Successful complete digestion of well lithified shale and extraction of microfossils from Devonian beds in western New York

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ABSTRACT: Researchers in paleontological and paleoecological sciences often need complete disaggregation of rock materials for certain lines of investigation. However, complete disaggregation of more lithified sedimentary rock is known to be problematic. A complete shale disaggregation method implementing quaternary ammonium surfactants, widely used in paleontological sciences for poorly lithified shale and mudstone, was successfully used on well lithified Devonian shale in the Appalachian Basin of Western New York. Over 50 Devonian gray and black shale samples were collected from multiple localities in western New York (Cashaqua, Rhinestreet, Skaneateles, Windom, and Ludlowville), coarsely crushed, and fully immersed in a quaternary ammonium surfactant until complete disaggregation was achieved (5–14 days); aliquots were run through a series of nested sieves. The sieved sediments contained hundreds of well-preserved microfossils released from the shale: ostracods, dacryoconarids, and previously unreported palymorphs, charophytes, agglutinated foraminifera, miospores, and other microspherules. These microfossils were easily found within disaggregated and sieved samples but were unrecognizable on the shale surface and destroyed in prior investigations of whole rock thin sections. In addition to more traditional approaches, inclusion of this complete rock disaggregation method may assist in a more complete analysis of material, increase our understandings of ancient basin systems and have important implications on our understanding of the paleoecology during the Late Devonian marine biotic crises.

Keywords: complete maceration, disaggregation, quaternary surfactant, well lithified, shale, Devonian, Appalachian

INTRODUCTION

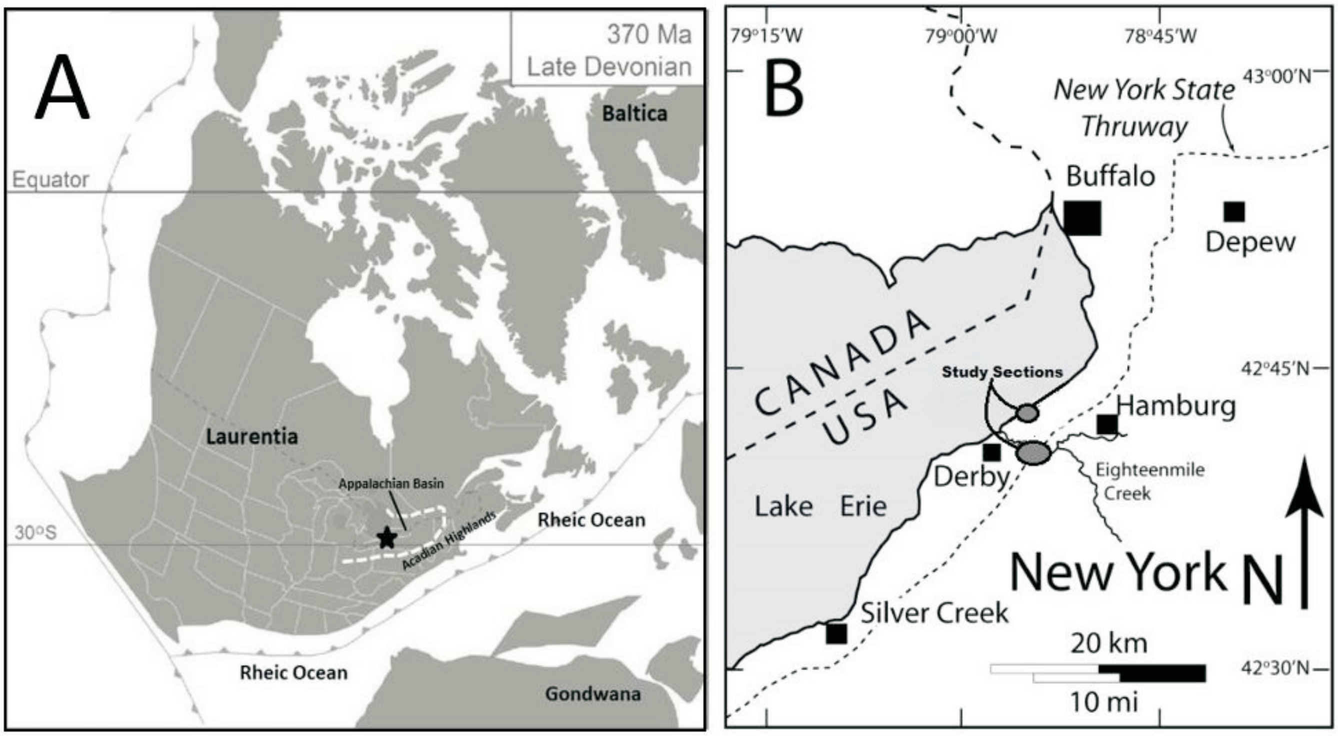
The methodology for disaggregating fine-grained sedimentary rocks has been studied for quite some time (Taylor and Georgesen, 1933; Krumbein 1933; Gipson 1963). However, variation among cementing compounds has hindered recognition of a common disaggregation method suitable for the range of fine-grained sedimentary rocks (Krumbein 1933), particularly for those that are well lithified. Thus, the search for better disaggregation approaches has continued (Gipson 1963; Lund 1970; Bennington 1993; Macquaker 1994; Yang and Aplin, 1997; Heilbronner and Keulen 2006). Prewash techniques have been proposed and implemented with positive results (Jiang and Liu 2011). However, the use of acids (Upshaw et al. 1957; Schopf 1965; Miller 1967; Chauff 1978; Grahn and Afzelius 1980; Jeppsson et al. 1985, 1999; Etherington and Austin 1993; Jeppsson and Anehus 1995; Ford and Lee 1997) and freeze-thaw techniques (Hanna and Church 1928; Pojeta and Balanc 1989; Remin et al. 2012) are known to be time consuming (Jarochowska et al. 2013) and, on occasion, destroy certain components of interest to investigators (e.g., biologicals, carbonates, etc.).

Non-invasive pretreatment techniques that involve sample exposure to brief hot hydrogen peroxide baths and varying concoctions of less hazardous and readily available household chemical (e.g. carpet cleaner, bleach, acetone, methylated spirits) have shown notable increases to palynomorph yields when compared to nitric acid and formic acid techniques (Riding et al. 2007; Riding and Kyffin-Hughes 2010). However, these techniques have shown that these approaches may also be corrosive to certain microfossils such as miospores, dinoflagellate cysts and kerogen macerals that are particularly susceptible to oxidation (Riding et al. 2010). Other non-invasive techniques used with success include formic acid pretreatments used in combination with multiple applications of solvents and bleach have been successfully applied to slightly older Appalachian Basin deltaic samples (Chamberlain et al. 2016). While Chamberlain et al.'s (2016) methodology yielded numerous previously unreported specimens, commonly lost through strong acid reduction techniques, their approach is equally time consuming as established methodologies.

Micropaleontological and palynological investigations, in particular, rely on complete disaggregation of lithified materials with little damage to components. A variety of time saving and less hazardous disaggregation techniques have been used with great success on poorly lithified shale and mudstone (Lierl 1992; Holbourn and Kuhnt 1998; Nagy 2005; Heldt et al. 2008, Babinot and Colin 2011; Jarochowska et al. 2013). This paper discusses the success of implementing the quaternary ammonium surfactant complete disaggregation technique on well lithified shale samples recovered from the Devonian gray and black shale beds of Western New York and the potential paleoecological impact of the varying types of microfossils recovered from this technique.

GEOLOGIC BACKGROUND

Five transgressive/regressive cycles have been recognized in the Late Devonian Appalachian Basin, then connected to the global Rheic Ocean (Arthur and Sageman 2005; text-fig. 1A). The beds investigated herein accumulated in the relatively enclosed north-



TEXT-FIGURE 1
A. Paleogeographical reconstruction of Laurentian during the Devonian (based on Cocks and Tursvik 2011; Bingham-Koslowski 2015); star denotes the three general localities sampled in this investigation. B. Map of sampling localities in western New York (adapted from Lash 2018).

ern part of the northeast-southwest trending Appalachian foreland basin bounded on its east and southeast by the rising Acadian Highlands (Cocks and Torsvik 2011; Bingham-Koslowski 2015; text-fig. 1A). Crustal loading by the inboard fold and thrust belt caused subsidence of the foreland basin (Quinlan and Beaumont 1984; Beaumont et al. 1988), which was dominantly filled by siliciclastic material eroded from the uplifted Acadian orogen (Arthur and Sageman 2005; Hupp and Weislogel 2018; Fritz 2019).

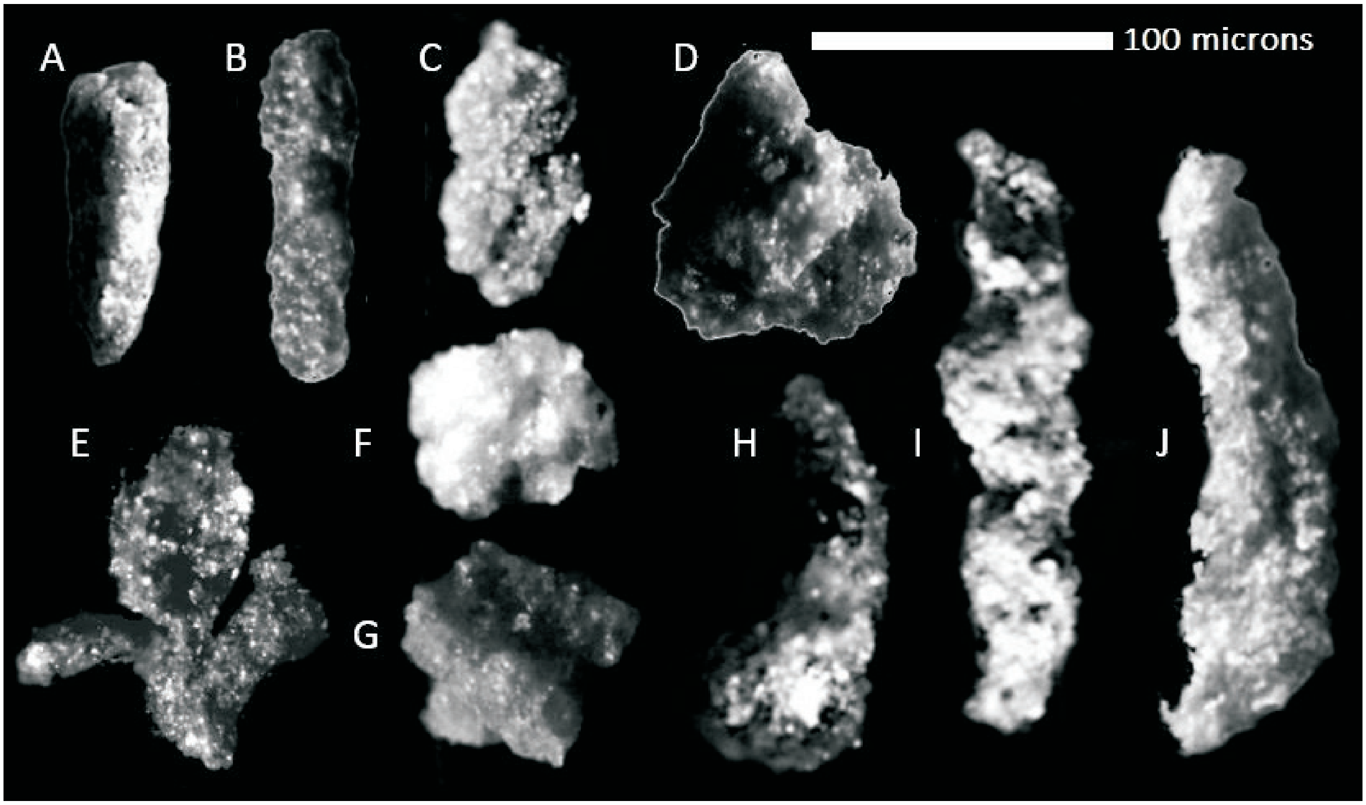
The basic lithology of the Rhinestreet and Cashaqua formations were first described by paleontological researchers and later summarized and compiled by Buehler and Tesmer (1963). More recently, work attempting to constrain the ecological conditions (e.g. freshwater inundation, primary production, and oxygen conditions) and relative sea level change have been published (Arthur and Sageman 2005, Ver Straeten et al. 2011; Hupp and Weislogel 2018; Fritz 2019; Lash 2016, 2018). These distal marine shales recorded relative sea level changes in alternating beds of deeper water, dark gray to black organic-rich shale, suspected to be deposited in dysoxic or anoxic bottom waters and light gray organic-poor shale, deposited in shallower, more oxygenated water (Ver Straeten et al. 2011; Fritz 2019). The shale members investigated here represent a few of many gray to black shale sequences previously identified in this area.

METHODS AND MATERIALS

Samples of gray and black shale from several Devonian formations (Cashaqua, Rhinestreet, Pipe Creek, Hanover, Skaneateles, Windom, Wanakah, and Ludlowville) were collected from well exposed outcrops along creek beds in Erie County, New York (text-fig. 1B) and three samples from each of the Skaneateles, Windom, Wanakah, and Ludlowville were selected at random along road cuts and creek beds. The samples from the Cashaqua-Rhinestreet and Rhinestreet-Angola contacts on Eighteenmile Creek were sampled at 3 cm (Rhinestreet-Angola) and 10 cm (Cashaqua-Rhinestreet) intervals spanning 2–6 m, respectively.

Paleontologists have employed surfactants, including Rewoquat, with great success in complete disaggregation of shale material for fossil extraction (Holbourn and Kuhnt 1998; Dzygiel and Wieczorek 2000; Nagy 2005; Heldt et al. 2008; Jarochowska et al. 2013, 2016; Habermann et al. 2019). Rewoquat W 3690 PG is the trade name for a highly concentrated quaternary ammonium surfactant that has been widely used to clean fossils for well over two decades (Lierl 1992; Babinot and Colin 2011). Rewoquat is known to disintegrate rock substantially faster (days) than traditional acid digestion methods (months) (Jarochowski et al. 2013). The enhanced fossil content of sediment residue obtained by use of Rewoquat likely reflects the dispersion of clay aggregates (Jarochowski et al. 2013). However, importation of Rewoquat to certain countries, including the United States, has been problematic due to chemical importation and safety restrictions. The present study used an industrial grade quaternary ammonium surfactant with comparable ingredients but at a much lower concentration (Quat Stat 5 (5–10%); Rewoquat (75%)).

Shale samples were coarsely crushed with a mortar and pestle, 100 cc (~135 gm) of the sample material was then completely



TEXT-FIGURE 2
Marine agglutinated and calcareous foraminifera specimens. A. *Hyperammina constricta* – Rhinestreet. B. *Bathysiphon* sp. – Rhinestreet C. *Webbinelloidea similis*. – Cashaqua. D. *Ammobaculites beveridgei* – Angola. E. *Schizammina* sp. – Ludlowville. F. *Sorosphaeroides pentachora* – Skanateateles. G. *Psuedoastrorhiza conica* – Windom. H. *Tolypammina bulbosa* – Rhinestreet. I. *Tolypammina jacobschapelensis* – Rhinestreet. J. *Tolypammina* sp. – Hanover.

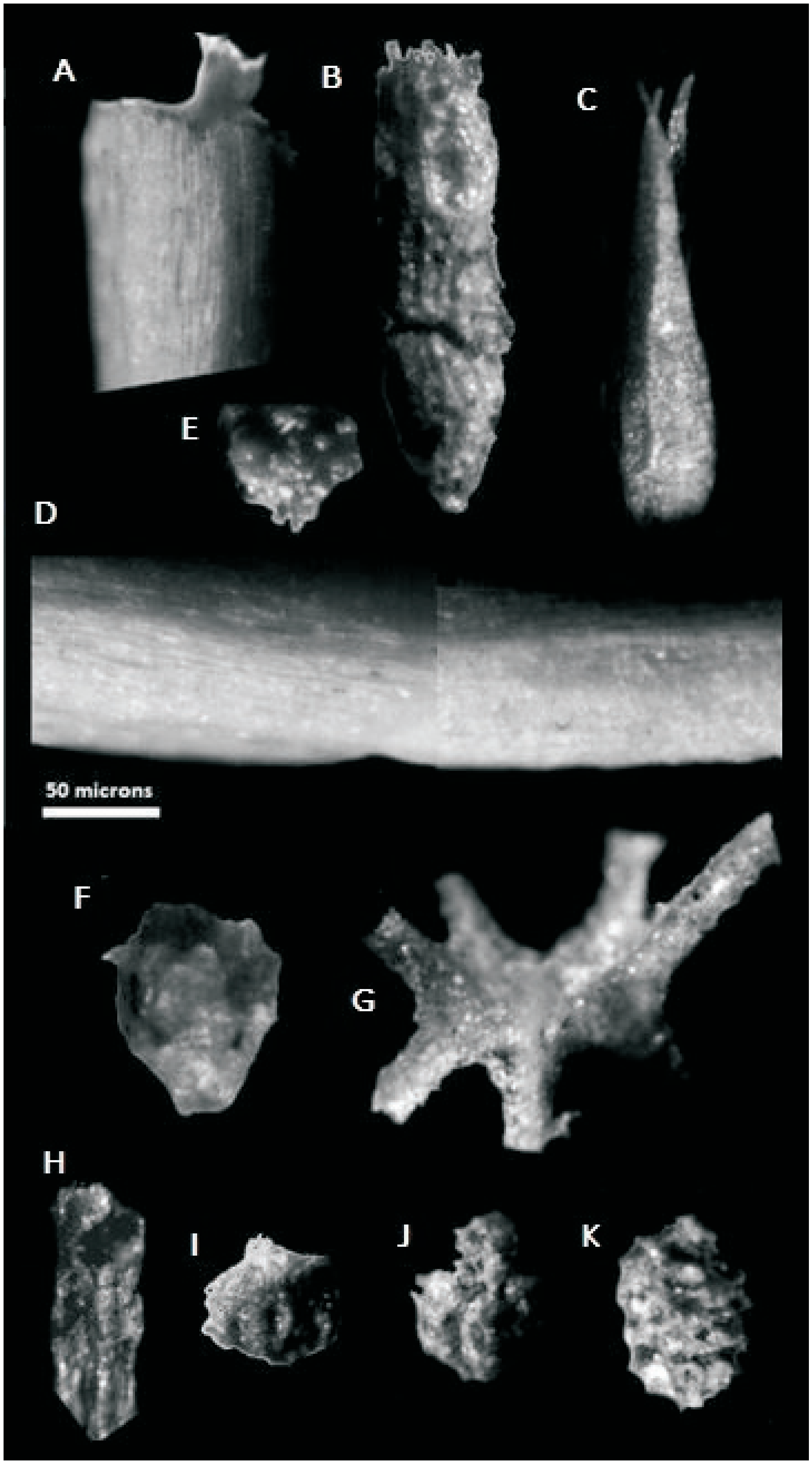
submerged in the industrial grade quaternary ammonium surfactant [Betco Quat-Stat 5 (Dioctyl dimethyl ammonium chloride 16.11%), Alkyl (67% C12, 25% C14, 7% C16, 1% C18)] Dimethyl benzyl ammonium chloride (10.74%)), and placed in a low frequency (~20kHz) sonic bath for 7 to 14 days until individual shale samples completely dissolved. Aliquots were then run through a series of nested sieves (250, 150, 90, and 63 µm), dried at room temperature (~20°C), and weighed out to 0.05 gm for specimen counts and collection. Individual microspherule specimens found in sieved sediments were mounted on double-sided adhesive carbon tape and analyzed on a Phenom ProX scanning electron microscope (SEM) operating at acceleration voltages between 5 and 15 keV. Excess sieved sediments were also utilized for resin thin sections. Larger shale samples from Eighteenmile Creek were used to make traditional thin sections. Thin sections were made both along and perpendicular to the bedding planes. The samples chosen for thin sectioning were lithified enough to not require impregnation.

RESULTS

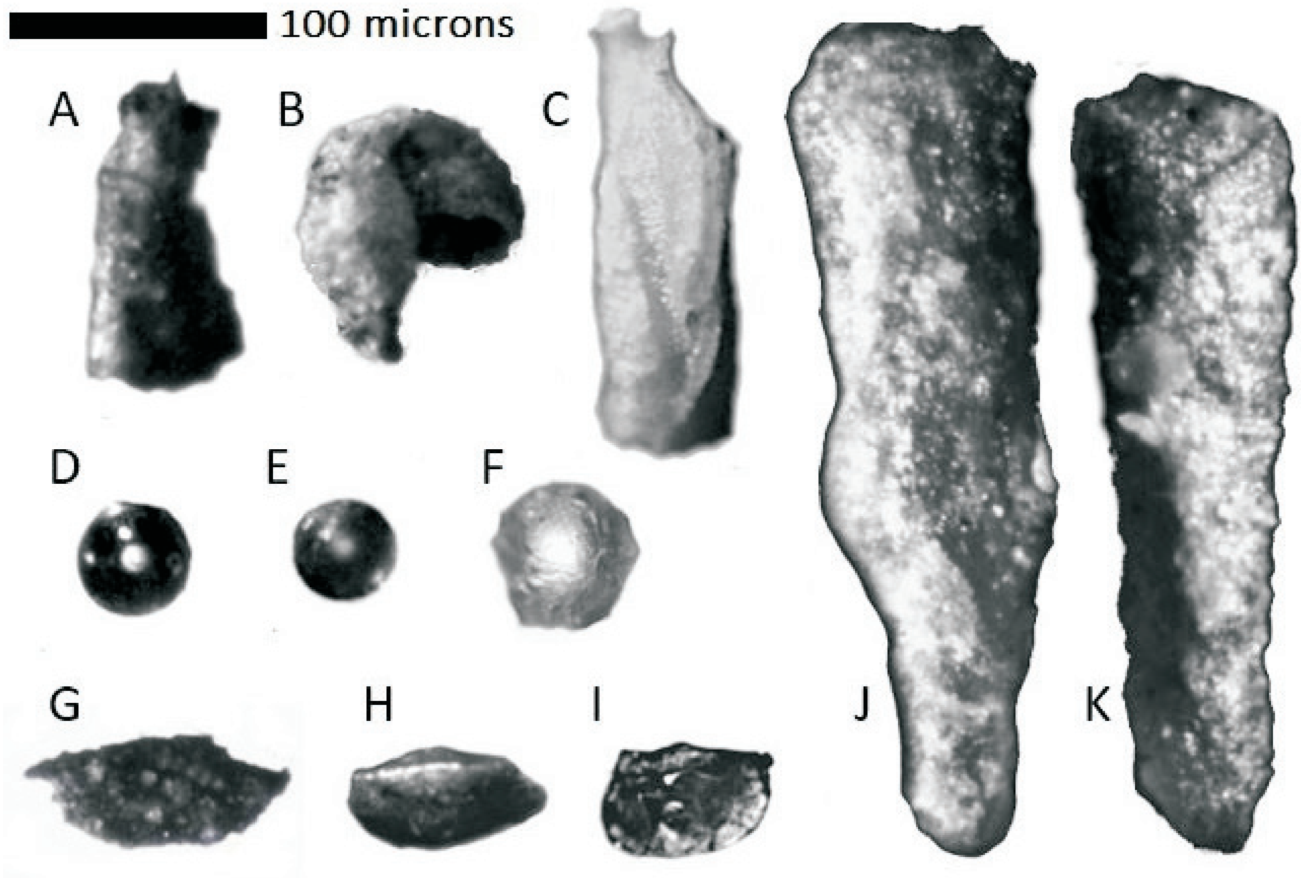
Thin sections rendered virtually no distinguishable microfossils; only several enigmatic and unidentifiable foraminifera, twelve shattered microspherules, and no palynomorphs were found in thin sections. Sediment retrieved from sieves ranges in size from 63–500 µm. All formations contained microfossils. The most prolific formations were gray shale formations and beds of the Windom, Skaneateles, Ludlowville, Hanover, Angola, and Cashaqua. While all black shale members (Rhinestreet and Pipe Creek) contained microfossils, the numbers and diversity of genera and species was greatly reduced comparatively to gray shale members (Cashaqua, Angola, Hanover, etc.) through this quaternary surfactant maceration technique. Extracted microfossils included those previously reported (agglutinated foraminifera, miospores, chitinazoans, dacryoconarids, ostracods: text-figs. 2-3), as well as others that have not been reported in the literature for Western New York (charophytes, fresh water palymorphs, and calcareous foraminifera; text-figs. 2 and 4). All microfossils vary in preservational quality between formations. The best preservation came from microfossils of the gray shale beds (Windom, Skaneateles, Ludlowville, Hanover (gray members), Angola, Cashaqua). Notably, miospores were predominately found in black shales and were of high preservational quality whereas all other microfossils from black shales were poorly preserved or frequently unidentifiable most likely due to conditions during preservation.

DISCUSSION

Paleontologic investigations of the Middle and Upper Devonian shale successions in the Western New York State region of the Appalachian Basin, particularly of the Hamilton Group, have focused on macrofossil groups, including ammonites (House 1965;



TEXT-FIGURE 3
Select palymorphs specimens of Characeae retrieved from specified associated shale members; A, D. branchlet – Cashaqua. B, C. partial stipule – Cashaqua and Rhinestreet respectively. E. antheridia (male reproductive organ) – Rhinestreet. F, G. stipulodes – Hanover. H, K. oogonium (female reproductive organ Characeae). H. *Sycidium* sp. indet. – Cashaqua. I. *Chovanella burgessi* – Cashaqua J. *Moellerina* sp. – Cashaqua–Rhinestreet contact. K. *Ascidiella cruciata* – Rhinestreet.



TEXT-FIGURE 4
Previously unidentified in microfossils 'traditional' prep techniques. A, C. Chitinozoans – Cashaqua. D, F. Miospores – Cashaqua, Rhinestreet, Pipe Creek. G, H. indeterminate ostracods and their carapaces – Rhinestreet, Pipe Creek. J, K. dacryoconarids – Cashaqua, Rhinestreet.

Berry et al 1989; Becker and Kirchgasser 2007), brachiopods (e.g. Sutton et al. 1970; Brett and Baird 1985; Smith et al. 1985; Vogel et al. 1987; Goldman and Mitchell 1990), and trilobites (Speyer and Brett 1985, 1987; Babcock and Speyer 1987; Brett et al. 2007). Micropaleontological work in these deposits has focused on conodonts (Klapper and Phillip 1971; Huddle and Repetski 1981; Kirchgasser et al. 1988; Over 1997) with limited discussion of dacryoconarid tentaculites (Yochelson and Kirchgasser 1986), and graptolites (Baird et al. 1988). While micropaleontological work has been conducted (Over 1997) specifically on conodonts in the Rhinestreet, microfossil extraction was limited to fossils visible with the naked eye, on rock surfaces and removed with fine knives and pin tools, and select samples exposed to hydrocholic or acetic acid baths with some success. While the Cashaqua is rich in macrofossils, the Rhinestreet is comparably barren and so has attracted little attention by paleontologists. In addition, there is a notable and near absence of foraminiferal research in western New York. Perhaps by default in the difficultly of extraction and the diminutive size of specimens, these beds have not been subjected to complete disaggregation techniques. This technique will enhance microfossil recovery in these, and similar formations allowing for increased research and understandings of paleontology and paleoecology.

The disaggregation of sedimentary rock is especially applicable to micropaleontologic investigations and fine-grained marine deposits, especially those deposited under reducing conditions, which may often contain a robust and well preserved microfaunal record. However, the tendency of phyllosilicate minerals to form clay floccules deposited in low pH values makes the use of acids for rock digestion inefficient and time-consuming (Upshaw et al. 1957; Schopf 1965; Miller 1967; Chauff 1978; Grahn and Afzelius 1980; Jeppsson et al. 1985, 1999; Etherington and Austin 1993; Jeppsson and Anehus 1995; Ford and Lee 1997). Disaggregation of rock by expansion through freeze-thaw (Hanna and Church 1928; Pojeta and Balanc 1989; Remin et al. 2012) can be just as daunting and equally as damaging to brittle fossil structures and so it is not regularly employed. Following suit, paleontologists have been actively searching for less time consuming and hazardous approaches to this problem.

When utilizing a less concentrated quaternary ammonium surfactant, as in this methodology, the time required to completely disaggregate moderately to well lithified gray and black shale was extended by about 7 days (e.g., complete disaggregation of organic-rich shale averaged 14 days) from previously reported timelines with Rewoquat which averages 7 days to complete disaggregation (Hodgkinson 1991; Wisshak 2012; Jarochowski et al. 2013). The difference of disaggregation time may reflect either or both the lower concentration of ammonium salts or the degree of lithification. However, the additional time required for complete disaggregation is nominal and only one sample remained partially disaggregated after two weeks. This sample was collected from a very dark, extremely well lithified 6 cm interval near the base of the Rhinestreet Formation, which rendered no microspherules but did release size equivalent sediments and rendered a few poorly preserved palymorphs, charophytes and foraminifera. The repeatability of a complete disaggregation using a quaternary ammonium surfactant method is nearly 100% for well lithified black and gray shale with an extended timeframe. Further, this slightly modified method allowed for collection of specimens never previously published on within this area of the Appalachian Basin. The implications of the microfossil assemblages found within the shale beds of Western New York, particularly fresh water microfossils, may provide greater understanding and insight of intercalated shale and carbonate sequences that continue to defy straightforward explanations (Arthur and Sageman 2005; Lash 2016).

CONCLUSIONS

The use of a commercially available, lower concentration, quaternary surfactant for highly repeatable and rapid sedimentary rock disaggregation can be successfully used on well lithified shale for micropaleontological research where previously used methods were limited to poorly lithified shale and mudstone. Despite the intense amount of previously published research in these beds of Western New York, use of this complete disaggregation method rendered microfossil assemblages that were previously unreported. Thus, employing this time saving method may provide new insights into the paleoecology of the ancient Appalachian Basin that may have gone undetected with more traditional methodologies.

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