

Surface Area Characterization of Suspended Sediments in Glacial Meltwater

Using “nano-BET”

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I. Abstract

Suspended flux is the greatest source of sediment to the ocean, so suspended sediments likely make a significant contribution to global element cycling and ocean chemistry. However, the contribution of suspended material to the ocean is not solely dependent on mass; it is the sediment's reactivity which determines to what degree mineral grains will dissolve and contribute to the chemistry of the water transporting it. Reactivity is largely determined by grain surface area, and glacial suspended sediments are believed to have higher surface areas than riverine suspended material, for glacial weathering often produces very fine-grained material known as "rock flour". If the surface area characteristics and, therefore, reactivity of glacial suspended is better understood, then that information can be used to assess the impact of glacial cycles on seawater chemistry. Conventional BET surface area measurements using N₂ adsorption isotherms are readily available, but established methods use a volumetric approach which requires at least 0.5-1 grams of material for reliable results. Since existing sampling methods in the field do not always yield sufficient suspended material in glaciated catchments, our experiment utilizes a new technique for measuring BET surface area which uses a mass rather than volume-based method. The technique, dubbed "nano-BET" is capable of measuring nanogram-sized variations in mass, which permits surface area analysis for sample sizes of a milligram or less. Through a series of gas adsorption experiments, we have improved the procedures for sample analysis and data processing and demonstrated that nano-BET produces reasonable surface area measurements for glacial suspended sediments.

II. Introduction

Role of suspended sediment for global element fluxes

River-transported sediment can be described by three main categories: dissolved, suspended, and bedload. Bedload makes up largest grain size fraction of sediment, and moves down stream by either rolling or saltating along the riverbed. Suspended load is the finest-grained portion of sediment transported and is light enough to be carried by a river's current. Finally, dissolved load is the material which has dissolved and formed an aqueous solution with the surrounding water. Understanding sediment fluxes is important to constrain global element cycling, for the annual flux of fluvial sediments is one of the largest sources of particulate material and elements to the ocean. The effect of dissolved load on ocean chemistry has often received the greatest attention since most dissolved elements are immediately incorporated into seawater upon reaching the ocean. However, dissolved load actually contributes the least material of the three types of sediment transport. Dissolved flux is only 1 Gigaton per year (Gt/yr). After accounting for material loss from natural sediment traps, the annual flux of bedload sediment is approximately 1.6-10 Gt/yr, and suspended sediment has by far the greatest flux, ranging from 15-20 Gt/yr (Jones et al. 2012a and references therein).

Since suspended load is the greatest source, by mass, of material to the oceans it is likely suspended sediment makes a significant contribution to ocean chemistry and dissolved element concentrations. Several recent studies have demonstrated the importance of suspended sediment for global element cycling. For example, measurements of suspended calcium (Ca) flux indicate that it is both comparable to the dissolved flux and much more dependent on river discharge (Gislason et al. 2006). This suggests that suspended Ca flux could serve as significant negative feedback for the greenhouse effect. Similarly, suspended flux is estimated to be greater than dissolved flux for every element except sodium (Oelkers et al. 2011). Some elements (e.g. Ca,

Sr, Li, and Mg) have a particulate flux comparable to that of dissolved elements while aluminum, zircon, niobium, and titanium all have particulate fluxes which are more than 1000 times greater.

However, the greater annual flux of suspended material does not automatically prove that suspended sediment has a greater impact on ocean element concentrations than the dissolved load, for grain reactivity must be taken into account. Only the portion of a suspended sediment particle which dissolves into the surrounding water will have an effect on water chemistry. In addition to partial dissolution of suspended particulates, interactions with seawater can also cause re-precipitation of secondary mineral phases from the dissolved flux (Jones et al. 2012a). Therefore, understanding the contribution of suspended sediment global element fluxes requires a thorough understanding of the reactivity of transported sediments. Several factors affect grain reactivity. The mineralogical composition of a sediment grain will determine grain solubility. For example, quartz grains are far less soluble than calcite, so calcite grains will tend to dissolve more rapidly in freshwater. Also, temperature plays an important role. Weathering rates tend to increase as air temperatures rise, and it is likely that there is a strong feedback between weathering rates and climate change (Gislason et al. 2009). Additionally, grain geometry can help determine reaction rates. When only considering grain geometries, blocky minerals such as calcite and quartz will be much less reactive than platy minerals such as micas.

One of the most common methods for assessing sediment reactivity is by measuring a sample's surface area. As the average size of sediment grains decreases, the surface area will increase. High surface area provides additional reaction sites for water-rock interactions, which means that bulk surface area is positively correlated with sediment reactivity. Previous studies (e.g. Fairchild et al. 1999) have calculated the surface area of suspended sediments by using ideal grain geometries. However, this approach risks underestimating the sample's surface area, for

assuming a uniform grain shape does not account for the pitting, fractures and partial dissolution of grain surfaces that will increase grain surface areas in nature. Therefore, gas adsorption experiments (e.g. Jones et al. 2012a) which account for these factors are more reliable. When combined with sediment composition, knowledge of regional geology and *in situ* measurements, surface area measurements can provide a great deal of information about sediment reactivity in a catchment or river system.

Suspended Flux in Glaciated Environments

Surface area measurements for fluvial suspended and bedload sediments (fig. 1) are present in existing literature (Jones et al. 2012a,b). However few, if any, published surface area measurements for suspended sediment in glaciated environments exist. Glacial weathering produces extremely fine-grained suspended material, known as “rock flour”, which is highly reactive (Brown et al. 1996) and should have a higher surface area than riverine suspended sediments. As a result, rivers draining glaciated catchments should have suspended sediments with higher reactive surface areas than suspended sediments in rivers draining non-glaciated catchments. Thus, glacial rivers likely have a significant impact on ocean chemistry over glacial/interglacial timescales.

Despite the lack of surface area measurements, there have been several studies of sediment reactivity and transport in glaciated catchments (e.g. Anderson et al. 1997, Hosein et al. 2004, Anderson et al. 2005, Gislason et al. 2009, and Li et al. 2012). One of the greatest challenges for evaluating the contribution of glacial versus riverine suspended sediments to element cycling is understanding the effects of chemical and physical weathering in glaciated environments. Physical weathering dominates glaciated catchments, and the rates of erosion for

glaciated environments can be an order of magnitude greater than comparable non-glaciated catchments (Anderson et al. 2005, Hosein et al. 2004). Chemical weathering rates, in contrast, tend to be lower than the global average, especially in terms of silica flux, although Ca^{2+} and K^+ concentrations tend to be high due to enhanced weathering of carbonates and micas (Anderson et al. 1997, Anderson et al. 2005, Hosein et al. 2004). This is primarily due to the dependence of silicate weathering on temperature, for the lower temperature of glacial meltwater greatly reduces silicate dissolution. Nevertheless, it has been suggested that changes in local climate can have a strong effect on chemical weathering rates. A recent study of glacial and non-glacial catchments at the Urumqi River in central Asia revealed that the glaciated catchment had an annual dissolved flux nearly two times greater than the non-glacial catchment which was correlated with higher average air temperatures and precipitation rates at the glacial catchment (Li et al. 2012). Additionally increases in temperature, such as the present state of anthropogenically-induced climate change tend to have a greater effect on mechanical weathering for glaciated environments. In a study of several Icelandic catchments, glaciated terrains experienced an increase of 17-30% for inorganic particulate flux per degree Celsius of warming compared 5-16% for non-glaciated catchments (Gislason et al. 2009).

Despite the low dissolution rates in meltwater channels, glacial suspended sediments should be very reactive due to their high surface areas. As a result, these sediments could make a significant contribution to water chemistry in locations further downstream, such as major rivers and the ocean. Having a series of surface area measurements for glacial suspended sediments would help better constrain the contribution of these sediments to global element cycling. Unfortunately, existing sampling methods make it difficult to collect enough suspended sediment in the field for conventional surface area analysis, especially during the beginning and end of the

melt season. Our study utilizes traditional methodology for measuring surface areas as well as a new technique (Aciego et al. 2011) capable of measuring surface area at the nanoscale, which requires less than a milligram of material for analysis. Using the two methods, we have measured the surface area of suspended sediments from two glacial catchments in the Canadian Rockies and the Juneau Icefields in Alaska. Qualitative measurements of bulk mineralogy for samples were also conducted using X-ray powder diffraction (XRD) to evaluate the effect of mineralogy on sediment surface area.

Sampling Locations

Samples were collected from two field sites: the Lemon Creek Glacier in the Juneau Icefield and the Athabasca and Saskatchewan glaciers from the Columbia Icefield, all alpine glaciers. Lemon Creek (fig. 2) overlies predominantly silicate bedrock. A late Cretaceous to early Paleogene tonalite is covered by the glacier (Ingram and Hutton 1994) with carbonaceous shale/mudstone and high-grade metamorphic rocks cover the upper and lower parts, respectively, of the catchment. Studying the reactivity of silicate-rich suspended sediments is more important for evaluating the potential feedback between suspended Ca flux and the greenhouse effect, for weathering of carbonate sediments does not affect the net balance of CO₂ between the atmosphere and the oceans (Gislason et al. 2006). Nevertheless, carbonate weathering greatly contributes to the net transfer of Ca ions to the ocean and could affect fluxes of trace elements, such as strontium. Therefore, suspended sediment samples were also taken from the Columbia Icefield glaciers (fig. 3) during the 2011 and 2012 melt seasons. The Columbia Icefield overlies carbonate-rich bedrock.

III. Methods

Sample Collection and Preparation

Initial samples were collected from the Athabasca Glacier in Alberta, Canada during the 2011 melt season. In the field, meltwater was collected once daily by a filtration apparatus designed at GIGL (fig. 4). Once activated, a vacuum pump drew the meltwater up through a tube and both a coarse (100 micron) and fine (0.2 micron) filter to separate suspended sediments from the water sample. The filters were then placed in ziplock bags for storage and transportation back to the lab.

When the filters arrived from the field, the suspended sediments were separated from the filters using a Branson 5510 ultrasonic machine. The coarse-grained filter was first placed on a wire-mesh filter holder and secured inside a plastic container. Next, ~2 liters of 18.2 M Ω (SDIS) water was added until the filter was just barely submerged, and the container was covered with plastic wrap to protect it from contamination. Then, the sample was sonicated for 30 minutes or until all sediment was removed from the filter. Finally, the fine-grained filter was sonicated for an additional 15 minutes, and the resulting slurry was poured into two 1-liter Nalgene containers.

After sonication, sediments were separated from the slurry using an Eppendorf 5702 centrifuge. The slurry was poured into four 50-mL vials and centrifuged at 4000 revolutions per minute for 15-minute intervals until all of the sediment had settled to the bottom. Each vial was then decanted and refilled and the process continued until all of the slurry had been processed. After that, the collected sediment was poured into a pre-weighed Pyrex® petri dish and oven-dried at no higher than 100°C. Lastly, the dried petri dish was weighed to calculate sample weight and the sediment was scraped into a glass vial for storage using a metal scraping tool.

Unfortunately, the initial sample preparation method had several disadvantages. First, the coarse filters proved extremely fragile during the sonication process. When they arrived from the field, these filters had a consistency similar to paper pulp and were easily torn when transferred to the plastic container for sonication, so it is possible that some samples were contaminated when they were sonicated. Additionally, centrifuging the resulting slurry was both time-intensive and inefficient at collecting the entire sample. Processing just 200 mL of sample required anywhere from 45 minutes to an hour and a half of centrifugation and even at that point the supernatant still contained the finest size-fraction of sediment. As a result, a new procedure for sample collection and processing was developed for the summer, 2012 field season. In the field, samples were collected using the same method from the previous field season, but only the fine-grained filters were used. Back at the University of Michigan, samples were prepared in a Class-100 clean lab. Initially, Savillex® teflon beakers were pre-cleaned using a 3-step acid wash. The beakers were first rinsed three times with SDIS water and then placed in a ~6M HNO₃ bath and left on a hotplate overnight. This procedure was followed by an additional overnight bath in ~6M HCl, and then concentrated HNO₃ with trace HF was added to each beaker, the beakers were capped, and were left on a hotplate for three days. Before and after each acid-cleaning step, the beakers underwent three more rinses with SDIS water. Finally, the beakers were left in a drying rack overnight.

Once the cleaned beakers were dry they were labeled and weighted, and sediment processing began. SDIS water was added to the plastic bags containing the filters and the bags were manually agitated to remove as much sediment from the filters as possible. The slurry was then poured into the beakers, an aluminum foil jacket was affixed to the beakers to decrease dry-down time, and the beakers were placed on a hot plate to dry. Additional SDIS rinses were used

until all of the sediment was removed from the filter and the plastic bags. After the final dry-down, the beakers were capped, removed from the hot plate, and allowed to cool for 15-20 minutes. Each beaker was then re-weighed, and the difference between the initial and final masses was used to calculate the sample mass. 10-20 mg splits were taken for chemical analysis and the samples were then transferred to pre-cleaned glass vials using a teflon scraping tool and weigh paper. Next, the beakers were rinsed three times with SDIS, and then cleaned with organic solvents to remove any residual sediment.

From this point onward, the beakers were cleaned using a different method. The beakers were first filled with 1 mL of HCl and left on a hot plate overnight. Afterwards, the acid was immediately discarded into the HCl waste container. Each beaker was then rinsed three times with SDIS and then underwent the first two steps of the original cleaning process, with one modification. Unlike the original method only the inside of the beakers was cleaned, for they were considered too dirty to place in the cleaning vials. After the final HCl bath, the beakers were once more rinsed three times with SDIS and allowed to dry, and sediment processing continued.

BET Analysis

One of the most common types of surface area analysis is the Brunauer, Emmett and Teller (BET) method. Originally developed by Brunauer et al. (1938), BET analysis relies on nitrogen gas adsorption to calculate the specific surface area (SSA), or surface area per unit mass of a sample. BET surface area is determined by the number of adsorbed nitrogen gas molecules (n) which, in turn, is calculated by the following equation:

$$\frac{P/P^0}{n(1 - \frac{P}{P^0})} = \frac{1}{n_m c} + \frac{(c - 1) \frac{P}{P^0}}{n_m c}$$

where P is the pressure of the system, P^0 is the saturation pressure of the gas used in the adsorption experiment (in this case, nitrogen), and n_m is the number of gas molecules that can be adsorbed in a monolayer. The BET constant c is expressed as:

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

E_1 is the heat of adsorption for the first monolayer, E_L is the heat of adsorption for each subsequent layer, and R and T are the universal gas constant and temperature, respectively. Both n_m and c are empirically determined constants. During a measurement, data for P , P^0 , and n are collected and an isotherm is plotted using the ratio between P/P^0 and $(P/P^0)/n(1-(P/P^0))$. When the slope of the isotherm is linear, it can be used with the intercept to calculate n_m and c :

$$n_m = \frac{1}{s + i}$$

$$c = \frac{s}{i} + 1$$

Once n_m and c are known, the SSA can be calculated using these two constants, the mass of the sample, and the known area of a nitrogen gas molecule (Aciego et al. 2011).

Conventional BET analysis of samples

Conventional BET analysis uses a volumetric method to calculate n , and several samples from the 2011 field season were measured this way along with the standard SRM-1900, a silicon nitride powder. Samples are first loaded into a glass vial of known volume (fig. 5a) and then

outgassed at 200°C. Next, a maximum of four vials are loaded into a NOVA 4200e Surface Area and Pore analyzer (fig. 5b) and the “bulbs” at the bottom of the vials which contained the sediments were immersed in liquid nitrogen, creating isothermal conditions. Finally, the gas adsorption experiments were conducted and the resulting isotherm used to calculate the samples’ SSA.

Unfortunately, the precision of a volumetric approach is limited by the mass of sample used for analysis. For conventional, BET at least 1 – 0.5 grams of material is needed to produce reliable results. This is problematic when collecting glacial suspended sediment samples, for the filtering procedure will often yield far less than a gram of sediment.

Nano-BET analysis of samples

Recent developments have made it possible to measure the BET surface area of sample sizes less than a milligram (Aciego et al. 2011). Originally developed to analyze dust from ice cores the new method, referred to as “Nano-BET”, uses a gravimetric approach to measure n . In order to account for the surface area and mass of the gold boat used to hold the samples, a blank run is first conducted using the empty boat during each measurement. Also the standard BAM-PM-103, an aluminum oxide, was utilized before the first measurement and after every couple of measurements. When loading material into the boat, a representative split of the sample, usually from 0.5-1.5 mg, is placed in a pre-cleaned savillex beaker and suspended in ~20 μm of distilled ethanol. The suspension is then pipetted into the gold boat that has been placed securely on a metal sample holder, and is taken to the nanobalance for analysis.

During a measurement (fig. 6a), the nanobalance chamber is brought to room pressure (~1000 mbar), turned off, and the chamber is unscrewed and lowered. A gold boat containing the

sample is picked up with rust-resistant forceps and loaded onto the wire diamond or “stirrup” suspended from the top of the machine. The sample chamber is then raised, sealed and placed under vacuum. Once the chamber was under vacuum the sample was outgassed at 200 °C for four hours and then allowed to cool back to room temperature for two hours. Next the sample chamber was immersed in a dewar of liquid nitrogen and allowed to cool to the temperature of liquid nitrogen in order to achieve isothermal conditions. When the nanobalance is activated (fig. 6b), a magnetic rod attached by a wire to the stirrup is raised and lowered by direct current while the sample position is measured using alternating current. From this process, a sample mass is calculated to nanogram precision. By magnetically levitating/lowering the sample boat throughout the adsorption experiment, n can be calculated for every data point.

Before and after each set of measurements, the gold boats are cleaned inside their beakers using SDIS, distilled ethanol, and dilute HNO₃. After three initial rinses with SDIS, the beaker is filled with ethanol and sonicated for one hour. Next the ethanol is decanted, and after 3 more SDIS rinses the beaker is filled with 1ml of 1.5M HNO₃ and placed on a hot plate at no higher than 100 °C to clean overnight. Finally, the HNO₃ was discarded, and after a final set of SDIS rinses the beaker was filled with ethanol and capped for storage. Nano-BET, like the conventional method, is a non-destructive process. To preserve the sample after analysis, simply skip the initial SDIS rinse and proceed directly to the sonication step. After sonicating the gold boat, the resulting suspension can be poured into another Savillex® beaker and dried down to recover the sample.

Data Processing for Nano-BET

Raw data from the nanobalance was downloaded from the Nelixon website as a Microsoft Excel spreadsheet. Since the nanobalance collects pressure and current readings continuously, the raw data contains every part of the measurement process, including the up, down, and transition phases. Since the only data needed is from the up and down positions, the transition data must be removed. An add-in from Rubotherm is used to organize the raw data into a table relating chamber pressure and the current weights for the up and down positions, respectively. While the add-in removes most of the transition data, the file must be fine-tuned by hand to remove any additional outliers. Excel's sort command can be used to filter out excessively high or low current values. Once enough outliers have been removed the graphs of up and down current weight versus pressure should look like two fairly identical curves (fig. 7). Next, averages of each block of "up" and "down" data are taken, and the difference between the sample (up) and calibration (down) measurements are calculated by subtracting each sample measurement from the average of the two calibration measurements which bracket the sample. This value is the mass of the sample in current units mentioned above, which is then plotted against pressure (fig. 8). If the run was successful, the sample plot should have a positive linear correlation at some point between 0 and 300 mbar.

Once we have verified the sample has run correctly and no issues are found with the blank run, then the data can be further processed to calculate the BET surface area. Using the linear fit from fig. 6, a new plot is generated (fig. 9) plotting the y-fit over P/P_0 . The y-fit is the function

$$y = \frac{c-1}{n_m * c} * x + \frac{1}{n_m * c} = S * x + 1$$

where x is P/P_0 . By plotting y against x , a positive, linear correlation is generated which is used to calculate the BET constant and slope and, in turn, the BET surface area.

With the surface area calculated, the only value needed is the mass of the sample in order to report the results in m^2/g . Prior to the standard and sample measurements, a mass calibration was conducted using standard weights of 1, 2, 5, and 10 mg. When the blank and sample are measured by the nanobalance, the mass is recorded as current units. By measuring the standard weights a linear plot is generated (fig. 10) which can be used to convert the sample mass from current units to grams.

XRD Powder Diffraction

The XRD measurements from both the Lemon Creek and Columbia Icefield sampling sites were measured using powder diffraction. 100-500mg splits of approximately 20 samples were powdered using a mortar and pestle, and transferred to glass sample holders. Each measurement was made using a Rigaku Ultima IV X-ray diffractometer. Raw data was then analyzed using PDXL and minerals were identified using peak standards from the ICDD PDF-2 2008 database.

IV. Results

Mineralogy of Lemon Creek and Columbia Icefield Suspended Sediments

For both Athabasca and Lemon Creek suspended sediments, the minerals present did not vary significantly from sample to sample. Each sediment sample measured from Lemon Creek (fig. 11) contained quartz, plagioclase, biotite, hornblende, and chlorite minerals, and most contained clinopyroxene. Additionally, calcite was detected for four of the thirteen samples

analyzed. The clay mineral corrensite was present in two of the samples but did not appear to have any correlation with any changes in element concentrations. Suspended sediments collected during from Athabasca during the 2012 melt season showed virtually identical mineralogy between samples (fig. 12). Each sample contained calcite, dolomite, quartz, plagioclase and micas. Curiously, while the X-ray diffraction profiles for each sample overlapped almost perfectly, the relative intensity of characteristic peaks varied greatly from sample to sample.

Conventional BET Measurements – Athabasca Glacier

Samples measured using conventional BET (fig. 13) had surface areas ranging from approximately 1-9 m²/g. These values are of comparable order of magnitude to existing surface area measurements from fluvial suspended sediments (e.g. Jones et al. 2012 a, b). However, this was unexpected, for glacial suspended sediments were believed to have higher surface areas than suspended riverine material. Additionally, there was no correlation between BET surface area and other measurements taken in the field such as meltwater discharge, velocity, and pH.

Nanobalance Troubleshooting

The nanobalance arrived at the University of Michigan last winter, and much of the time since then has been spent fine-tuning the device to make sure it is functioning properly. As prototype technology, issues with data collection and analysis inevitably occurred. With the balance itself, the main issue was caused by malfunctions with the Gas Dosing System (GDS), which controls the rate and amount of N₂ gas pumped into the sample chamber. When a measurement works perfectly the GDS should allow the chamber to gain pressure from vacuum to 1000 mbar over several hours, stopping at a pre-determined number of pressure steps. While each run only needs to get up to 600 mbar to be usable, it is best if the entire process is

completed so the entire adsorption isotherm can be recorded. Unfortunately, glitches in the software often caused the GDS system to malfunction before the pressure even reaches 600 mbar. This past summer, while I worked on the nanobalance for the Honors Summer Fellowship, the machine's graphical user interface (GUI) would freeze mid-run, requiring us to contact Rubotherm to remotely reboot the nanobalance. A software upgrade later that fall eventually stopped the GUI from freezing, but the GDS continued to crash frequently, meaning that many measurements had to be re-run.

Two main problems were also encountered with the process of downloading and analyzing the data. First, the add-in used to organize the blocks of data would cut large sections of the measurement when evaluating the data, so these data had to be manually found in the raw data file and edited to remove the transition stages. Since this added up to several hours to the analysis of each measurement, it was imperative that a solution be found. During the winter semester, an updated add-in from Rubotherm was made available, and the process became much more streamlined. The other problem experienced was with the Nelixon site used to download data. Until this spring, the website would crash frequently and data downloaded extremely slowly. Ultimately, it was determined that the problem affecting the nanobalance GDS was the same reason the Nelixon website was having trouble downloading data. Originally, the Nelixon site had a public IP address that could be accessed from any computer, which left the Nelixon site and nanobalance GDS vulnerable to outside attacks. By restricting access to the Nelixon website to a few lab computers, most of the problems disappeared and the nanobalance has been running fairly smoothly ever since.

Nanobalance BET Measurements – Lemon Creek Glacier

By the time the major issues with the nanobalance had been resolved, it was already early April, so the machine could only be run a limited number of times. Fortunately, we were able to successfully run and process data for two standard measurements and a sample and a mass calibration (fig. 14). While one of the standard measurements was slightly outside of the certified error range for PM-103, the two measurements demonstrate that the nanobalance is producing reliable results. Additionally, the sample's measured surface area of $\sim 4 \text{ m}^2/\text{g}$ is of the same order of magnitude as the samples from Athabasca, which means this value is also reasonable. When the sample run was processed, the resulting linear plots (fig. 15) had a low r^2 value. This is likely due to the low specific surface area of the Lemon Creek sediments, which constrains the lower limit for surface area measurements.

V. Discussion

Mineralogy

While only three samples from the Athabasca Glacier were analyzed, the XRD results for the Lemon Creek Glacier clearly demonstrate that the minerals present do not change significantly over the period of the melt season studied. This suggests that the types of bedrock being eroded remain the same over the study period. In contrast, changes in the relative intensities of peaks from sample to sample indicate that the bulk mineralogy may change significantly. However, a semi-qualitative analysis is needed to estimate the percentage of each mineral present.

BET Measurements

Modeling of chemical weathering fluxes from glacial meltwater suggests that there should be a relationship between sediment surface area and discharge (e.g. Anderson et al. 2005)

which was not observed in the Athabasca samples. Similarly, the surface area measurements for both Athabasca and Lemon Creek were much lower than expected. In terms of Athabasca, several factors may have affected the results. First, pieces of the coarse filter could have contaminated the samples, but this is unlikely. The most logical source of error would be the centrifugation process. By losing the finest size fraction, our measurements for Athabasca could significantly underestimate the true bulk surface area. Nevertheless, the measurement from Lemon Creek was the same order of magnitude. While the Athabasca and Lemon Creek glaciers overlie entirely different bedrock material, the result from Lemon Creek suggests that the Athabasca data is, at the very least, reasonable. Ultimately, the greatest barrier to understanding our results is the lack of sufficient data. To fully understand changes in surface area at the Lemon Creek and Athabasca glaciers, many more measurements must be made at multiple intervals across the melt season.

Future Work

To improve the amount of data available, additional measurements should be taken either over the course of the melt season at Athabasca and Lemon Creek or as individual samples from a variety of alpine glaciers. Samples from the same catchment would help us understand how much suspended sediment surface area varies over the melt season and determine if there is any relationship between surface area and discharge. Collecting samples from additional glaciers would demonstrate how bulk surface area changes from catchment to catchment.

There are also several steps which could be taken to improve the process of analyzing the sediments. First, all samples possible should be run using conventional BET if a sufficient amount of material is available both for the analysis and chemical digestion. Each nanobalance

measurement takes two days, while four samples can be measured each day using conventional BET. Nevertheless, a significant portion of filters collected during the 2012 field season contained less than a gram of sediment, so the nanobalance will continue to be an essential tool for surface area measurements. Additionally, steps could be taken to automate data processing. Having a program which would perform the calculations would significantly reduce the amount of time spent on each sample, for data analysis for each run currently takes three hours. Finally, an additional mass calibration is needed. The current calibration is for 1-10 mg, but each gold boat weighs over 50 mg. While the 1-10mg mass calibration proved sufficient, future measurements should also use calibration weights at and greater than 50 mg.

VI. Conclusion

Clearly there is much more work that needs to be done. As a result of technical difficulties there was only a short period of time to generate data at the end of the winter, 2014 semester, so the data generated is not robust enough to being understanding overall trends throughout the melt season at Lemon Creek. Nevertheless, several significant milestones have been met. The mineralogy of both the Lemon Creek and Athabasca glaciers have been well characterized, and it is clear that the minerals present do not change significantly over the course of the study period. Despite concerns over potential contamination, samples from the Athabasca glacier have produced reasonable surface area values using conventional BET. Finally, efforts over the past year have both alleviated the vast majority of problems with the nanobalance and demonstrated that nano-BET can produce reliable results. Future work will undoubtedly produce a more robust dataset while continuing to refine the process of collecting and processing data from the nanobalance.

VII. Acknowledgements

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VIII. Figures

Location	BET Surface Area (m ² /g)	Hydrologic Setting	Geologic Setting	Sediment Type
Borgarfjörður Estuary	7.357	Estuary	Mouth of Hvítá River	Estuarine
Hvítá River	6.358	River	Volcanic	Bedload
Mississippi River	3.05	River	Continental	Bedload
Orange River	18.23	River	Continental	Bedload
Amazon River	7.32	River	Continental	Composite
Madeira River	11.35	River	Continental	Suspended
Etna	1.49	River	Volcanic	Bedload
Sveinsgil River	17.35	River	Volcanic	Bedload
Jökulsá River	22.26	River	Volcanic	Suspended

Figure 1: Suspended and bedload sediment surface area measurements for several river systems. Data compiled from Jones et al. 2012 a,b.

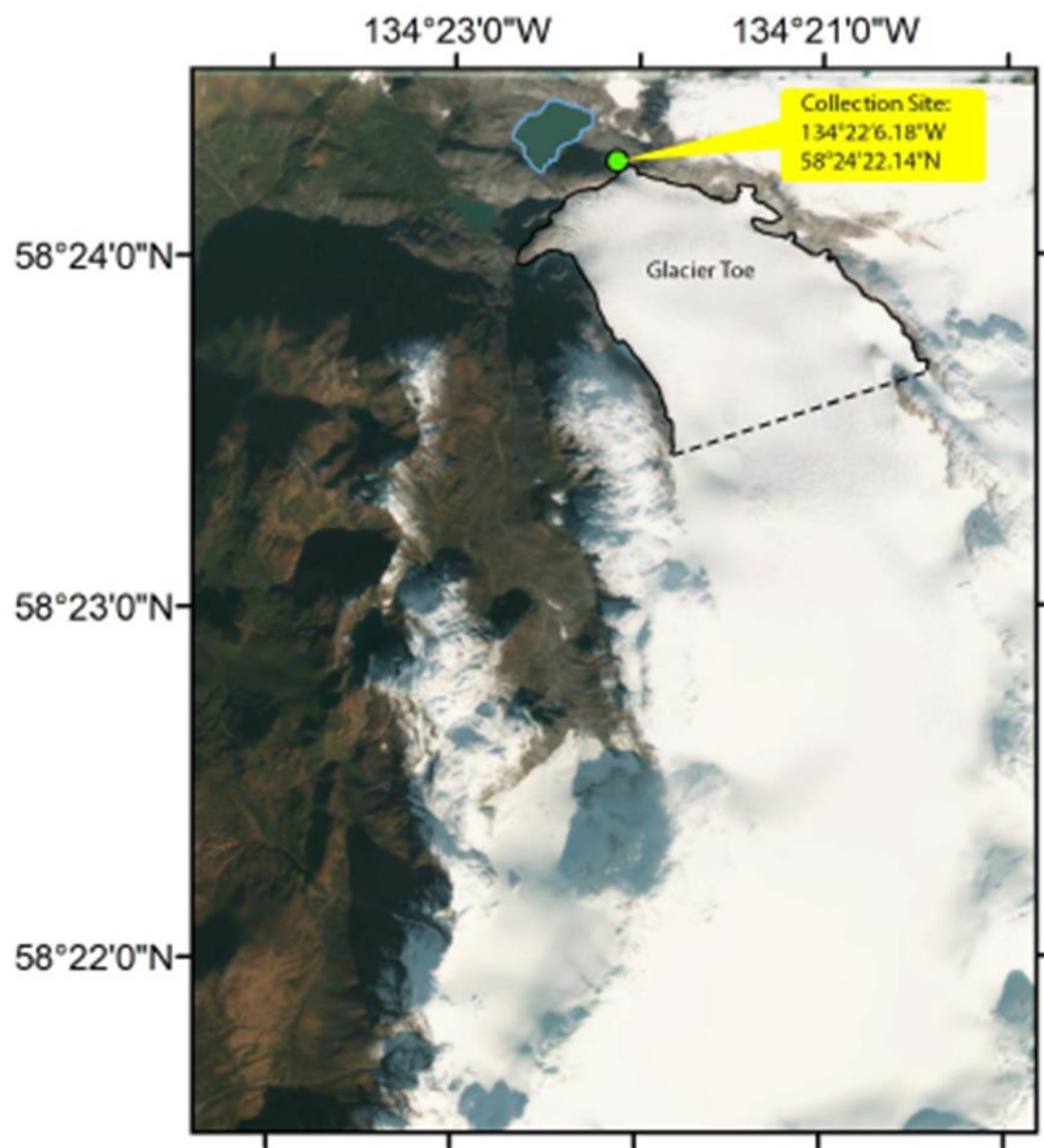


Figure 2: Area map of the Lemon Creek Glacier. Suspended sediment samples were collected from a meltwater channel at the toe of the glacier (denoted by a green dot).

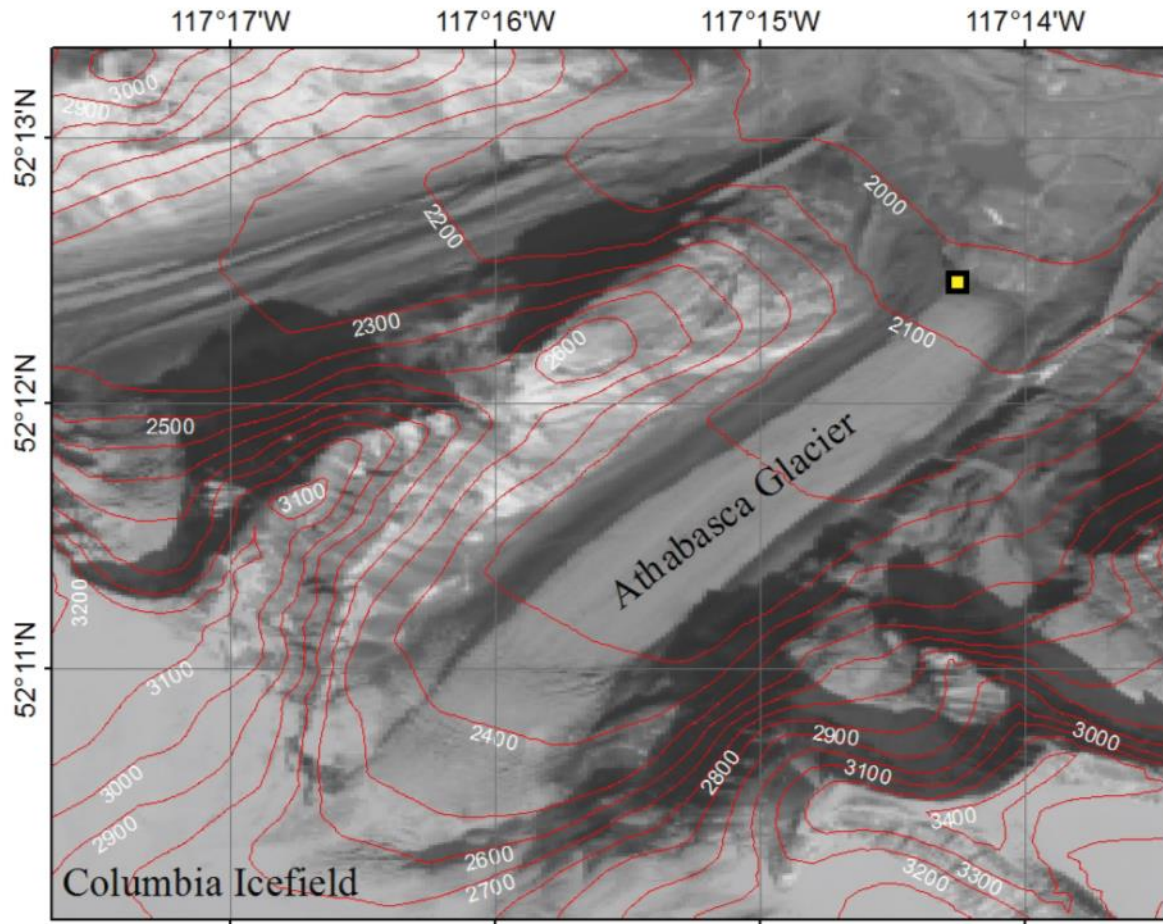


Figure 3: Area map of the Athabasca Glacier. The collection site is marked by the yellow square.



Figure 4: The filtration apparatus separates suspended sediment and water sampled directly from the meltwater channel as graduate student Carli Arendt collects field measurements in the background.

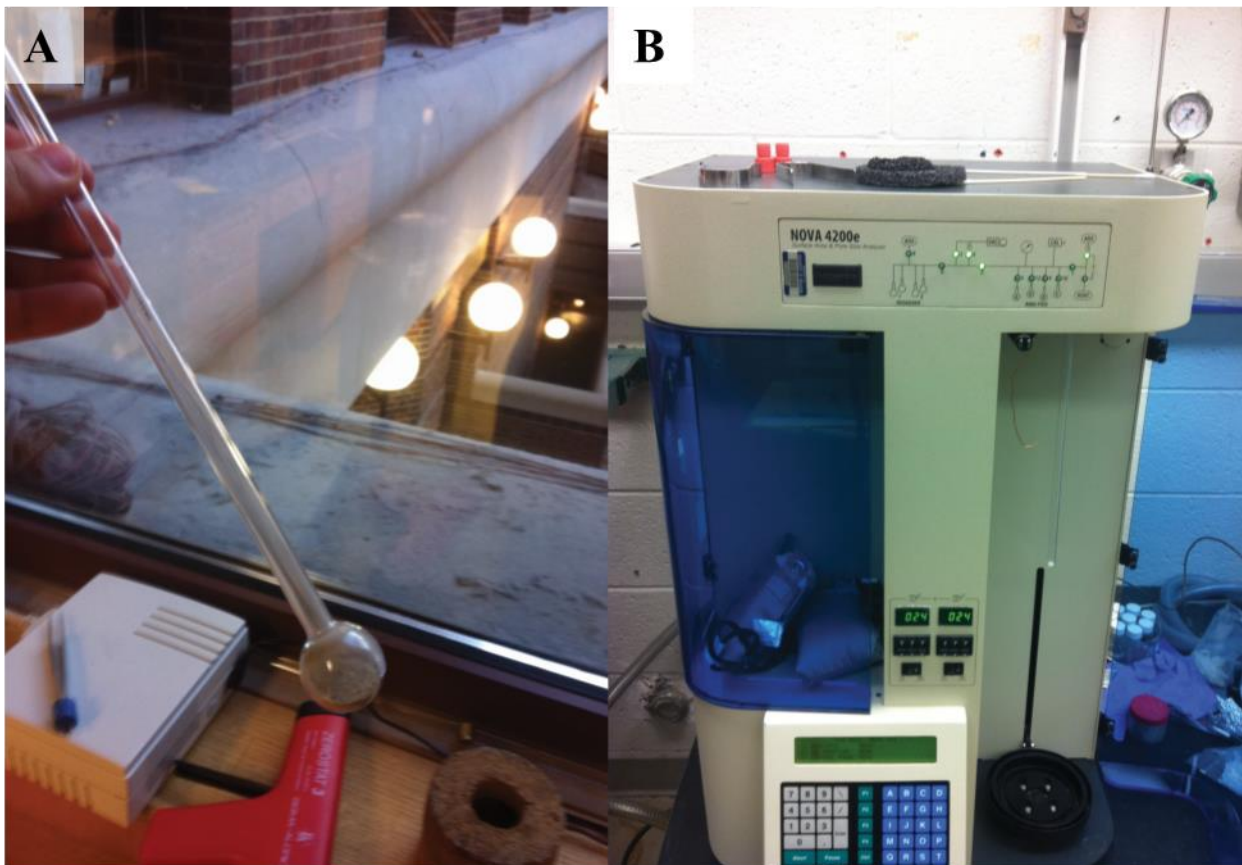


Figure 5: Equipment used for conventional BET measurements. Samples are first loaded into glass vials of known volume (a) and then outgassed. Then, they are analyzed using a NOVA 4200e Surface Area and Pore analyzer (b).

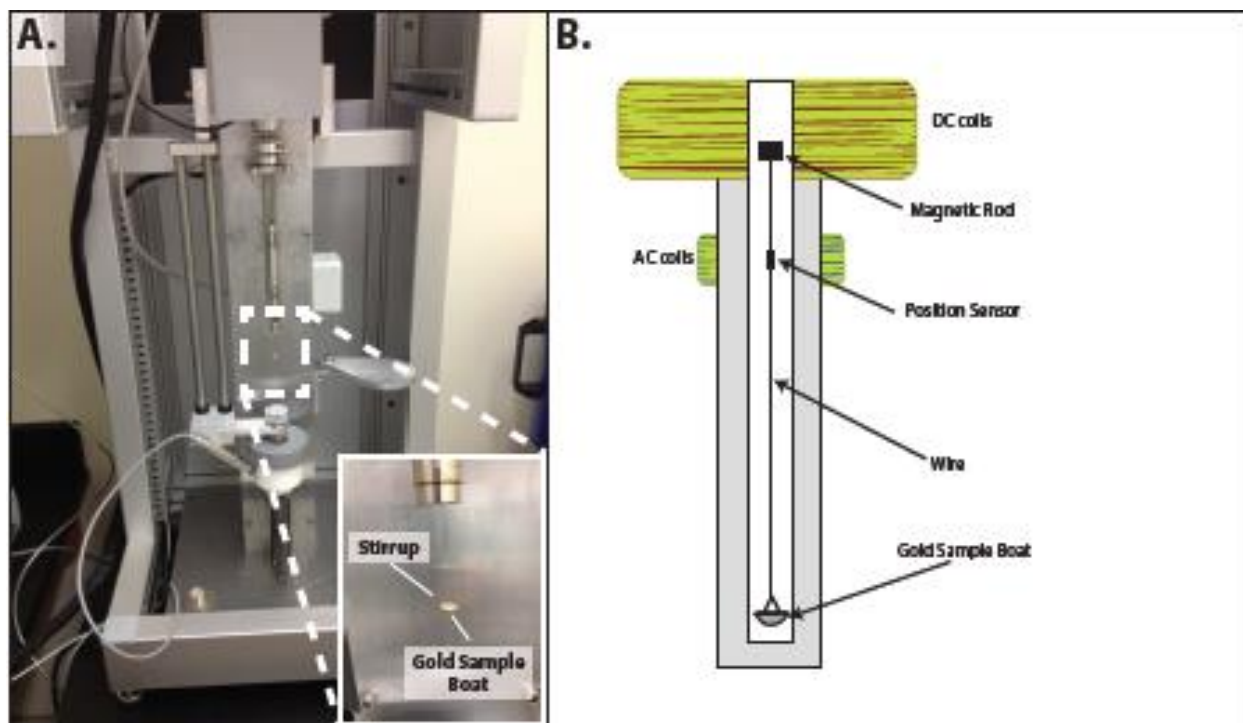


Fig. 6: The nanobalance. In (A), the sample chamber is lowered and the gold sample boat has been loaded into the stirrup. (B) is the nanobalance in schematic form as depicted by Aciego et al (2011).

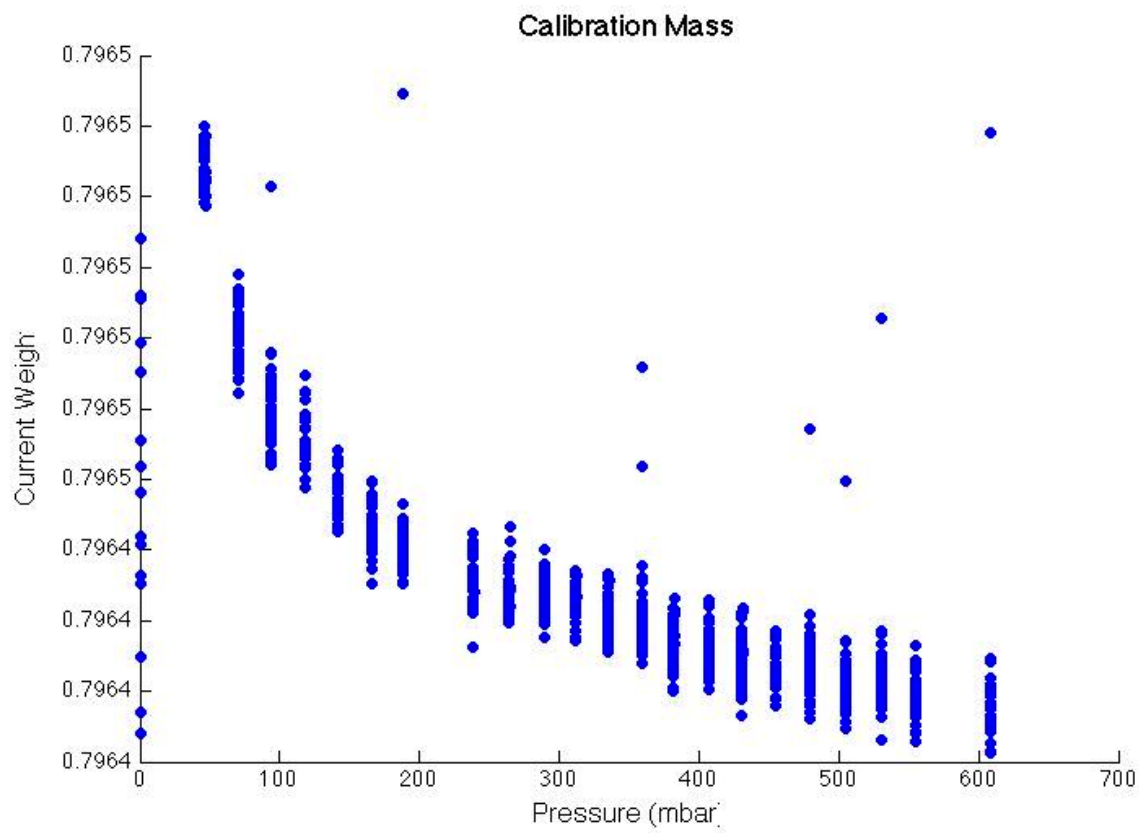
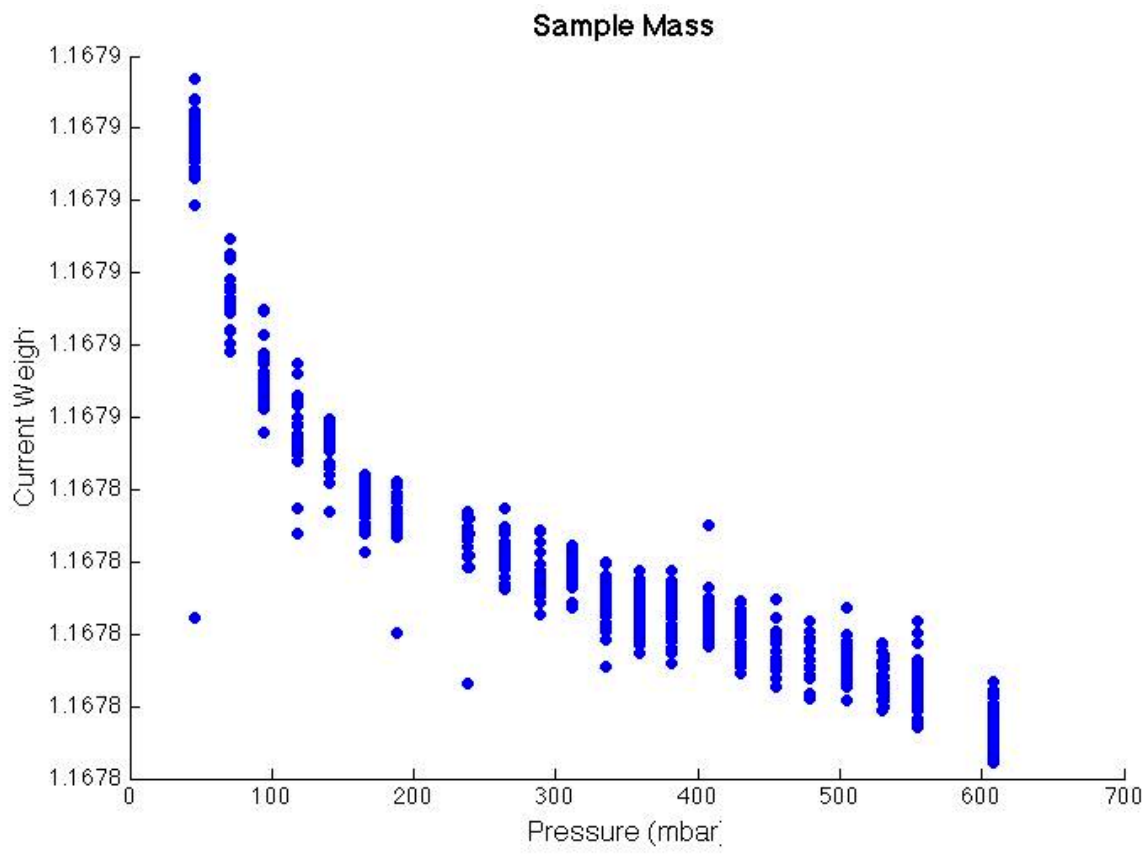


Fig. 7: Sample and calibration weights.

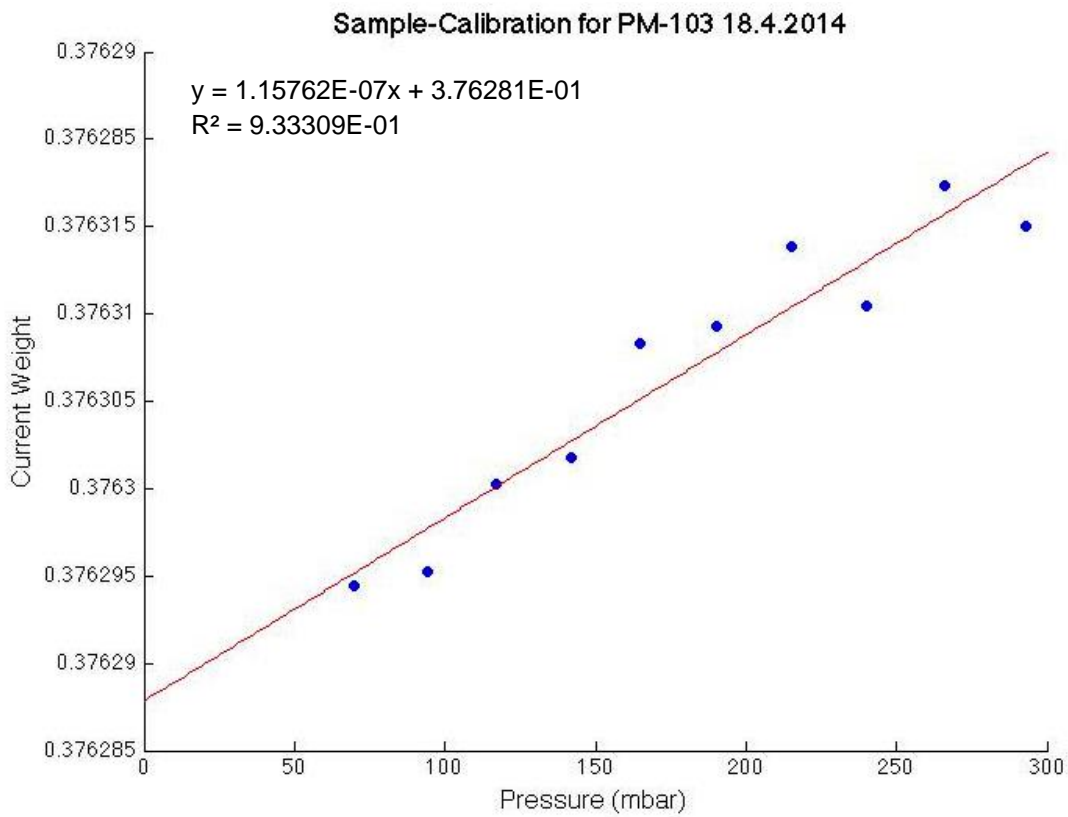
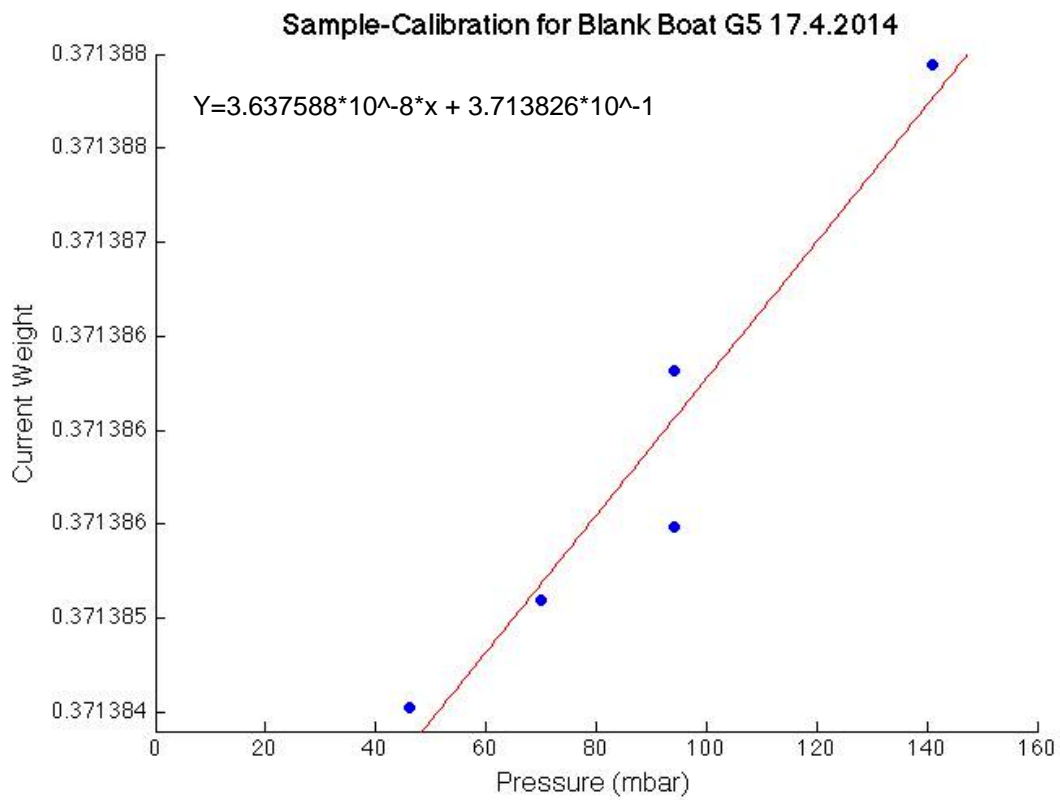


Figure 8: Sample minus calibration for standard (PM-103) and blank boat G5.

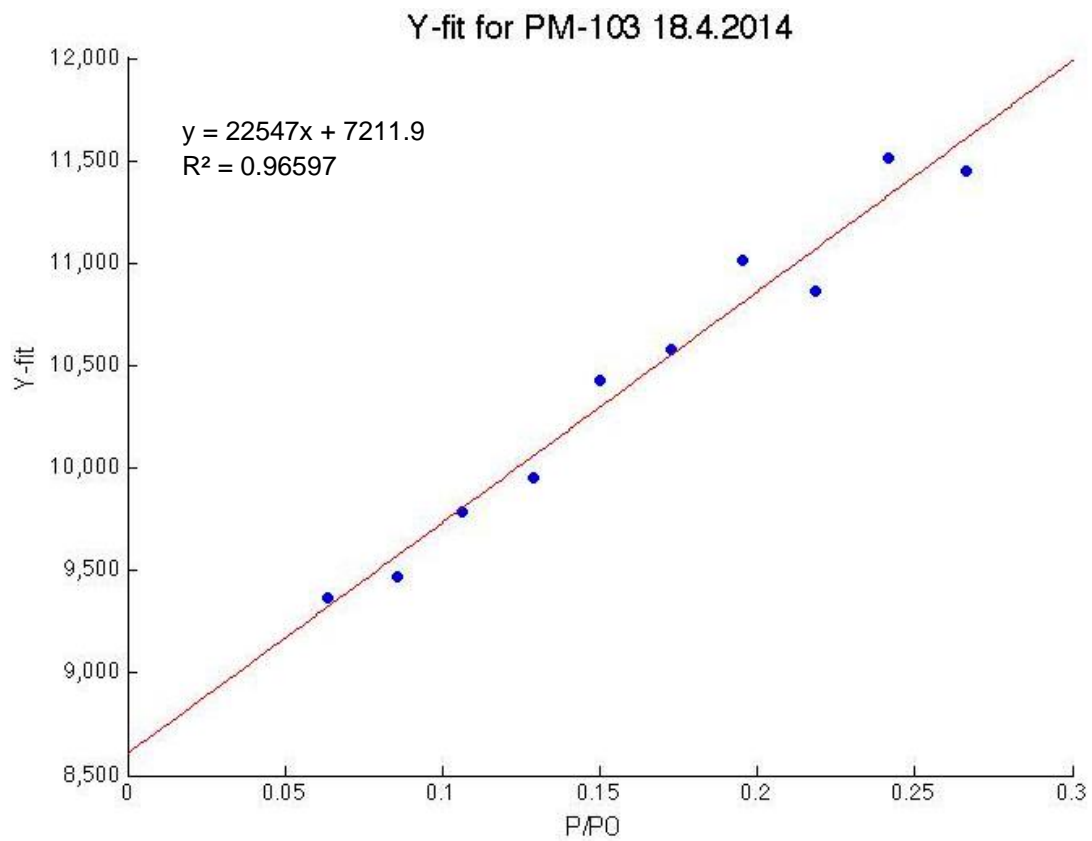


Figure 9: Y-fit for standard. The BET surface area is calculated from this plot.

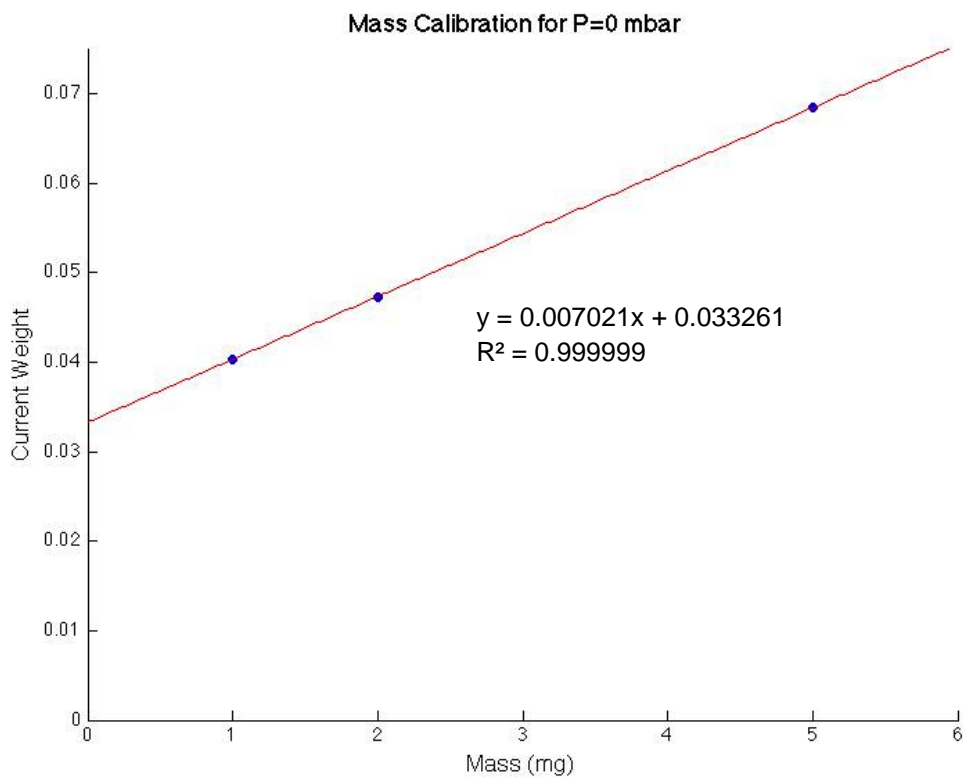
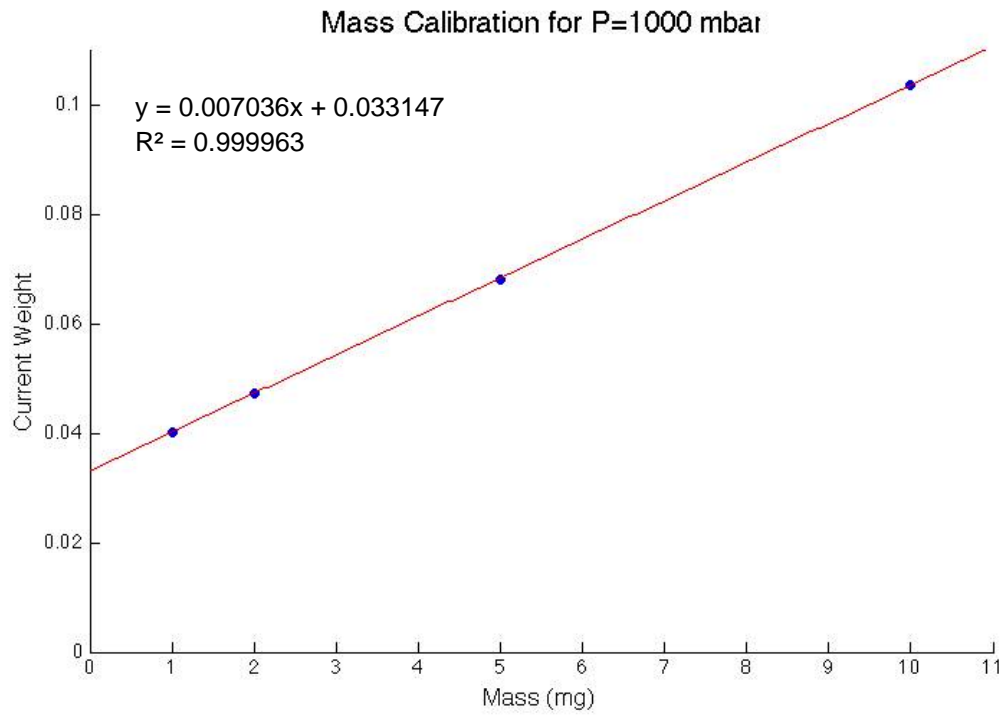


Figure 10: Mass calibration for the nanobalance. The linear relationship allows us to convert the measured mass from current units to milligrams.

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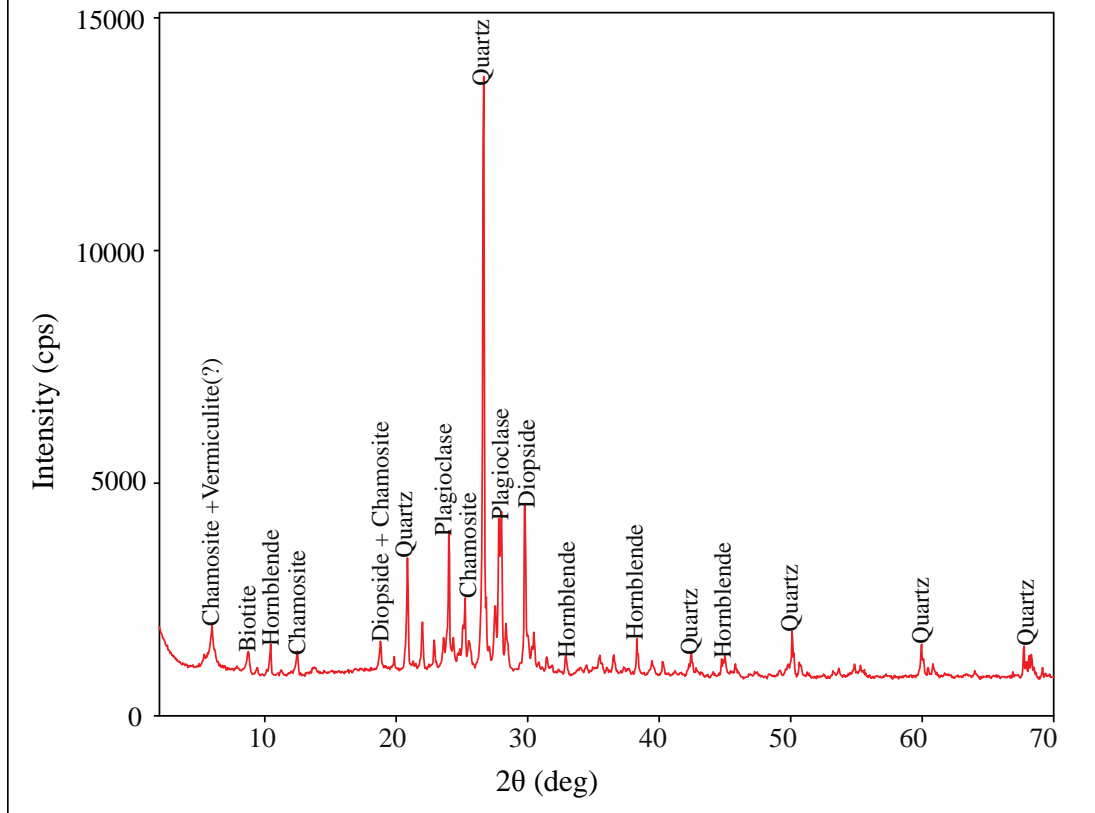


Figure 11: Sample XRD profile for the Lemon Creek Glacier

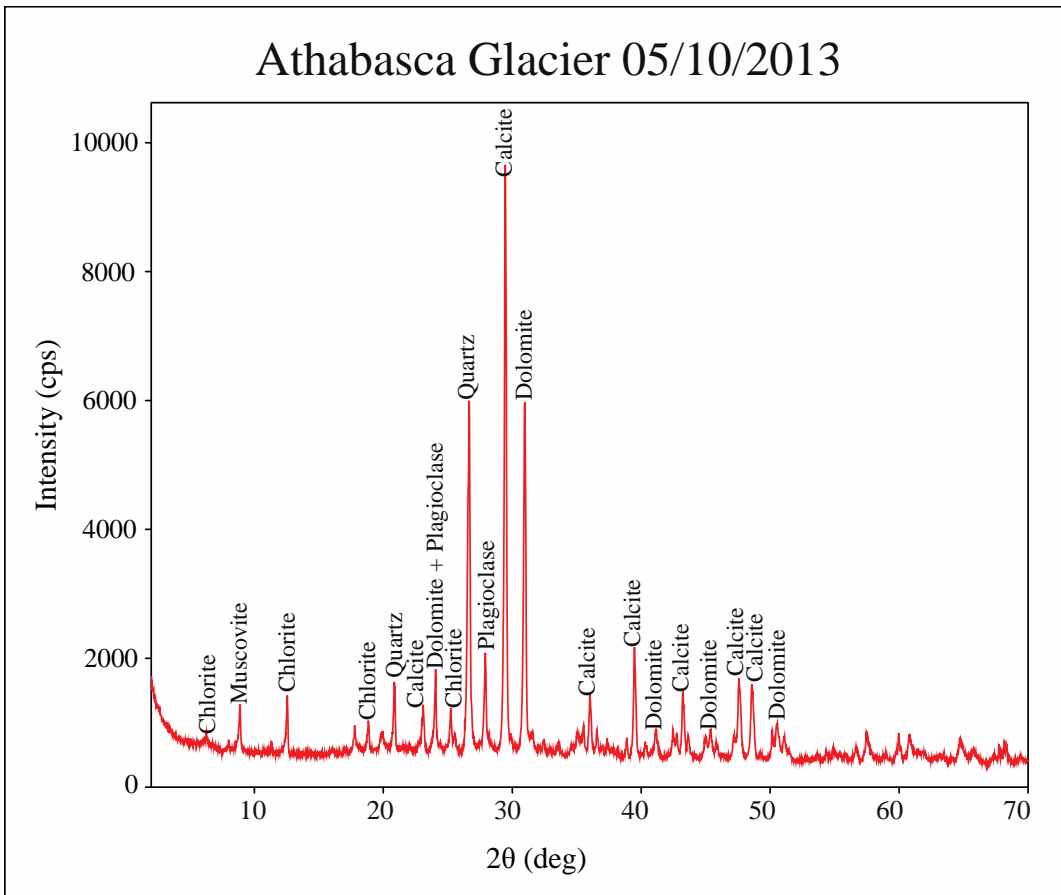


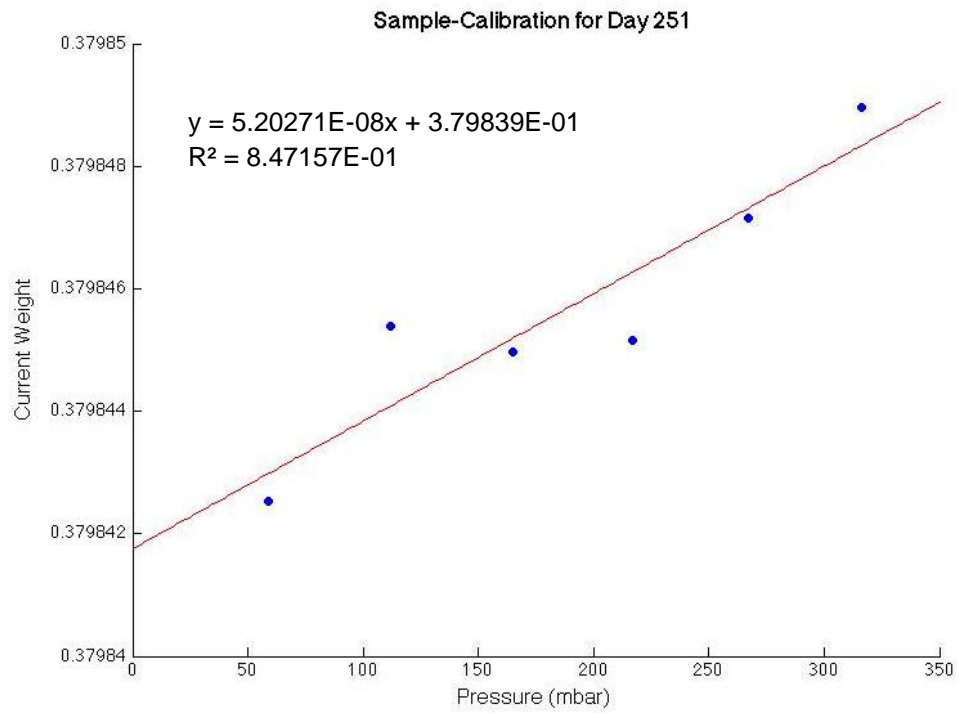
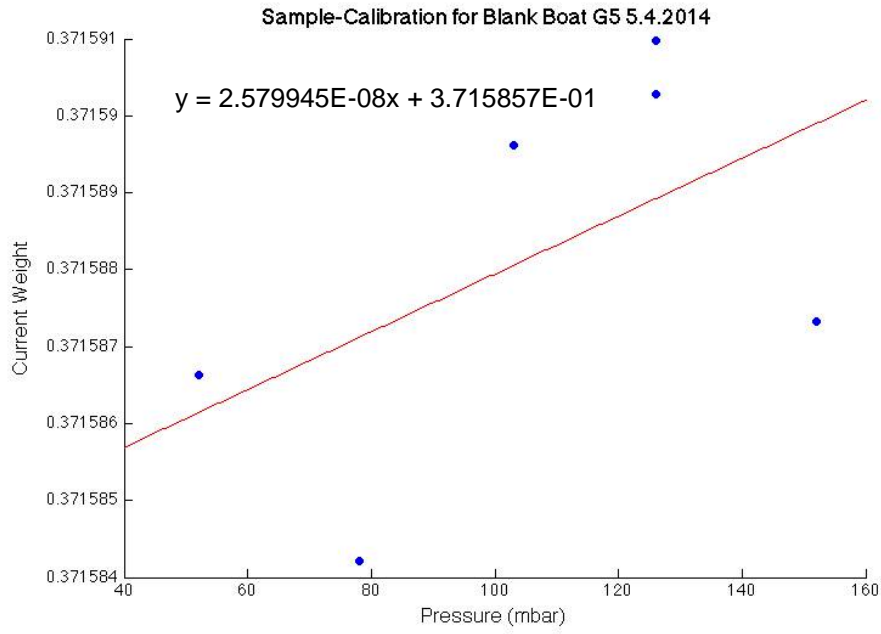
Figure 12: XRD figures for Athabasca from samples taken during the 2013 melt season.

Date (2011)	Specific Surface Area (m ² *g ⁻¹)
14-May	1.921
24-May	8.284
11-Jul	6.97
24-Jul	3.86
Standard (SRM-1900) Certified SSA	Average: 2.646 +/- 0.252 2.85 +/- 0.09 multipoint 2.79 +/- 0.07 singlepoint

Figure 13: SSA measurements from 2011 Athabasca field season.

Day of the Year (2012)	BET Surface Area (m ² /g)	Certified Surface Area
Standard Measurement 1	164.47	156.0 +/- 1.3
Standard Measurement 2	159.02	156.0 +/- 1.4
251	4.91	

Figure 14: SSA measurements for standard BAM PM-103 and Lemon Creek Glacier sample.



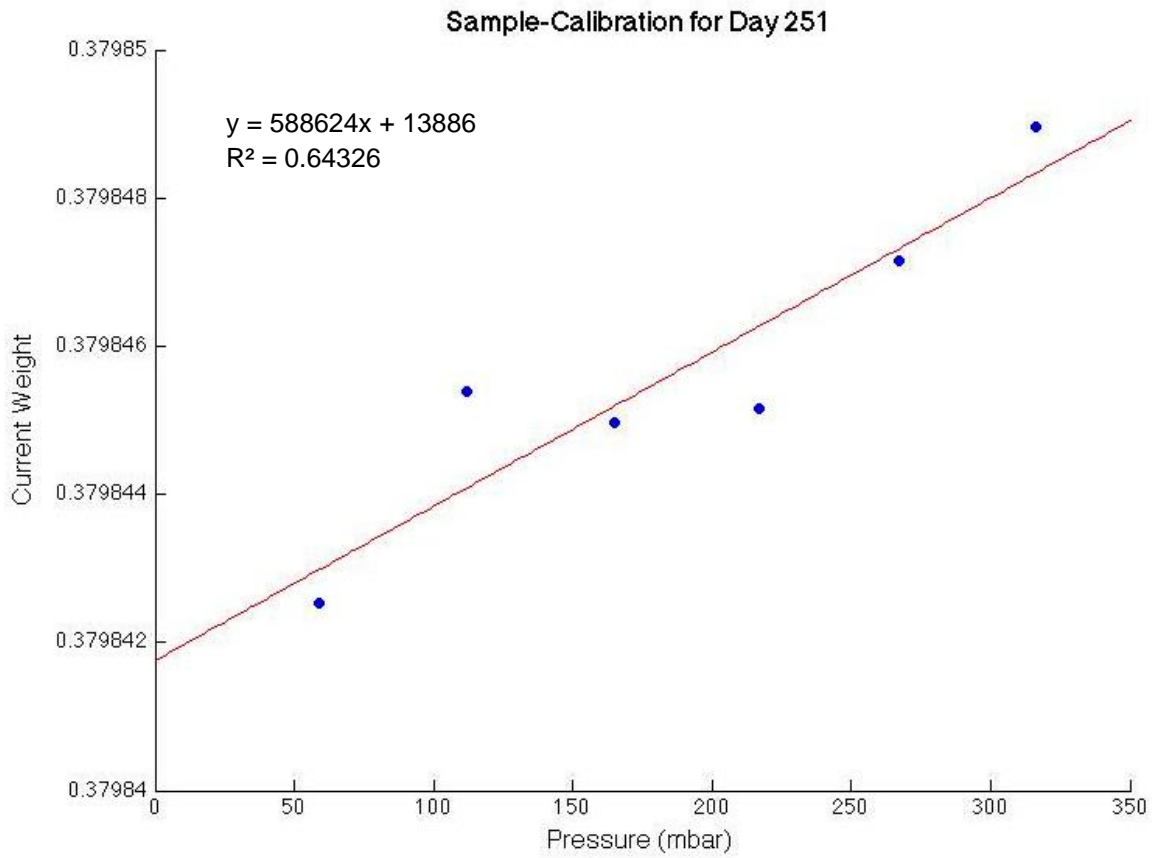


Figure 15: Plots of Sample-Calibration for boat G5, Sample-Calibration for Day 251, and Y-fit for Day 251.

VIII. References

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