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Extraction of calcareous dacryoconarid microfossils from limestones and mudrocks by surfactants paired with freeze-thaw processing

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ABSTRACT

Microfossils offer a wealth of paleoenvironmental information, but their extraction from consolidated material, especially ancient rocks, is time-consuming and often lacks systematic methodological development. This study examined the efficacy of repeated freeze-thaw processing paired with different surfactants (anionic, cationic, and detergent) on the extraction of fossils from the order Dacryoconarida, conically shaped calcareous microfossils that occur in diverse marine facies of the Devonian Period. A stepwise technique was developed involving saturation of rocks in either 18 Ω water or 25% NaCl, followed by freezing and then boiling in surfactant (Pinequat, Decon 90, or Calgon in Na_2CO_3 solution). In comparison with saturation in NaCl solution, saturation in water generally had higher yields of disaggregated material and more intact fossils. All surfactants performed better at extraction compared to boiling in pure water. Across all lithologies examined, Na_2CO_3-buffered Calgon (sodium hexametaphosphate) disaggregated rock most efficiently, but Na_2CO_3 solution alone generally had the highest yield of total and intact fossil specimens. Pinequat, a cationic surfactant, yielded more disaggregate for siliclastic samples compared to calcareous samples, but had lower fossil yield. Decon 90, an anionic surfactant, performed better at disaggregating limestones and had higher fossil extraction efficiency than Pinequat across all lithologies. Freeze-thaw processing pairing water saturation and 5% Na_2CO_3 simmering is an effective treatment for the disaggregation of rocks to extract analytically viable amounts of dacryoconarids from fossiliferous samples. This pairing had greater fossil extraction potential than surfactants at the concentrations tested in this study and is recommended if the elemental composition of the target rocks is unconstrained.

1. Introduction

Valuable paleontological and geochemical information is preserved in microfossils that can be used for the reconstruction of ancient environments. The fragility of microfossils and the time-consuming nature of effective extraction means that methodologies to extract them has been often revisited. Many challenges arise due to compositional complexity and degree of lithification of the matrix and the preservation and chemical nature of the fossilized material (Tarsilli and Warne, 1997; Feldman, 2004; Vodrážka, 2009). Consequently, some studies on calcareous forms preclude extraction, especially from limestones, due to high degree of lithification (Tarsilli and Warne, 1997; Gessa and Lecuyer, 1998). A promising fossil taxon for geochemical study of the early Paleozoic is the Order Dacryoconarida (Frappier et al., 2015). These conical calcareous plankton (Fig. 1C) were abundant and globally distributed, but disappeared during the end Devonian extinction event (Lindemann, 2002; Wittmer and Miller, 2011). They are found in diverse lithofacies, sometimes in rock forming quantities (Lindemann and Yochelson, 1984; Bond, 2006), and the spatiotemporal distributions of genera have been shown to reflect regional environmental conditions (Gessa and Lecuyer, 1998; Wei, 2019). One study on the carbon and oxygen stable isotope ratios of dacryoconarids through a continuous interval of Middle Devonian stage strata showed that they are sensitive to carbon cycle perturbations coincident with well-known biocrises and changes in temperature regime (Frappier et al., 2015). Skeletal carbonates are a paleoenvironmental archive that allows for carbonate-based proxies to be applied to any rock compositions in which they occur; however, to facilitate future studies, the elongate shape of dacryoconarid conches and presence in variable marine facies necessitates revisitation of extraction procedures.

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Chemicals historically used to macerate rocks fall into two groups: matrix dissolution enhancers and physical dispersants (Hodgkinson, 1991). Matrix dissolution can be further divided into acids/alkalis, organics (spirits) and oxidants/reductants; whereas dispersants are divided into surfactants, detergents, and salts. Many matrix dissolution chemicals are hazardous to users and often, unless carefully monitored, result in pitting of the fossils and are best implemented if the matrix composition is known and differs from the target fossils (Hodgkinson, 1991; Tarsilli and Warne, 1997; Cureton et al., 2010; Kennedy and Coe, 2014). Furthermore, some acids have been shown to influence stable isotope values of fossils if exposure is not limited to <24 h, often not long enough to fully disintegrate the matrix (Hellawell and Nicholas, 2012). Because future studies intend to utilize dacryoconarids for isotopic analysis we focus on physical dispersants, which are less likely to alter fossil chemical compositions. Surfactants, surface active agents, are a class of chemicals that have also been routinely utilized to disaggregate rocks and have been found to exhume fossils with little alteration, but no systematic approach has been taken to understand the mechanism.

The traditional method employed to extract dacryoconarids involves boiling or soaking bulk rock in a quaternary ammonium surfactant, which is time consuming (days to months) depending on the resistivity of the rock (Jarochowska et al., 2013; Frappier et al., 2015). It is difficult to ascertain from the literature what rock composition/surfactant pairings would provide for optimal extraction. Intercomparison between different published methodologies is currently infeasible due to inconsistencies in factors such as different concentrations, starting sizes, equipment and multi-step processes that elude the primary mechanism of disaggregation (Thomas and Murney, 1985; Kennedy and Coe, 2014; Beasley et al., 2020). Recently, important advances have been made toward more rapid disaggregation of the surrounding matrix by testing different surfactants combined with sonication (Meehan et al., 2020), however mechanical disaggregation by sonication can cause fragmentation or erosion of delicate fossils (Hodgkinson, 1991). Now a systematic approach is warranted to understand the mechanism by which different surfactants interact with varying rock compositions and their capacity to extract microfossils without damaging them. This study seeks to further develop a cost-effective method using surfactants paired with freeze-thaw mechanical disaggregation adapting an approach developed by Kennedy and Coe (2014).

It would be impractical to test all the thousands of surfactants; rather, it is reasonable to test categories of dispersants already in use for paleontology and geochemistry. The primary focus of this research was to compare the combined use of freeze-thaw with different dispersing agents already employed in the geosciences – a quaternary ammonium (Pinequat), an anionic-nonionic surfactant mixture (Decon 90) and a detergent (sodium hexametaphosphate historically called Calgon). Additionally, the influence of saturating solution prior to freezing is addressed. Salt solutions, especially those containing sodium, purportedly mimic the natural weathering process of shales (Hanken, 1979), and are employed in mechanical disaggregation for fossil extraction (Kirchner, 1958; Hodgkinson, 1991). Objectives of this study were to 1) systematically compare disaggregating potential of common surfactants employed in the geological discipline on different lithologies, 2) to examine the contribution of repeated freeze-thaw toward mechanical disaggregation, and 3) to compare the influence of saturation by sodium chloride solution and pure water on the freeze-thaw process. The goal is to provide a first order understanding of how surfactants work at removing different matrices surrounding calcareous fossils, and to establish which chemical treatments are recommended for specific situations.

2. Materials and methods

2.1. Samples

All samples were sourced from the Middle and Late Devonian Appalachian Basin Hamilton and Genesee Groups of New York (Table 1). See Frappier et al. (2015) for detailed description of field collections. Percent carbonate was determined gravimetrically for all samples by weighing powdered sample before and after digesting in 10% HCl. Samples matrices were broadly classified as calcareous (CV, OC) or siliclastic (GL, BS-5, BS-25) based on carbonate composition and

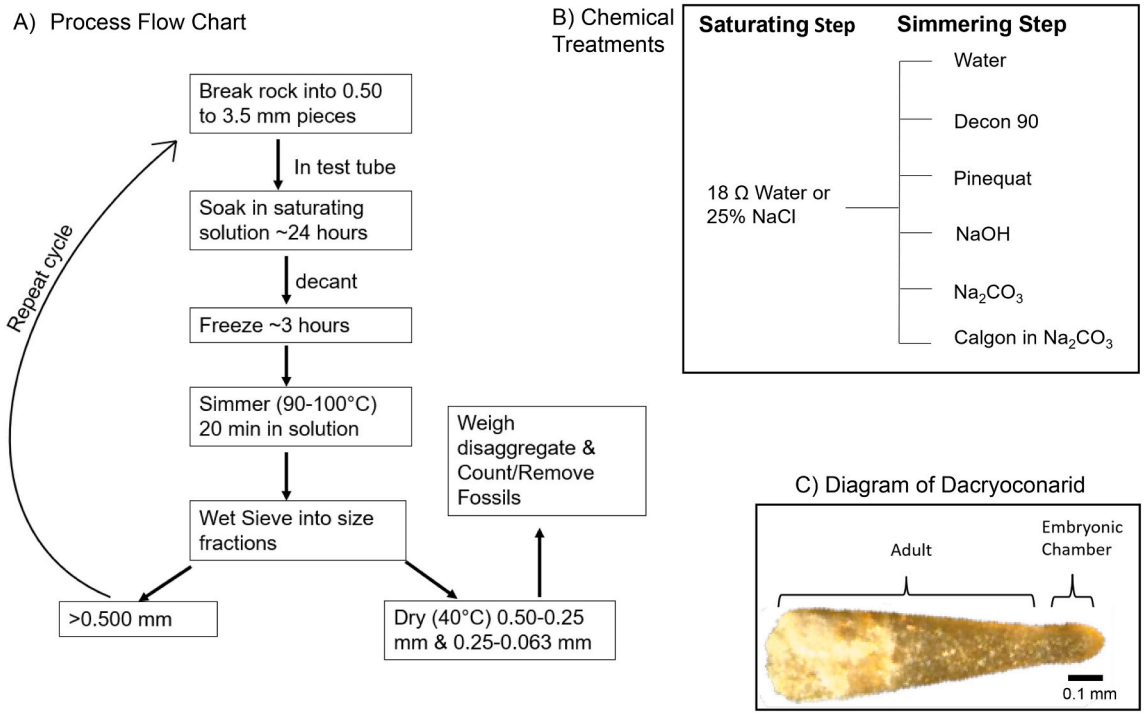


Fig. 1. A) Flow chart of one cycle of freeze-thaw processing, B) the bracketing of the chemical treatments which differ by only one component (either the saturating solution or simmering solution) for a total of 12 treatments, C) A simplified diagram of an intact styliolinid dacryoconarid with adult and embryonic chamber labeled.

Table 1
Sample characteristics and localities.

Sample name	Member/formation	Age	Description	% Carbonate
CV	Cherry Valley limestone, Marcellus Formation	Eifelian	Cherty Limestone/ glauconitic marlstone [a]	86.6
OC	Oatka Creek, Marcellus Formation	Eifelian	Argillaceous limestone [b]	79.3
BS-5	Bakoven Shale (lower 5 cm), Marcellus Formation	Eifelian	Carbonaceous black shale	46.9
BS-25	Bakoven Shale (25–30 cm), Marcellus Formation	Eifelian	Laminated Black shale	29.4
GL	Genundewa Limestone, Ludlowville Formation	Frasnian	styliolinid arenaceous packstone [c]	30.8

Approximate percent carbonate was determined gravimetrically by weighing powered sample before and after digestion in 10% HCl (no replicates). Sample nomenclature constitutes two initials for the member followed by a number if there was more than one for the unit. a. (Oliver, 1956) b. (Lindemann, 2002) c. (Baird et al., 2006).

primary grain mineralogy. Representatives of three dacryoconarid families (Nowakiidae, Styliolinidae, Striatostyliolinidae) abound in many Devonian units of the Appalachian Basin, but this study did not distinguish between taxa when counting conches.

2.2. Methods

2.2.1. Chemical preparation

Surfactants work by adsorption of the polar functional group by electrostatic attraction to oppositely charged sites on the material. Hydrogen bonding between adjacent surfactant tails neutralizes the charge of the complex and induces micellization, or aggregation, of surfactant molecules to minimize electrostatic repulsion, thereby encasing and removing surface charged particles (Chen et al., 1998). Factors that affect the adsorption capacity alter the electrostatic potential of the surface of a material or surfactant head by protonation and include pH, ionic strength, temperature, and surfactant concentration (Belhaj et al., 2020). Therefore, these conditions are considered for chemical preparation.

Each sample was processed through two main chemical steps – saturating and simmering (90–100 °C) (Fig. 1A). The saturating solutions were 25% NaCl and 18 Ω purified water (Fig. 1B). Publications differ or do not report concentrations used for salt solutions in fossil extraction (Kirchner, 1958; Haynes and Bassuoi, 2017; Alves et al., 2021), so a saturated solution (at room temperature) was prepared. The six simmering solutions represented the main classes of surfactants typically employed in the literature (cationic, anionic and a detergent) and controls for pH. Chemicals were prepared (Table 2) and stored in amber polyethene plastic bottles. High purity (18 Ω) water is the solvent for all preparations.

Surfactants operate on equilibrium principles and therefore dilute solutions in the range of 0.10 to 0.01 M favor their dissociation into an ionic state and high concentration inhibit micellization (Peterson et al., 1983; Harris, 2007; Belhaj et al., 2020). Hodgkinson (1991) found damage to calcareous fossils at a concentration of Decon 90 up to 25%. Thus, following manufacturers recommendation a 5% dilution was followed for both Pinequat and Decon 90, the active ingredient concentration of which is unknown. Pinequat (5% *v*/v) prepared in pure water has a pH of 7. Decon 90 (5% v/v) is a proprietary blend of anionic and nonionic surfactants in KOH and has a pH of 13, so a solution of NaOH at the same pH was prepared to control for the effect pH alone. Following the preparation by Theisen et al. (1968), Calgon (5% wt/v) was made up in (5% wt/v) Na_2CO_3, which was also tested independently. Saturating and simmering in pure water was considered the baseline for intra-sample comparison. Bracketing saturation and simmering solutions gives a total of 12 combinations tested against each sample (Fig. 1B).

Grain size and mineralogical heterogeneity even within the same sample can impose considerable variation in results on mass evolution studies; therefore, following the methodological suggestions by Alves et al. (2021), initial sample fragments were randomly divided into test tubes and two trials were performed for each treatment.

2.2.2. Modified disaggregation procedure

Samples were crushed by percussion mortar and dry sieved to collect the fragments between 3.5 mm and 0.5 mm that would be taken through processing. This size interval was selected based on preliminary experimentation on the effects of starting size outlined below. Approximately 10-g aliquots of separated sample were weighed, added to 15 mL test tubes, and covered in saturating solution (Fig. 1A). After 24 h the

Table 2
Prepared chemical solutions.

Chemical	Formula/structure	Preparation	Solution pH	Proposed mechanism	Hazards
Saturating					
Water (18 Ω)	H_2O		5–6	Frost wedging	None
Saline	NaCl	25% NaCl	5–6	Na^+ disrupts clay structure (Hanken, 1979)	None
Simmering					
Water	H_2O		5–6	Control	none
Decon 90	A mixture of anionic and non-ionic surface-active agents, stabilizing agents, alkalis in 0.5–2% KOH non-phosphate detergent builders and sequestering agents	5% *v*/v	>13	Clay dispersant, KOH removes organics (Hodgkinson, 1991)	Caustic at high concentration
Sodium Hydroxide	NaOH	2 mL/L	>13	Removes some acid insoluble contaminants (Hodgkinson, 1991)	Caustic
PineQuat	Primary active ingredient 3% Didecyldimethylammonium chloride	5% *v*/v	7–8	Clay dispersant (Peterson et al., 1983)	Skin/eye irritant
Sodium Carbonate	Na_2CO_3	5% v/v	12–13	Removes silica and aluminum from clay (Hodgkinson, 1991)	Caustic at high concentration
Calgon	Sodium hexametaphosphate	1% Calgon in 5% sodium carbonate	12–13	Clay dispersant (Wintermyer and Kinter, 1955)	Inhalant, irritant

Note: pH was estimated using litmus paper and monitored regularly for stored chemicals. All solutions prepared in 18 Ω water.

solution was decanted and the sample frozen at −14 °C for at least 3 h. Before removing frozen samples, a hot water bath, as well as the simmering solutions, were prepared at 90–100 °C. The warm surfactant was poured directly into the test tube, capped lightly, and then immediately submerged in the water bath right out of the freezer. The duration of simmering was determined by preliminary tests that monitored pH of solutions, so that surfactants remained within working range without buffering. The simmered contents were then immediately wet sieved with 18 Ω water into targeted size fractions (>0.500 mm, 0 0.500–0.250 mm, and 0.250–0.063 mm) and dried at 40 °C, to avoid thermal alteration of clay minerals (Thomas and Murney, 1985), in an oven until the mass difference between subsequent weighing was zero. Each dried collection was weighed and the dacryoconarids were counted. The >0.500 mm size fraction was returned to the test tube and the disaggregation process repeated and the <0.500 mm residue was archived. Any fossils from the >0.500 mm size were removed to avoid recounting in the next cycle. A complete cycle under this protocol starts with saturation and ends with fossil counting (Fig. 1A).

2.2.3. Assessment of extraction efficiency

Adult dacryoconarids grew to between 5 mm and 1 mm (Wei et al., 2012), but most average <1.0 mm with the embryonic chamber typically ranging from 0.15 mm to 0.08 mm in diameter (Li, 2000; Brocke et al., 2016). The size range of the residue collected after each cycle of the process was 0.500–0.063 mm. This was further divided into two approximately equal size fractions, 0.500–0.250 mm and 0.250–0.063 mm, each collected separately. The two size bins facilitated more efficient counting under light microscope, and assessment of the size frequency (larger or smaller rock fragments) of the disaggregate. Intact fossil specimens are defined as having both embryonic chamber and adult conch, which permits species level identification, whereas a fragment is either part (Fig. 1C). The number of intact and fragmented specimens were counted for the >0.500 mm, 0.500–0.250 mm, and 0.250–0.063 mm fractions and recorded each cycle. Counts were used as a means of inter-sample comparison on the fragmentary nature and extraction potential of the chemical application on specific matrices, since intra-sample comparison cannot be made without accounting for fossil abundances and preservation. The present study was limited by material availability to using only 10-g samples, which was effective in this case because the approximate fossils concentration was known from previous investigation using traditional methods (Richard Lindemann, personal communication). Our use of consistent rock sample mass allows for quick assessment of the disaggregation rate of chemical treatments between different matrices. However, because the small sample size in this study might not be representative of fossil abundances found elsewhere, 10 g should not be relied upon as guide to sampling plans. In real fossil disaggregation applications that begin with rock samples having unknown fossil abundance, a test run that applies the recommended extraction protocol with 100–200 g (or more) of rock will be necessary to gauge the amount of raw material required to extract sufficient numbers of fossils depending on their abundance.

Five cycles were performed for each treatment (Fig. 1B) to observe a general trend. Disaggregation efficiency of the treatments was assessed by calculating percent gain of the mass removed each cycle, which is expressed as

$$\text{Percent Gain} = \frac{\text{mass size fraction collected (g)}}{\text{initial sample mass (g)}} \times 100\% \quad (1)$$

Cumulative percent gain was tracked over five cycles and plotted to compare treatments on each sample (Fig. 3).

2.2.4. Traditional method

All previously used methods with documented dacryoconarid recovery employed a different cationic surfactant and mode of maceration (Jarochowska et al., 2013; Frappier et al., 2015; Meehan et al., 2020). For most direct comparison to the current study, the method outlined in Frappier et al. (2015) was replicated due to similarities in the processing steps and equivalent rock samples. Neither starting size nor concentration of surfactant was reported in that study and the agent used, Quaternary-O, is no longer available, so these parameters were chosen from literature that used comparable surfactant-based protocols. To approximate the traditional method, two replicates of ~10 g samples of CV and GL were coarsely crushed to between 2 and 3 cm^3 (Peterson et al., 1983; Kennedy and Coe, 2014) and simmered in open vessels (90–100 °C) on a hot plate in either 5% Pinequat or 5% Decon 90 (Hodgkinson, 1991) for a total of 16 h (Frappier et al., 2015). The resulting material, colloquially known as “stone soup”, was sieved into 0.500–0.063 mm fractions after 8 h and the surfactant solution was replaced.

3. Results

3.1. Starting size fragments

Surface area is well-known as an important factor in physical and chemical weathering of rocks. Mechanical crushing has the desirable effect of increasing surface area providing a simple and quick mechanism to separate some fossils from rock matrices (Fig. 2). But, excessive crushing can also fragment delicate microfossils. Both whole and broken dacryoconarid shells found in thin-sections from deep drill cores of the (Mason, 2017), show that all shell fragments are not produced by physical sample processing and highly fragmented styliolinids can be a post-depositional product of environment (Sageman et al., 2003). Preliminary tests on CV, a limestone, established the influence of initial grain size on the rate of rock disaggregation and intact fossil extraction. Approximately 1.5 g of rock fragments were sorted into roughly four size intervals (0.5–1 mm, 1–5 mm, 5–10 mm, and 10–15 mm) and processed by water/water treatment for 5 cycles (Fig. 2A). The smallest starting size (0.5 to 1.0 mm) yielded the highest fossil counts (10 shells) as well as highest percent gain (7%). To further test this observation, we carried out a similar set of experiments with narrower size intervals (1–3 mm, 3–5 mm, 5–8 mm and 8–10 mm). The smaller intervals show a more consistent trend of cumulative percent gain. Although the 0.5–1 mm interval showed over all best results in terms of total and intact fossil counts (Fig. 2B) and percent gain after 5 cycles, it was deemed appropriate to start with a larger size range because some dacryoconarids can be up to 5 mm long (Wei, 2019). Sieve sizes of 3.36 mm and 0.500 mm were used as the upper and lower starting size limits for the remaining trials and two replicates of each treatment was performed to account for heterogeneity in sampling.

3.2. Trends in percent gain

The samples can be categorized broadly into siliclastic (GL, BS-5, and BS-25) and calcareous (CV and OC) that differ by varying degrees of clay content (Table 1). For the water saturation treatments, BS-5 had the highest percent gain among all samples after five cycles, ranging between 27% (Decon 90) and 33% (Calgon) (Fig. 3). The laminated black shale, BS-25 had the lowest gain among samples ranging from <2% (water, Decon 90, NaOH) to 8% (Calgon). Percent gain for the remaining siliclastic sample, GL, ranged from 4% (NaOH) to almost 12% (Calgon). For limestones, gain ranged from 3% (NaOH) to 13% (Calgon) for CV and 3% (Decon 90) to 17% (Calgon) for OC. For all rock types, Calgon had the highest gain followed by Na_2CO_3 which both increased in gain quadratically across 5 cycles, whereas the other treatments increase linearly except for sample BS-5 where all treatments increase gain logarithmically.

All sodium chloride saturation treatments had logarithmic percent gain (Fig. 3). The siliclastic samples had comparable gains between saturation solutions, whereas the calcareous samples had half as much gain for saline solution as the water saturation treatments. Except for the two shales, the addition of salt reduced the gain of the water simmering

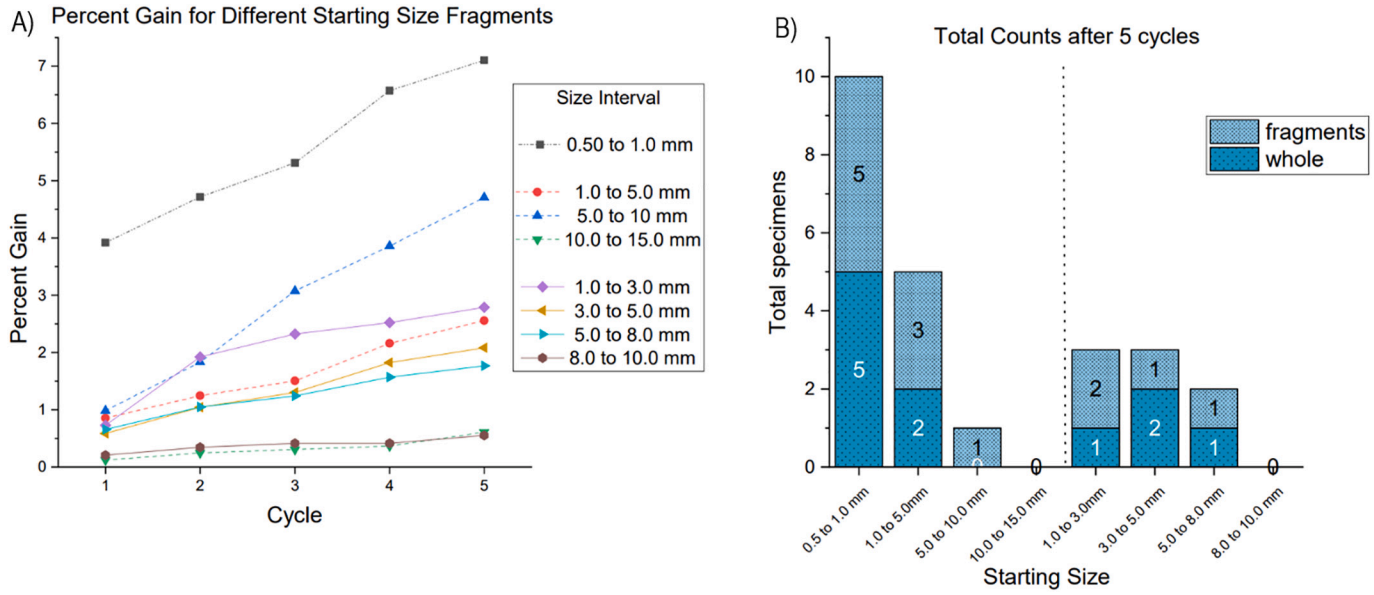


Fig. 2. A) Cumulative percent gain of disaggregated residue for sample CV with different intervals for starting size rock fragments. Only one trial was performed for each. Dotted lines are size intervals of 5 mm and solid lines are intervals of 2–3 mm. B) Stacked bar chart of cumulative intact (dark blue) and fragmented (light blue) specimen counts after the 5 cycles for each starting size interval. Superimposed values show counts. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

treatments and it furthermore reduced the gain of Calgon and sodium carbonate for all samples. For the shales (BS-25 and BS-5), water and NaOH achieved the highest percent gains within uncertainty with overall percent gain comparable to Calgon for the water saturation treatments. For both GL and CV Decon 90 paired with sodium chloride had the highest percent gain.

Undergoing the traditional method, CV yielded <0.1% gain for both Decon 90 and Pinequat after simmering for 16 h (Fig. 6). GL yielded an average of <0.3% gain using Decon 90 and 1.75% gain using Pinequat. Overall percent gain was lower for both samples using the traditional method compared to the first cycle of the new method, which take about the same amount of total time.

3.3. Size frequency of disaggregation

One of the goals of this experiment was to determine if cumulative disaggregation after 5 cycles for each treatment favored a larger (0.500–0.250 mm) or smaller (0.250–0.063 mm) size fraction, which may indicate if a size-preparation step adds utility in extracting target fossils at certain sizes. The cumulative frequency of the larger size fraction (0.500 mm to 0.250 mm) to the smaller (0.250–0.063 mm) collected each cycle was calculated (Fig. 4). For the water saturation treatments, all samples had >55% frequency for the larger size. CV had the narrowest range of differences in highest to lowest frequency ranging from 61.5% (Pinequat) to 67.5% (water) and BS-25 had the largest range of differences of 56.1% (water) to 76.4% (Calgon). The other samples are uniform with no distinguishing patterns between lithology and chemical treatment. For BS-25, salt saturation in general resulted in a slightly higher frequency of smaller fragments across treatments, but there is no discernable trend among the other samples.

3.4. Fossil counts

Cumulative intact and fragmented fossil counts were recorded and the ratio of intact to fragmented specimens was calculated for each treatment (Fig. 5). No fossils were extracted from BS-5 of any kind and no intact fossils were found in OC. For sample OC under water saturation, Na_2CO_3 and Calgon have considerably higher counts (406 and 306 respectively) than the other treatments, which extracted the same number of fossils (~90 to 100) within error. For CV, Decon 90 extracted more total fossils (~80) than NaOH (~69), water (~68), and Pinequat (~36), but within error of Na_2CO_3. The two non-surfactant alkaline solutions, NaOH and Na_2CO_3, had the highest ratio of intact fossils for this sample. For both calcareous samples, Calgon extracted fewer fossils than Na_2CO_3. For the black shale, B-25, water (~26) followed by NaOH (~12) had the highest total counts, but so few specimens were extracted that the error between each treatment is large. For GL, a similar pattern to OC sample was revealed, but Calgon (~3743) extracted more than Na_2CO_3 (~2935). Pinequat had the lowest ratio of intact fossils for both GL and CV. In general, NaCl saturation led to fewer fossils counts for all samples and lower intact ratio. Only BS-25 had higher intact fossil recovery, but total counts between saturation solutions were within error for most treatments.

4. Discussion

Several studies have individually examined the utility of surfactants on fossil extraction compared to matrix dissolution methods; however, it is difficult to isolate the individual effect of several important factors in the process of disaggregation (Peterson et al., 1983; Kennedy and Coe, 2014; Beasley et al., 2020; Meehan et al., 2020). We aim to tease apart the physical/chemical influences projected onto the sample materials by individual reagents and experimental steps.

4.1. Influence of mechanical crushing and repeated freeze-thaw

Part of our investigation evaluated the effect of mechanical crushing, specifically what starting sample particle sizes would best accelerate fossil-matrix disaggregation while minimizing fossil fragmentation. We find that while crushing into such fine fragments was suitable for the current study based on our results, if in future studies reconnaissance sampling reveals high proportions of larger specimens it is recommended to start with 2–3 cm^3 size fragments and proceeding with a few cycles before crushing to the smaller size range.

One aim of this study was to test the efficiency of freeze-thaw as a mechanical treatment, without additional chemicals. This was examined by using pure water to saturate and boil samples in. Every treatment above or below the water/water trend line outside of its uncertainty can

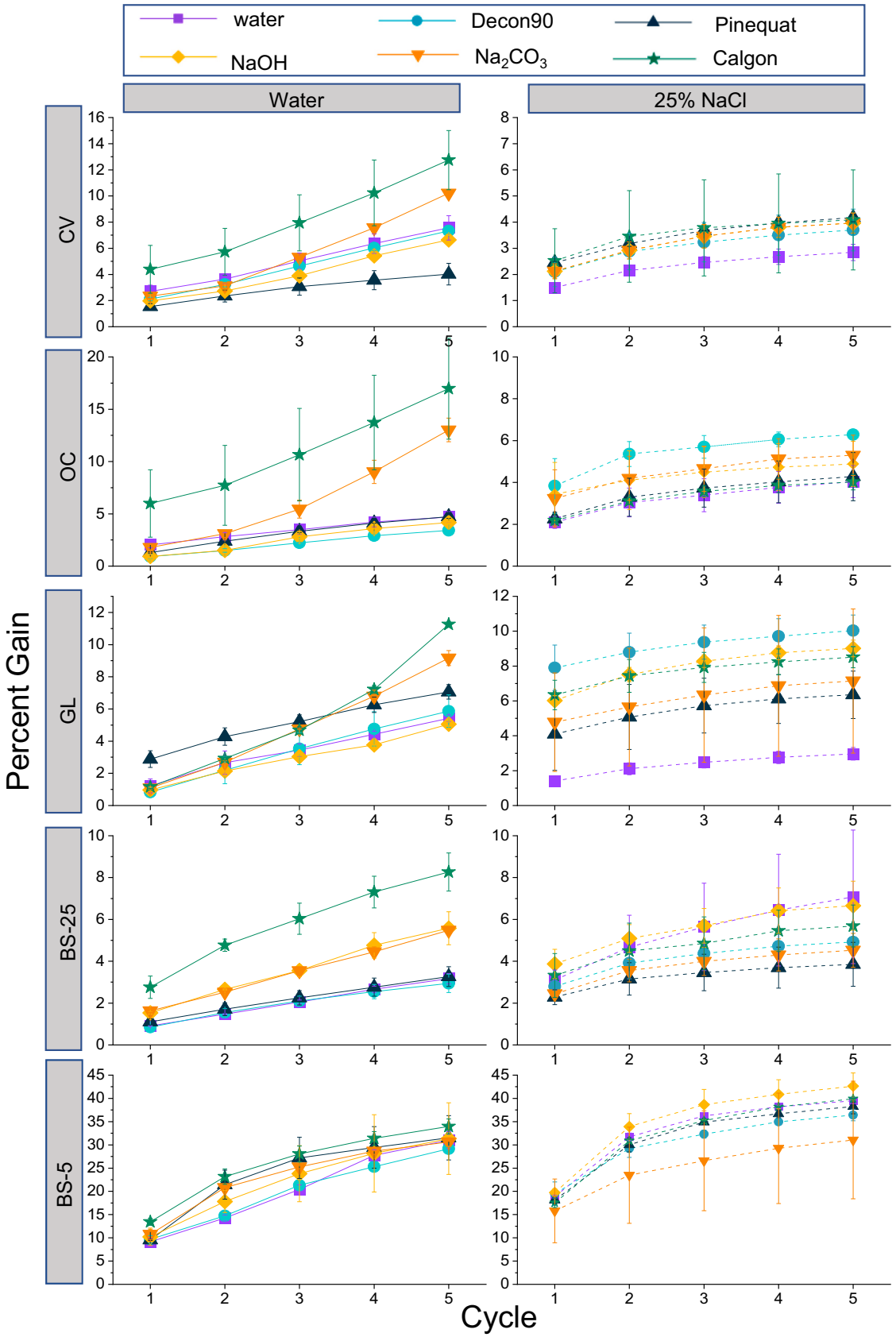


Fig. 3. Average trends in cumulative percent gain for water-saturation (left, solid lines) and saline-saturation (right, dotted lines) methods on each sample across 5 cycles, where each line colour/symbol represents one chemical agent. Error bars are calculated as the minimum and maximum from the midpoint of two trial average.

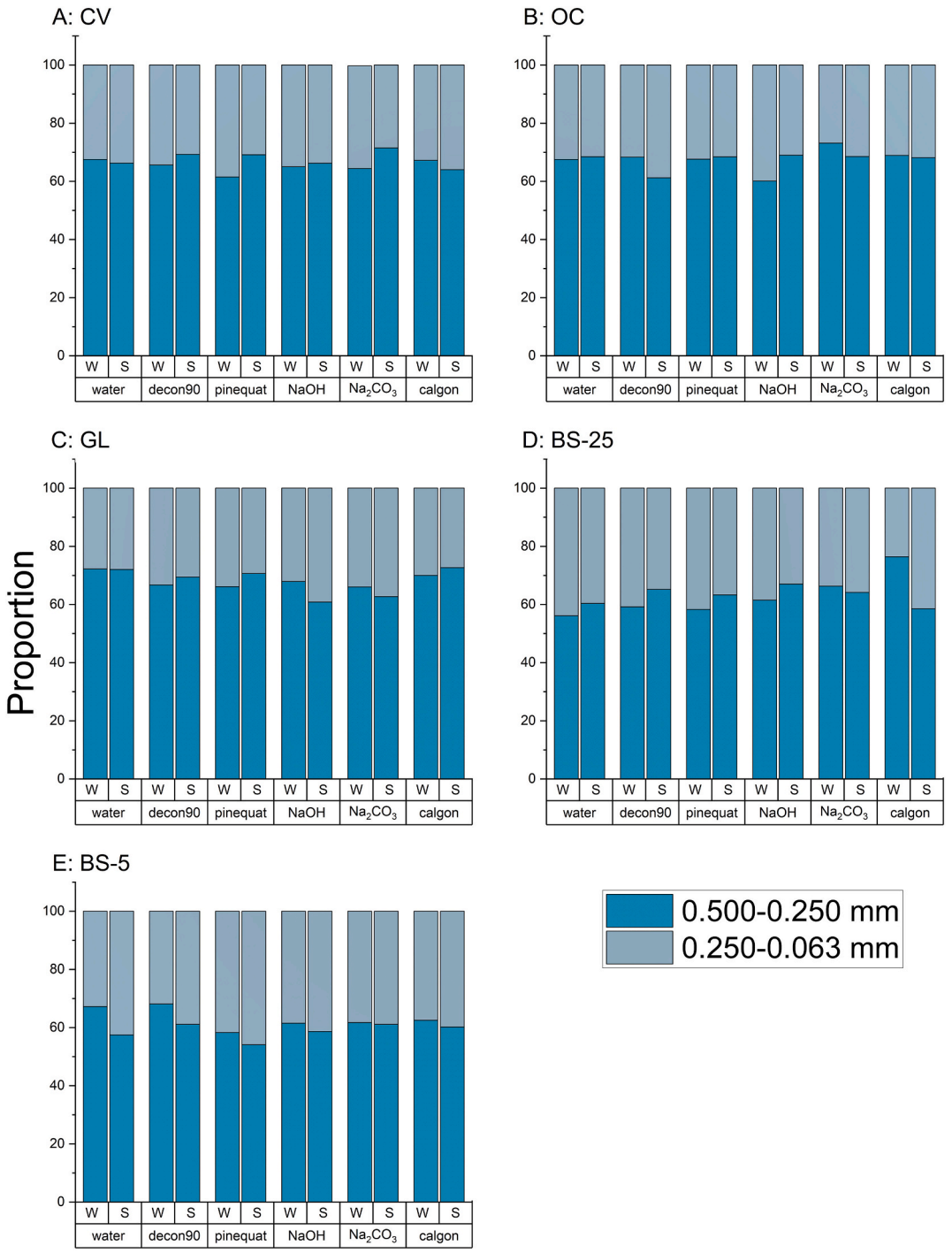


Fig. 4. Cumulative proportion by rock sample (A-D) of larger (0.500–0.250 mm, dark blue shading) and smaller (0.250–0.063 mm, light blue shading) size fractions disaggregated after 5 cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

be viewed as the effect of chemicals (Fig. 3). For every sample, repeated freeze-thaw produces a linear trend by disaggregating a consistent amount each cycle. BS-25 had the lowest slope (0.33% per cycle) and the lowest frequency large size fraction (56.1%). We attribute this to its low porosity and limited infiltration (Fig. 4). Freeze-thaw alone extracted generally low amounts of fossils and proportion of intact fossils, except for the black shale. Freeze-thaw extracted the most intact specimens from the black shale BS-25 despite the treatment having the lowest total gain for that rock sample (Fig. 5).

Laboratory studies on the durability of limestones and sandstones subjected to repeated freeze-thaw cycling have shown that its role on disaggregation is generally independent of composition of the rock, but dependent on degree of saturation (Nicholson and Nicholson, 2000; Al-Omari et al., 2015; Eslami et al., 2018). This parameter depends on permeability rather than porosity. Furthermore, under the high pressure of small pore space the freezing temperature of ice is drastically lowered and the time it takes for critical saturation may take up to 48 h or longer (Al-Omari et al., 2015). Several parameters including material (grain size and shape, preexisting flaws, compressibility, permeability), environmental conditions (temperature, rate of cooling, water pressure) and time are all contributors to the degree of fracturing by freeze-thaw (Walder and Hallet, 1985; Eslami et al., 2018). Therefore, the

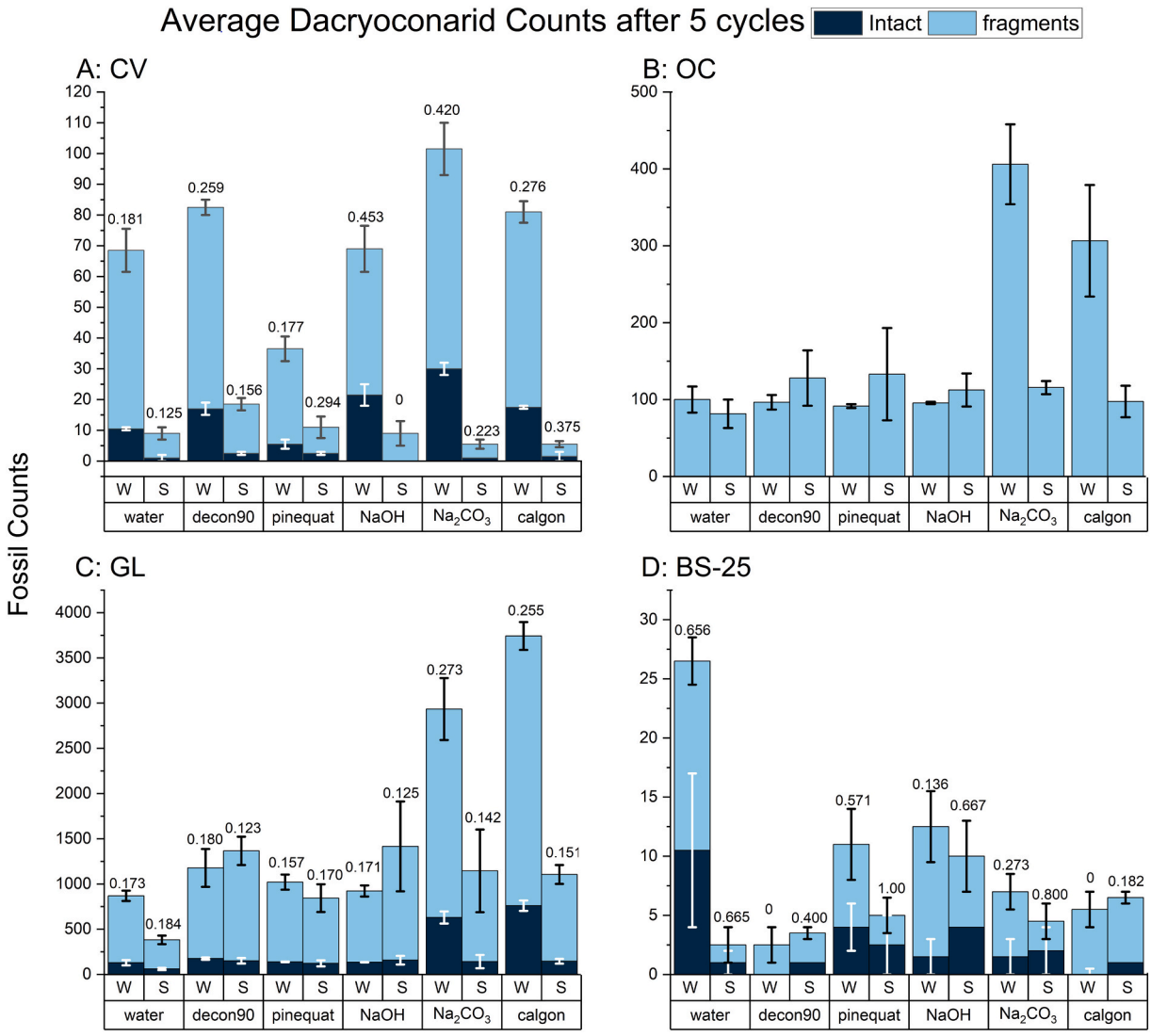


Fig. 5. Average cumulative dacryoconarid counts by rock sample (A-D) after 5 cycles for water (W) and saline (S) methods and by surfactant. Numbers above the bars are the average ratio of intact (dark blue) to fragmented (light blue) specimens. Error bars are the maximum and minimum counts of the duplicate trials for intact and fragmented specimens. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

efficiency of freeze-thaw as a mechanical process is not predictable unless permeability of the samples is known, which will be a matrix specific rather than grain specific characteristic. The highly compacted black shale yielded the lowest percent gain for freeze-thaw (2%), but most samples yielded <4%.

4.2. Influence of solution pH

An important parameter on the adsorption dynamics of surfactants is pH, which dictates its working range and the speciation of minor components on the surface of the rock with which they react (Harris, 2007). We assess the influence of pH alone on disaggregation by pairing a surfactant with a solution of a similar pH. Sodium Hydroxide (pH 12) performed better than Decon 90 only on the black shale BS-25, where NaOH achieved the same gain as Na_2CO_3 (pH 13). Water (pH 5) and Pinequat (pH 7) had the highest ratio of intact to fragmented fossils for BS-25 (Fig. 5D), but this trend is not seen in the other siliclastic sample, GL. For the limestone CV, percent gain for NaOH was similar to Decon 90, but a higher proportion of intact fossils was extracted for both alkaline solutions NaOH and Na_2CO_3. The other calcareous sample, OC, had no difference in fossil counts for NaOH compared to Decon 90 but Na_2CO_3 was the most effective at almost 3 times higher (Fig. 5A). These observations suggests that the identity of conjugate ions is the primary driver in extraction of fossils rather than the hydroxide concentration exclusively. Thus, the attack of hydroxide on the rock at these exposure times (20 min.) is minimal and ineffective at extracting fossils. The main contribution of solution pH on disaggregation is through the speciation of surface species and the surfactants, not on dissolution of matrix.

4.3. Influence of surfactant type

During experimentation, both Calgon and Na_2CO_3 reacted violently with BS-5, and to a lesser extent with BS-25, on contact for the first two cycles. A layer of red sediment <0.063 mm, presumed to be clay minerals evolved and was removed during rinsing. This observation is supported by studies on the clay dispersing properties of Calgon and Na_2CO_3 from soils (Wintermyer and Kinter, 1955; Theisen et al., 1968). Polyphosphates, like Calgon, are employed in soil particle size analysis because they dissociate in solution providing cations and polyatomic anions that can complex with components of clay minerals and separate them from the rest of the sediment (Hatch and Rice, 1939; Green, 2001). Calgon provides Na^+ ions that disrupt the interlayer of clay minerals by cationic exchange with K^+ causing them to expand and damage the structure (Wintermyer and Kinter, 1955); furthermore, Calgon absorbs

rock surface cations like Ca^{2+} and Mg^{2+} and leaves the surface exposed to further chemical aggression (Andreola et al., 2004). This could explain the quadratic nature of the percent gain for Calgon on the calcareous samples. A study on the dispersive properties of Calgon on kaolinite found that following 4 h of reaction at room temperature the concentration of Al in solution was greater than that of Si, which suggests it also disrupts the octahedral planes of kaolinite rather than the tetrahedral silicon planes (Andreola et al., 2004). This was noted in early studies comparing Calgon and Na_2CO_3 which found that Na_2CO_3 had a better potential for dispersing soil cemented with high amounts of silicon and aluminum, but was not always consistent and therefore pairing the two was suggested (Wintermyer and Kinter, 1955; Theisen et al., 1968). Furthermore, Calgon quickly degrades in solutions less than pH 7 and among excess cations, so long exposure times would be expected to reduce the effect of Calgon (Andreola et al., 2004). Buffering in Na_2CO_3 and shorter exposure times in this study may promote the disaggregating potential of Calgon on all rock types.

Another study that examined the amount of disaggregation following repeated 24 h soaking in Calgon buffered by Na_2CO_3 at room temperature found that the combination performed best on coarse grain sandstone in clay matrix, but did not achieve >5% gain of fossiliferous fraction (Beasley et al., 2020). In comparison, the current study ranged from 8% to 35% gain for the same pairing. This indicates that freeze-thaw processing and/or the addition of heat might be contributing to the activity of the solution by reducing the reprecipitation of carbonate compounds (Hatch and Rice, 1939). Comparing Na_2CO_3 and Calgon solutions independently, the presence of Calgon is contributing to improved gain, but may also be fragmenting the fossils more since Na_2CO_3 generally had either higher total counts or higher ratio of intact fossils (Figs. 2 and 4).

Several studies have investigated the adsorption dynamics of surfactants onto natural surfaces (ShamsiJazeyi et al., 2014; Daghlian Sofla et al., 2016; Tagavifar et al., 2018). Anionic surfactants are typically used for extraction from sandstone reservoirs in the field of oil recovery due to low adsorption resulting from negative charge repulsion between the surfactant and silica (Belhaj et al., 2020). Cationic surfactants are typically used with limestone due to the limited interaction with positive charges on calcite (Sanchez-Martin et al., 2008). However, it has been found that trace mineralogical heterogeneity and accessory minerals can drastically change the electrostatic potential of rock surfaces and therefore the ability of surfactant adsorption (Ma et al., 2013; Tagavifar et al., 2018).

Assessment of the trends in disaggregation of Pinequat and Decon 90 requires consideration of the dynamics of surfactant adsorption. When a charged particle is hydrated an electrostatic double layer forms (Ma, 2012). The first layer adsorbed to the surface is a monolayer of ions of opposite charge. However, this layer does not entirely negate the surface charge of the particle so a second 'diffuse' layer forms which permits the exchange of ions from solution. The point of zero charge (pzc) is the pH at which the net charge of the surface of a material is zero (Tagavifar et al., 2018). This varies between materials where metal oxides have a higher pH-pzc than calcite, for instance. In a study on the adsorption dynamics of anionic surfactants on natural limestones across a range of pH it was found that adsorption decreases linearly with pH and ionic strength (Tagavifar et al., 2018). Independent of concentration, at low pH adsorption of both anionic surfactants is pH dominated by the interaction of the surfactant head group, with positively charged sites on clay and calcite surfaces. At pH >10 the hydrated surface species become negatively charged due to the loss of hydrogen from hydroxyl groups, but promotes hydrogen bonding with the surfactant tail to the surface, which is a weaker bond. Therefore, concentration of surfactant is not an important factor for limestones with clay or metal oxide contents, but the surfactant structure, presence of competing cations and clay mineralogy is important. The exact structure of Decon 90 is unknown, but its pH of 12 suggests that it performs no better than the water treatments for any sample due to surface charge reactions promoting hydrogen bonding onto calcite rather than adsorption of the surfactant onto trace minerals. Cationic surfactants exhibit negligible adsorption onto synthetic calcite, but significant adsorption onto natural carbonates due primarily to silica composition and therefore the choice of cationic or anionic surfactant is best determined if silica composition is known (Ma et al., 2013). This is supported by our results which show that Pinequat performs better than Decon 90 for the siliclastic sample GL, but is least effective for the sample with the highest carbonate composition, CV. However, Decon 90 extracted more fossils than both water and Pinequat for both GL and CV, but not the black shale (BS-25) or the argillaceous limestone (OC) (Fig. 5). It is possible that slight compositional differences between the fossil and matrix permitted Decon 90 to extract more fossils these two samples. In addition, there is likely a narrow pH working range for surfactants that would promote more effective extraction of calcareous fossils. The safe pH range for calcium carbonate fossils without dissolution is 8.6 to 9.4; therefore, in principle a suitable dispersant for calcareous fossil extraction might have a similar working pH range, so as to not erode the fossils.

4.4. *Influence of saturating solution*

Sodium chloride saturation had the least impact on CV (limestone) with only half as much cumulative yield as the water saturating treatments (Fig. 3) and considerably fewer fossil counts (Fig. 5). For OC and GL, counts for salt saturation were within error for all treatments except Na_2CO_3 and Calgon, which have nearly half the total counts. Several studies have addressed the role of brine on the disintegration of different materials (Haynes and Bassuoi, 2017; Alves et al., 2021 and references therein) and have shown that the two most important parameters are pore size and degree of saturation, similar to freeze-thaw. Small pore space in the case of salt crystallization promotes greater fracturing due to high pore pressures and most salt weathering occurs subsurface to the extent it can permeate resulting in irregular pitting and scaling. Fracturing is done primarily by crystal expansion rather than disruption of clays by the sodium. More significant erosion occurs with cyclic conditions (wet to dry) than allowing total permeation (Haynes and Bassuoi, 2017). However, in this study the NaCl saturation altered the trends of all treatments toward logarithmic reducing fossils counts as well. In addition, for all samples but the shales, NaCl saturation led to reduced gain for all water simmering treatments. This may be related to the diffusion of water compared to brine, which would have a large hydrated sphere around each ion (Yu et al., 2022). This large hydration sphere may prevent the salt from invading pore space in the 24-h saturation time frame. Salt efflorescence, the apparent whiting on the surface of rocks due to repeated recrystallization, was observed after 5 cycles. This may be the cause of diminishing percent gain. If redissolution of surface deposits is not occurring due to the high concentration of the brine, then this could be preventing subsequent erosion.

A study on the dispersive effects of Calgon on colloidal kaolinite in the presence of alkali salt solutions reported decreasing dispersion at higher ionic strengths (Ma, 2012). This is because at higher ionic strength the diffuse layer becomes contracted so that only smaller ions can exchange. At high enough ionic strength this layer becomes permeable only to Na^+ so that Calgon cannot interact with the surface. They found the highest dispersion potential for Calgon was in pure water which is supported by this study.

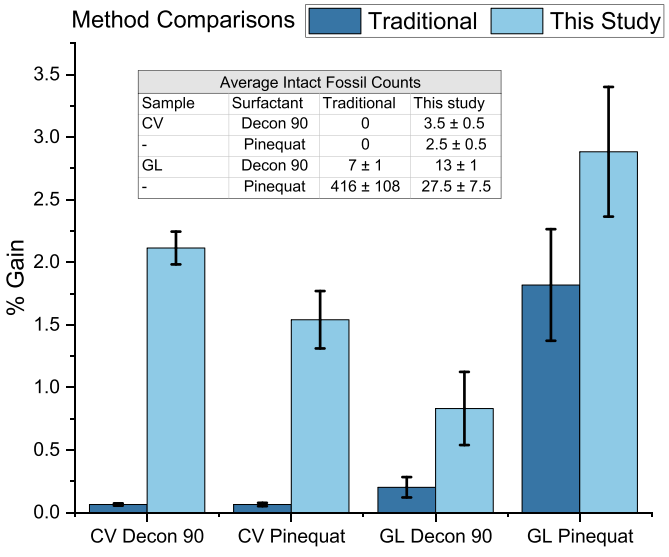
Decon 90 had higher fossil counts for OC, GL and OC in salt saturation compared to water saturation, but the opposite trend was observed for Pinequat (Fig. 5). Likewise for these samples, percent gain was much higher for Decon 90 (up to 5% cumulative gain, but Pinequat gain was largely unaffected. For GL and OC, the NaCl-Decon 90 pairing had the highest gain for any treatment. A review on the effects of salinity on surfactant adsorption behavior indicates that at moderate salinity anionic surfactants may have higher adsorption onto surfaces with higher silica content by protonation of some of the surface charges by salt ions, thus reducing surfactant repulsion. But at high salt

concentrations contraction of the double layer at the surface of the rock prevents adsorption of surfactants, like Decon 90 and Calgon, that are too large to be permitted (Belhaj et al., 2020 and references therein). Cationic surfactants, like Pinequat, having the same charge as Na^+ would be affected by competition for binding sites.

4.5. Comparison with traditional method

For disaggregating carbonate fossils from rocks of different composition, comparison of the present method with the traditional corroborates our findings that cationic surfactants more readily disaggregate arenaceous matrices, and that anionic surfactant are generally better paired with rocks that have calcareous cements (Peterson et al., 1983). GL was fissile and readily disaggregated just by simmering in Pinequat without any crushing.

The highly cemented CV had <0.5% gain employing either Decon 90 or Pinequat under the traditional protocol (Fig. 6), but a clear difference arose when comparing the surfactants under the present method. This result further illustrates that crushing the limestone into smaller starting pieces can improve extraction efficiency for highly cemented rocks, like CV, but might not be necessary for laminated facies such as GL. Furthermore, some tight lithologies are reported to be resistant to the traditional "stone soup" method, even after extended continuous simmering for more than two weeks (R. H. Lindemann, personal communication, 2020). The traditional method extracted considerably more whole fossils (416 ± 108) compared to the current method (27 ± 7.5) from GL using Pinequat despite disaggregating less total material (Fig. 6). For some applications, this may be a desirable result that warrants the loss of processing efficiency due to the more time-consuming traditional process. The following caveat applies: the current study is limited by small sample sizes used, and the small number of replicates, and it is difficult to ascertain the true extraction potential with small sample sizes, which leads to large discrepancies in fossil counts. That could result from either real methodological differences in extraction potential or subsamples with differing fossil concentrations. Furthermore, the new method is more effective with several cycles rather than only one. There are several disadvantages to the traditional method. It requires more active hands-on time as simmering solutions must be regularly monitored and the solution replenished. Evaporation from open containers meant that not only were pH and concentration not controlled and highly variable, but also a larger quantity of solution was required for the traditional method, whereas only enough to cover the material is required of the new method.



Average Intact Fossil Counts

Sample	Surfactant	Traditional	This study
CV	Decon 90	0	3.5 ± 0.5
-	Pinequat	0	2.5 ± 0.5
GL	Decon 90	7 ± 1	13 ± 1
-	Pinequat	416 ± 108	27.5 ± 7.5

Fig. 6. Cumulative percent gain for samples CV and GL after one cycle of the new method using water saturation compared 16 h of simmering via the traditional method in either 5% Decon 90 or 5% Pinequat. Error bars are the minimum and maximum values calculated from two replicates.

4.6. Future research

Future research could investigate the influence of concentration or functional group of surfactants on rate of disaggregation. This study chose surfactants currently employed and easily accessible. However, because the structure and the composition of the active ingredients in Decon 90 is proprietary by diluting the solution to 5% it might have reduced its effect. At low concentrations surfactant adsorption forms a monolayer on the surface, as concentration increases intermolecular interactions cause the formation of micelles (Belhaj et al., 2020). There is a concentration at which this behavior plateaus and increasing surfactant concentration becomes disruptive to micellation. Further steps can be taken to improve efficiency of extraction aided with the knowledge of correct surfactant-lithology pairings. Studies on sodium salts suggest that sulfate followed by sodium carbonate then chloride salts yield most rapid erosion for sedimentary rocks. Dehydration of sodium sulfate in pore space is accompanied by a phase change with 300% volume expansion whereas NaCl is strictly a recrystallization process (Haynes and Bassuoi, 2017). Further research could systematically examine both the optimal anionic surfactant and salt concentrations or identities for more rapid disaggregation of limestones. The optimal initial mechanical processing size could be further evaluated. Improved assessments of the compositional properties of limestones, such as thin sections, could be used to facilitate understanding of calcareous microfossil extraction from this rock type using surfactants. Last, the application of this methodology to other microfossils groups could broaden its scope of use.

5. Conclusion

This study systematically investigated the role of surfactant type on rock disaggregation and fossil extraction to understand a first order mechanism. Depending on composition, surfactants may improve extraction efficiency in combination with cyclic freeze-thaw mechanical disaggregation by selectively removing specific contaminants. For limestones, Decon 90, an anionic surfactant, had greater total and intact fossils extraction compared to Pinequat, a cationic surfactant, and freeze-thaw alone likely because Decon 90 can react with positively charged surface species. Pinequat, alternatively, performed better for siliclastic samples by selectively attacking negative surface species. For maximum extraction potential using surfactants knowledge of rock composition is essential as even minor contaminants and the speciation of those contaminants due to solution pH or high ionic strength can drastically reduce disaggregation efficiency. Calgon and Na_2CO_3 performed optimally for more argillaceous samples as they both disrupt the bonding of clay minerals, but they also performed well on carbonates and siliclastic samples as both can also dispel surface species on these rock types. Nevertheless, Na_2CO_3 solution alone generally extracted more total fossils or higher proportion of intact fossils across all rock compositions compared to any surfactant. The recommended method for extraction of calcareous dacryoconarid fossils from most rock types is water saturation freeze-thaw processing followed by boiling in 5% Na_2CO_3. For black shales specifically water saturation followed by boiling in water is recommended. Altogether, the most efficient saturating/simmering solution pairing assessed in this study was pure water/Na_2CO_3. Despite the Calgon disintegrating variable matrices more rapidly, it was more fragmentary than other chemical treatments. For each sample that contained dacryoconarids an analytically viable amount (at least 10 mg) (Frappier et al., 2015) of fossil material was extracted in 5 cycles with only 10 g of starting material. This was calculated from estimates of average body mass of intact dacryoconarid conches found in sample GL (Fig. 7). Total hands-on time for one cycle is

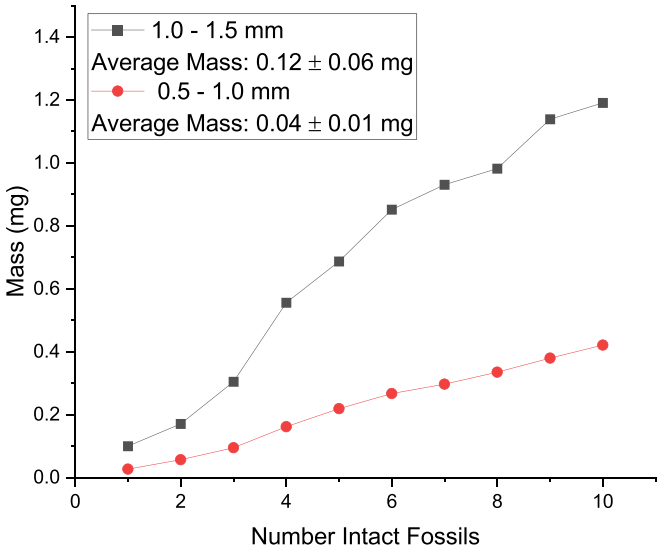


Fig. 7. Plot of mass trends of dacryoconarids sequentially added to a balance of two intact fossil size classes by conch length, 1.0 to 1.5 mm (black squares) and 0.5 to 1.5 mm (red circles), extracted from GL. Uncertainty of average mass reported as ±1σ. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

estimated to be 30 min with total estimated time extraction time <36 h per cycle.

CRediT authorship contribution statement

Ashley N. Prow: Conceptualization, Methodology, Investigation, Data curation, Visualization, Project administration, Formal analysis, Writing - original draft, Writing - review & editing. **Zunli Lu:** Formal analysis, Supervision, Funding acquisition, Resources, Writing - review & editing. **Amy B. Frappier:** Resources, Writing – review & editing. **Lucy E. Weisbeck:** Validation, Investigation, Writing – review & editing. **Caroline R. Underwood:** Validation, Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marmicro.2023.102216.

References

Al-Omari, A., Beck, K., Brunetaud, X., Török, Á., Al-Mukhtar, M., 2015. Critical degree of saturation: a control factor of freeze-thaw damage of porous limestones at Castle of Chambord, France. Eng. Geol. 185, 71–80. https://doi.org/10.1016/j.enggeo.2014.11.018.

Alves, C., Figueiredo, C.A.M., Sanjurjo-Sánchez, J., Hernández, A.C., 2021. Salt weathering of natural stone: a review of comparative laboratory studies. Heritage 4, 1554–1565. https://doi.org/10.3390/heritage4030086.

Andreola, F., Castellini, E., Manfredini, T., Romagnoli, M., 2004. The role of sodium hexametaphosphate in the dissolution process of kaolinite and kaolin. J. Eur. Ceram. Soc. 24, 2113–2124. https://doi.org/10.1016/S0955-2219(03)00366-2.

Baird, G.C., Kischgasser, W.T., Over, D.J., 2006. An early late devonian bone bed-pelagic limestone sucession: the North Evans-Genundewa Limestone story. In: New York State Geological Association Field Trips (Guidebook), pp. 354–395.

Beasley, C., Parvaz, D.B., Cotton, L., Littler, K., 2020. Liberating microfossils from indurated carbonates: comparison of three disaggregation methods. J. Micropalaeontol. 39, 169–181. https://doi.org/10.5194/jm-39-169-2020.

Belhaj, A.F., Elraies, K.A., Mahmood, S.M., Zulkifli, N.N., Akbari, S., Hussien, O.S.E., 2020. The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: a review. J. Pet. Explor. Prod. Technol. 10, 125–137. https://doi.org/10.1007/s13202-019-0685-y.

Bond, P.G., 2006. The fate of the homoctenids (Tentaculitoidea) during the Frasnian-Famennian mass extinction (late Devonian). Geobiology 4, 167–177. https://doi.org/10.1111/j.1472-4669.2006.00078.x.

Brocke, R., Fatka, O., Lindemann, R.H., Schindler, E., Ver Straeten, C.A., 2016. Palynology, dacryoconarids and the lower Eifelian (Middle Devonian) asal Choteč Event: case studies from the Prague and Appalachian basins. Geol. Soc. Spec. Publ. 423, 123–169. https://doi.org/10.1144/SP423.8.

Chen, L.J., Lin, S.Y., Huang, C.C., 1998. Effect of hydrophobic chain length of surfactants on enthalpy-entropy compensation of micellization. J. Phys. Chem. B 102, 4350–4356. https://doi.org/10.1021/jp9804345.

Cureton, J.C., Lewis, P.J., Thies, M.L., 2010. Evaluating acetic acid for removing microvertebrate fossils from Cave Breccia. In: Botswana Notes and Records, 42, pp. 172–178.

Daghlian Sofla, S.J., Sharifi, M., Hemmati Sarapardeh, A., 2016. Toward mechanistic understanding of natural surfactant flooding in enhanced oil recovery processes: the role of salinity, surfactant concentration and rock type. J. Mol. Liq. 222, 632–639. https://doi.org/10.1016/j.molliq.2016.07.086.

Eslami, J., Walbert, C., Beaucour, A., Bourges, A., Noumowe, A., 2018. Influence of physical and mechanical properties on the durability of limestone subjected to freeze-thaw cycles. Constr. Build. Mater. 162, 420–429. https://doi.org/10.1016/j.conbuildmat.2017.12.031.

Feldman, 2004. A review of the laboratory preparation of palynomorphs with a description of an effective non-acid technique. Rev. Bras. Paleontol. 7, 13–44. https://doi.org/10.4072/rbp.2004.1.02.

Frappier, A.B., Lindemann, R.H., Frappier, B.R., 2015. Stable isotope analysis of Dacryoconarid carbonate microfossils: a new tool for Devonian oxygen and carbon isotope stratigraphy. Rapid Commun. Mass Spectrom. 29, 764–774. https://doi.org/10.1002/rcm.7159.

Gessa, S., Lecuyer, C., 1998. Evolutionary dynamics of Pragian Dacryoconarida (lower Devonian, Tentaculitoidea) evidence from palaeontological data and 813C of marine carbonates from Czech Republic. Palaeogeogr. Palaeoclimatol. Palaeoecol. 138, 69–83.

Green, O.R., 2001. Extraction Techniques for Palaeobotanical and Palynological Material, pp. 256–287. https://doi.org/10.1007/978-94-017-0581-3_25.

Hanken, N., 1979. The use of Sodium Tetraphenylborate and Sodium Chloride in the extraction of fossils from Shales, 53, 738–741.

Harris, D.C., 2007. Quantitative Chemical Anaylsis. W.H. Freeman and Company, New York.

Hatch, G.B., Rice, O., 1939. Surface-active properties of hexametaphosphate. Ind. Eng. Chem. 31, 51–58. https://doi.org/10.1021/ie50349a012.

Haynes, H., Bassuoi, M.T., 2017. Physical salt attack on concrete. J. Sustain. Cem. Based Mater. 6, 195–216. https://doi.org/10.1080/21650373.2016.1218802.

Hellawell, J., Nicholas, C.J., 2012. Acid treatment effects on the stable isotopic signatures of fossils. Palaeontology 55, 1–10. https://doi.org/10.1111/j.1475-4983.2011.01108.x.

Hodgkinson, R.L., 1991. Microfossil processing: a damage report. Micropaleontology 37, 320–326. https://doi.org/10.2307/1485894.

Jarochowska, E., Tonarova, P., Munnecke, A., Ferrova, L., Sklenar, J., Vodrazkova, S., 2013. An acid-free method of microfossil extraction from clay-rich lithologies using surfactant Rewoquat. In: Examples of Application to Silurian and Devonican fossils, pp. 141–143.

Kennedy, A.E., Coe, A.L., 2014. Development of the freeze–thaw processing technique for disaggregation of indurated mudrocks and enhanced recovery of calcareous microfossils. J. Micropalaeontol. 33, 193–203. https://doi.org/10.1144/jmpaleo2013-020.

Kirchner, Z.M., 1958. A new method of hard-rock maceration. Micropaleontology 4, 327–328.

Li, Y.X., 2000. Famennian Tentaculitids of China. J. Paleontol. 74, 969–975.

Lindemann, R.H., 2002. Dacryoconarid bioevents of the Onondaga formation and the Marcellus subgroup, Cherry Valley, New York. In: Guidebooks for Fieldtrips in New York and Vermont. B7.1-B.7.17.

Lindemann, R.H., Yochelson, E.L., 1984. Styliolines from the Onondaga Limestone (Middle Devonian) of New York. J. Paleontol. 58, 1251–1259.

Ma, M., 2012. The dispersive effect of sodium hexametaphosphate on kaolinite in saline water. Clay Clay Miner. 60, 405–410. https://doi.org/10.1346/ccmn.2012.0600406.

Ma, K., Cui, L., Dong, Y., Wang, T., Da, C., Hirasaki, G.J., Biswal, S.L., 2013. Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials. J. Colloid Interface Sci. 408, 164–172. https://doi.org/10.1016/j.jcis.2013.07.006.

Mason, J.L., 2017. High-Resolution Facies Variability and Connections to Compositional and Mechanical Heterogeneity in the Union Springs Formation of Central New York. Cornell University.

Meehan, K.C., Kowalski, C., Bartlett, K., Li, I., Bembia, P., 2020. Successful complete digestion of well lithified shale and extraction of microfossils from Devonian beds in western New York. Stratigraphy 17, 205–212. https://doi.org/10.29041/strat.17.3.205-212.

Nicholson, D.T., Nicholson, F.H., 2000. Physical deterioration of sedimentary rocks subjected to experimental freeze-thaw weathering. Earth Surf. Process. Landf. 1307, 1295–1307.

Oliver, W.A.J., 1956. Stratigraphy of the Onondaga Limestone in Eastern New York. Bull. Geol. Soc. Am. 67, 1441–1474.

Peterson, S., Maples, C.G., Lane, N.G., Peterson, S., Maples, C.G., Lane, N.G., 1983. Use of surfactants in disaggregation of argillaceous rocks. Micropaleontology 29, 467–469.

Sageman, B.B., Murphy, A.E., Werne, J.P., Ver Straeten, C.A., Hollander, D.J., Lyons, T. W., 2003. A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, middle-upper Devonian, Appalachian basin. Chem. Geol. 195, 229–273. https://doi.org/10.1016/S0009-2541(02)00397-2.

Sanchez-Martin, M.J., Dorado, M.C., del Hoyo, C., Rodriguez-Cruz, M.S., 2008. Influence of clay mineral structure and surfactant nature on the adsorption capacity of surfactants by clays. J. Hazard. Mater. 150, 115–123. https://doi.org/10.1016/j.jhazmat.2007.04.093.

ShamsiJazeyi, H., Verduzco, R., Hirasaki, G.J., 2014. Reducing adsorption of anionic surfactant for enhanced oil recovery: part II. Applied aspects. Colloids Surf. A Physicochem. Eng. Asp. 453, 168–175. https://doi.org/10.1016/j.colsurfa.2014.02.021.

Tagavifar, M., Jang, S.H., Sharma, H., Wang, D., Chang, L.Y., Mohanty, K., Pope, G.A., 2018. Effect of pH on adsorption of anionic surfactants on limestone: experimental study and surface complexation modeling. Colloids Surf. A Physicochem. Eng. Asp. 538, 549–558. https://doi.org/10.1016/j.colsurfa.2017.11.050.

Tarsilli, A., Warne, M.T., 1997. An improved technique for extracting calcareous microfossils from Palaeozoic limestones. Alcheringa 21, 57–64. https://doi.org/10.1080/03115519708619184.

Theisen, A.A., Evans, D.D., Harward, M.E., 1968. Effect of dispersion techniques on mechanical analysis of Oregon soils. Tech. Bull. 104.

Thomas, F.C., Murney, M.G., 1985. Techniques for extraction of foraminifers and ostracodes from sediment samples. In: Canadian Technical Report of Hydrography and Ocean Sciences, 54, pp. 1–24.

Vodrážka, R., 2009. A new method for the extraction of macrofossils from calcareous rocks using sulphuric acid. Palaeontology 52, 187–192. https://doi.org/10.1111/j.1475-4983.2008.00829.x.

Walder, J., Hallet, B., 1985. Theoretical model of the fracture of rock during freezing. Bull. Geol. Soc. Am. 96, 336–346.

Wei, F., 2019. Conch size evolution of Silurian–Devonian tentaculitoids. Lethaia 52, 454–463. https://doi.org/10.1111/let.12324.

Wei, F., Gong, Y., Yang, H., 2012. Biogeography, ecology and extinction of Silurian and Devonian tentaculitoids. Palaeogeogr. Palaeoclimatol. Palaeoecol. 358–360, 40–50. https://doi.org/10.1016/j.palaeo.2012.07.019.

Wintermyer, A.M., Kinter, E.B., 1955. Dispersing Agents for Particle-Size Analysis of Soils. Highway Research Board Bulletin.

Wittmer, J.M., Miller, A.I., 2011. Dissecting the global diversity trajectory of an enigmatic group: the paleogeographic history of tentaculitoids. Palaeogeogr. Palaeoclimatol. Palaeoecol. 312, 54–65. https://doi.org/10.1016/j.palaeo.2011.09.009.

Yu, T., Li, Q., Hu, H., Tan, Y., Xu, L., 2022. Molecular dynamics simulation of the interfacial wetting behavior of brine/sandstone with different salinities. Colloids Surf. A Physicochem. Eng. Asp. 632 https://doi.org/10.1016/j.colsurfa.2021.127807.