of these formations ranges from 0.5 to 6.9% (average ~2.0-4.5%; Zumberge, 1984; Hammes & Carr, 2009; Dawson & Almon, 2010).

Many of the background components in these lithologies hinder nannofossil identification by both obscuring individual specimens and by clumping multiple specimens together with other particles, such as carbonate and quartz grains, land-derived phytoclasts, AOM and opaque minerals. Nannofossil specimens from untreated samples can be difficult to identify to species level, and meaningful abundance and diversity counts can be compromised. Here, we compare results for residual organic content and for abundance and species richness of nannofossil assemblages for several of the preparation variations discussed above.

3.1 Residual organics

Residual organics were compared for each sample under a variety of treatments, including variations in pH, the number of wash iterations, and with and without the use of an ultrasonic bath. The relative abundance of residual organics was estimated using Compton (1962) for abundances of 2-50% per field of view (FOV) and Reid (1985) for abundances of 1% or less per FOV. Estimates were made at 630x magnification in plane polarised light (PPL), where N = 50 FOV. Results are summarised in Figure 2 and Table 1.

In untreated slurry-smear slides, organic material comprised an average of ~7-14% of the FOV. Treatments at 9.5pH showed a reduction in organic material (μ = ~4-9%); however, significant organic material remained, even with three iterations of the treatment. Pure bleach was most successful in lightening and dispersing organic matter. A single iteration of the treatment with pure bleach gives results similar to 9.5pH after three treatments (Figure 2). Optimum results were achieved with two and three iterations, both consistently giving an average organic

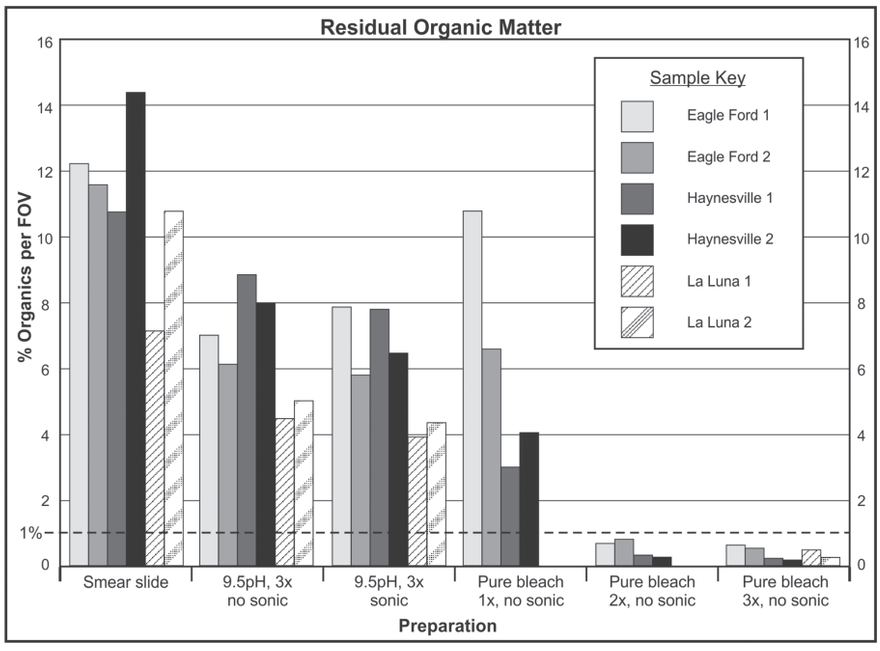


Figure 2: Illustration of average residual organics per FOV after various treatment procedures. Estimates based on Compton (1962) and Reid (1985). N = 50 FOV at 630x magnification in PPL. Ideal results (<1% residual organics/FOV) achieved with 2-3 iterations of cleaning/washing procedure

Average Residual Organics (%) / FOV						
Formation/Sample	Preparation					
	A	B	C	D	E	F
Eagle Ford A	12.2	7.2	7.9	10.8	0.7	0.7
Eagle Ford B	11.5	6.1	5.8	6.6	0.8	0.6
Haynesville A	10.7	8.7	7.9	3.0	0.3	0.2
Haynesville B	14.4	8.0	6.4	4.1	0.3	0.2
La Luna A	7.4	4.5	4.0	NA	NA	0.6
La Luna B	11.0	5.1	4.4	NA	NA	0.3

A = Untreated slurry-smear slide
B = 9.5pH, 3 iterations, no sonic
C = 9.5pH, 3 iterations, sonic
D = Pure bleach, 1 iteration, no sonic
E = Pure bleach, 2 iterations, no sonic
F = Pure bleach, 3 iterations, no sonic

Table 1: Residual organic matter per FOV after various treatments. Estimates based on Compton (1962) and Reid (1985). N = 50 FOV at 630x magnification in PPL

matter content of <1% per FOV (N = 50 FOV). Ideally, samples should undergo as little processing as possible, with two iterations sufficient to achieve the desired results. Results for each formation are summarised in Table 1. Decreasing background organic matter, increasing sediment dispersion and cleaner individual specimens are illustrated in Plates 2-4 for the Eagle Ford, La Luna and Haynesville Fms, respectively. Remaining background material obscuring nannofossil specimens is predominantly limited to opaque minerals. Photomicrographs are all taken at 630x magnification in cross-polarised light (XPL, left) and PPL (right).

3.2 Nannofossil abundance and species richness

One of the greatest challenges of working with untreated samples from organic-rich mudstones is the species-level identification of obscured specimens. Many species require an unobscured view of the central-area structure for positive identification. Subsequently, numerous specimens in an untreated sample may be labeled 'unidentifiable'. In addition, aggregates of multiple specimens, along with other background components, result in tentative relative abundance estimates.

In this study, nannofossil relative abundance and species richness is based on one full traverse at 1000x (~250 FOV). Two additional traverses were completed to scan for rare taxa, which were given a value of one. As the main goal of this portion of the study was to compare changes in relative abundance and species richness in one sample under a variety of preparations, care was taken to make all slides to a consistent thickness. We noted a significant increase in the number of identifiable specimens in treated samples (Figure 3). In addition, we observed an increase in species richness, likely due to improved visibility and greater confidence in species-level identification (Table 2). Treated samples also showed a modest increase in total nannofossil abundance, either due to an underestimation of the number contained in untreated aggregates, or due to a slight concentration of nannofossils in samples treated for organics and clays (Figure 3, Table 2).

3.3 Cost/benefit

Although there is a slight increase in processing time, this cost is significantly offset by the increased quality of the sample preparations. This reduces total microscope time

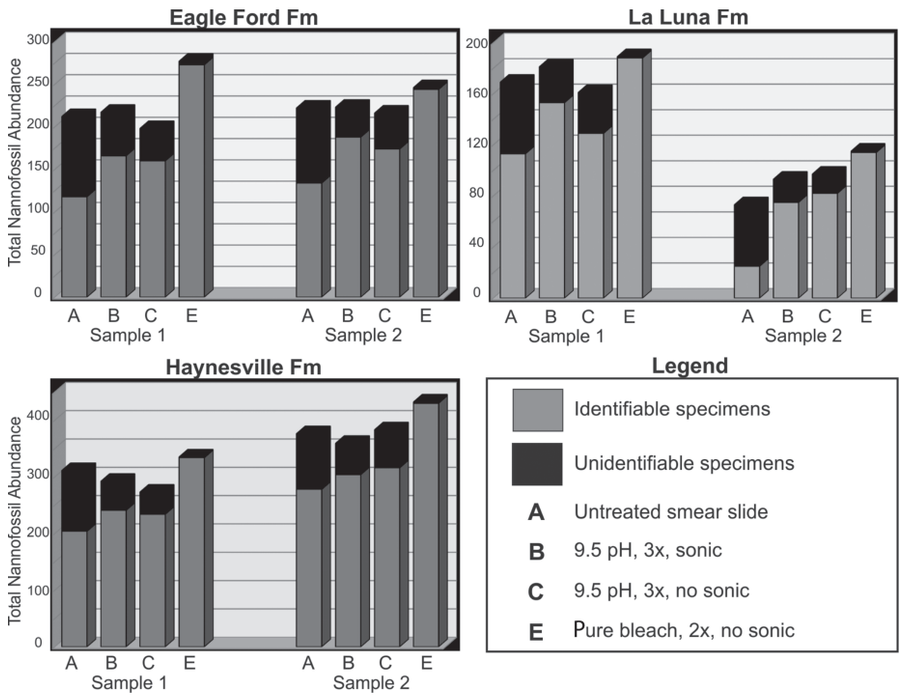
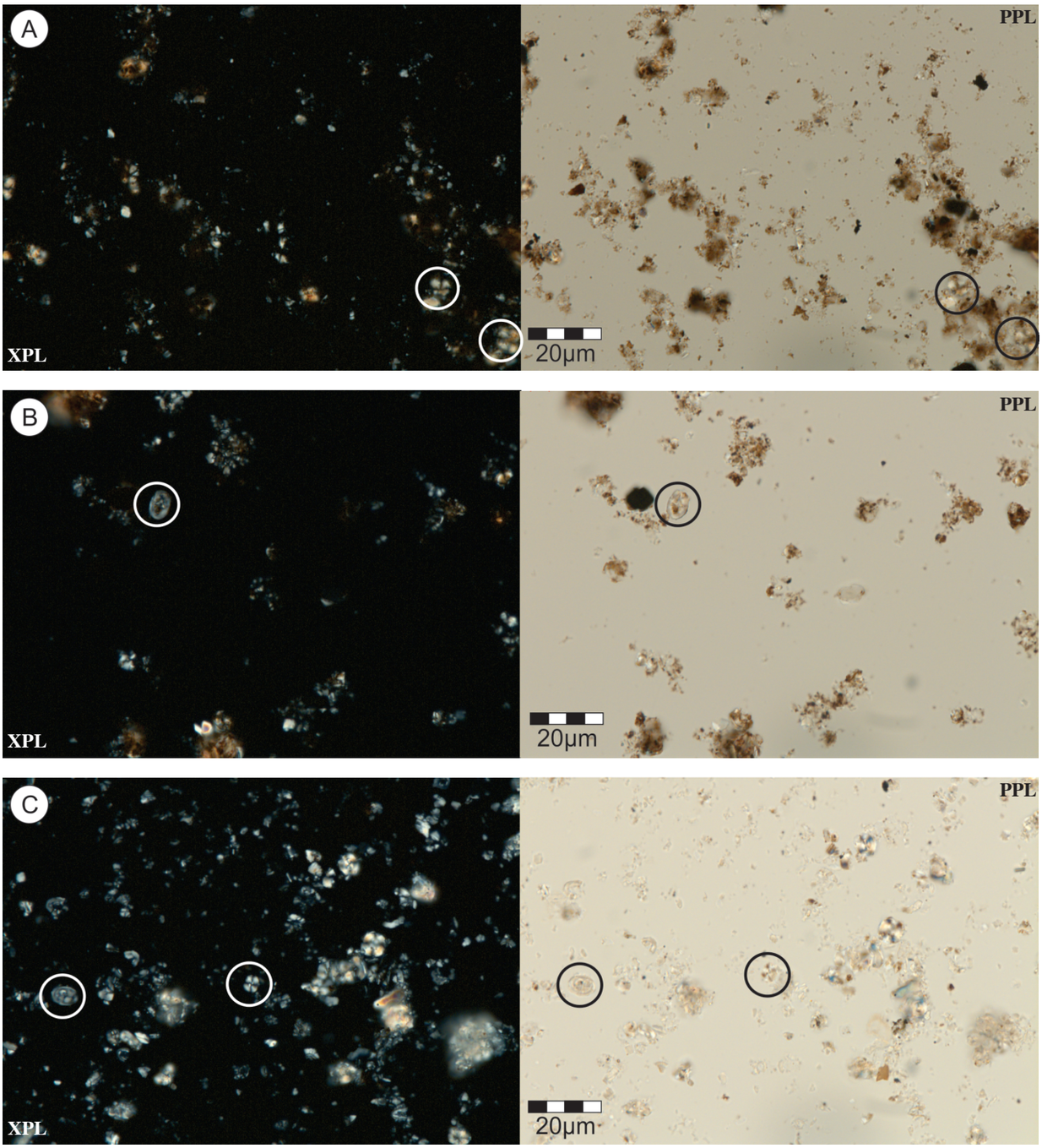


Figure 3: Abundance data for Eagle Ford, La Luna and Haynesville Fms, showing relative changes in proportion of unidentifiable *vs*. identifiable nannofossil specimens, and total nannofossil abundance after varying sample treatments. Unidentifiable specimens refer to those obscured by organic matter or those adhering to background sediment, and does not include broken specimens with incomplete morphology

Plate 2

Comparison of sample Eagle Ford 1 with (**A**) untreated slurry-smear slide, (**B**) 9.5pH, 3 iterations, no sonic and (**C**) pure bleach, 2 iterations, no sonic
Organic matter particularly evident in PPL. Selected specimens highlighted for comparison
Photomicrographs taken at 630x magnification for wider FOV



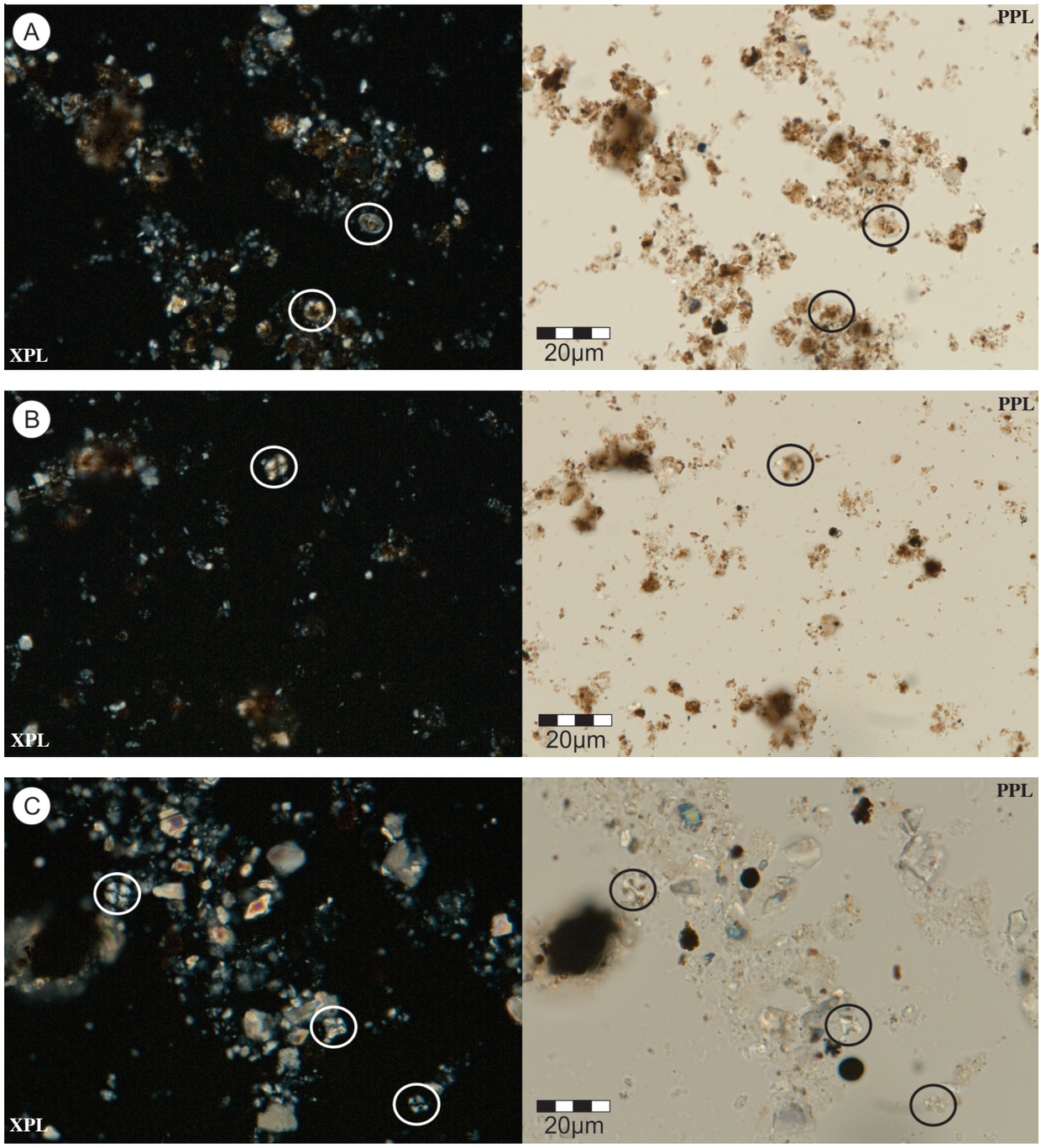
needed for analysis and produces biostratigraphic data with greater accuracy. In addition, the procedure uses household bleach as the primary reagent, which is mild enough to permit use of the procedure on drilling rigs, and is inexpensive.

4. Conclusions

We have presented a method of calcareous nannofossil sample preparation that lightens organic matter and increases liberation of individual nannofossil specimens from background sediment in organic-rich mudstones.

Plate 3

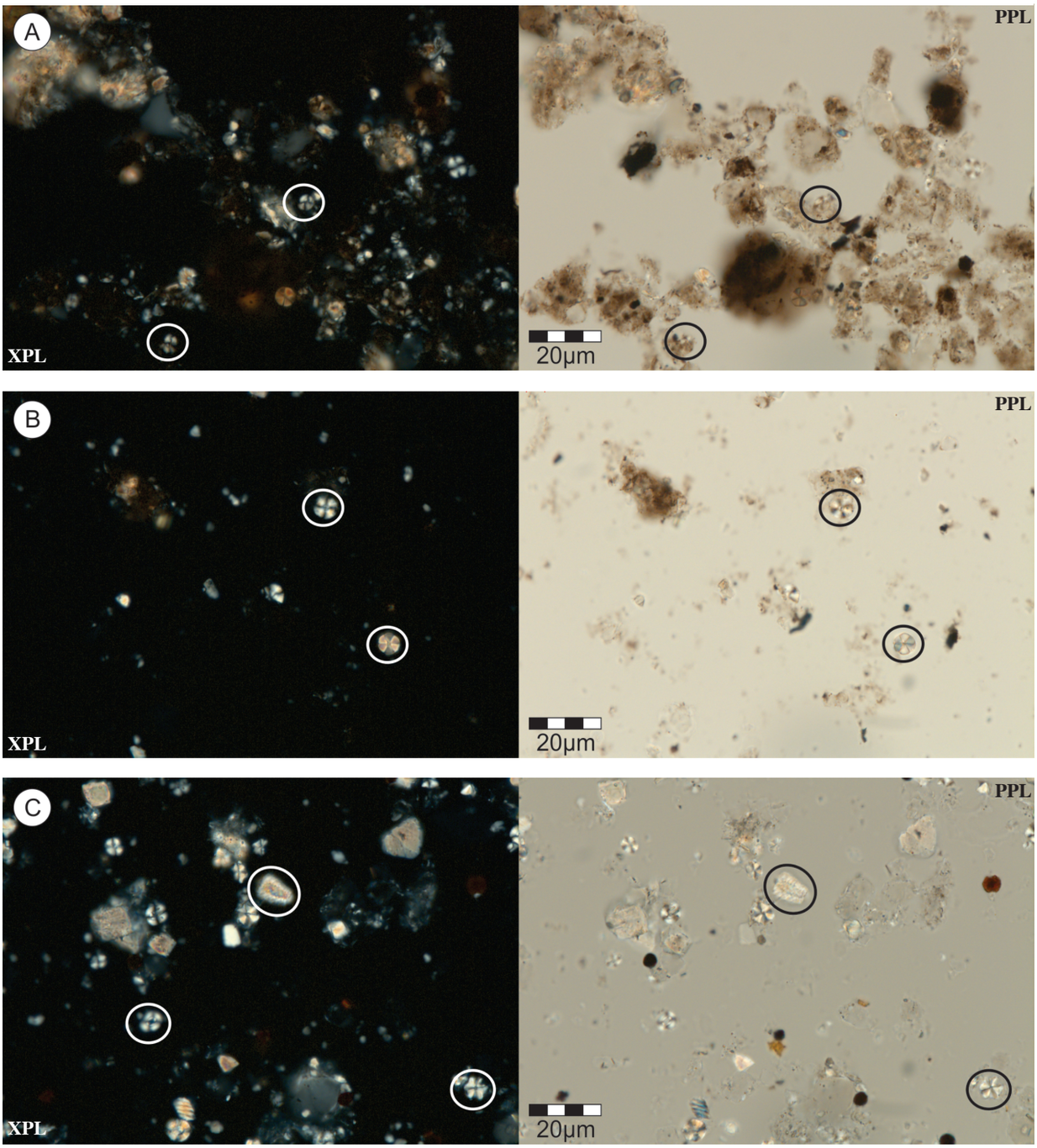
Comparison of sample La Luna 1 with (**A**) untreated slurry-smear slide, (**B**) 9.5pH, 3 iterations, no sonic and (**C**) pure bleach, 2 iterations, no sonic
Organic matter particularly evident in PPL. Selected specimens highlighted for comparison
Photomicrographs taken at 630x magnification for wider FOV



This procedure is modeled after foraminifer cleaning techniques, but was modified to be sufficient for basic light-microscopy at ~1000x magnification. Through numerous revisions and tests of the process, we have detailed a relatively quick and simple procedure that maximises nannofossil recovery and identification with minimal processing. This pretreatment uses pure bleach (NaClO ~5.25-6.0% by volume), followed by washes with bicarbonate solu-

Plate 4

Comparison of sample Haynesville 2 with (**A**) untreated slurry-smear slide, (**B**) 9.5pH, 3 iterations, no sonic and (**C**) pure bleach, 2 iterations, no sonic
Organic matter particularly evident in PPL. Selected specimens highlighted for comparison
Photomicrographs taken at 630x magnification for wider FOV



tion and deionised water. Up to 24 nannofossil samples can be prepared per day with batch processing. We believe the procedure provides significantly improved data and decreases total microscope time for a relatively modest increase in processing time and cost of laboratory supplies.

With increased assets in unconventional resources, a greater number of calcareous nannofossil biostratigraphy projects are derived from organic-rich mudstones. While

Formation/Sample	Preparation	Nannofossil Abundance	Unidentifiable Specimens	Identifiable Specimens	Species Richness
Eagle Ford A	A	212	94	118	30
	B	217	51	166	38
	C	198	38	160	35
	E	277	4	273	50
Eagle Ford B	A	222	88	134	33
	B	223	35	188	39
	C	216	42	174	39
	E	246	2	244	49
Haynesville A	A	311	107	204	26
	B	292	51	241	27
	C	273	39	234	29
	E	335	1	334	35
Haynesville B	A	376	98	278	33
	B	359	55	304	35
	C	383	67	316	32
	E	432	2	430	39
La Luna A	A	169	56	113	30
	B	181	28	153	36
	C	161	32	129	33
	E	189	1	188	40
La Luna B	A	73	48	25	10
	B	93	18	75	31
	C	97	15	82	33
	E	115	1	114	44

A = Untreated slurry-smear slide
B = 9.5pH, 3 iterations, no sonic
C = 9.5pH, 3 iterations, sonic
E = Pure bleach, 2 iterations, no sonic

Table 2: Detail of relative abundance data for Eagle Ford, La Luna and Haynesville Fms, showing changes in relative proportions of unidentifiable *versus* identifiable nannofossil specimens, as well as total nannofossil abundance and species richness after varying sample treatments

traditional methods of industrial sample preparation are excellent for most lithologies, they are insufficient for sediments rich in marine and terrestrial organic matter. We document significant decreases in organic matter, and concomitant increases in both the number of identifiable specimens and species richness, in all treated samples. This methodology can increase species-level identification, improve biostratigraphic data and significantly raise confidence in biostratigraphic interpretations.

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