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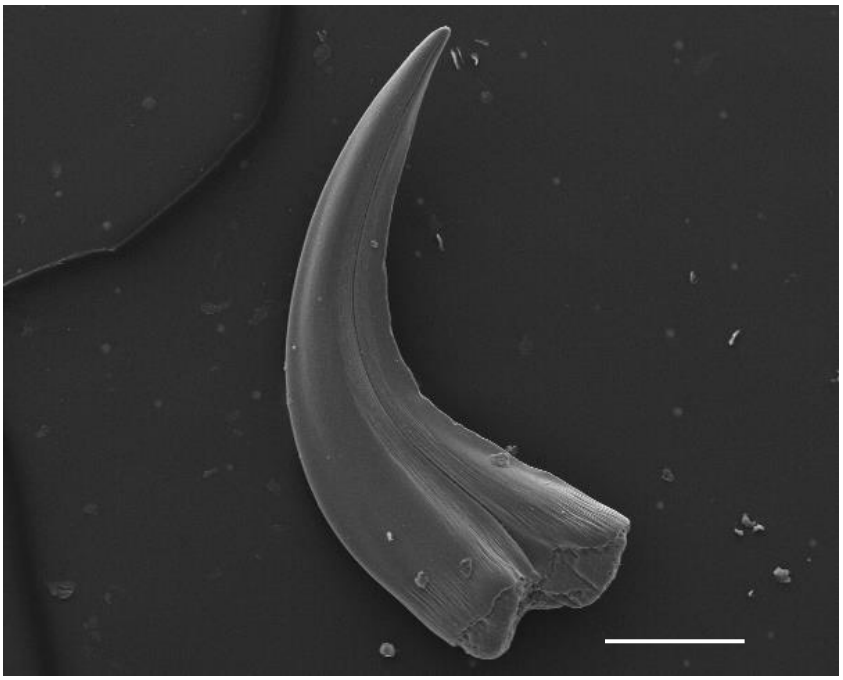
Evaluation and optimization of acid processing procedures for the extraction of conodont elements from calcareous rock



C. Gallotta, S.A. Gouwy, and L. Komaromi

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ABSTRACT

The purpose of this study was to identify alternative methods which would improve current conodont processing times and cost at the GSC-Calgary paleontology lab. Conodont processing consists of several stages, most of which are completed within a single day. Acid digestion, however, is the longest processing stage and is also conveniently the most variable in terms of processing techniques. Therefore, this is where this study seeks to improve. The current sample digestion technique utilizes an acetic acid solution which take a notably long time to completely process samples therefore, investigation into quicker techniques commonly used in other labs utilizing formic acid were explored. Formic acid processing improved digestion time to 3 days compared to acetic acid processing's maximum of 56 days. Processing cost results favored acetic acid which totaled $126.41 for full processing of 2.5kg samples, compared to formic processing cost of $101.73 for 1.0kg of sample which theoretically totals $127.99 per 2.5kg of sample. Lab productivity significantly improved using formic acid, capable of producing 350 samples per year opposed to 195 samples processed via acetic acid. Observing extracted specimen under a scanning electron microscope showed no difference between the processing methods. Both methods could produce pristine sample quality which was completely indistinguishable. Based on these findings, the formic acid processing method can be used as a viable technique for the extraction of conodonts from calcareous rock and should be offered as a fast-track, but slightly more expensive alternative for sample processing.

Cover image: ***Panderodus unicostatus*** **(Branson and Mehl 1933), C-468285, Bad Cache Rapids Group, Albany River, northern Ontario. 042-M-16; 51° 45' 40.59" N, 86° 12' 56.73" W. Overview scan, scale bar is 200µm.**

INTRODUCTION

The process of extracting conodonts from their parent rock can be both strenuous and time consuming. This is particularly true at the Geological Survey of Canada's Calgary office where total processing time largely exceeds 8 weeks per sample. The larger portion of this processing time comes from the acid digestion which takes a staggering 8 weeks maximum to complete. As this 8-week cut-off is the maximum that a sample can digest, a substantial price is attached to each sample to cover cost associated with the long processing time. This severely limits the productivity of the Calgary conodont lab. Therefore, it is of interest to investigate potential replacement or alternative methodologies for processing conodont samples. While the final steps of the conodont processing can also be investigated for effectiveness, the purpose of this project was to study the impact of changing the type of acid used in processing with regards to digestion time, impact on quality, and ultimately price difference.

Currently, the GSC-Calgary lab uses glacial acetic acid, which is viewed as the safer and more common option (Green 2001; Hellawell and Nicholas 2012). The glacial acetic acid technique has been perfected over the years of use at the GSC, however the processing time each sample takes, using the acid, limits the yearly output of samples. With the standard 8-week digestion time, the lab was slowly reducing its backlog of samples that accumulated during the 2017-2019 facility upgrades. Acid digestion is currently the longest step in conodont processing and finding optimality and ways to reduce processing time is critical to vastly improve productivity while reducing processing costs. The most impactful way to reduce digestion time would be to use a stronger more aggressive acid, notably formic acid (Hellawell and Nicholas 2012; Wheeley et al. 2012; Ralston 1971). Formic acid in conodont processing has been thoroughly investigated, mainly for the impact on the quality of yielded microfossils (Hunt 2017, Jeppsson 1995). This comparison between the two acids has been made numerous times, notably studies from Hellawell and Nicholas (2012) and Ralson (1971) illustrate how formic acid is commonly viewed as the quicker more aggressive methodology which requires much more intensive work over short periods of

time. On the contrary, acetic acid is very hands-off however much more time consuming (Hellawell and Nicholas 2012).

This project was also tailored to investigate several other key differences between acid treatments. The first of which is the difference in productivity of the methods. As processing rate is related to how many samples can be completed in a year, knowledge of the maximum potential of each methodology could help shape decisions of what process to use if tight time restrictions are in place. One major issue brought up during preliminary meetings with the GSC staff was the overtly expensive conodont processing cost, thus price was identified as a fundamental factor for this study. The final area of investigation was overall quality of the sample post-digestion. Formic acid has been observed to cause some etching on the conodont surface due to the aggressive reaction with calcareous rocks (Müller, 1998). Quality of the retrieved conodonts is the major driving force in methodology selection as samples from the GSC-Calgary lab are used for biostratigraphy and taxonomy and must be kept to the highest quality, regardless of the other variables.

METHODOLOGY

Sample selection

The samples used in this study are archival GSC rock samples from the Hudson Bay Lowlands of Ontario. As the success of the testing largely depended on the quality and yield of conodont material in the samples, archived spare rock material of already studied samples was chosen. GSC reports on those archival samples provided information on yields and the associated archival conodont slides allowed checking the quality of the retrieved conodont elements. The selected samples with high yields of good quality conodonts and with of course enough rock material available for both acid procedures, were the best available starting material for these comparative tests. In total, 8 samples were selected to determine differences between acetic and formic processes. The location, age, lithology, expected breakdown and conodonts per kilogram of sample are displayed in table 1.

Table 1. Samples chosen for this study. These were selected due to their notable high breakdown and conodont yield. All samples collected by Derek Armstrong (Ontario Geological Survey). Modified sample numbers used in this study were the lab processing number prefixed with rather an F or A denoting processing from rather formic acid or acetic acid, respectively.

Sample	C#	Location	Strata	Age	Lithology	Expected Breakdown (%)[1]
1786-03	C-468285	Albany River	*Bad Cache Rapid Group*	*Late Ordovician*	Limestone	93.4
1786-04	C-468286	Albany River	*Bad Cache Rapid Group*	*Late Ordovician*	Limestone	100
1787-05	C-468295	Little Current River	*Ekwan River Formation*	*Llandovery*	Limestone	100
1787-10	C-468300	Drowning River	*Ekwan River Formation*	*Llandovery*	Limestone	100
1800-5	C-591609	Kenogami River	*Ekwan River Formation*	*Llandovery*	Limestone	97.2
1800-6	C-591610	Kenogami River	*Ekwan River Formation*	*Llandovery*	Limestone	95.3
1800-8	C-591612	Fort Albany	*Stooping River Formation*	*Llandovery*	Limestone	96.7
1800-11	C-591615	Ekwan River	*Ekwan River Formation*	*Llandovery*	Limestone	97.3

[1]: Expected breakdown is what was previously observed when samples underwent original acid digestion. As these samples were previously processed at the GSC-Calgary conodont lab, a level of expectation to how well samples digested over an 8-week period were generated.

Method selection

99.5% Glacial acetic acid procedure

Acetic acid (CH_3COOH) treated samples followed the standard procedure currently used at the GSC-Calgary lab with a few slight modifications. Current standard procedure entails a 10 litre plastic sample pail to be first filled with 2.5kg of crushed walnut size sample. Then approximately 8.5L of water is added to the pail, followed by 1L of 99.5% analytical grade glacial acetic acid generating a 10.5 % acetic acid concentration allowing fluctuation within 10-12% concentration margins, the approximate accepted solution concentration range used at the GSC-Calgary conodont lab. No buffer is initially used in this procedure although a portion of the almost inert first week acid solution is added to the fresh solution of the second week to act as a buffer. This extra step is repeated with every change of acid. Since most test samples were under the standard size of 2.5kg, less volume of liquids is needed for the processing thus a mass-solution correction was determined as shown below. Equation 1 allows the calculation of the desired volume for the same acid/water concentration. Equations 2-3 allow the calculation of the needed volumes of acid and water for a certain volume of solution.

Equation 1

$$\left(Sample\ Mass\ (kg) \times \left({}^{9.5\ (L)}\!/_{2.5\ (kg)}\right)\right) = Corrected\ Total\ Solution\ (L)$$

Equation 2

$$Corrected\ Total\ Solution\ (L) \times 0.18 = Glacial\ Acetic\ Portion\ (L)$$

Equation 3

$$Corrected\ Total\ Solution\ (L) \times 0.82 = Tap\ Water\ Portion\ (L)$$

Formic acid procedure

Samples designated for formic acid (HCOOH) processing were subjected to a similar double buffer methodology examined by Jeppsson and Anehus (1995) who suggest 11L of 10% formic acid solution per kg to achieve 24hr breakdown. We opted for a somewhat slower procedure that was more feasible for our lab and uses less acid per kg, a modified methodology of Jeppsson and Anehus (1995) combined with the processing method used at J. E. Day's conodont lab at the Illinois State University in Normal (IL). This procedure would only require a 3.0L solution of formic acid in water per kilogram of rock sample. Additionally, the modified procedure used a repetitive treatment, adding new acid every day until complete digestion was obtained, or 3 days had passed, giving a total of 9L per kg of sample instead of 11L in Jeppsson and Anehus (1995). To determine quantities of reagents as well as mass corrections, the solution composition was first derived on a proportion per 1.0L scale. The identified proportions within every 1.0L of solution consisted of 87% (870mL) of tap water and 13% (130mL) of 85% analytical grade formic acid which gives a solution concentration of about 11% as opposed to the 10% concentration used in the Jeppsson and Anehus (1995) processing method. The dual buffer, 30g of calcium carbonate and 0.7g of tricalcium phosphate was also added per liter of solution.

The total volume of solution needed is calculated by taking the weighed sample mass and multiplying it by 3L of solution / kilogram. Volumes of liquids were calculated using equations 5-6. Although extraneous, this process was done to ensure flexibility in increasing sample mass along with ensuring that every

processed sample, regardless of mass, would have the same acid concentration. To compare with the formic acid procedure used by the Illinois lab, samples designated for formic processing weighed between 1.0 – 1.25kgs depending on quantity of archival sample left over at the GSC-Lab.

Equation 4

$$\frac{\left(3.0L \times Sample\ Weight\ (g)\right)}{1000g} = Total\ Solution\ (L)$$

Equation 5

$$Total\ Solution\ (L) \times 0.87 = Tap\ Water\ Portion\ (L)$$

Equation 6

$$Total\ Solution\ (L) \times 0.13 = 85\%\ Formic\ Acid\ Portion\ (L)$$

$$Total\ Solution\ (L) \times 30\ \left(\frac{g}{L}\right) = Cacium\ Carbonate\ Portion\ (g)$$

$$Total\ Solution\ (L) \times 0.7\ \left(\frac{g}{L}\right) = Tricalcium\ Phosphate\ Portion\ (g)$$

Crushing

Using a standard hammer, samples were crushed to approximately walnut size and divided into pails, one deemed for acetic acid processing, the other for formic acid processing. To replicate the current processing procedure observed at the GSC as a control, acetic acid samples' weight was ~2.5kg. Formic samples were further split into two separate pails, each weighing 1.0 – 1.25kg.

Initial acidizing

Acetic acidizing

Samples that were processed via the GSC-Calgary procedure were first weighed, then portions of acid and water were calculated by sample mass corrections *(Equation 1-3)*. The desired amount of water was first added to the sample pail, followed by the calculated acetic acid for that specific sample mass. For a typical 2.5 kg sample that would be 0.99L of acetic acid added to 8.5L of tap water giving an initial concentration of about 10.5% for the water-acid solution. The sample's pH was recorded, and the sample was placed inside the walk-in fume hood.

Formic acidizing

Using the determined reagent quantities via formulas 4-6, a standard 1kg sample would consist of 2.6L tap water, 0.4L of 85% formic acid, 90.0g of calcium carbonate and 2.1g of tricalcium phosphate. Proponents were added to the pails and monitored to ensure initial reaction of the formic acid and sample was not overtly intense. Once the initial reaction subsided and stabilized, samples were placed on shelves in the walk-in fume hood.

pH monitoring

Following initial acidization, the sample's pH was closely monitored to track changes which can be indicative of reaction progress and sample quality (Jeppsson et al. 1999; Quinto et al. 2016; Sobolev 1996). Every day, an Orion 5 Star pH meter was calibrated (±0.01pH) then used to measure pH of the sample. The meter probe was placed approximately 5cm below the solution surface to ensure accurate reading of solution pH. To prevent any contamination between samples, the probe was rinsed with distilled water in between measurements. This was done 3 times a day, at fixed 3-hour intervals of 9:00am, 12:00pm, and

finally 3:00pm until the sample was either digested completely or the maximum time allotted was reached.

Acid changes

An acid change for acetic samples occurred every 7 days or until the solution reached a pH of 5.5. The standard acid changing procedure at GSC-Calgary, has samples poured out onto stacked US standard No. 10 and No. 200 sieves, and a small catch basin for the solution. The top No. 10 sieve was used to catch the larger undissolved chunks, while smaller residue would wash into the finer No. 200 sieve bellow. Chunks of sample within this larger sieve were rubbed and rinsed using tap water to remove all stuck-on sediment. Once rinsed, these were returned to the pail for further digestion. Finer residue caught in the lower sieve was rinsed thoroughly to remove the clayey fraction. Once the sieve runoff was clear, residue was poured into a labeled beaker that was filled with water to prevent desiccation. Solution in the catch basin was returned to the pail and fresh acetic acid equal to the initial amount of acid was added to the sample. Sample solution was periodically mixed following measurements of pH every 3 hours to prevent density layering however were largely let to settle overnight and over weekends.

Formic samples maintained the same technical procedure for sieving and rinsing of samples. However formic sample were changed every day rather than every week or when the solution reached a pH of 5.5 as is the case for acetic acid. This was done to ensure the stronger acid solution would not cause damage to released conodont elements. Additionally, samples containing formic acid were shaken every time the pH was measured to avoid concentrated density layering within the solution.

Acid removal

Acid changes continued until the sample had completely dissolved, or the maximum time limit of digestion was reached. For acetic acid processing samples, the maximum time allowed for samples was 8 continuous weeks of acid changes. Formic acid processed samples, however, were allowed 3 days of acid digestion, resulting in 2 acid changes before being removed. When a sample was removed from acid, it was sieved and rinsed then left-over chunks caught in the no. 10 sieve were set on a plate and left to dry. These left-over portions of the sample were then weighed and recorded as +10's or "Final Mass". Captured acid was neutralized to a pH of 5.5 then disposed of via hazardous waste removal program.

Bleaching

Captured residue from both processing methods were then boiled in a bleach bath to remove any organics residing in the sample post acid digestion. Approximately 200mL of sample residue was moved to glass bleaching pots. Then 2.0L of water and 30mL of standard sodium hypochlorite was added to each pot. The sample was then gently boiled for 6 hours on a medium low heat in a 12 % bleach solution. Samples were then poured into a US standard no. 200 sieve where they were rinsed until drippings ran clear. Clean residue was poured onto a 180-shark skin filter paper residing within a funnel to drain out any excess water. The filter paper was placed on a plate and left to dry. Once dried, samples were put in labeled jars and sent for picking.

Picking

Sample residue placed in jars following bleaching were picked though, extracting all conodont elements present. Residue was distributed evenly over a picking tray, ensuring no residue would be covered. The picking plate was then examined under a stereoscopic microscope at x60 magnification. The picking plate was manually moved throughout the field of view until the entire picking tray was examined. If any conodont element was identified within the tray, it was removed and placed in a labeled microfossil slide

using a fine tip painters brush. Excess residue on the tray was then placed in a small Whirl-Pak™ residue bag. Sample residue in the jars were completely picked.

DISCUSSION

Analysis of sample properties

Sample mass

A total of 21 samples were processed for this study (Table 2). Eight for analysis of acetic acid processing, 13 for formic acid processing. The difference in sample number relates to relative sample weight and amount of sample remaining at the GSC lab. Sample weight was divided into two, half for formic analysis and the other half for acetic analysis. Due to formic analysis requiring only 1.0 – 1.25kgs of sample, most of the formic samples were further split between into two pails. This is opposed to acetic analysis which required 2.5kgs of sample to conduct. Formic samples which had less than 1.5kg of sample after division were only processed in one pail. The average weight of formic samples was 1043.0 ±0.1g (*n=8*). As calculations were made to correct for sample mass, the lowest mass, 730.0g had the same acid ratio added to the sample as the largest sample of 1180.5g. The average weight for acetic processing samples was 1701.3g ±0.1g (*n=13*). Similarly, with formic processing, mass corrections were applied to all samples to ensure that the smaller samples had the same relative acid to mass ratio as the larger samples. Compositions of all acid solutions are listed in *Appendix A2*.

Table 2. Total samples (*n=21*) and respective sample weight (g) and acid test conducted.

Sample	Acid Test	Sample Mass (g) (±0.5)
F178603	Formic	1163.5
A178603	Acetic	1160.0
F178604	Formic	1060.0
A178604	Acetic	1101.5
F178705	Formic	730.0
A178705	Acetic	720.5
F178710A	Formic	868.5
F178710B	Formic	877.0
A178710	Acetic	1744.0
F18005A	Formic	1180.5
F18005B	Formic	1119.0
A18005	Acetic	2312.0
F18006A	Formic	1144.5
F18006B	Formic	1102.0
A18006	Acetic	2252.0
F18008A	Formic	1143.5
F18008B	Formic	1126.5
A18008	Acetic	2269.0
F18011A	Formic	1024.0
F18011B	Formic	1020.0
A18011	Acetic	2051.0

Processing time

Formic acid processing time was restricted to 3 days (Fig. 1). No sample was broken down completely before the 3-day maximum was reached. Samples that underwent acetic acid processing range from 24 to the maximum 56 days in processing time. Only 5 samples achieved >95% breakdown before reaching the maximum 8-week (56 day) processing time. The remaining 3 samples did not reach full breakdown before the maximum allowed digestion time. Average digestion time taken for all acetic acid samples was 44 days or about 6.5 weeks (Fig. 1).

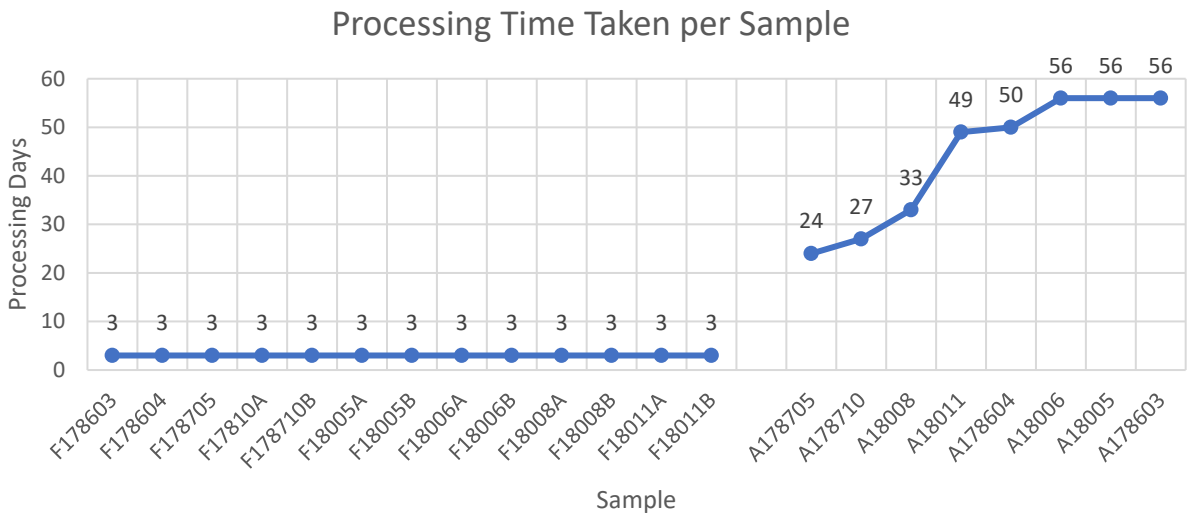

Figure 1. Processing time of samples. *Left* indicates formic samples processing time set at a maximum of 3 days. *Right* indicates acetic samples processing time set at a maximum of 56 days.

Digestion time

Digestion time observed for both procedures was outlined as a critical outcome and factor determining a superior methodology. Samples subject to formic acid digestion required to be completed within one week due to limitations of GSC laboratory operations during weekends. Formic acid digestion remained preset at 3 days to guarantee those limitations were met. This preset 3 days is however highly modular. In fact, similar studies, such as those described by Jeppsson et al. (1999) and Sobolev (1996) illustrate how formic acid processing can also be modified to completely digest samples within 2 days. This range in flexibility of formic processing is superior to that observed by acetic processing as the minimum observed time to complete digestion via acetic acid was 24 days. Furthermore, samples which underwent acetic acid treatment were also observed to hit its maximum allotted digestion time of 56 days. Digestion of samples using the designated formic methods could be completed 6 times over before the average acetic acid sample (44 days) was completed. Assuming both methods take their maximum allowed time in digestion, these numbers increase with formic processing is nearly 14 times faster while outpacing its acetic counterpart 8:1. There is a hypothetical scenario to which may expedite digestion time which involves the combined use of both formic and acetic acid. Theoretically a potential procedure which would use a combination would first subject samples formic acid digestion for one to two days then, a conversion to acetic acid would occur until samples are fully digested. An immediate identified issue with this procedure is the risk of complications if samples undergo stable oxygen isotope analysis due to interference that acids may have on samples. Such potential complications should be carefully considered

and true benefits of using this hypothetical procedure should be further investigated before fully committing to this experimental method.

Breakdown

Percentage of sample breakdown (Fig. 2) was calculated by dividing the mass of the dissolved portion (original sample mass minus the mass of the +10's) by the original mass of the sample. The formic acid samples ranged from 59% to a maximum 85% breakdown averaging 69.6% ±0.1% (*n=13)* over the three days of acid digestion. Acetic acid samples ranged from 62% breakdown to 100%, averaging 89.0% ±0.1% (*n=8*) over 44 days.

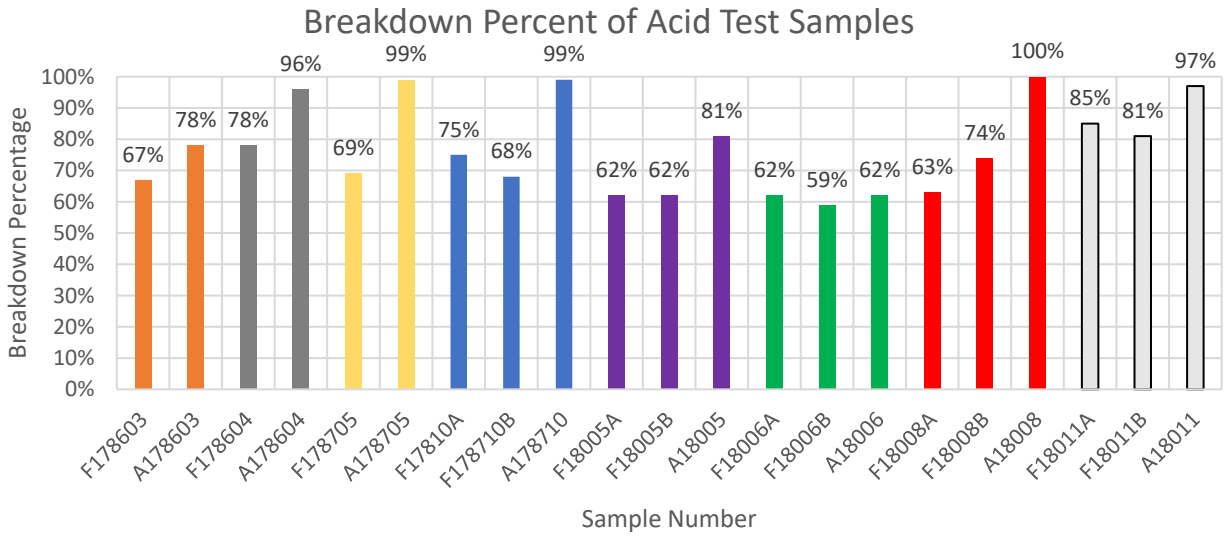

Figure 2. Breakdown percentages of samples given left over sample mass post acid digestion. Samples sharing the same sample ID number are twin samples which were split into different tests.

Breakdown percentage

Breakdown percentages observed in both acetic and formic acid methods widely varied (Table 3). Variation was predominantly observed in formic acid samples where samples ranged from 59% breakdown to 85%. Samples subjected to formic acid testing typically achieved on average 62% breakdown. In other words, approximately 600 grams of the sample dissolved from the 1kg original mass. Acetic acid samples also exhibited a variation in breakdown percentage between 79% to 100%. This equates to a digestion of approximately 2kg of sample from its 2.5kg original mass. When comparing identical samples between the two methods, all acetic acid samples maintained higher breakdown percentages than their formic acid counterparts. Based on these observations we can hypothesize that acetic acid processing leads to higher amounts of sample being broken down over longer periods of time. Particularly seen in the 1787-05 sample series, digestion via acetic acid resulted in complete dissolution of the sample over 24 days. This was the fastest sample of the acetic series to reach 100% digestion.

Table 3. Sample breakdown percentages compared to total time taken to dissolve. Acetic acid sample maximum digestion time allotted 56 days. Formic acid sample maximum digestion time allotted 3 days.

Percent Breakdown over Time

Sample	Acid Test	Breakdown (%)	Time (Days)
F178603	Formic	67	3
A178603	Acetic	78	57
F178604	Formic	78	3
A178604	Acetic	96	50
F178705	Formic	69	3
A178705	Acetic	99	24
F178710A	Formic	75	3
F178710B	Formic	68	3
A178710	Acetic	99	27
F18005A	Formic	62	3
F18005B	Formic	62	3
A18005	Acetic	81	56
F18006A	Formic	62	3
F18006B	Formic	59	3
A18006	Acetic	62	56
F18008A	Formic	63	3
F18008B	Formic	74	3
A18008	Acetic	100	33
F18011A	Formic	85	3
F18011B	Formic	81	3
A18011	Acetic	97	49

This compared to the formic acid processing of the identical sample resulted in 69% digestion over 3 days. Although complete dissolution was accomplished via acetic acid, formic acid processing accomplished 69% dissolution in an eighth of the time taken. Additionally, average digestion rates amongst all acetic and formic acid samples maintain a daily breakdown rate of 2.02% and 23.2% respectively. Further enforcing the capability of formic acid to digest samples at a quicker rate. If formic acid processing were to continue for a fourth day, samples could potentially see a breakdown percentage above 90% at a fraction of the time.

Although presumptive projections for formic acid processing state +90% breakdown over four days, these are only projections and achieving this percentage are strongly dependent on total mineral composition of the sample. A notable observation which may alter this projection of formic acid processing was made during daily acid changes. Larger digested sample chunks formed a hard-shell-like coating resulting in lower daily residue yields. Typically, this observation has been known to occur in samples which have higher proportions of clay where calcium carbonate within the rock dissolves at an expedited rate, while the more acid resistant clay particulate remains. Evidence of this was supported by holes in the shell structure leading to an interior structure which was showing signs on continual digestion on the inside. Furthermore, leftover samples that exhibited this trait were tested with several drops of 10% HCl. This test indicated nominal amounts of carbonate presence in the shell portion and large carbonate presence

within the matrix core. Samples which had this feature notably had lower breakdown percentages across both types of acid thus it is likely that these samples contained high potions of clayey material.

Caution should be assumed when projecting breakdown percentages, as a noted trend across all samples is the slowdown of digestion following the first initial changes. This is common with both processes as the longer samples take, the slower breakdown occurs. Typically, maximum breakdown occurs in the first one to two acid changes. During these changes, most of the carbonate portion breakdown occurs thus producing large volumes of free residue. With maximum yields being seen early on, it is not uncommon to see a total halt in produced free residue later. This trend is due to the rapid loss of readily available calcareous material to react, leaving only siliciclastic material. Acetic acid samples see this lack of yield at approximately week 6 while formic acid samples gradually produced less residue over the week depending on lithology of the sample.

Lithology impacts

Substantial variation in breakdown and time for both methods is apparent when sample lithology is considered. Seen in studies such as Hunt (2017) and Purnell and Donoghue (2005), samples which are comprised of predominantly calcareous material digest quicker while more siliciclastic samples digest slower. Similarly, samples that contain large amounts of calcareous material observe greater breakdown percentages. This is due to calcium carbonate reacting strongly in the presence of acid to form (*Equation 8*).

Equation 8

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + H_2O + CO_2$$

This increase in calcium carbonate within highly proportioned samples leads to quicker dissolution rates and greater breakdown. Samples containing a disproportionately high amount of clay, or other siliciclastic material are much more challenging to digest as lack of readily available calcium carbonate reduces the rate to which digestion can occur. Predominantly siliciclastic samples submitted to the GSC have been historically observed to take the full 56 days and have very little breakdown in acetic digestion. Evidence within our study of lithology driving dissolution time and breakdown is prevalent when comparing samples such as A178705 and A18008 which contained high proportions of calcareous material compared to others such as A18006 and A178603. Formic processing results within our study suggested that lithology of samples is less of a driving force to expedite the dissolution time needed. None of the samples which underwent formic processing achieved 100% dissolution prior to the 3-day processing maximum. Regardless whether a sample contains mostly calcareous material or not, samples will still require all 3 days to maximize breakdown percentage.

pH over time and pH significance

The reaction rate of both formic and acetic processing was monitored throughout the study via pH measurements of the solution at any given time (Figs. 3, 4). Suggested by Jeppsson and Anehus (1995), the reaction process can be monitored via pH measurements. When the pH reaches more than 5.0, the reaction between acid and calcium carbonate is likely nearing completion Jeppsson and Anehus (1995). As a result, pH evolutions for both sample methods were monitored and recorded and if a sample reached

a pH of 5.0, an acid change would be required. Although this was implemented to expedite the dissolution process and ensure digestion was always occurring, it was only utilized once. Only one acetic acid sample within its first week of digestion ever reached the pH threshold required. Following the first several weeks of digestion, sample's pH stayed relatively stagnant, only decreasing when new acid was added via acid change. This flat lining of the pH level exemplifies that following the first several weeks of digestion, the reaction and digestion of the sample slows due to lack of available calcium carbonate. With the removal of free residue every acid change, the remaining samples rock lithology changes to favor siliciclastic material which releases minimal amounts of additional calcium carbonate into the solution. This phenomenon explains why pH levels fail to increase in later processing weeks.

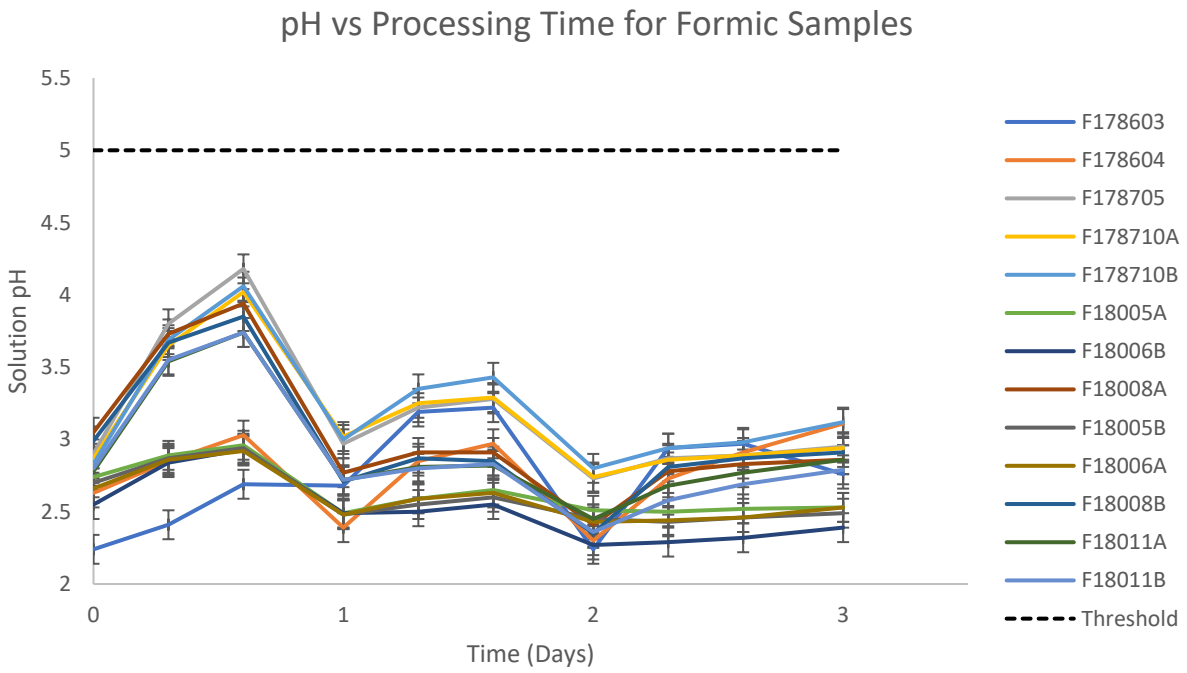

Figure 3. Formic acid test samples' pH measurements over their 3-day acid digestion period. Measurements were taken at 9am, 12pm, and 3pm every weekday. Dashed line indicates the preset 5.0pH threshold which if reached would warrant an acid change.

The pH levels observed in formic acid processing shared characteristics similar to those of their acetic acid counterparts with the rapid increase in pH over the day. All pH's observed in formic acid samples see large spikes over the course of their first 2 days, then slowly tapering off over the course of day three. The lowering intensity of these spikes is once again likely due to the sample containing less calcium carbonate following its initial reaction. The main difference between the two processes is mainly the degree to which pH resulted in acid changes. With only one acetic acid sample and zero formic acid samples reaching the 5.0 threshold, it can be advised that pH monitoring is slightly more effective in acetic acid processing to track progress of reaction. There were several samples which came close to reaching the 5.0 pH threshold however never fully reached the pH level prior to their 7-day schedule. The lack of formic acid samples reaching the pH threshold is due to the short time frame between adding new acid and rinsing the samples. With active reaction times limited to 24 hours, samples containing a high portion non-calcareous

material on the rock's surface may obstruct progress of the reaction. This obstruction restricts any substantial pH increases of the sample within a 24-hour period resulting in lower pH spike intensity. Monitoring of pH could also theoretically be used to detect when pH levels are too low. This form of monitoring would allow addition of a neutralizer such as water to dilute solution above a certain pH level. Lower pH's could potentially pose a risk in damaging conodont elements. Although evidence of an optimal pH level was not identified within this study, we recommend the solution pH should be no lower than what we used to prevent potential damage.

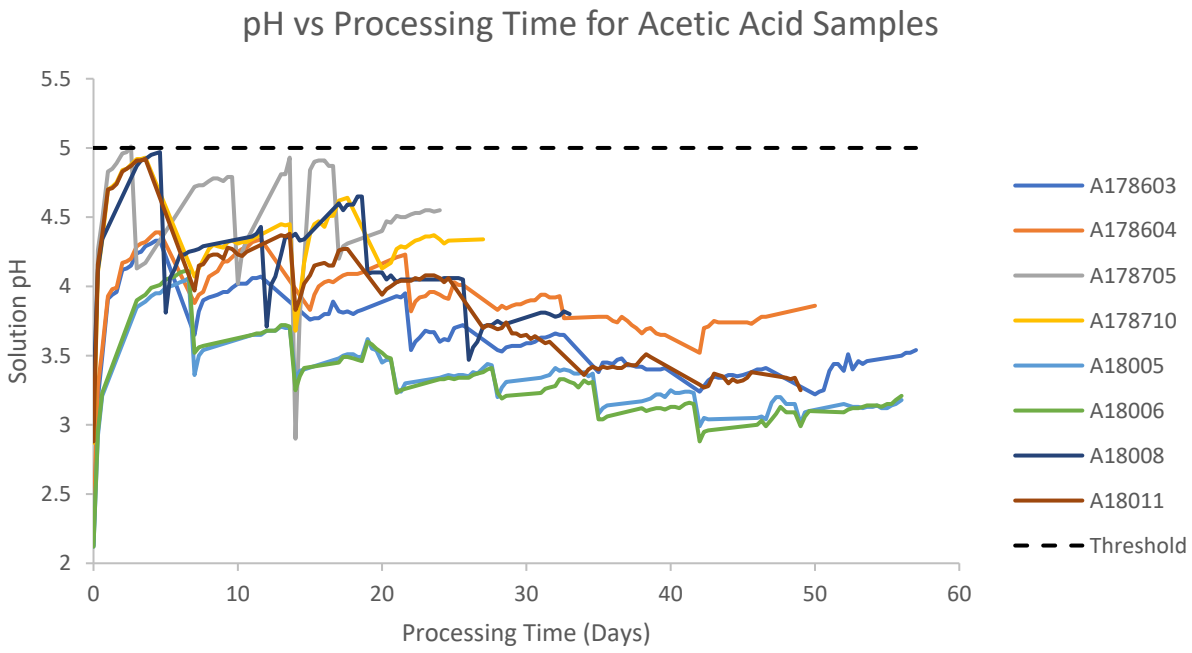

Figure 4. Acetic acid test samples' pH measurements over their 3-day acid digestion period. Measurements were taken at 9am, 12pm, and 3pm every weekday. Dashed line indicates the 5.0pH threshold which if reached would warrant an acid change.

Optimal pH cutoffs can be identified by successful monitoring of the sample solution throughout sample digestion. Particularly for processing via acetic acid pH, monitoring proved to be a useful tool in tracking progress of digestion. In the initial weeks of acid digestion, monitoring of pH allowed expedited acid changes by several days. In turn, this allowed samples to finish quicker than they would have, ultimately saving on processing cost. After the initial weeks of acidization pH monitoring became less relevant as pH spikes were reduced, then eventually flattened due to lower reaction rates or complete digestion of the calcareous fraction. Theoretically these mechanisms can be a good identifier when processing of a sample can end, however the constant monitoring of acetic acid samples makes the procedure much more hands-on.

Digestion limitations

Limitations of methods arise when comparing the two processes based on time. One identified limitation in formic acid processing with respect to time is the maintenance samples require. Formic acid shows characteristics of an aggressive acid (Quinton et al. 2016), thus maintenance needs to be held at higher standards which include; acid changes every day, stirring or shaking the sample pails every few hours to prevent density layering (Jeppsson and Anehus 1995), and hourly monitoring of pH to prevent damage to

conodont elements. These additional requirements are detrimental as over a 3-day period, the technician in charge of maintaining samples becomes more hands on than comparted to acetic processing. The more hands on work to successfully maintain formic acid processing may require a designated worker who would be needed to operate the acid changes daily, something that may not be feasible. Although time spent in the digestion phase is substantially lowered, formic acid fails to allow major flexibility in completion of other daily laboratory activities. Many of the required maintenance procedures are? also conducted on samples in acetic acid, however the weekly acid changes allow superior flexibility when samples are not due for a change. This 'change and wait' type of processing allows laboratory workers to fulfill other designated tasks while digestion is occurring. Acetic acid is also far less aggressive than its formic counterpart thus chances of causing major damage to conodont elements if not attended to daily become negligible (Gault 1955). For this reason, acetic acid processing was observed as a more hands-off passive digestion method which outputs lower sample counts at longer rates. Formic acid processing was observed as the more hands on active digestion method which outputs higher sample counts at shorter rates.

Sample quality

Formic acid processing has been identified as a harsher acid which can cause moderate to severe surface etching to conodont elements (Müller, 1998). To evaluate if our tested formic procedures caused surface etching on our extracted conodont elements, they were taken to the scanning electron microscope at the Foothills hospital, in Calgary, Alberta where they were titanium-coated, then imaged. Out of the processed samples, 4 parent samples (C-468285, C-468286, C468295, and C-468300) were selected based on productivity and range of picked conodont elements. Chosen samples had conodonts which underwent formic and acetic digestion. Selection of conodonts for each sample included 3 ramiforms and 3 coniforms to provide adequate variation and quality of scans. Due to time constraints at the SEM microscope, two coniforms and two ramiforms per sample were selected for imaging. Observing surface x2500 magnification scans provided detail to the extent of damage that may have been caused during its extraction process. Scans were classified as pristine preservation due to their original structural integrity and lack of any observable recrystallization (Fig. 5). Furthermore, these samples had no observable surface damage from acid digestion regardless of procedural method. Scans also captured small distinctive features such as striation lines in samples F178604 and A178603 (C-468286 and C-468285 respectively) which capture original shape and characteristics of the conodont. As these features are seen on conodonts from our acetic and formic acid processing, it was determined that there was no damage or surface etching when comparing our different procedures.

Samples seen in Figures 6 and 7 were classified as conodonts which did not maintain pristine preservation. Samples given this designation were structurally altered after viewing under a picking monocular microscope. Upon further observation of surface magnification, samples were likely recrystallized following deposition. This determination was based on the shape and cubic like mineral structures which were embedded in the specimen. Similarly, as we had no control for what the original specimen looked like, we cannot confirm the extent to which formic acid processing had on the specimen. It can be inferred however that both acetic and formic acid samples were nearly identical as both displayed a similar degree of recrystallization. Based on these results, there is no clear evidence in our study that our formic acid processing resulted in surface etching. Thus, we can suggest that our methods in formic acid processing are a valid methodology in the extraction of conodonts which causes little to no degree of damage to conodont elements. Refer to appendix section A5 for a complete collection of all scans taken for this study.

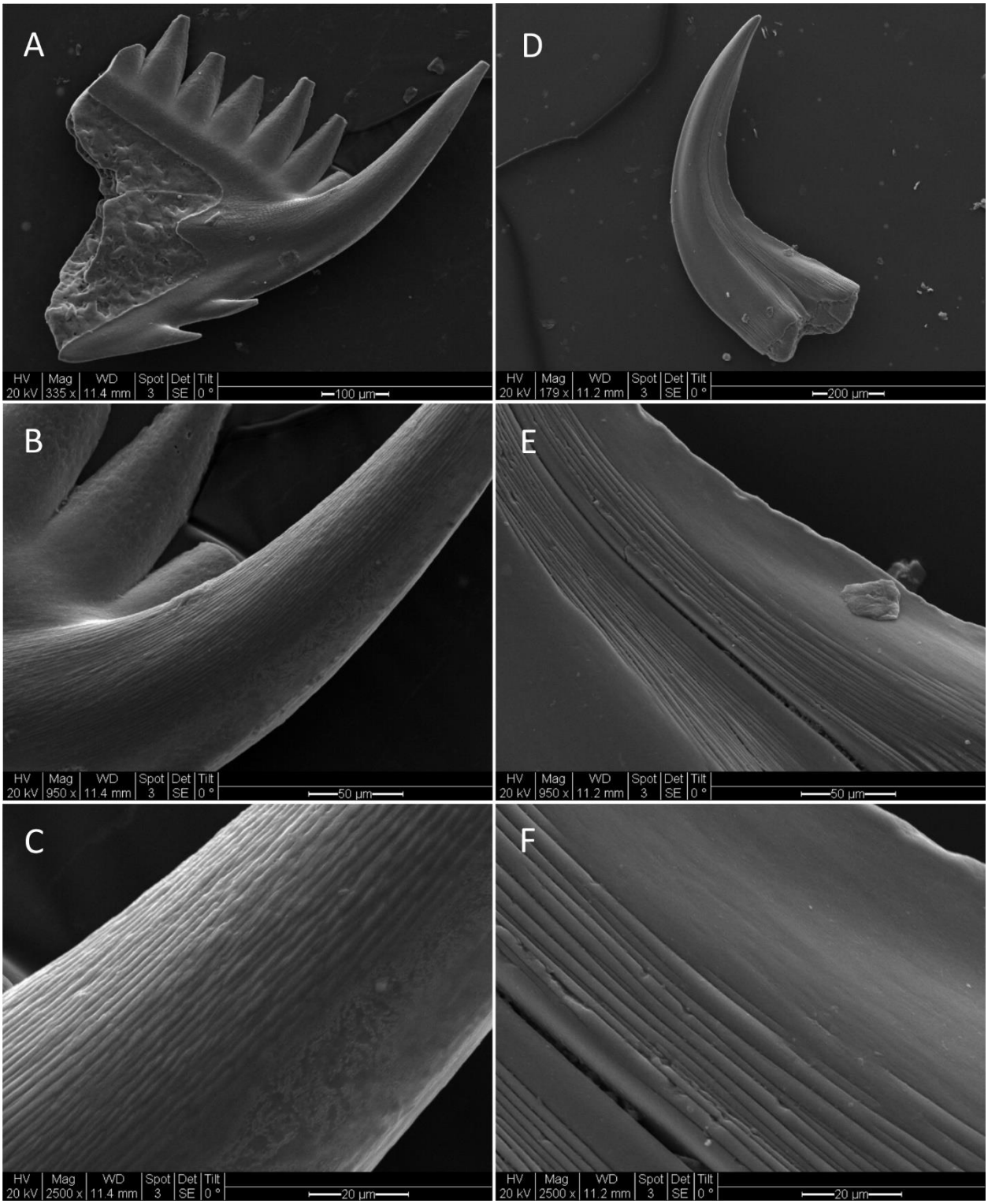

Figure 5. *Left* (A, B, C) *Aphelognathus* sp. aff. *A. pyramidalis* (Branson, Mehl and Branson 1951), (GSC 141425). Overview, x950, x2500 respectively surface SEM scans of sample A178603 processed via acetic acid. Textures observed in (c) of original feature to specimen. *Right* (D, E, F) *Panderodus unicostatus* (Branson and Mehl 1933), (GSC 141430). Overview, x950, x2500 respectively surface SEM scans of sample F178604 processed via formic acid. Striations are of original feature to specimen.

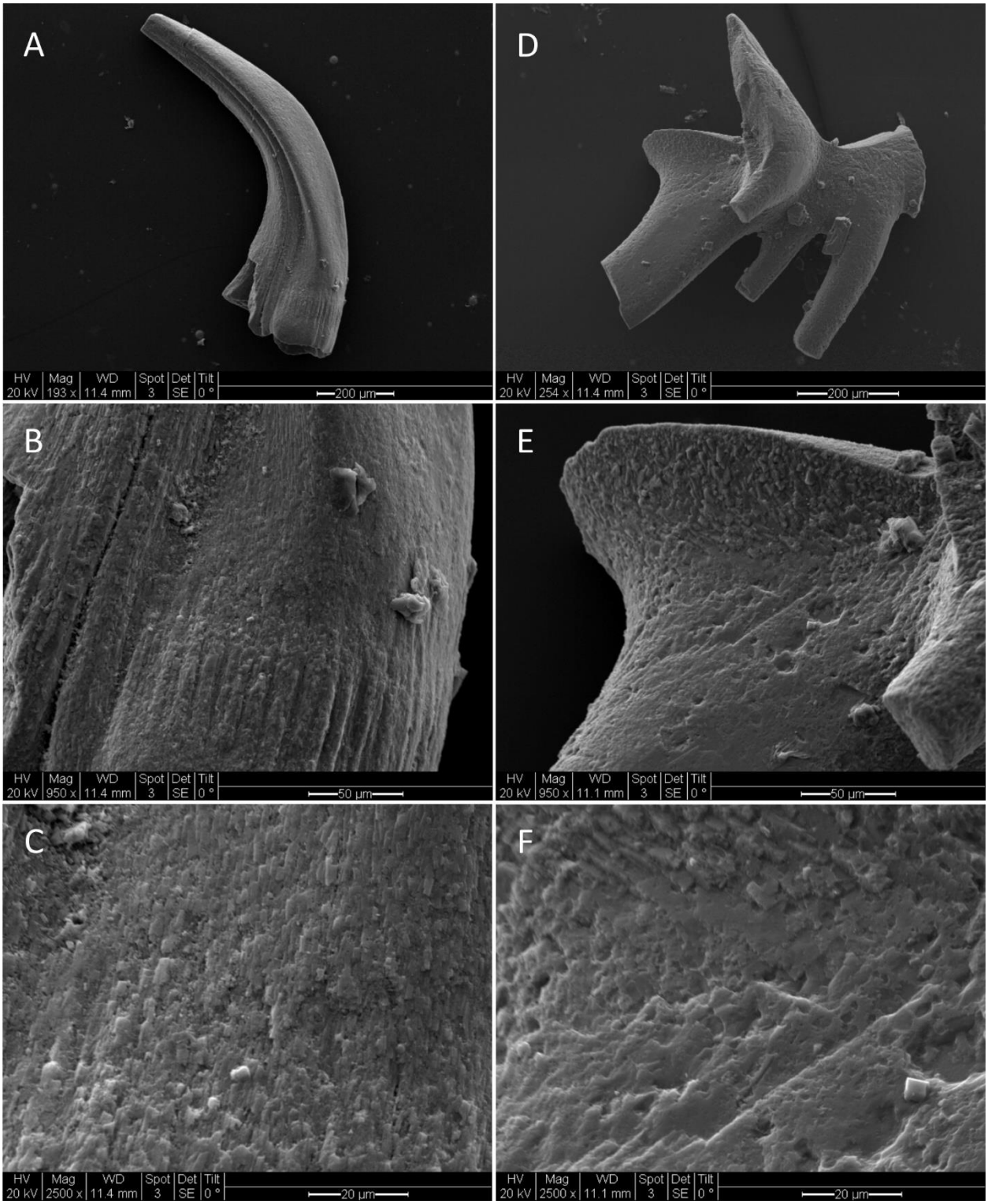

Figure 6. *Left* (A, B, C) *Panderodus unicostatus* (Branson and Mehl 1933), (GSC 141433) and *Right (*D, E, F*) Distomodus* sp. (GSC 141435). Overview, x950, x2500 scans respectively of sample A178705 processed via acetic acid. Cubic like structures indicative of recrystallization and not representative of etching due to acid.

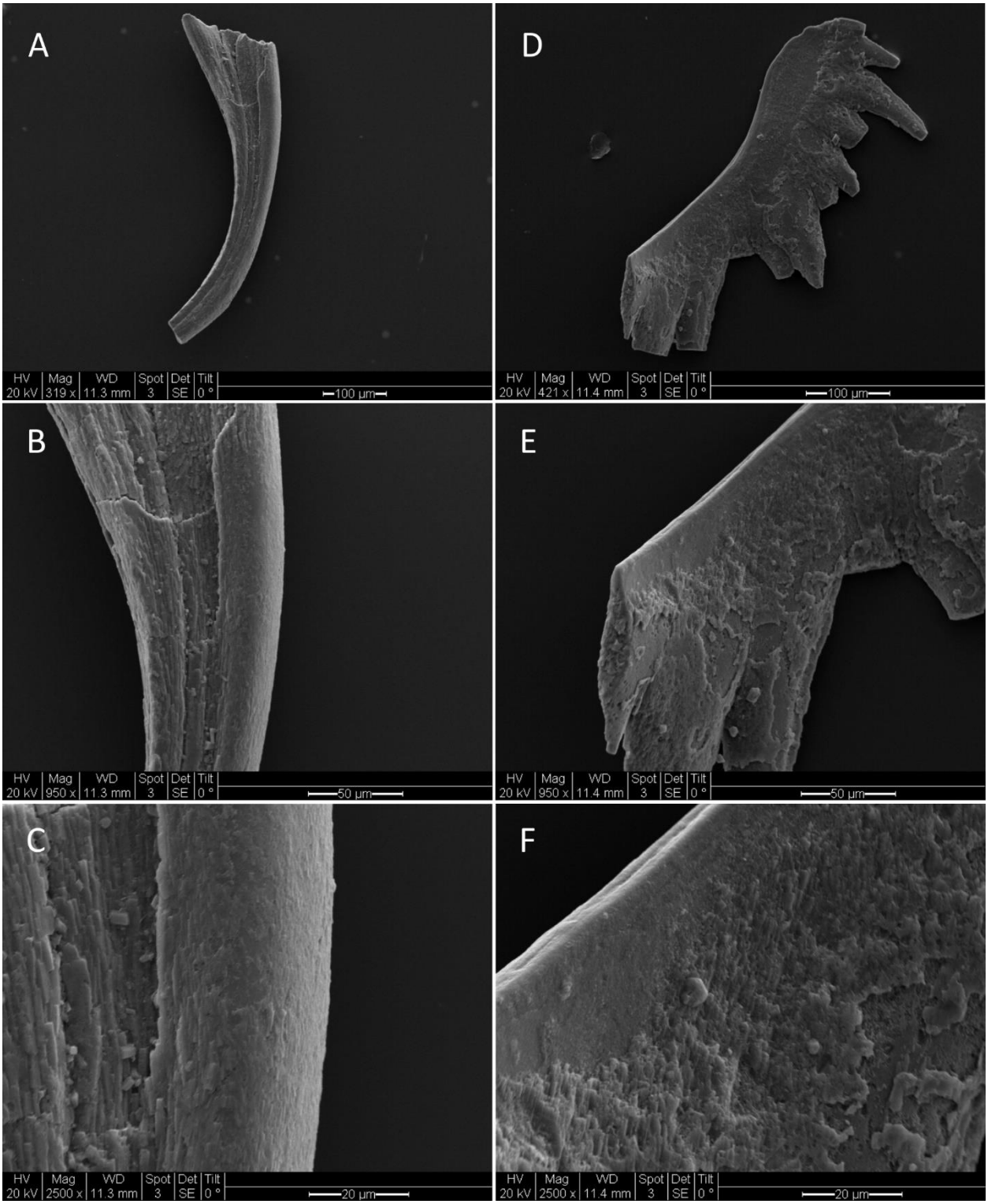

Figure 7. *Left* (A, B, C) *Panderodus unicostatus* (Branson and Mehl 1933), (GSC 141434) and *Right* (D, E, F) *Ozarkodina pirata* Uyeno in Uyeno and Barnes 1983 (GSC 141436). Overview, x950, x2500 scans respectively of sample F178705 processed via formic acid. Cubic structure and worn-down features indicative of recrystallization not representative of etching.

Analysis of laboratory costs

Sample cost

The approximate acid cost to process one sample using the formic acid method costs approximately $22.32 for a 1.0kg sample, and $48.20 for a 2.5kg sample. This is compared to acetic acid processing cost which costs approximately $28.84 for a 2.5kg sample. Including all other variables according to the current GSC-Calgary cost list, the presumptive cost to process a 1.0kg formic sample is $101.73 and $127.99 for a 2.5kg sample, whereas a 2.5kg acetic sample would cost $126.41. A short cost list summary for both Formic and Acetic acid processing is listed in Table 4 and Table 5 respectively. For the full detailed list of cost breakdown, refer to Appendix A4: Tables A14 and A15.

Table 4. Cost associated with processing samples via formic acid. These values only include costs of acid solutions used and do not include any other costs that may be associated with the total sample cost.

1.0kg Formic Acid Sample		**2.5kg Formic Acid Sample[5]**	
Acid Solution Cost / Sample		**Acid Solution Cost / Sample**	
Avg. Acid Added (L)	1.5	Acid Added (L)	3
Acid Cost / Liter	$ 3.51	Acid Cost / Liter	$ 3.51
Acid Cost[1]	$ 8.92	Acid Cost[1]	$ 17.84
Avg. Calcium Carbonate Added (kg)	0.1	Calcium Carbonate Added (kg)	0.225
Calcium Carbonate Cost / kg	$ 128.87	Calcium Carbonate Cost / kg	$ 128.87
Calcium Carbonate Cost[2]	$ 12.89	Calcium Carbonate Cost[2]	$ 29.00
Avg. Tri Phosphate Added (kg)	0.002	Tri Phosphate Added (kg)	0.0053
Tri Phosphate Cost / kg	$ 255.70	Tri Phosphate Cost / kg	$ 255.70
Tri Phosphate Cost[3]	$ 0.51	Tri Phosphate Cost[3]	$ 1.36
Total Acid Solution Cost / Sample[4]	$ 22.32	Total Cost / Sample[4]	$ 48.20

[1] Cost of formic acid added to sample over duration of acid digestion process. Cost calculated by taking acid added then multiplying by Acid Cost / Liter, then adding additional variables such as shipping, environmental fees, and US surcharges associated with delivery and procurement of acid. Acid added is the sum of all acid which samples require to digest.
[2] Cost of calcium carbonate added to sample. Cost calculated by multiplying calcium carbonate added (kg) by cost of calcium carbonate. Calcium carbonate was only added in initial stage of digestion as a buffer and not added again in following acid changes.
[3] Cost of tri phosphate added to sample. Cost calculated by multiplying tri phosphate added (kg) by cost of tri phosphate. Tri phosphate was only added in initial stage of digestion as a buffer and not added again in following acid changes.
[4] Total cost of acid solution is the sum of; Acid, Calcium Carbonate, and Tri-phosphate costs per sample.
[5] 2.5kg formic acid sample was not tested in this study therefore effectiveness of solution is unknown. Values of constituents determined by calculating required amounts to process a theoretical 2.5kg sample opposed to the 1.0kg samples used in this study. This theoretical 2.5kg sample was created to provide a comparison of price to process an equivalent weight of sample processed via Acetic acid.

Table 5. Cost associated with processing samples via acetic acid. Theses values only include cost of acid solution and do not include any other costs that may be associated with the total sample cost.

2.5kg Acetic Acid Sample	
Avg. Acid Added (L)[1]	6.3
Acid Cost / Liter	$ 3.51
Total Acid Cost / Sample[2]	$ 28.84
Total Acid Solution Cost / Sample[3]	$ 28.84

[1] Average acid added to samples processed via acetic acid. This is an average of all acetic acid samples (n=8) processed in this study.
[2] Cost of acetic acid added per sample. Calculated by multiplying the average acid added (L) by acid cost / Liter, then adding additional variables such as environmental fees, shipping, and US surcharges associated with the delivery and procurement of acid.
[3] Total cost of acid solution for a sample processed via acetic acid.

Sample cost analysis

A cost analysis was conducted on each processing method to identify any significant differences. This analysis was conducted on the premise of identifying which methodology costs less to conduct, which in turn would provide adequate opportunities for future processing options. Using the GSC price breakdown lists which uses quotes from suppliers to the GSC as of winter 2020. Costs for formic, acetic study average, and acetic maximum were calculated. It was determined that the formic acid processing cost for digestion per sample was $22.32 CDN for 1kg of sample and $48.20 for 2.5kgs of sample. This cost included various factors such as environmental and shipment fees, as well as cost of the buffers required for processing which were broken down to cost contribution per sample. Acetic acid processing was divided into two separate categories, one based on the project digestion time average, the other for full time digestion. Assuming samples take the maximum 56 days, costs for acid digestion was determined to be $36.63 per sample. Likewise, the average time taken for our study samples was 6.3 weeks, resulting in a total of 7 acid changes costing $28.84 per sample. Based on the cost of acid digestion alone, formic acid processing is slightly cheaper than the cost of its acetic counterpart only when comparing processing costs of 1.0kg of formic acid processing to 2.5kg of sample via acetic acid processing. When comparing both methods in terms of processing 2.5kg samples, acetic acid ($28.84 per sample) is significantly cheaper than its formic counterpart ($48.20 per sample). As we did not test the effectiveness of processing 2.5kg of sample via our tested formic acid procedure, we cannot state conclusively if this is viable option or that this theoretical cost would provide the same results seen in the 1.0kg samples. Regardless of the weight of sample processed, several observations can be made with regards to cost implications. Firstly, formic acid processing does have a major disadvantage in use as it requires a greater amount of materials (buffers) to digest samples, which in turn also increases general cost. This increase in general cost however is limited by; the short 3-day digestion time requiring less acid added per sample, and buffers are only added one time to the sample pail initially. Acetic acid processing however is advantageous in use requires no additional materials to conduct digestion. However, the process has a hindrance by the quantity of acid added to the sample over its processing time which is far more than what is seen in formic acid processing. This is disadvantage in the use of acetic acid processing as regardless of rather a 1.0kg or 2.5kg of sample processed via formic acid, the amount of acetic acid added to the sample is double to six times more than the amount of formic acid used per sample. When accounting for all other steps of processing in extraction of conodonts, the total cost for formic acid processing samples equivalents to $101.73 per 1.0kg sample and approximately $127.99 for a 2.5kg sample. This is cheaper compared to the full time (8 weeks of digestion) and slightly more than project average (6.3 weeks of digestion) acetic samples at $145.32 and $126.41, respectively. This large increase in price for acetic acid samples is due to the number of samples per year each procedure can complete. With yearly total lab costs excluding acid digestion being approximately $10,000 (Yearly costs accounting for equipment, lithium meta tungstate, and bleach) coverage of these costs must be determined by dividing total costs over number of samples completed every year. Samples processed via acetic acid per year (~154) is less than the number of samples formic acid digestion can produce (350). Therefore, to account for yearly laboratory costs, acetic acid samples costed approximately $30.00 more than their formic counterparts.

Cost variation and cost per kilogram

Other factors which were not included in the cost analysis include costs incurred via disposal of hazardous waste. Although this will inevitably increase cost attributed / sample, hazardous waste would only be necessary if there is not possibility to neutralize the solution to an acceptable pH. Both types of acid are considered weak acids thus drain disposal is acceptable provided concentrations are low and pH is neutral.

Furthermore, drain disposal should only be conducted if it is within acceptable parameters and is permitted by local, provincial, or federal legislation. For the purposes of this study, hazardous waste was neutralized, then disposed of using local removal services. Another factor when examining costs is the quantity of sample being processed. Formic acid processing in this study used on average 1.0kg of sample, whereas acetic acid processing used the standard GSC procedure of 2.5kg of sample. Although cost of acid digestion in formic acid processing is cheaper, it is processing 1.5kg less of sample therefore is not nearly as cost efficient at digesting large quantities of sample. Furthermore, if costs were adjusted to account for costs per 1.0kg of sample, full time acetic acid processing would cost $14.65 which is cheaper than the determined formic cost. Based on this correction, acetic acid is the cheaper method per kg of sample processed. An additional variable is the differential in time as formic acid processing only required 3 days to complete whereas acetic processing can take up to 56 days to complete. This meaning formic acid processing takes nearly 19 times faster than acetic acid processing. This differential in cost per kg of sample can be quickly brushed aside by researchers if samples are completed at a substantially faster rate, thus providing data for their research more quickly

Laboratory productivity

Assuming 10 formic acid samples can be processed at one time, the maximum number of samples that can be processed via formic acid is 520 per year. When realistic variables such as sick days, vacation days and lab catch up periods, the realistic amount of samples that can be processed from the formic method is about 350. The maximum amount of sample that acetic acid processing can yield each year is 248 assuming 30 samples are run at a time. With a reduction of lab catch up weeks to only 4 weeks each year, the realistic number of samples that can be produced is about 195. Assuming samples take 8 full weeks to process, the lab would only realistically produce about 154 samples each year (Table 6). The number of samples processed at a time was determined by several factors including the type of acid digestion and physical constraints observed within the lab. It was determined for best optimality in acid digestion, only 10 samples of formic acid would be run at a time while 30 acetic acid samples could be run at a time. The lower sample count in formic acid processing is due to how formic samples are processed. As one sample batch is to be maintained for 3 consecutive days, a logistical amount of samples that can be completed within one day must be used, which based off observations of current processing in the lab totals approximately 10 samples a day. On higher yield years, this count may be increased to 15 samples a day however doing so may put a strain on the lab technician's ability to complete other tasks. Contrarily samples processed via acetic acid can have upwards of 30 samples at a time. This is due to acetic acid samples requiring an acid change every week rather than every day thus, multiple samples can be processed over several days. This works out to approximately 10 samples a day, for 3 different designated acid change days (Tuesday to Thursday) for a total of 30 samples every acid digestion cycle. The physical constraints involved with the quantity of samples being processed in a day particularly involves laboratory space. Samples must be stored within fume hoods therefore laboratory space, more specifically fume hood space, becomes a major limiting factor when increasing concurrent samples. Another physical constraint as previously mentioned is the workers ability to complete that quantity within a single day. This was identified as a major limitation with large sample count batches as little to no time was left for other laboratory tasks to be completed when conducting 15-20 acid changes a day, thus a lesser more current count was chosen. This limitation also puts a strain on the workers physical health as conducting 15-20 acid changes daily involves a large amount of labor work. This amount of labor work may not be obtainable by some individuals due to strain put on the body, therefore a lesser amount of 10 acid changes was selected as the optimal amount.

Table 6. Productivity determination of the GSC-Calgary conodont lab. Values used mirror values seen throughout regular operating procedures.

Procedure	Samples / Batch	Processing Weeks (per Year)	Digestion Cycles[1] (per Year)	Total Samples (per Year)
		Maximum[2]		
Acetic	30	52	8	248
Formic	10	52	52	520
		Realistic[3]		
Acetic	30	41	6.5	195
Formic	10	35	35	350

[1] Digestion cycles refers to the number of weeks in a year where acid treatment can be conducted. Acetic acid processing takes 8 weeks maximum to complete, thus there are only 8 cycles that digestion is completed in a year. This method assumes no new samples are added during the digestion time of the previous sample batch.
[2] Maximum values disregard any discontinuities in laboratory procedures. These values assume processing can be completed 365 days a **year**.
[3] Realistic values account for several weeks throughout the year where processing cannot be completed. These include; Sick Leave (4 weeks maximum), Vacation Leave (3 weeks), Statutory Holidays (2 weeks, only applies to formic processing), and lab catch up weeks (8 weeks for formic, 4 weeks for acetic). Lab catch up weeks differ due to the difference in speed of output thus allowing submitted samples to be completed quicker, allowing greater downtime between lab submissions. Lab catch up weeks are defined by days where no processing is done, and work can be focused on other things not related to processing. These values widely vary year to year due to how many days of leave are taken.

The number of samples that the lab can produce in a fiscal year is also of importance when comparing both methodologies. Productivity for the lab must be calculated to determine the number of samples that can be accepted by the lab to ensure completion in an acceptable timeframe. Formic acid processing only takes 3 days to complete samples so, a sample batch round can be fully completed within one week. To ensure the amount samples being processed is not overwhelming and can be effectively changed within a 7.5-hour workday, 10 samples on average can be run daily thus producing 10 samples every 1 week of acid digestion. Theoretically, assuming maximum efficiency and production, samples could be processed all 52 weeks of the year, resulting in a maximum of 520 samples completed within one fiscal year. Acetic processing however takes a maximum of 56 days to complete. Within this 56-day window, no new samples are added, and acid changes only occur 3 days a week. On average 10 samples a day results in 30 samples in acid digestion during the 56-day timeframe. Assuming maximum production of the lab, only 6.5 eight-week cycles occur within the year, thus a maximum of 195 samples can be completed. Both processing numbers however are unrealistic as mandatory shutdowns, vacation days, sick days, and lab catchup days are inevitable within a given year. After these variables are considered, 35 designated formic acid processing weeks can output 350 samples in a year. Using similar variables, 41 realistic acetic acid processing weeks can output 154 samples a year. Differences in realistic processing weeks arise from slight variation in how both methods handle stat days and amount of lab catch up weeks. While these numbers change every year, formic processing cannot commence if there is a statutory holiday in the middle of the week due to the cut off from daily acid changes. Acetic processing however is relatively unaffected by these days due to the flexibility of acid changes which can be completed a day after due. Additionally, lab catch up weeks are also different amongst the processes, with 8 devoted weeks for formic and 4 devoted weeks for acetic acid processes. This is due to inclusion of statutory holidays for formic acid as well as 4 definite weeks of shutdown due to holidays or other work done to the lab. With the capability to output

350 samples within a given year, formic acid processing is nearly 2 times more productive than its acetic acid counterpart. This productivity entails samples can be produced at relatively low turnover times, something acetic processing struggles to accomplish. Lab productivity was calculated with the assumption that a full-time technician is dedicated to only the conodont lab thus if conditions are changed, calculated lab production amounts will be different.

CONCLUSIONS AND RECOMMENDATIONS

Based on evidence presented within this study, we can infer that both acetic and formic acid processing methods are valid techniques in the extraction of conodonts as is confirmed by the use of these techniques in many conodont processing labs. The goal of this study was to determine what techniques would be better for the GSC-Calgary lab with respect to processing time, cost, and sample quality. Although processing with formic acid is carried with the apparent risk of surface etching, there was no clear evidence in our study that this was the case using our formic acid processing method. There were however many pros and cons for using one method over the other based on observations during the study. Acetic acid processing has plenty of beneficial aspects. The more hands-off approach of acetic acid processing formulates a less work intensive procedure, which allows laboratory staff to complete non-associate tasks when samples are not being worked on. Acetic acid was also determined to be cheaper per kilogram when compared to formic acid. The increase in sample weight processed by acetic acid per pail was also an identified beneficial trait of acetic acid as it allows all 2.5kg of sample to be processed in one pail. For the same weight of sample to be processed using our tested formic acid procedure, it would have to be divided into two pails, each weighing 1.25kg which ultimately doubles processing cost. Although there is potential for 2.5kg of sample to be processed in a single pail, While 2.5kg of sample in one formic acid pail, costing $127.99 no investigation into how to accomplish this or effectiveness was done in this study. The major limitation imposed by using acetic acid is the dissolution time of the sample requiring up to 8 weeks makes the method 8 times longer than its formic counterpart. This is a major hindrance as the increase in processing time limits the ability to complete large quantities of samples within a year, something that is apparent in the calculated lab productivity.

For our identified formic acid methodology there were also many benefits and limitations. In particular, the most beneficial aspect in utilizing the formic acid procedure is digestion time and efficiency. Samples were out pacing the rate of breakdown seen in acetic acid processing by nearly 20% a day. Effectiveness in time also directly increases the productivity potential of the lab, allowing greater quantities of samples being processed in a year. We believe that use of formic acid processing in this study was well maintained and thus likely contributed to no observable damage to the specimen themselves. There are several limitations as identified in our study. The first of which is the increase in cost per sample being ~30% higher than acetic acid processing per kilogram of sample. We believe that this increase in price however can likely be negated due to the time taken to complete sample processing being drastically reduced. The second limitation identified is the nature of formic acid processing requiring an increased amount of work in a concentrated time frame of 4 days. This increase in maintenance for processing samples makes it difficult to complete other non-acid digestion related tasks which the technician may have to complete in weeks of acid digestion. A potential integration to help fix this challenge is to change the way planning and preparation is done. With integration of designated weekly tasks, other components of the technicians' role could be worked on off week or weeks which have no acid digestion planned. Formic acid processing also demands a much more intense monitoring system in the form of pH monitoring and sample mixing to ensure acid strength and layering doesn't compromise laboratory grade results which

once again is a hindrance on the flexibility of the technicians' daily tasks. The hazards for the use of formic acid have also been identified as a limitation for the procedure. Unlike acetic acid which is generally a safer acid to handle when diluted, formic acid is more hazardous as it not only more flammable in both liquid and vapor form, but it can also more reactive and can cause severe burns to the skin and eyes if exposed. Additionally, formic acid is toxic if inhaled and may cause respiratory irritation to a greater degree than what can be caused by acetic acid. Due to these hazards, formic acid also requires greater amounts of laboratory equipment such; as ventilation snorkels, well ventilated fume hoods, and fire suppression units. Although these limitations may hinder formic acid's true capabilities, we believe that our formic acid procedural methods are a valid technique in the extraction of conodonts.

Concluding Remarks

As the result of this study, the GSC-Calgary conodont lab is to include the use of formic acid processing into standard operating procedures. The ability to offer both methods as valid processing practices will allow greater choice for researchers submitting samples to the laboratory. Additionally, the introduction of the alternative formic acid processing provides the option for samples to be completed at a quicker pace thus increasing the number of samples the laboratory could complete each year. Albeit slightly ($1.50) more expensive per sample when compared to acetic acid, the quick processing time of formic acid may be an interest to researchers that need their samples quickly. The cheaper option of the two processing types based off the results of this study, would be acetic acid costing $126.41 for 2.5kg sample. In the case of the present situation at GSC-Calgary, time saved processing conodonts using formic acid processing will vastly enhance the ability for technicians to complete other laboratory activities. With respect to quality of conodont elements based off the evidence observed in this study, we conclusively determined that type of acid had no impact on surface quality of the conodont specimen. Therefore, the result will still maintain high quality samples that the GSC is known to output.

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APPENDIX

A1. Sample properties

Table A1. Properties of samples chosen for this study. A total of 8 parent samples were selected based of reported conodont productivity. Parent samples Location of sample collection, age, lithology, and expected breakdown percentage of chosen samples are provided.

Sample	Treatment	Parent Sample	C#	Location	Age	Lithology	Expected Breakdown (%)[1]
A178603 F178603	Acetic Acid Formic Acid	1786-03	C-468285	N/A	*Middle Ordovician*	Limestone	93.4
A178604 F178604	Acetic Acid Formic Acid	1786-04	C-468286	N/A	*Middle Ordovician*	Limestone	100
A178705 F178705	Acetic Acid Formic Acid	1787-05	C-468295	Little Current River	*Wenlock - Ludlow*	Limestone	100
A178710 F178710A F178710B	Acetic Acid Formic Acid Formic Acid	1787-10	C-468300	Drowning River	*Wenlock - Ludlow*	Limestone	100
A18005 F18005A F18005B	Acetic Acid Formic Acid Formic Acid	1800-5	C-591619	Kenogami River	*Early Silurian*	Limestone	97.2
A18006 F18006A F18006B	Acetic Acid Formic Acid Formic Acid	1800-6	C-591610	Kenogami River	*Early Silurian*	Limestone	95.3
A18008 F18008A F18008B	Acetic Acid Formic Acid Formic Acid	1800-8	C-5916120	Fort Albany	*Early Devonian*	Limestone	96.7
A18011 F18011A F18011B	Acetic Acid Formic Acid Formic Acid	1800-11	C-591615	Ekwan River	*Early Silurian*	Limestone	97.3

[1] Expected breakdown is what was previously recoded when samples underwent acid digestion. As these samples were previously processed at the GSC-Calgary conodont lab, the expected breakdown is the level of expectation to how well samples digested over an 8-week period.

A2. Acid solution compositions

A2.1 Acetic acid solution

Table A2. Composition of acid solution including sample mass, amount of water, and total acid added. Acid added amount was re-occurring every acid change as "fresh acid" into previous solution.

Sample	Sample Mass (g) ±0.5g	Total Solution (L)[1] ±0.01L	Water (L) ±0.01L	99.5% Glacial Acetic Acid (L) ±0.01L
A178603	1163.5	2.4	2.0	0.4
A178604	1060.0	2.6	2.1	0.5
A178705	720.5	1.6	1.3	0.3
A178710	1744.0	3.8	3.1	0.7
A18005	2312.0	5.1	4.2	0.9
A18006	2252.0	5.0	4.1	0.9
A18008	2269.0	5.0	4.1	0.9
A18011	2051.0	4.5	3.7	0.8

[1] Total solution adjusted for variable sample mass. Each sample maintains a 5.5 : 2.5 solution to mass ratio

A2.2 Formic acid solution

Table A3. Composition of acid solution including sample mass, amount of water, weight of dual buffers added, and total acid added. Acid added amount was re-occurring every acid change as "fresh acid" into previous solution. Calcium Carbonate and Tricalcium Phosphate were only initially added in original composition, not in following acid changes.

Sample	Sample Mass (g) ±0.5g	Total[1] Solution (L) ±0.01L	Water (L) ±0.01L	85% Formic Acid (L) ±0.01L	Calcium Carbonate (g) ±0.1g	Tricalcium Phosphate (g) ±0.1g
F178603	1163.5	3.5	3.0	0.5	104.7	2.4
F178604	1060.0	3.2	2.8	0.4	95.4	2.2
F178705	730.0	2.2	1.9	0.3	65.7	1.5
F178710A	868.5	2.6	2.3	0.3	78.2	1.8
F178710B	877.0	2.6	2.3	0.3	78.9	1.8
F18005A	1180.5	3.5	3.1	0.4	106.2	2.5
F18005B	1119.0	3.4	2.9	0.4	100.7	2.3
F18006A	1144.5	3.4	3.0	0.4	103.0	2.4
F18006B	1102.0	3.2	2.9	0.4	99.2	2.3
F18008A	1143.5	3.4	3.0	0.4	102.9	2.4
F18008B	1126.5	3.4	2.9	0.4	101.4	2.4
F18011A	1024.0	3.1	2.7	0.4	92.2	2.2
F18011B	1020.0	3.1	2.7	0.4	91.8	2.1

[1] Total solution adjusted for variable sample mass. Each sample maintains a 5.5 : 2.5 solution to mass ratio

A3. pH measurements over time

A3.1 Formic acid pH measurements

Table A4. Measurements of pH, acid changes, and processing time for formic samples from parent samples 1786-03, 1786-04, 1787-05, and 1787-10. pH measurements occurred every 3 hours in a standard operating day.

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
Sample: *F178603*					
June 17 2019	2.24	2.41	2.69	0	0
June 18 2019	3.19	3.22	2.68	1	1
June 19 2019	2.94	2.97	2.24	2	2
June 20 2019	2.76	2.77	NA	2	3
Sample: *F178604*					
June 18 2019	2.63	2.85	3.03	0	0
June 19 2019	2.39	2.85	2.97	1	1
June 20 2019	2.30	2.73	2.91	2	2
June 21 2019	3.11	NA	NA	2	3
Sample: *F178705*					
July 9 2019	2.9	3.8	4.18	0	0
July 10 2019	2.97	3.22	3.28	1	1
July 11 2019	2.73	2.87	2.89	2	2
July 12 2019	2.95	NA	NA	2	3
Sample: *F178710A*					
July 9 2019	2.87	3.65	4.02	0	0
July 10 2019	3.02	3.25	3.29	1	1
July 11 2019	2.74	2.86	2.89	2	2
July 12 2019	2.94	NA	NA	2	3
Sample: *F178710B*					
July 9 2019	2.83	3.69	4.06	0	0
July 10 2019	3.00	3.35	3.43	1	1
July 11 2019	2.80	2.94	2.98	2	2
July 12 2019	3.12	NA	NA	2	3

Table A5. Measurements of pH, acid changes, and processing time for formic samples from parent samples 1800-05 and 1800-06. pH measurements occurred every 3 hours in a standard operating day.

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
Sample: *F18005A*					
July 16 2019	2.74	2.89	2.96	0	0
July 17 2019	2.49	2.59	2.65	1	1
July 18 2019	2.51	2.50	2.52	2	2
July 19 2019	2.53	NA	NA	2	3
Sample: *F18005B*					
July 16 2019	2.70	2.87	2.94	0	0
July 17 2019	2.48	2.55	2.60	1	1
July 18 2019	2.45	2.43	2.46	2	2
July 19 2019	2.49	NA	NA	2	3
Sample: *F18006A*					
July 16 2019	2.66	2.86	2.92	0	0
July 17 2019	2.48	2.59	2.63	1	1
July 18 2019	2.43	2.44	2.46	2	2
July 19 2019	2.53	NA	NA	2	3
Sample: *F18006B*					
July 16 2019	2.55	2.84	2.93	0	0
July 17 2019	2.49	2.5	2.55	1	1
July 18 2019	2.27	2.29	2.32	2	2
July 19 2019	2.39	NA	NA	2	3

Table A6. Measurements of pH, acid changes, and processing time for formic samples from parent samples 1800-08 and 1800-11. pH measurements occurred every 3 hours in a standard operating day.

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
Sample: *F18008A*					
July 23 2019	3.05	3.73	3.94	0	0
July 24 2019	2.77	2.91	2.91	1	1
July 25 2019	2.41	2.78	2.83	2	2
July 26 2019	2.86	NA	NA	2	3
Sample*: F18008B*					
July 23 2019	2.99	3.67	3.85	0	0
July 24 2019	2.71	2.87	2.85	1	1
July 25 2019	2.35	2.81	2.87	2	2
July 26 2019	2.91	NA	NA	2	3
Sample: *F18011A*					
July 23 2019	2.78	3.54	3.74	0	0
July 24 2019	2.72	2.81	2.82	1	1
July 25 2019	2.45	2.68	2.77	2	2
July 26 2019	2.86	NA	NA	2	3
Sample: *F18011B*					
July 23 2019	2.8	3.55	3.74	0	0
July 24 2019	2.72	2.8	2.83	1	1
July 25 2019	2.36	2.58	2.69	2	2
July 26 2019	2.79	NA	NA	2	3

A3.2 Acetic acid pH measurements

Table A7. Lab sheet measurements for acetic acid sample A178603 (1786-03).

Sample: *A178603*					
		pH (±0.01)			**Processing Time**
Date	***9 am***	***12 pm***	***3pm***	**Acid Changes**	**(Days)**
June 17 2019	2.13	3.19	3.49	0	0
June 18 2019	3.91	3.94	3.96	0	1
June 19 2019	4.12	4.13	4.15	0	2
June 20 2019	4.24	4.25	4.28	0	3
June 21 2019	4.31	4.33	4.33	0	4
June 24 2019	3.65	3.82	3.90	1	7
June 25 2019	3.92	3.93	3.94	1	8
June 26 2019	3.96	3.96	3.99	1	9
June 27 2019	4.02	4.02	4.02	1	10
June 28 2019	4.06	4.06	4.07	1	11
July 2 2019	3.76	3.77	3.77	2	15
July 3 2019	3.80	3.80	3.89	2	16
July 4 2019	3.82	3.81	3.82	2	17
July 5 2019	3.80	3.82	3.83	2	18
July 8 2019	3.93	3.92	3.95	2	21
July 9 2019	3.54	3.60	3.63	3	22
July 10 2019	3.68	3.67	3.67	3	23
July 11 2019	3.60	3.62	3.61	3	24
July 12 2019	3.70	3.71	3.72	3	25
July 15 2019	3.54	3.53	3.56	4	28
July 16 2019	3.57	3.57	3.57	4	29
July 17 2019	3.59	3.59	3.60	4	30
July 18 2019	3.63	3.63	3.64	4	31
July 19 2019	3.66	3.65	3.65	4	32
July 22 2019	3.38	3.45	3.45	5	35
July 23 2019	3.44	3.47	3.48	5	36
July 24 2019	3.43	3.43	3.42	5	37
July 25 2019	3.42	3.40	3.40	5	38
July 26 2019	3.40	3.40	3.41	5	39
July 29 2019	3.24	3.28	3.32	6	42
July 30 2019	3.35	3.34	3.34	6	43
July 31 2019	3.36	3.36	3.35	6	44
Aug 1 2019	3.36	3.37	3.38	6	45
Aug 2 2019	3.40	3.40	3.41	6	46
Aug 6 2019	3.22	3.24	3.25	7	50
Aug 7 2019	3.39	3.44	3.44	7	51
Aug 8 2019	3.39	3.51	3.40	7	52
Aug 9 2019	3.46	3.44	3.46	7	53
Aug 12 2019	3.50	3.52	3.52	7	56
Aug 13 2019	3.54	NA	NA	7	57

Table A8. Lab sheet measurements for acetic acid sample A178604 (1786-04).

Sample: *A178604*

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
June 17 2019	2.29	3.28	3.54	0	0
June 18 2019	3.93	3.98	3.99	0	1
June 19 2019	4.17	4.18	4.20	0	2
June 20 2019	4.29	4.31	4.32	0	3
June 21 2019	4.36	4.39	4.39	0	4
June 24 2019	3.88	3.94	3.96	1	7
June 25 2019	4.07	4.09	4.11	1	8
June 26 2019	4.18	4.18	4.21	1	9
June 27 2019	4.25	4.27	4.28	1	10
June 28 2019	4.32	4.33	4.34	1	11
July 2 2019	3.83	3.94	4.00	2	15
July 3 2019	4.03	4.04	4.03	2	16
July 4 2019	4.06	4.08	4.09	2	17
July 5 2019	4.09	4.09	4.10	2	18
July 8 2019	4.21	4.22	4.23	2	21
July 9 2019	3.82	3.89	3.92	3	22
July 10 2019	3.93	3.96	3.96	3	23
July 11 2019	3.94	3.92	3.91	3	24
July 12 2019	4.03	4.01	4.01	3	25
July 15 2019	3.83	3.86	3.84	4	28
July 16 2019	3.86	3.87	3.87	4	29
July 17 2019	3.89	3.90	3.90	4	30
July 18 2019	3.94	3.94	3.94	4	31
July 19 2019	3.92	3.92	3.93	4	32
July 22 2019	3.77	3.78	3.78	5	35
July 23 2019	3.75	3.74	3.78	5	36
July 24 2019	3.75	3.72	3.70	5	37
July 25 2019	3.70	3.69	3.70	5	38
July 26 2019	3.66	3.65	3.65	5	39
July 29 2019	3.52	3.70	3.71	6	42
July 30 2019	3.75	3.74	3.74	6	43
July 31 2019	3.74	3.74	3.74	6	44
Aug 1 2019	3.74	3.74	3.73	6	45
Aug 2 2019	3.76	3.78	3.78	6	46
Aug 6 2019	3.86	NA	NA	6	50

Table A9. Lab sheet measurements for acetic acid sample A178705 (1787-05).

Sample: *A178705*

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
June 25 2019	3.00	4.26	4.48	0	0
June 26 2019	4.83	4.85	4.89	0	1
June 27 2019	4.96	4.97	4.99	0	2
June 28 2019	4.13	4.15	4.17	1	3
July 2 2019	4.72	4.73	4.73	1	7
July 3 2019	4.76	4.78	4.78	1	8
July 4 2019	4.76	4.79	4.79	1	9
July 5 2019	4.02	4.25	4.33	2	10
July 8 2019	4.81	4.81	4.93	2	13
July 9 2019	2.90	3.80	4.18	2	14
July 10 2019	4.84	4.90	4.91	2	15
July 11 2019	4.91	4.87	4.87	2	16
July 12 2019	4.20	4.29	4.31	3	17
July 15 2019	4.40	4.47	4.46	3	20
July 16 2019	4.51	4.50	4.50	3	21
July 17 2019	4.52	4.53	4.53	3	22
July 18 2019	4.55	4.55	4.54	3	23
July 18 2019	4.55	NA	NA	3	24

Table A10. Lab sheet measurements for acetic acid sample A178710 (1787-10).

Sample: *A178710*

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
A178710	2.87	4.10	4.33	0	0
A178710	4.70	4.72	4.75	0	1
A178710	4.84	4.85	4.88	0	2
A178710	4.92	4.92	4.93	0	3
A178710	4.07	4.13	4.19	1	7
A178710	4.27	4.30	4.29	1	8
A178710	4.28	4.32	4.33	1	9
A178710	4.31	4.32	4.32	1	10
A178710	4.45	4.44	4.45	1	13
A178710	3.68	3.91	4.17	2	14
A178710	4.38	4.45	4.47	2	15
A178710	4.43	4.51	4.51	2	16
A178710	4.62	4.63	4.64	2	17
A178710	4.13	4.15	4.17	3	20
A178710	4.27	4.29	4.28	3	21
A178710	4.31	4.33	4.34	3	22
A178710	4.36	4.36	4.37	3	23
A178710	4.34	4.31	4.33	3	24
A178710	4.34	NA	NA	3	27

Table A11. Lab sheet measurements for acetic acid sample A18005 (1800-05).

Sample: *A18005*

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
June 21 2019	2.12	2.92	3.21	0	0
June 24 2019	3.85	3.87	3.89	0	3
June 25 2019	3.93	3.95	3.95	0	4
June 26 2019	3.99	4.00	4.01	0	5
June 27 2019	4.03	4.04	4.06	0	6
June 28 2019	3.36	3.5	3.54	1	7
July 2 2019	3.65	3.65	3.65	1	11
July 3 2019	3.68	3.68	3.68	1	12
July 4 2019	3.71	3.70	3.70	1	13
July 5 2019	3.33	3.39	3.40	2	14
July 8 2019	3.48	3.50	3.51	2	17
July 9 2019	3.51	3.49	3.49	2	18
July 10 2019	3.62	3.55	3.54	2	19
July 11 2019	3.45	3.47	3.47	2	20
July 12 2019	3.26	3.24	3.3	3	21
July 15 2019	3.34	3.35	3.36	3	24
July 16 2019	3.35	3.36	3.36	3	25
July 17 2019	3.35	3.38	3.37	3	26
July 18 2019	3.41	3.44	3.43	3	27
July 19 2019	3.20	3.27	3.31	4	28
July 22 2019	3.34	3.35	3.36	4	31
July 23 2019	3.41	3.39	3.40	4	32
July 24 2019	3.39	3.37	3.37	4	33
July 25 2019	3.38	3.35	3.37	4	34
July 26 2019	3.08	3.12	3.14	5	35
July 29 2019	3.17	3.18	3.19	5	38
July 30 2019	3.22	3.22	3.20	5	39
July 31 2019	3.25	3.23	3.23	5	40
Aug 1 2019	3.24	3.24	3.23	5	41
Aug 2 2019	2.99	3.05	3.04	6	42
Aug 6 2019	3.05	3.06	3.04	6	46
Aug 7 2019	3.16	3.20	3.20	6	47
Aug 8 2019	3.15	3.15	3.15	6	48
Aug 9 2019	3.01	3.09	3.10	7	49
Aug 12 2019	3.15	3.14	3.13	7	52
Aug 13 2019	3.13	3.12	3.13	7	53
Aug 14 2019	3.13	3.14	3.12	7	54
Aug 15 2019	3.12	3.14	3.15	7	55
Aug 16 2019	3.18	NA	NA	7	56

Table A12. Lab sheet measurements for acetic acid sample A18006 (1800-06)

Sample: *A18006*

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
June 21 2019	2.12	2.95	3.23	0	0
June 24 2019	3.90	3.92	3.94	0	3
June 25 2019	3.99	4.00	4.01	0	4
June 26 2019	4.05	4.06	4.07	0	5
June 27 2019	4.10	4.11	4.11	0	6
June 28 2019	3.52	3.56	3.57	1	7
July 2 2019	3.65	3.66	3.66	1	11
July 3 2019	3.68	3.68	3.68	1	12
July 4 2019	3.72	3.72	3.71	1	13
July 5 2019	3.25	3.35	3.41	2	14
July 8 2019	3.45	3.49	3.49	2	17
July 9 2019	3.48	3.47	3.46	2	18
July 10 2019	3.60	3.58	3.55	2	19
July 11 2019	3.52	3.49	3.48	2	20
July 12 2019	3.23	3.25	3.26	3	21
July 15 2019	3.33	3.33	3.34	3	24
July 16 2019	3.33	3.34	3.34	3	25
July 17 2019	3.34	3.36	3.37	3	26
July 18 2019	3.38	3.40	3.41	3	27
July 19 2019	3.23	3.19	3.21	4	28
July 22 2019	3.23	3.26	3.27	4	31
July 23 2019	3.28	3.33	3.33	4	32
July 24 2019	3.31	3.30	3.27	4	33
July 25 2019	3.32	3.30	3.31	4	34
July 26 2019	3.04	3.04	3.06	5	35
July 29 2019	3.12	3.10	3.11	5	38
July 30 2019	3.12	3.12	3.11	5	39
July 31 2019	3.13	3.13	3.12	5	40
Aug 1 2019	3.15	3.16	3.15	5	41
Aug 2 2019	2.88	2.95	2.96	6	42
Aug 6 2019	3.00	3.03	2.99	6	46
Aug 7 2019	3.04	3.08	3.13	6	47
Aug 8 2019	3.09	3.09	3.09	6	48
Aug 9 2019	2.99	3.06	3.10	7	49
Aug 12 2019	3.09	3.11	3.12	7	52
Aug 13 2019	3.12	3.13	3.14	7	53
Aug 14 2019	3.14	3.14	3.13	7	54
Aug 15 2019	3.15	3.15	3.18	7	55
Aug 16 2019	3.21	NA	NA	7	56

Table A13. Lab sheet measurements for acetic acid sample A18008 (1800-08)

Sample: *A18008*

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
June 21 2019	3.25	4.12	4.34	0	0
June 24 2019	4.87	4.91	4.92	0	3
June 25 2019	4.95	4.96	4.97	0	4
June 26 2019	3.81	4.06	4.12	1	5
June 27 2019	4.23	4.23	4.25	1	6
June 28 2019	4.26	4.27	4.29	1	7
July 2 2019	4.36	4.38	4.43	1	11
July 3 2019	3.71	4.01	4.07	2	12
July 4 2019	4.23	4.36	4.35	2	13
July 5 2019	4.38	4.33	4.34	2	14
July 8 2019	4.60	4.55	4.59	2	17
July 9 2019	4.59	4.65	4.65	2	18
July 10 2019	4.09	4.10	4.10	3	19
July 11 2019	4.10	4.05	4.08	3	20
July 12 2019	4.03	4.05	4.05	3	21
July 15 2019	4.05	4.06	4.06	3	24
July 16 2019	4.06	4.06	4.05	3	25
July 17 2019	3.47	3.56	3.60	4	26
July 18 2019	3.71	3.72	3.72	4	27
July 19 2019	3.75	3.73	3.73	4	28
July 22 2019	3.81	3.81	3.80	4	31
July 23 2019	3.78	3.79	3.82	4	32
July 24 2019	3.80	NA	NA	4	33

Table A14. Lab sheet measurements for acetic acid sample A1800-11 (1800-11)

Sample: *A18011*

Date	pH (±0.01) 9 am	12 pm	3pm	Acid Changes	Processing Time (Days)
June 25 2019	2.88	4.16	4.37	0	0
June 26 2019	4.7	4.71	4.74	0	1
June 27 2019	4.83	4.85	4.87	0	2
June 28 2019	4.91	4.91	4.92	0	3
July 2 2019	3.97	4.15	4.16	1	7
July 3 2019	4.22	4.23	4.23	1	8
July 4 2019	4.20	4.28	4.27	1	9
July 5 2019	4.23	4.22	4.25	1	10
July 8 2019	4.37	4.36	4.38	1	13
July 9 2019	3.83	3.91	4.02	2	14
July 10 2019	4.08	4.15	4.16	2	15
July 11 2019	4.17	4.15	4.15	2	16
July 12 2019	4.26	4.27	4.27	2	17
July 15 2019	3.94	3.98	4.00	3	20
July 16 2019	4.03	4.04	4.04	3	21
July 17 2019	4.04	4.06	4.05	3	22
July 18 2019	4.08	4.08	4.08	3	23
July 19 2019	4.06	4.03	4.06	3	24
July 22 2019	3.70	3.72	3.71	4	27
July 23 2019	3.69	3.70	3.74	4	28
July 24 2019	3.66	3.66	3.64	4	29
July 25 2019	3.65	3.62	3.64	4	30
July 26 2019	3.61	3.59	3.60	4	31
July 29 2019	3.36	3.40	3.42	5	34
July 30 2019	3.40	3.42	3.41	5	35
July 31 2019	3.42	3.41	3.41	5	36
Aug 1 2019	3.44	3.43	3.43	5	37
Aug 2 2019	3.48	3.51	3.49	5	38
Aug 6 2019	3.29	3.27	3.28	6	42
Aug 7 2019	3.37	3.36	3.35	6	43
Aug 8 2019	3.30	3.33	3.31	6	44
Aug 9 2019	3.32	3.34	3.38	6	45
Aug 12 2019	3.34	3.33	3.34	6	48
Aug 13 2019	3.25	NA	NA	6	49

A4. GSC cost lists

Table A15. Full processing cost calculated for conodont processing via formic acid procedure. Cost proportions broken down into cost per 1.0 kg sample.

Formic Processing Cost[1]	
Formic Acid Solution Cost / Sample	
85% Formic Acid Cost	$ 8.92
Calcium Carbonate	$ 12.89
Tri Phosphate	$ 0.51
Total Cost / Sample	$ 22.32
Bleach Solution Cost / Sample	
Bleach	$ 0.84
Heavy Liquid Solution Cost / Sample	
Total Lithium Meta Tungstate	$ 8.15
Equipment Cost / Sample[2]	
Filter paper	$ 1.68
Microfossil Slide	$ 1.09
Aluminum Bracket	$ 2.50
Glass Slide	$ 0.36
Sample Bags[3]	$ 24.00
Glassware	$ 7.14
Stationary	$ 2.86
PPE	$4.29
Total Equipment Cost	$ 43.92
Picking	
Cost Per Sample	$25.00
Total Processing Cost (1.0kg Sample)[4]	$101.73

[1] Total costs adjusted per quotes from suppliers to the GSC. Costs calculated for fall / winter 2019-2020 and are subject to change. Values equal costs to process 1.0 kg sample.

[2] Equipment costs account for approximate samples completed within a year. Total price is distributed over expected samples using productivity calculations.

[3] Sample bag cost is the sum of the 4-5 Whirl-Pak™ bags (Assorted size) used in both procedures. Average costs for these bags is $4.80/bag hence a total cost of $24.00 for all the bags used.

[4] Total Processing cost is the sum of; Total Acid cost / Sample, Bleach, Total Lithium Meta Tungstate, Total Equipment cost, and Picking cost. In addition to these values, a yearly 1.5% cost fluctuation rate is applied which covers alternative costs and yearly inflation values.

Table A16. Full processing cost calculated for conodont processing via formic acid procedure. Cost proportions broken down into cost per theoretical 2.5 kg sample.

Formic Processing Cost[1]	
Formic Acid Solution Cost / Sample	
85% Formic Acid Cost	$ 17.84
Calcium Carbonate	$ 29.00
Tri Phosphate	$ 1.36
Total Cost / Sample	$ 48.20
Bleach Solution Cost / Sample	
Bleach	$ 0.84
Heavy Liquid Solution Cost / Sample	
Total Lithium Meta Tungstate	$ 8.15
Equipment Cost / Sample[2]	
Filter paper	$ 1.68
Microfossil Slide	$ 1.09
Aluminum Bracket	$ 2.50
Glass Slide	$ 0.36
Sample Bags[3]	$ 24.00
Glassware	$ 7.14
Stationary & Pail	$ 2.86
PPE	$4.29
Total Equipment Cost	$ 43.92
Picking	
Cost Per Sample	$25.00
Total Processing Cost (2.5kg Sample)[4]	$127.99

[1] Total costs adjusted per quotes from suppliers to the GSC. Costs calculated for fall / winter 2019-2020 and are subject to change. Values equal costs to process a theoretical 2.5 kg sample.

[2] Equipment costs account for approximate samples completed within a year. Total price is distributed over expected samples using productivity calculations.

[3] Sample bag cost is the sum of the 4-5 Whirl-Pak™ bags (Assorted size) used in both procedures. Average costs for these bags is $4.80/bag hence a total cost of $24.00 for all the bags used.

[4] Total Processing cost is the sum of; Total Acid cost / Sample, Bleach, Total Lithium Meta Tungstate, Total Equipment cost, and Picking cost. In addition to these values, a yearly 1.5% cost fluctuation rate is applied which covers alternative costs and yearly inflation values.

Table A17. Full processing cost calculated for conodont processing via acetic acid procedure. Cost proportions broken down into cost per 2.5 kg sample.

Acetic Processing Cost[1]	
Acetic Acid Solution Cost / Sample[2]	
99.5% Glacial Acetic Acid Solution Cost	$28.84
Bleach Solution Cost / Sample	
Bleach	$ 0.84
Heavy Liquid Solution Cost / Sample	
Total Lithium Meta Tungstate	$ 14.62
Equipment Cost / Sample[3]	
Filter paper	$ 1.68
Microfossil Slide	$ 1.09
Aluminum Bracket	$ 2.50
Glass Slide	$ 0.36
Sample Bags[4]	$ 24.00
Glassware	$ 12.80
Stationary & Pail	$ 5.12
PPE	$7.68
Total Equipment Cost	$ 55.24
Picking	
Cost Per Sample	$25.00
Total Processing Cost[5]	$126.41

[1] Total costs adjusted per quotes from suppliers to the GSC. Costs calculated for fall / winter 2019-2020 and are subject to change

[2] Acetic acid costs accounted for shipment and delivery fees associated with import of the acid**.**

[3] Equipment costs account for approximate samples completed within a year. Total price is distributed over expected samples using productivity calculations.

[4] Sample bag cost is the sum of the 4-5 Whirl-Pak™ bags (Assorted size) used in both procedures. Average costs for these bags is $4.80/bag hence a total cost of $24.00 for all the bags used.

[5] Total Processing cost is the sum of; Total Acid cost / Sample, Bleach, Total Lithium Meta Tungstate, Total Equipment cost, and Picking cost. In addition to these values, a yearly 1.5% cost fluctuation rate is applied which covers alternative costs and yearly inflation values.

A5. Conodont SEM images

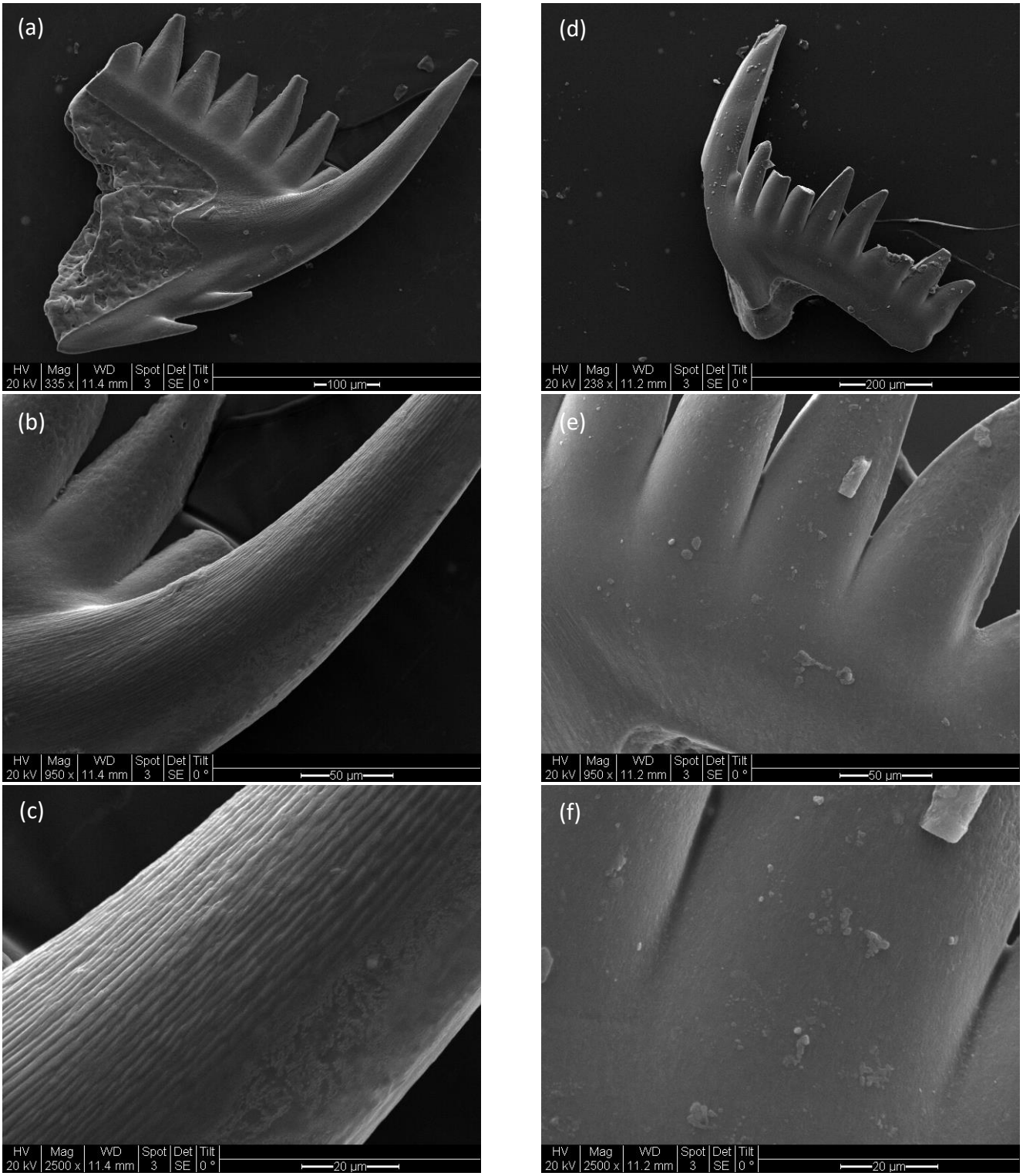

Figure A1. Ramiform elements from the 1786-03 (GSC Curation No. C-468285) sample series. *Aphelognathus* sp. aff. *A*. *pyramidalis* (Branson, Mehl and Branson 1951), left (GSC 141425) and right (GSC 141426). (a) Overview scan of specimen processed using acetic acid. Original structure well preserved. (b) x950 magnification of specimen illustrating well preserved original striation and textures. (c) x2500 magnification surface scan of specimen. No observable etching from acid present, original textures well preserved. (d) Overview scan of specimen processed using formic acid. Denticles broken off are not a result of acid treatment. (e) x950 magnification, surface residual mineral from host rock. No observable etching. (f) x2500 magnification surface scan of specimen. Mineral buildup from host rock observable, no etching due to acid treatment at surface level.

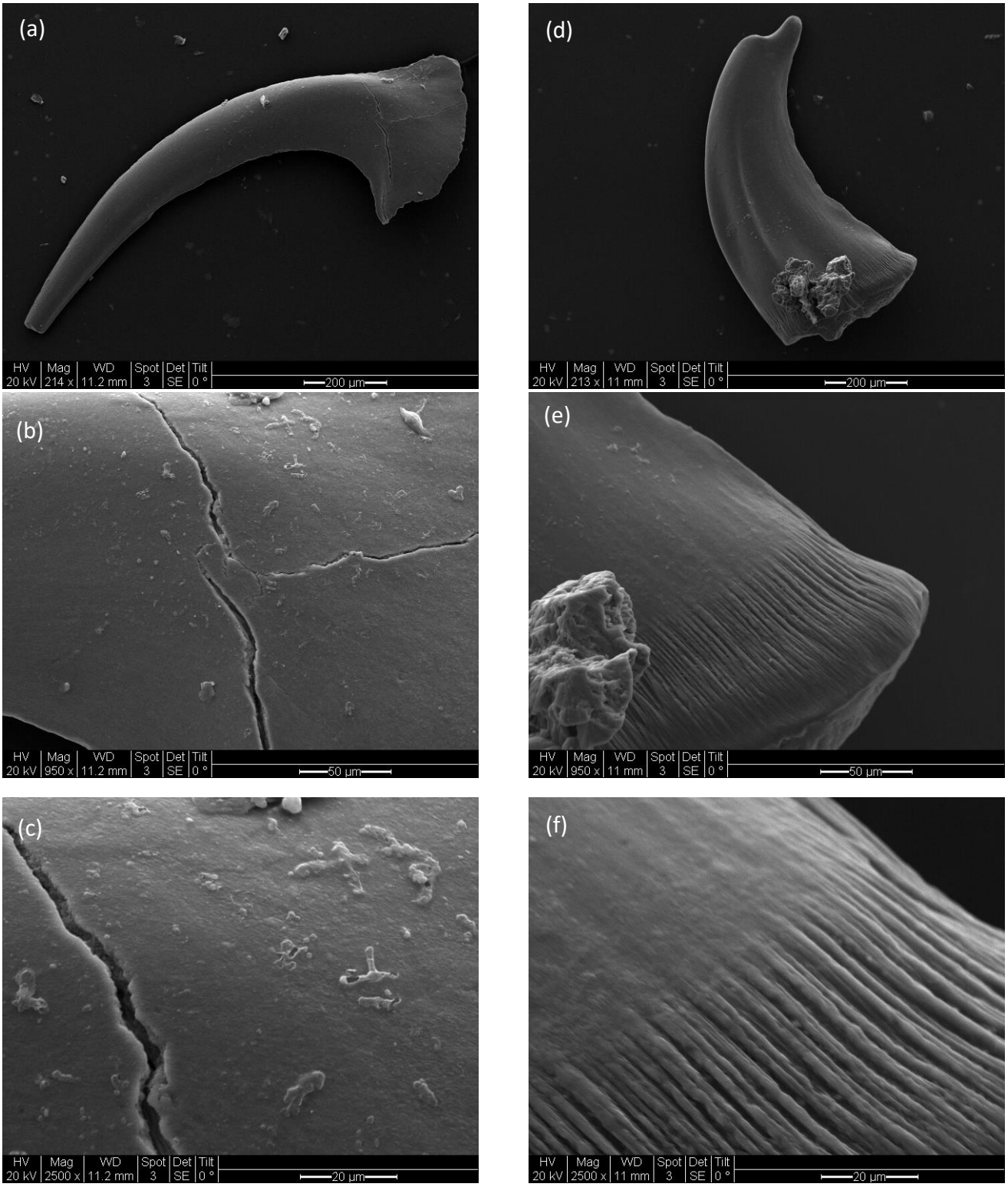

Figure A2. Coniform samples from the 1786-03 (GSC Curation No. C-468285) sample series. *Drepanoistodus suberectus* (Branson and Mehl 1933), left (GSC 141427), right *Panderodus unicostatus* (Branson and Mehl 1933) (GSC 141428) (a) Overview SEM scan of specimen processed via acetic acid. Fracture on surface not indicative of etching. (b) x950 magnification on specimen surface. Fracture was likely not caused by acidic treatment. No observable etching present. (c) x2500 magnification of specimens' surface features. Small mineralized residue likely from host rock, no surface etching due to acid treatment at surface level. (d) Overview scan of specimen processed via formic acid. Slight mineralized residue in basal region of the specimen is from host rock. (e) x950 magnification of specimen surface, no observable etching due to acid treatment. Striations from original conodont structure preserved at basal region. (f) x2500 magnification of surface features. Original striations preserved at basal region with no observable etching due to acid

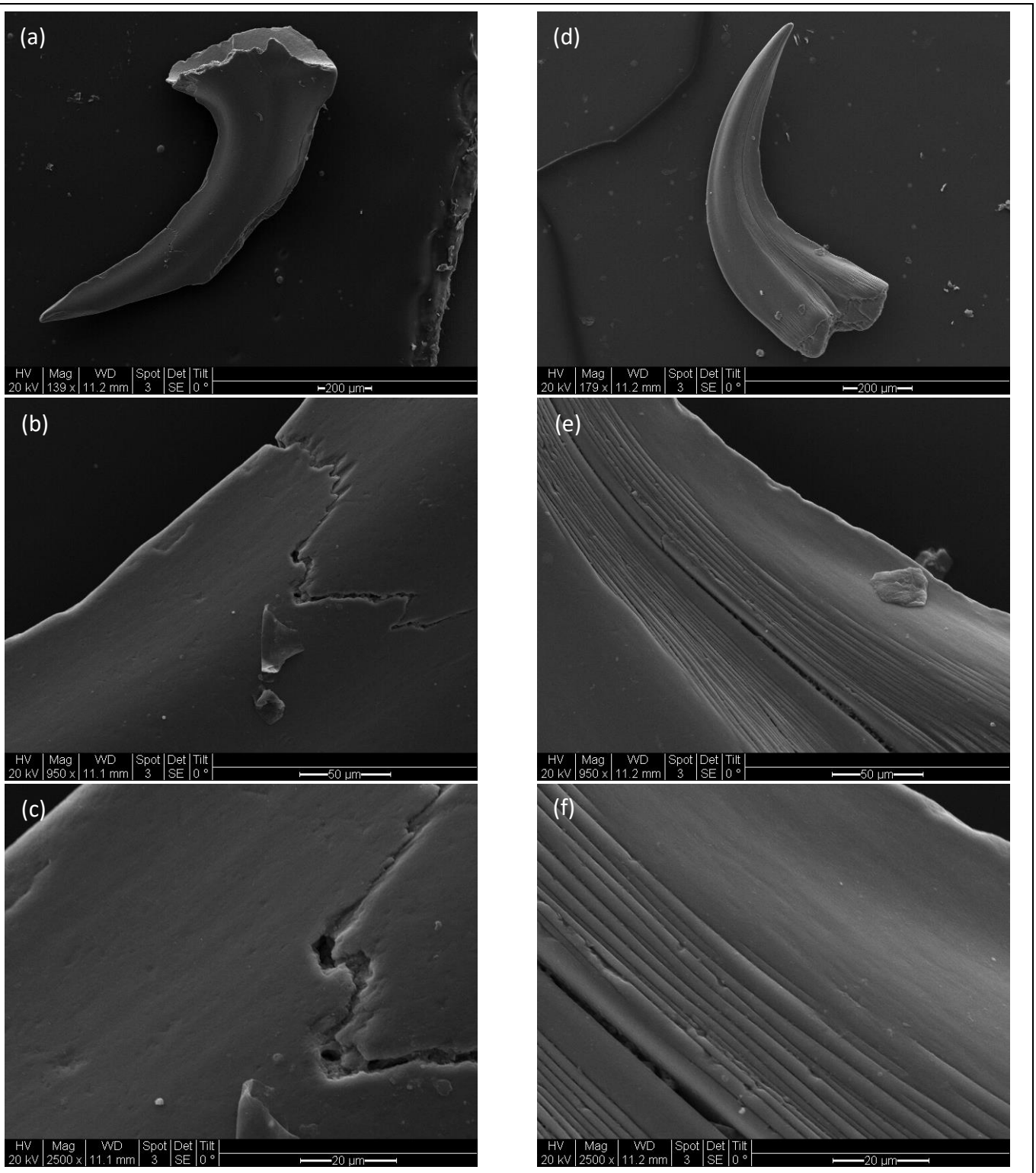

Figure A3. Coniform elements from the 1786-04 (GSC Curation No. C-468286) sample series. *Drepanoistodus suberectus* (Branson and Mehl 1933), left (GSC 141429), right *Panderodus unicostatus* (Branson and Mehl 1933) (GSC 141430) (a) Overview scan of specimen processed via acetic acid. Fragmentation and breakage prevalent throughout sample are not indictive of damage caused by acid treatment. (b) x950 magnification scan displaying surface features. Fracture imaged not caused by acid treatment, slight mineral residue from source rock. Smooth surface indicates no etching. (c) x2500 magnification of surface elements, no observable etching caused by acetic acid treatment. (d) Overview scan of specimen processed via formic acid treatment. Relatively pristine preservation of surface with moderate fracturing occurring at the basal region. (e) x950 magnification of surface features. Striations present are part of original surface texture of the specimen. Mineral build-up in right portion of the scan is from source rock. (f) x2500 magnification of surface striations displaying original texture of the conodont element. No surface etching from acid treatment observable at surface of

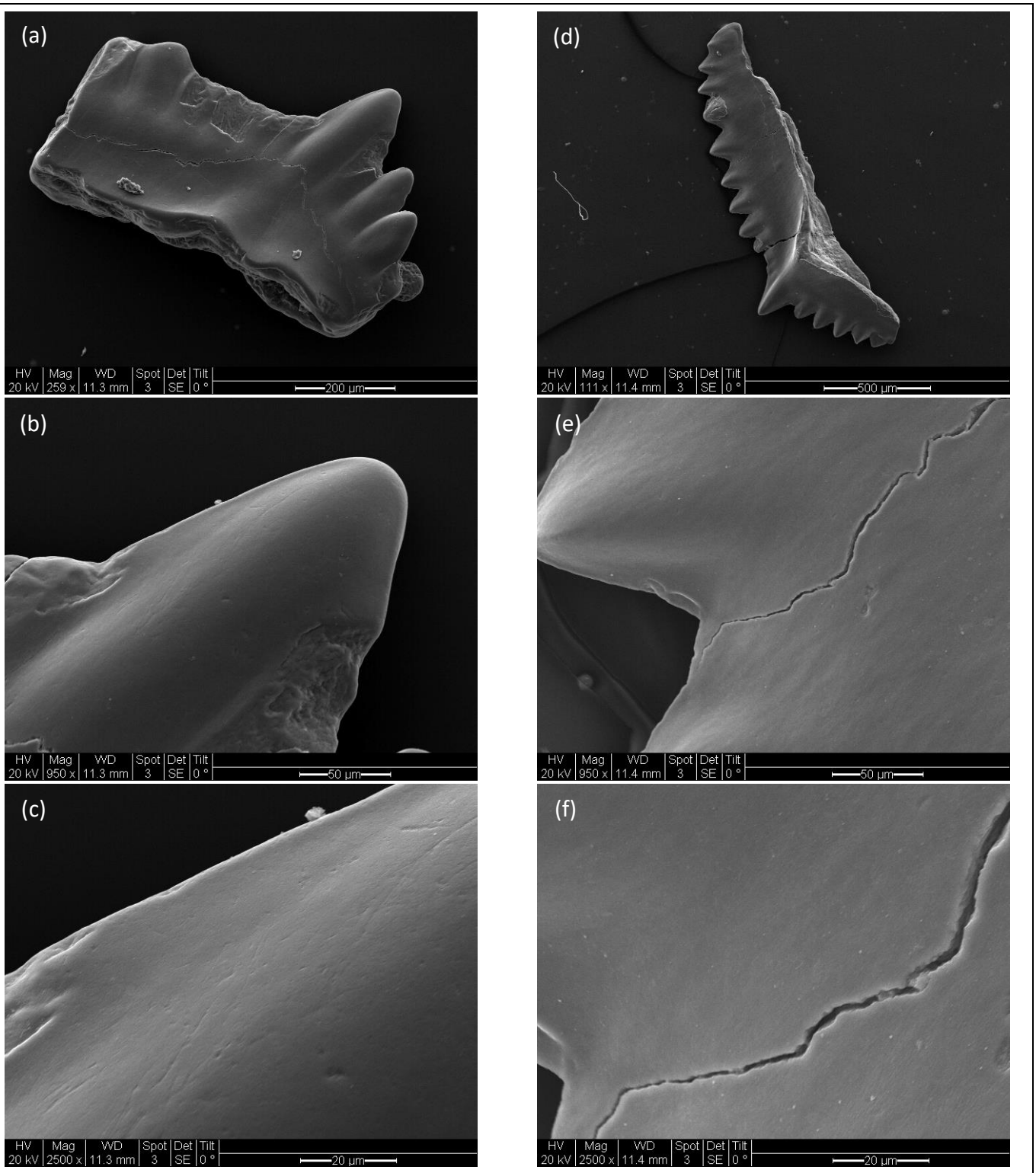

Figure A4. Ramiform elements from the 1786-04 (GSC Curation No. C-468286) sample series. *Aphelognathus* sp. aff. *A. pyramidalis* (Branson, Mehl and Branson 1951), left (GSC 141431) and right (GSC 141432). (a) Overview scan of specimen processed via acetic acid. Fracture running across specimen is not a result of acetic treatment. Slight mineral residue remained on element from source rock. (b) x950 magnification of surface features. Generally smooth surface with breakage occurring on the bottom portion of the feature. This breakage is not caused by acid treatment. (c) x2500 magnification of surface features, slight striations are likely original textures of the specimen. No observable etching from acid treatment is present. (d) Overview scan of specimen processed via formic acid. Structure relatively well preserved with minimal breakages on the denticles. Major fracture in the center of the conodont was likely the result of a mechanical breakage during processing, not caused by the acid. (e) x950 magnification of surface features. Smooth surfaces with slight divots resemble original features. (f) x2500 magnification of element surface. Fracture is not original however not a result of acid

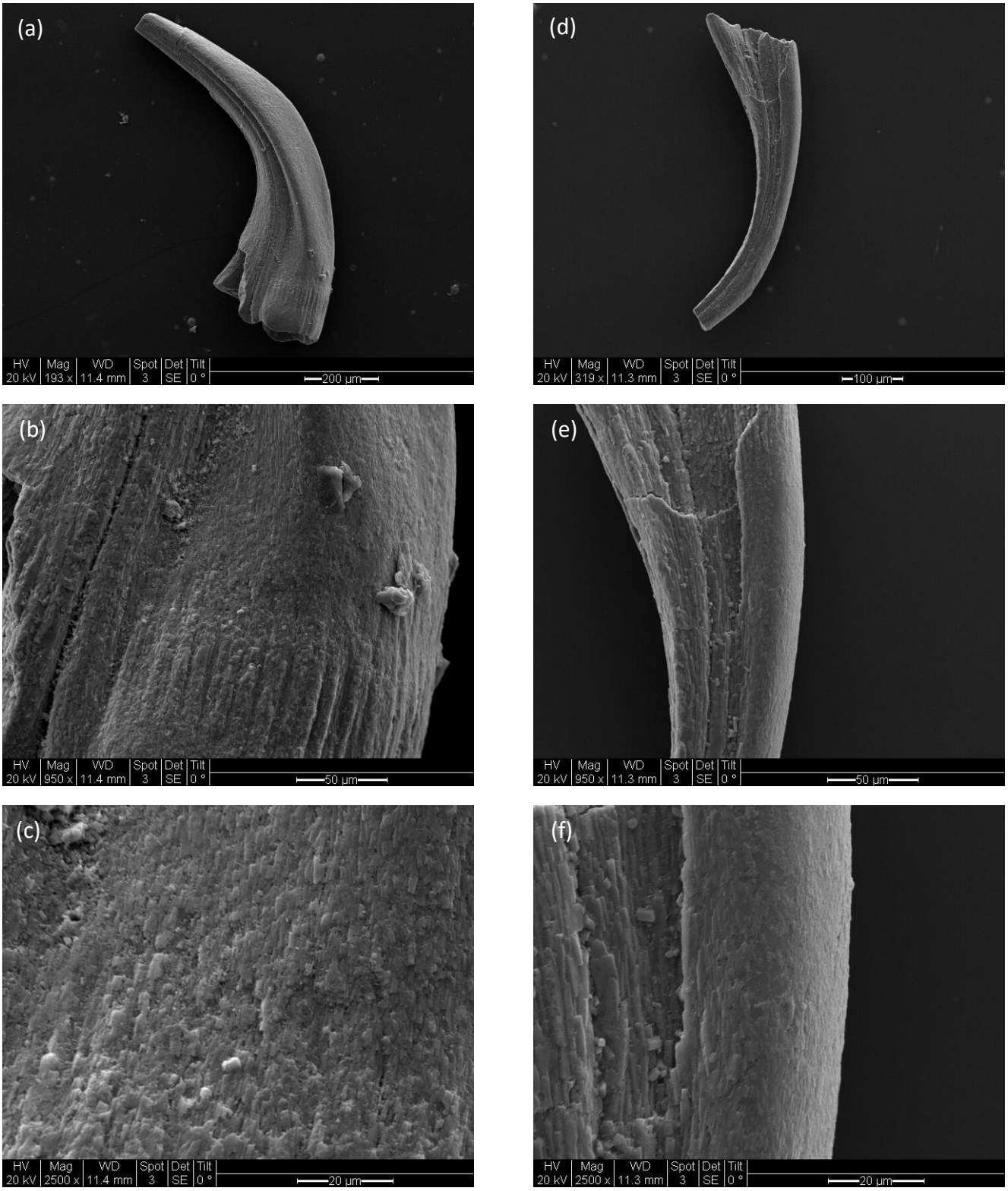

Figure A5. Coniform elements from the 1787-05 (GSC Curation No. C-468295) sample series *Panderodus unicostatus* (Branson and Mehl 1933) left (GSC 141433) and right (GSC 141434). (a) Overview scan of specimen which was processed using acetic acid. Fuzzy appearance is generally an indication of minor etching or re-crystallization of specimen. Original features visible at basal portion of the element. (b) x950 magnification of basal portion of the conodont element. Mineral residue observed on the right portion of the scan. Original features and striations are still prevalent but slightly obscured due to potential etching. (c) x2500 magnification capturing surface conditions. Present cubic structures indicate re-crystallization and slight etching due to acid treatment. (d) Overview scan of specimen which underwent formic processing. (e) x950 magnification of conodont features. Original textures present but slightly hard to distinguish due to potential etching. (f) x2500 magnification of conodont surface captures similar cubic like structures which indicate re-crystallization. Slight etching from acid treatment is also observed but original features still distinguishable.

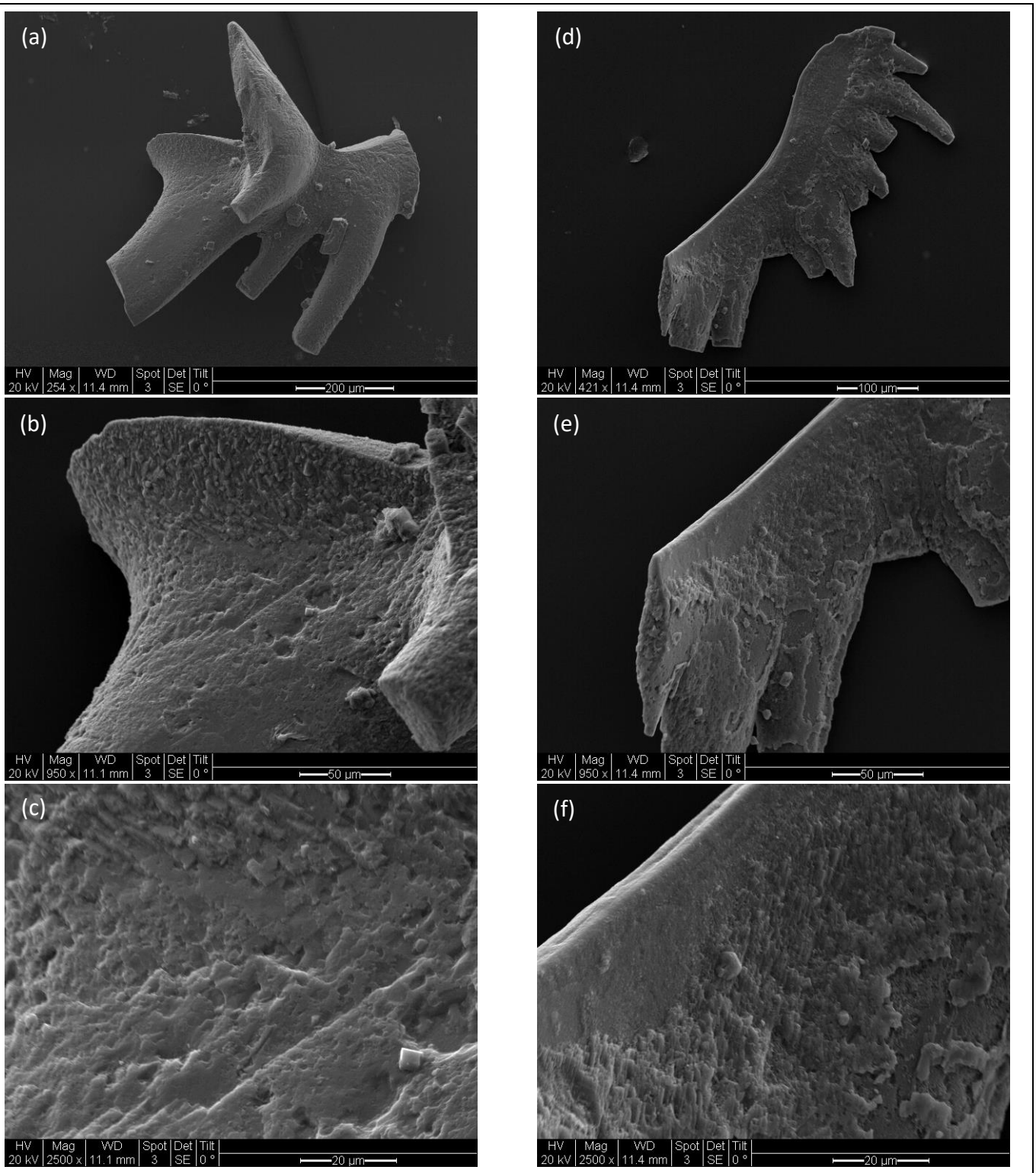

Figure A6. Ramiform elements from the 1787-05 (GSC Curation No. C-468295) sample series *Distomodus* sp. left (GSC 141435), and right *Ozarkodina pirata* Uyeno in Uyeno and Barnes 1983 (GSC 141436). (a) Overview scan of specimen which underwent acetic acid treatment. General structure is relatively well preserved. Slight fuzzy appearance suggests potential surface reworking or etching. (b) x950 magnification of surface conditions for conodont element. Groves and rough patches on element surface indicate etching or reworking of original elements. (c) x2500 magnification of surface conditions illustrate some cubic structures and pits suggesting conodont element likely underwent recrystallization. The extent of etching caused by acid is unknown. (d) Overview scan of specimen processed using formic acid. General appearance of structure suggests reworking or etching of original specimen. (e) x950 magnification of surface conditions illustrate a moderate degree of reworking. Original surface features not legible at this level of magnification. (f) x2500 magnification of surface displays some cubic like structures and rough patches. Degree to which these alterations were caused by acid treatment is unknown due to lack of original structure.