The American Pika: An Agent of Chemical Weathering?

By

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Abstract

The *Ochotona princeps*, also known as the American pika, are rock dwelling foragers who fall under the family of Lagomorphs. While they are only the size of an fist, these mammals play an important role in plant species biodiversity above the treeline. With climate change intensifying, the species are facing a population decline and are on the road to extinction. In order to bring more attention to pika from other fields of science, I wanted to examine an underexplored influence of pikas on their environment. This study examines the effect of pika urine on the metamorphic rocks of Niwot Ridge. Knowing more about this species and its impact on the Earth can help bring attention to protecting them. Even small-scale impacts these very tiny mammals make are fascinating and could open a door to studying more high alpine animals who are also at risk of endangerment. X-Ray Diffraction (XRD) was used to determine the chemical composition of the urine. A Stable Isotope Ratio Analysis was conducted to understand where the carbon in the urine coating originated from. Using a Scanning Electron Microscope (SEM), the rock sample was tested for the elemental composition of the rock at the surface impacted by the urine versus the center where it had never come into contact with pika urine. Alkaline urine would be required to have any chemical alterations of mineral grains in this situation. Minimal testing was done on the american pika but laboratory tests show that rabbits, a family of the pika, have a pH of around 8.2 (Suckow 2007) and mice, when fed the pika diet, have a pH around 5-6 (Böswald, 4) . Laboratory testing determined that pika urine does not directly cause chemical weathering of quartz, mica, and sillimanite but we did learn more about the processes that take place to create the urine stain that is found all over the world.

Introduction

Background: The American Pika

Pika are an individual territorial species, each encompassing their own talus pile. The radius of these piles is about 14-30 meters and contain rocks with a diameter ranging from 0.2 to 1.0 meters. These habitats include vegetation within approximately 10 meters from the center (Ray 2019).

Pika spend their long summer days foraging for nearby plants to store in their den for the winter, given the species does not hibernate. To mark each territory, pika chooses a few sheltered rocks where they leave behind urine and piles of feces pellets. The urine markings are very distinct and one of the main features you can notice to determine residency. Due to pika's short lifespan of three to four years, they only encompass a territory for a short period of time. What creates such thick layers of urine is the generations of pika that have lived in that territory. Pika are a very vocal species, if one dies or disappears others pick up on the lack of communication and can take over the territory. The territories that are most ideal for pika, which include nearby vegetation, a shelter, den space, and other nearby pika, are continuously reused (Ray 2019).

There are a few drivers that are involved in chemical weathering to soil formation, organic activity, is the one that would cause weathering in this scenario. Hydrolysis is the chemical process that takes place when silicate minerals interact with weakly acidic water. This process results in the formation of solid and aqueous products. In terms of the solid products, what is left is small quartz grains and kaolinite clays minerals. Quartz, which is very stable, is unweathered while biotite, which is found in silicate rocks, can be chemically altered into clay minerals (Harriss 1965). To determine if Pika urine has a pH low enough to cause hydrolysis to occur we had to console other animal studies. Similar species to the american pika's urine was tested to determine the pH. Mice, which were fed a similar diet to the american pika, showed a pH between 5-6 (Böswald, 4), which makes it a perfectly weak acid ideal for hydrolysis. The original prediction was that chemical weathering was taking place on biotite that is present in this rock and that quartz would be chemically resistant to hydrolysis.

Past Work on Pika Urine

Minimal research has been done on these white, chalky in texture, urine stains. Recent work has shown that urine stains mixed with old fecal pellets indicate recent occupancy within the last year to multiple decades ago (Beever 2016). Research has been limited on the *Ochotona princeps*, the pika that we find in the high alpine of the Western United States. The *Ochotona rufescens*, the Afghan pika, which is found in the high mountains of Afghanistan, Iran, Pakistan and Turkmenistan, however, has been more heavily researched. While the two are slightly different, they follow a similar diet which consists only of plants. In a past study it was found that the *Ochotona rufescens* excreted alkaline urine with high concentrations of chloride (296 ± 30 mmol/l), potassium (260 ± 30 mmol/l), and sodium (360 ± 30 mmol/l). However, no measurements regarding the concentration of calcite were measured (Matsuzawa 1981). Using this information, there is room for expansion on the study of the *Ochotona princeps* and what is creating the chalky texture of their urine stains.

Our Research

This study aims to determine the impact that American Pikas have on the surfaces of rocks in their dens. Using analyses with XRD, Stable Isotope Ratio Analysis, and SEM our goal was to offer more knowledge to different areas of science on the impacts of these small mammals. Are these urine spots causing enhanced chemical weathering at the surface of granites? Or alternatively, are interactions of microbes with the urine causing ions in the urine to precipitate as calcium carbonate, even if there is minimal chemical weathering? By characterizing the boundary of rock and urine, we can develop an understanding of the interaction between the two.

Methods

The rock sample that is the focus of this study is from Nederland, Colorado, in Indian Peaks Wilderness located at 40.0453598° N, 105.5701918° W. The rocks of Indian Peaks Wilderness are composed of silicate minerals. There are four different types of rocks located here. The two oldest rocks are metamorphic and the two youngest rocks are igneous intrusions. Considering the foliations present in our sample, we determined it must be one of the metamorphic rocks. Of those two, Schist is the oldest and Biotite Gneiss follows after both over a billion years old (Pearson 1980). The site is 10 m away from any fresh hay piles, indicating there is likely a current or very recent inhabitant (Ray 2019). The rock sample is also located in a sheltered area, with only 4 inches between the urine-covered rock and the overhanging rock (**Figure 1**). It was important to choose a rock that would only allow a very small animal to access it since other high alpine animals also leave similar markings. Considering that 4 inches of room was only generous enough for a Pika to fit under, we can confidently conclude that only Pika urine is present.

X-Ray Diffraction Analyses

The goal of using XRD was to determine both the composition of the chalky substance that was coating the rock as well as the overall rock composition. Using a dremel micro drill we removed 2 layers of pika urine powder, one at the surface and one at depth. We measured out 8 micrograms of each powder and added them to 2 different plastic microtubes (labeled: NWT-23-PPS and NWT-23-PPB). Each powder was then analyzed for mineralogical composition via XRD. In addition to the urine powder, XRD was also used to determine the mineralogical composition of the rock. Using a BRUKER D8 Advance powder X-ray diffractometer (**Figure 2**) the 3 powders were analyzed from 10° to 75° 2θ with an increment of 0.01° and a dwell time of 0.5 seconds. The minerals were identified by searching the Crystallography Open Database. The X-Ray generator was set to a voltage of 40 kV and a current of 40 mA. The data was then interpreted by selecting the best match to each of the peaks.

Stable Isotope Ratio Analysis

A Stable Isotope Ratio Analysis was conducted to understand where the carbon in the urine coating originated from. Results from XRD indicate that the powder is composed of calcium carbonate ($CaCO_3$). We were curious if the carbon that is found in the urine originated from the atmosphere or from pika excretion. $\delta^{13}C$ is an isotopic signature that compares the ratio of ^{13}C to ^{12}C. This can be tested from stable isotope ratio analysis and is a tool that can give us a relative time frame as well as the origin of the carbon isotopes. If the $\delta^{13}C$ value of the powder aligned with the $\delta^{13}C$ of the pika then the calcite could be a direct result of the pika. If the $\delta^{13}C$ value aligned more with the atmosphere then it was likely microbial activity was occurring. During microbially induced calcite precipitation (MICP) the urea from the pika could be creating a biofilm that the microbes feed off to produce calcite precipitation. In order to determine which was more likely we weighed out 250 µg (+/- 10 µg) each of NWT-23-PPS and NWT-23-PPB to run a stable carbon isotope test to determine its origin. All isotope ratios are reported using delta notation in parts per thousand. The carbonate carbon ($\delta^{13}C$) isotope values of carbonate samples were analyzed at the University of Colorado Boulder Stable Isotope Laboratory (CUBES-SIL) on a Thermo Delta V continuous flow isotope ratio mass spectrometer (CF-IRMS) (Thermo Fisher Scientific, Waltham, MA, USA). Carbonate samples and standards were digested in phosphoric acid in a Thermo Gasbench II (Thermo Fisher Scientific) heated to 70°C to release CO2 to be analyzed by CF-IRMS. Carbonate isotope values were corrected for sample size dependence and then normalized to the Vienna Pee Dee Belemnite (VPDB) scale with a three-point calibration using NBS-18, Yule marble (CU YULE) and Harding Icelandic Spar.

Scanning Electron Microscope

Using a Scanning Electron Microscope (SEM), the rock sample was tested for the elemental composition of the rock at the surface impacted by the urine versus the center where it had never come into contact with Pika urine. Since the sample was non-conductive we used a Cressington Sputter Coater from Ted Pella, INC. to coat the rock sample in 4µm platinum. This allowed us to use a scanning electron microscope, the TM4000Plus, HITACHI. Using SE (Secondary Electron) imaging, specific areas on the rock surface were examined. Using an Oxford Instruments energy-dispersive spectrometer (EDS), we were able to run an elemental analysis on the concentrations present in 3 different areas of the rock; the powder on the surface, the rock center, and the boundary of where the two come into contact (**Figures 3 and 4**).

Results

XRD

XRD results confirmed our expectation that the urine powder was composed mostly of calcite ($CaCO_3$). This was beneficial in determining how much powder to weigh out for the stable isotope ratio analysis (**Figures 5 and 6**).

The XRD spectrum of the rock sample played an important role in the identification of the rock type. With a few different basement rocks located near the study site, XRD results identified the minerals that compose the rock. The minerals that were found are quartz, muscovite, clinochlore, illite, and sillimanite (**Figure 7**). Biotite gneiss in the Indian Peaks Wilderness area is typically composed of mostly biotite, quartz, and plagioclase with varying amounts of sillimanite and garnet (Pearson 1980). The minerals found from XRD are similar to those found in Biotite Gneiss of Indian Peaks Wilderness, which we determined to be the rock type.

Zeiss AXIO Imager Microscope

Using our knowledge from the XRD results of the rock minerals, we used a Zeiss AXIO Imager microscope to take a closer look at the rock and minerals present and confirm the rock type. We were able to identify predominantly quartz, biotite and muscovite. We determined that the rock type is a biotite gneiss, roughly 1.7 billion years old, consistent with the bedrock geology of the Indian Peaks Wilderness (Pearson 1980).

Stable Isotope Ratio Analysis

Stable Isotope Analysis provided results that allowed us to compare the $\delta^{13}C$ values of the urine powder NWT-23-PPS (surface of coating) and NWT-23-PPB (base of coating). The $\delta^{13}C$

value of NWT-23-PPS was -8.43‰ (+/- 0.086‰) and the $\delta^{13}C$ value of NWT-23-PPB was -6.68‰ (+/- 0.86‰).

Secondary Electron Microscope

Results from SEM indicate that the coating on the rock is composed of oxygen, carbon, and calcium which supports the results from XRD that the urine powder is $CaCO_3$. SEM confirms no chemical weathering is taking place on the rock surface due to contact with pika urine. This was determined by comparing the elemental compositions that were found at both surface and depth. SEM showed different minerals located throughout the rock but there was no evidence of clay that would have been created during weathering. If there was a mineralogical change that had occurred, SEM would have shown a difference in elemental composition only along the boundary of contact, which was not the case.

Discussion

Zeiss AXIO Imager Microscope

Using our thin section of the rock sample, we were able to examine the individual minerals that were present throughout the rock. **Figure 8** shows the rock in normal light where the minerals we noted are labeled. **Figure 9** is a mosaic of the sample in XPL which was an important factor in determining which minerals are present. The foliations found after examining the thin section showed strong mica banding which is characteristic of Biotite Gneiss. Thus, microscopy, in combination with XRD, allowed us to confirm our observations that the rock sample is biotite gneiss.

We also looked at the minerals in a thin section along the boundary between pika urine and rock to determine if there was any noticeable difference. There did not appear to be any evidence of chemical alteration in the form of compositional differences compared to other locations of the rock.

Secondary Electron Microscope

SEM was used to look at the boundary of contact between the urine and rock surface at an elemental scale. The powder was composed of mostly carbon, oxygen, and calcium, which confirmed the XRD analysis (**Figure 10**). The highest weighted percentage elements present at NWT-23-PPB are carbon, oxygen, and silicon which can be seen mineralogically through XRD. The boundary of contact, however, shows minimal difference elementally from the rock at depth. The most common elements at the boundary are oxygen, silicon, and carbon. If chemical weathering had been occurring, we expected to see elemental changes at the boundary of the rock and the coating that are not present anywhere else in the rock. Calcium would have likely seen an increase in weight percentage along the contact versus at depth. Calcium experiences an increase in weathering during the early stages, with this process taking place on a geologically small time scale, there would have been a strong increase in calcium if chemical weathering was occurring. This occurs from dissolution where ions are created from calcite to calcium (Harriss 1965). **Figures 11 and 12** show that the percentage of calcium actually increases from deeper in the rock (0.76%) to the contact with the coating (3.24%). There are very small elemental percentage differences that can be seen in **Figures 11 and 12** between spectrum 10 and 11. These small differences are likely just differences in abundance of the main minerals between the two locations. We interpret that any compositional variation in the rock surface is much more likely from weathering that has taken place since the Laramide Orogeny, over the last 50 million years versus the time that pika have inhabited the field.

This biotite gneiss sample would likely not experience weathering to its quartz grains but much more likely to biotite. If biotite had been chemically altered there would have been a resultant smectite or kaolinite clay visible only along the boundary of contact. Both smectite and kaolinite are very high in oxygen which is not something that was interpreted on the SEM graph of contact.

A noticeable detail that can be seen in **Figure 10** is that there is significantly more carbon and oxygen than calcium. There should be an equal amount of calcium and carbon in the SEM graph given the chemical formula of calcite ($CaCO3$). Oxygen should be more prevalent than carbon and calcium. The most likely cause for this difference seen in carbon and calcium is the organics that are present in the urea.

Stable Isotope Ratio Analysis

Our original hypothesis was that the $\delta^{13}C$ values of the pika urine powder would reflect the pika diet. The expected $\delta^{13}C$ of plants is around -27‰ and the $\delta^{13}C$ of the plateau pika's back leg muscle is around -25‰ (Yi 2006). With altitude gradient, the $\delta^{13}C$ value of plants increases so in *Ochotona princeps,* the $\delta^{13}C$ value of urine could actually be larger than -27‰ (Yi 2006). Our results indicate a $\delta^{13}C$ value of -8.43‰ (top of coating) and -6.68‰ (base of coating), which is significantly different from what we expected for the $\delta^{13}C$ signature of the pika's plant-based diet. Considering that the $\delta^{13}C$ value was not constant at different depths of the powder, time had to be considered for what could cause this change. Pika are found to have a very stable isotopic diet across ranges and time so with a small change in $\delta^{13}C$, there was likely not a diet change that was recorded within the urine powder (Westover et al., 2020). These observations mean that the $\delta^{13}C$ values of pika and their diets have no role in the urine powder left behind. Instead, with values around -6 and -8, we interpret that there is likely involvement with atmospheric carbon (Graven et al., 2017).

Using this interpretation, we used the $\delta^{13}C$ values to determine a relative timeframe that pika have been using this specific rock. Results from stable isotope ratio analysis provided us with the $\delta^{13}C$ values for both the surface and depth of the urine stains. **Figure 13** is a graph repurposed from Graven et al. (2017), with both of our samples plotted horizontally. Based on where the lines of NWT-23-PPS and NWT-23-PPB were plotted on the image, we were able to develop an idea of the time that this rock was first in use by pika. NWT-23-PPB was likely from around the 1800's while NWT-23-PPS was much more recent and likely from the last decade. This gives us a period of around a century and a half that pika have been inhabiting this talus field and using this rock specifically. While, this is not an exact timeframe, this information can be used to guide future research to understanding how long it would take for weathering to take place on the surface level by comparing to longer lengths of time.

A possible interpretation of the formation of this coating is the addition of microbes. The isotopic results indicate exchange with the atmosphere which suggests that the crystallization does not occur straight from excretion. The microbes cause an exchange in carbon dioxide with the atmosphere as they feed which could offer an explanation for the unexpected $\delta^{13}C$ values. The $\delta^{13}C$ values would be from microbes feeding and exchanging with the atmosphere rather than from the pika muscles or hair and coming directly from excretion.

Future Work

While this project did not support the hypothesis that pika urine is an agent in chemical weathering, it does open the door to further work around the subject. Our rock sample is composed of minerals that are very resistant to chemical weathering including, quartz and sillimanite. This project could be expanded by examining rocks composed of different minerals from a variety of locations. Another rock type that would be worth examining to determine if chemical weathering does occur is limestone or marble, both of which are much more easily chemically weathered. Finding multiple test rocks that have been used for longer periods of time could aid in determining if time also has a play in the chemical breakdown from pika urine. Another possibility for future research on this project is by testing our $\delta^{13}C$ values with radiocarbon age dating to confirm our results.

Many parts remain unknown surrounding pika and their impact on the environment which leaves room for research to continue on this species. They could eventually be involved in the creation of a new type of carbonate record. With other carbonates being used for paleoenvironmental reconstruction by analyzing their isotopes, pika urine could be used in high alpine environments.

The calcite coating on the rock could be acting as a protective area. Testing could be done to determine if it is actually protecting the rock surface from chemical weathering. Also, a study could be done to see if chemical weathering would take place if the urine didn't leave the powdery surface we see.

Conclusion

The american pika was not found to cause any chemical alterations of biotite gneiss of the Indian Peaks Wilderness. In addition, the pika urine powder does not seem to record any information about their past diet and is instead strictly a record of atmospheric carbon. There is still much that can be learned about this species and if they have any impact on their environment. That can be shown in their $\delta^{15}N$ values and if there is the possibility of chemical alterations in more easily eroded rock types.

Figures

Image 1: Field site location, the rock with the pika urine powder can be seen in the center of the image with a pencil shown to scale.

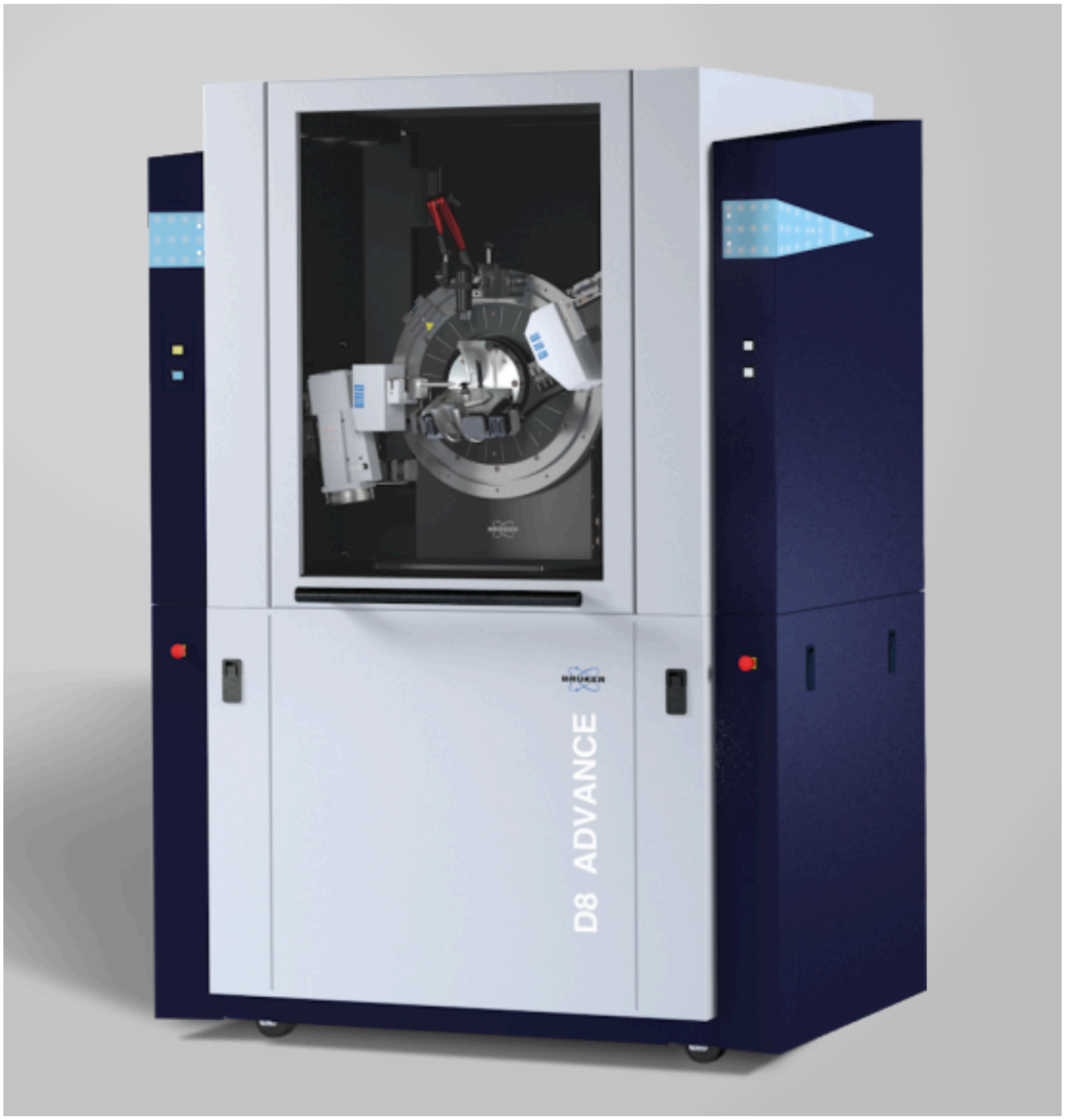


Image 2: X-Ray Diffraction (XRD) BRUKER D8 ADVANCE

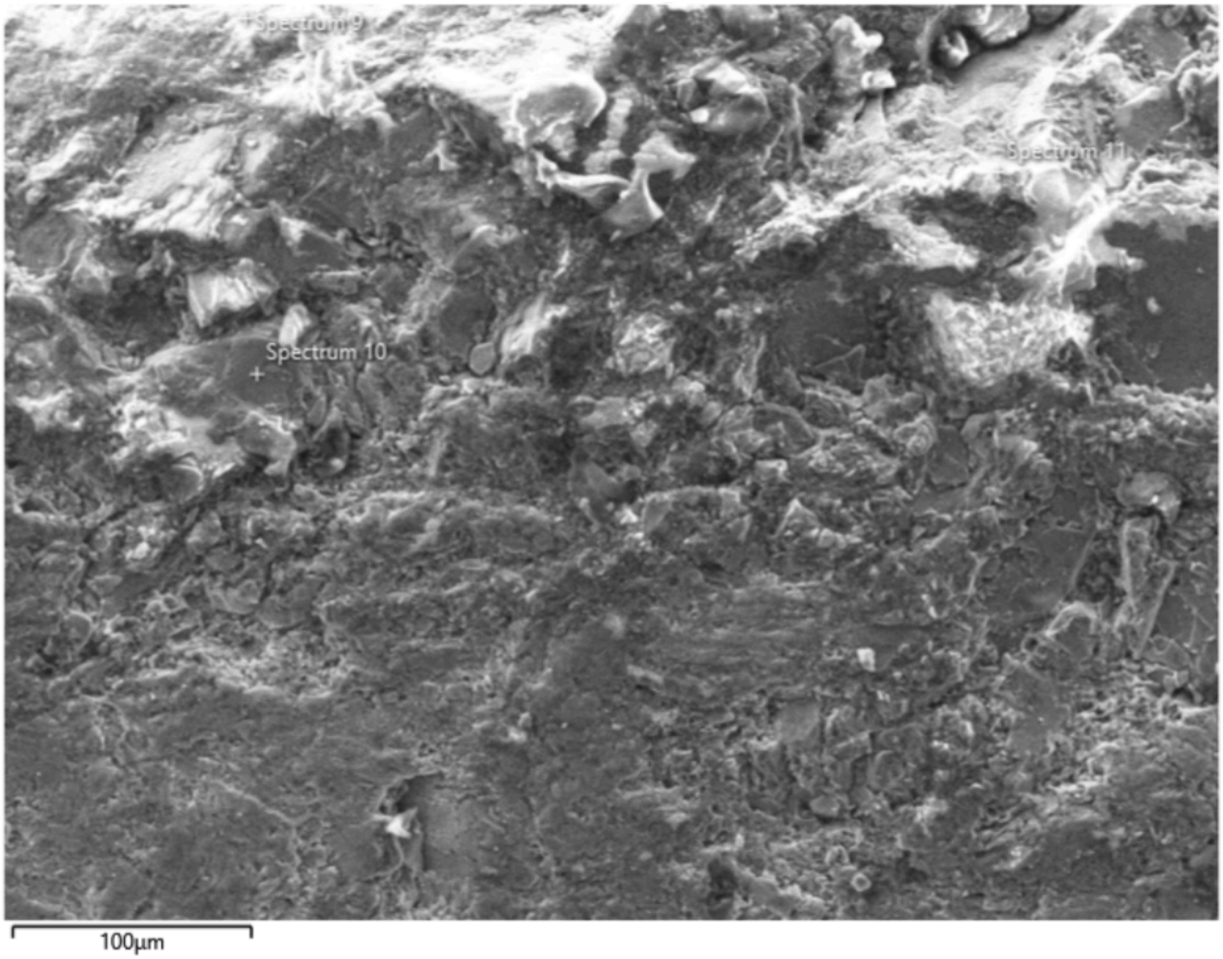


Image 3: Secondary electron image showing the boundary at which the pika urine comes into contact with the rock surface. The white at the top of the image is the urine powder and the gray at the bottom is the center of the rock.

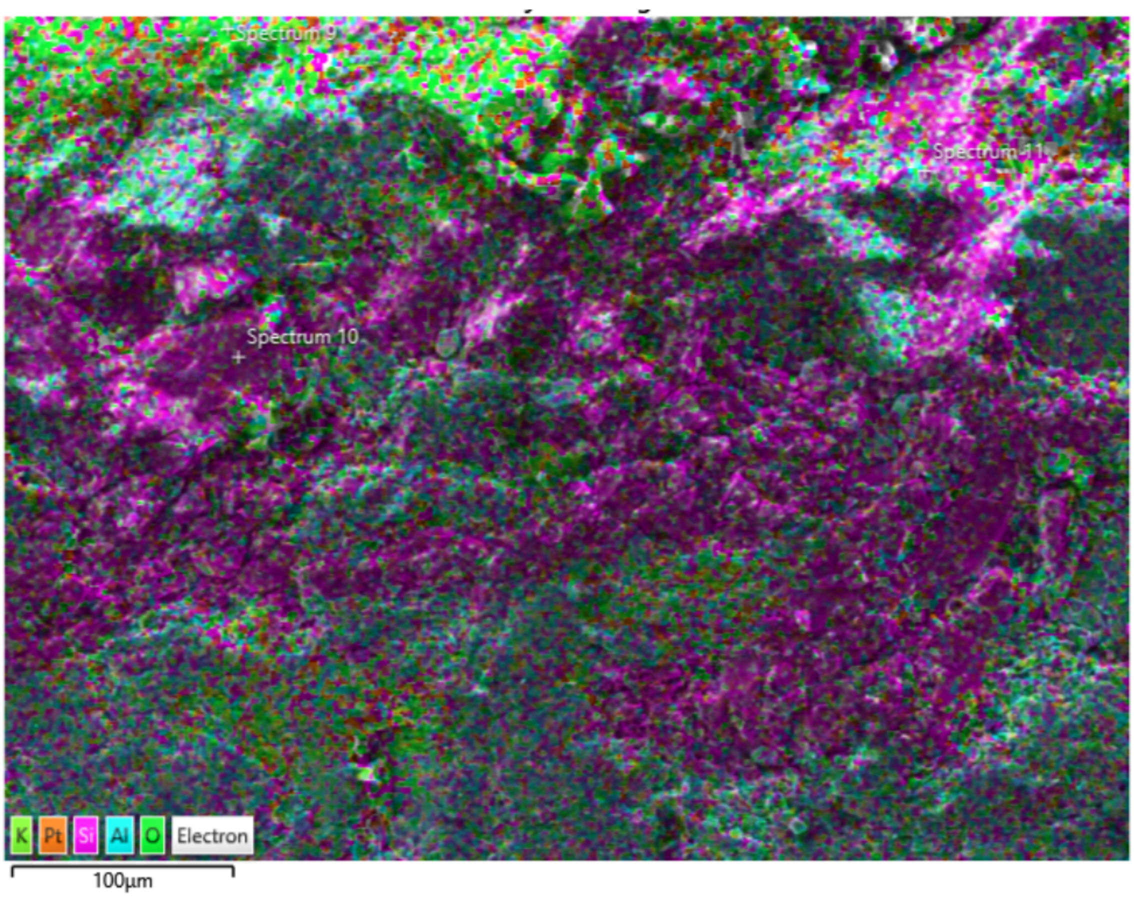


Image 4: EDS layered image showing the elemental composition of the boundary at which the pika urine comes into contact with the rock surface.

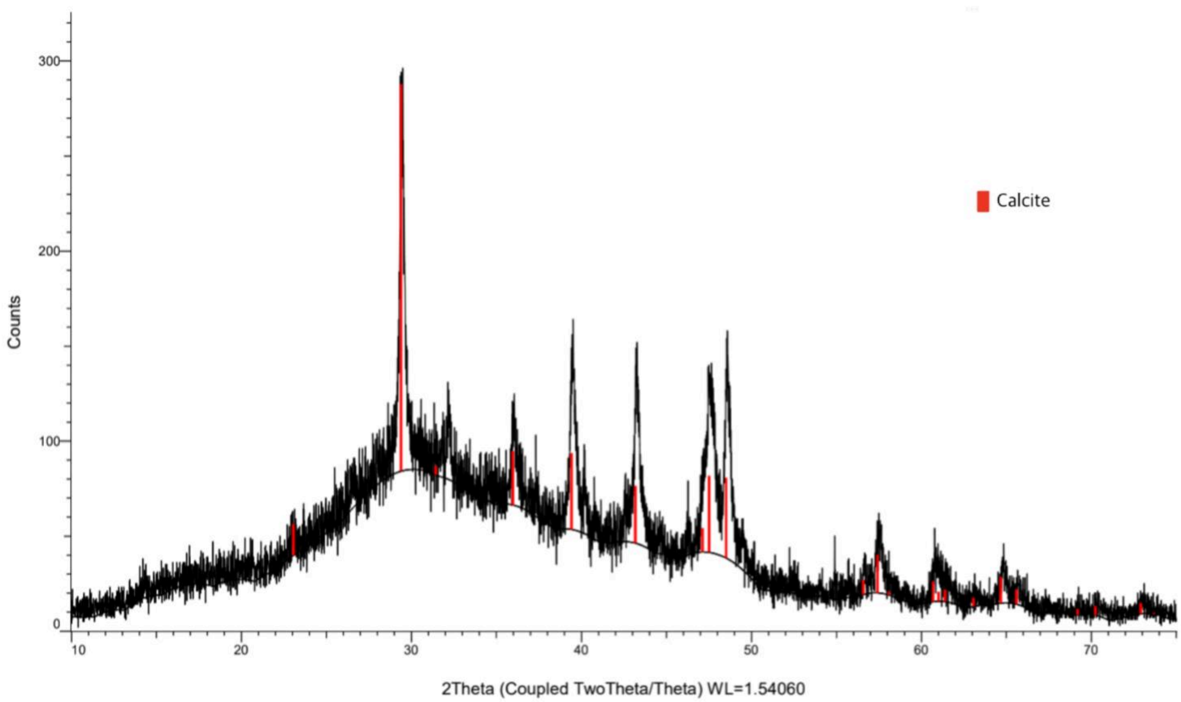


Image 5: XRD scan showing the composition of NWT-23-PPB.

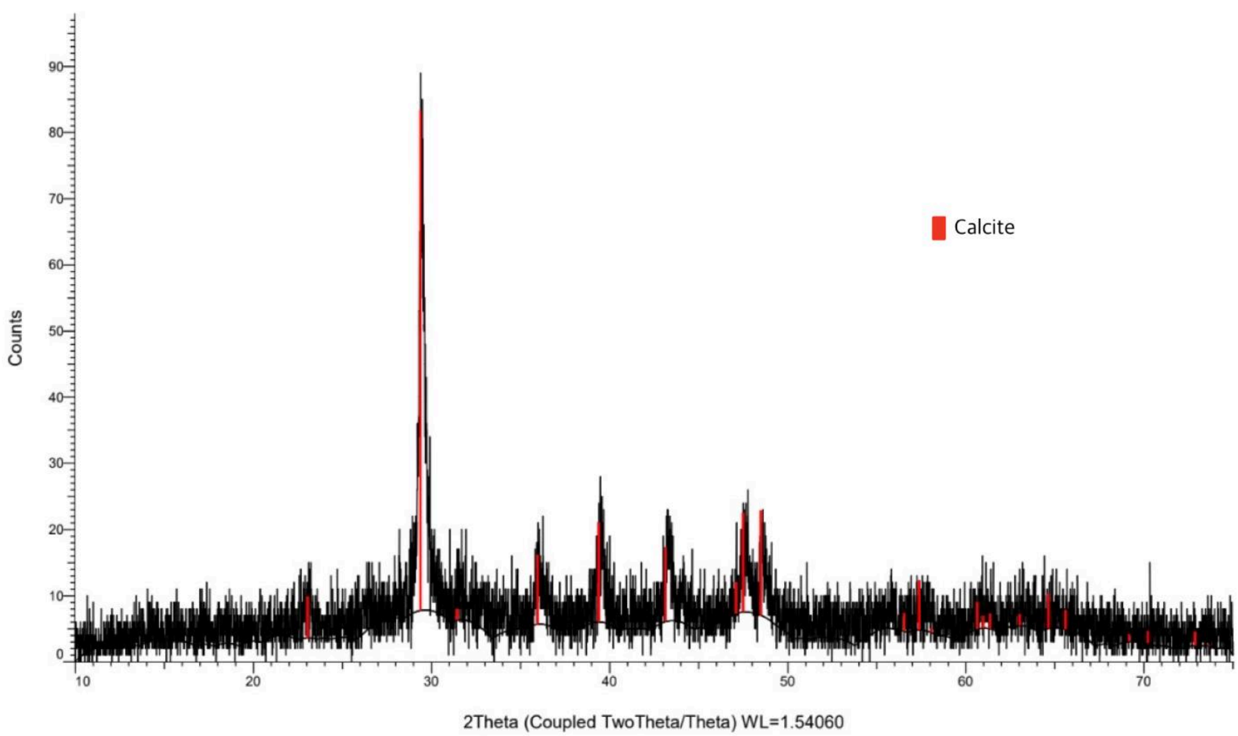


Image 6: XRD scan showing the composition of NWT-23-PPS.

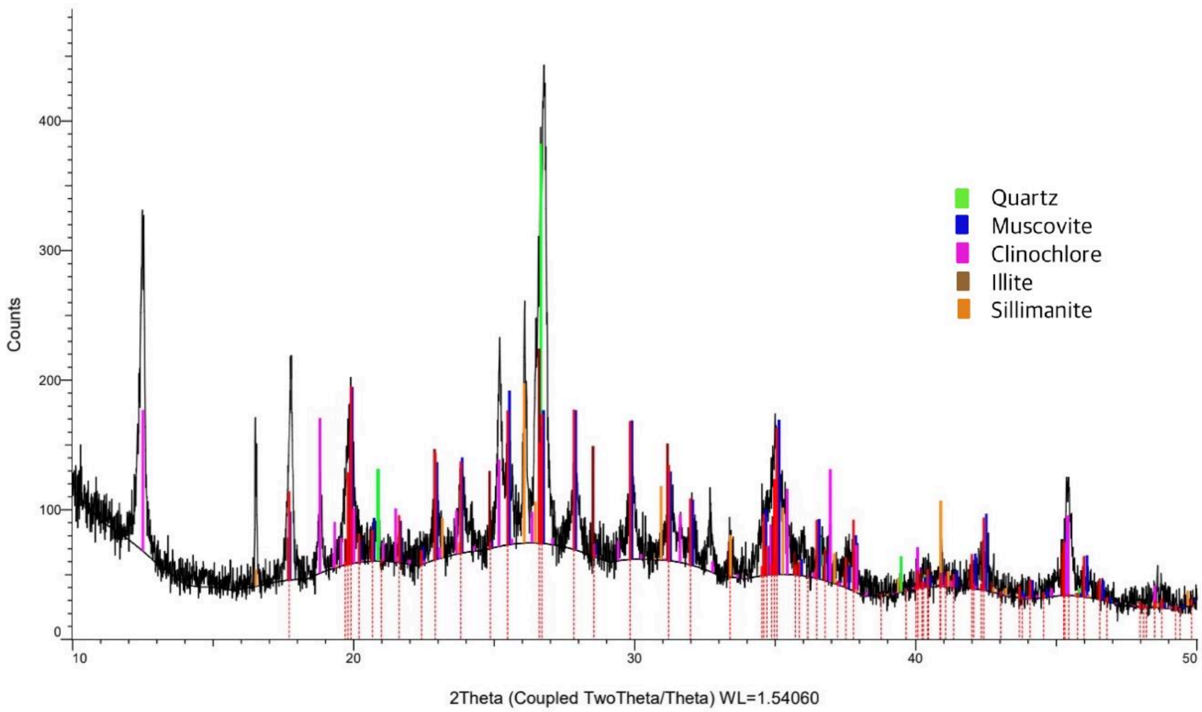


Image 7: XRD scan showing the composition of the rock sample.

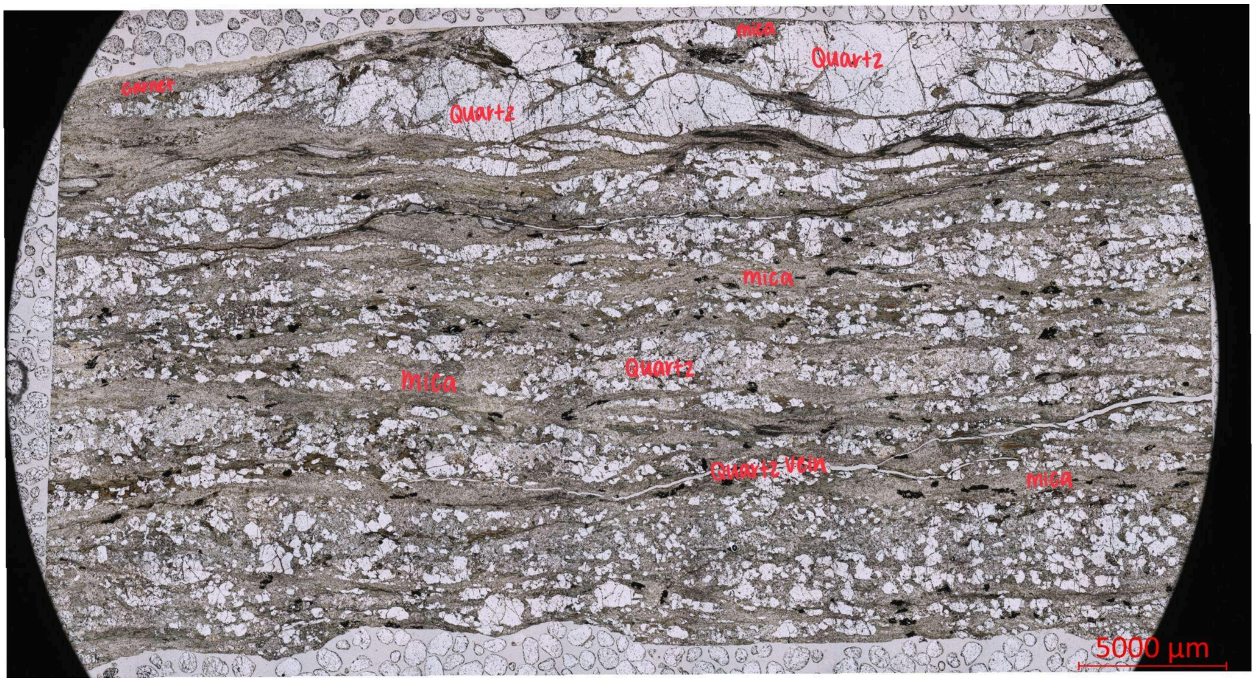


Image 8: Mosaic of rock sample seen as a thin section under normal light. Specific minerals are labeled which show it is predominantly composed of quartz and mica.

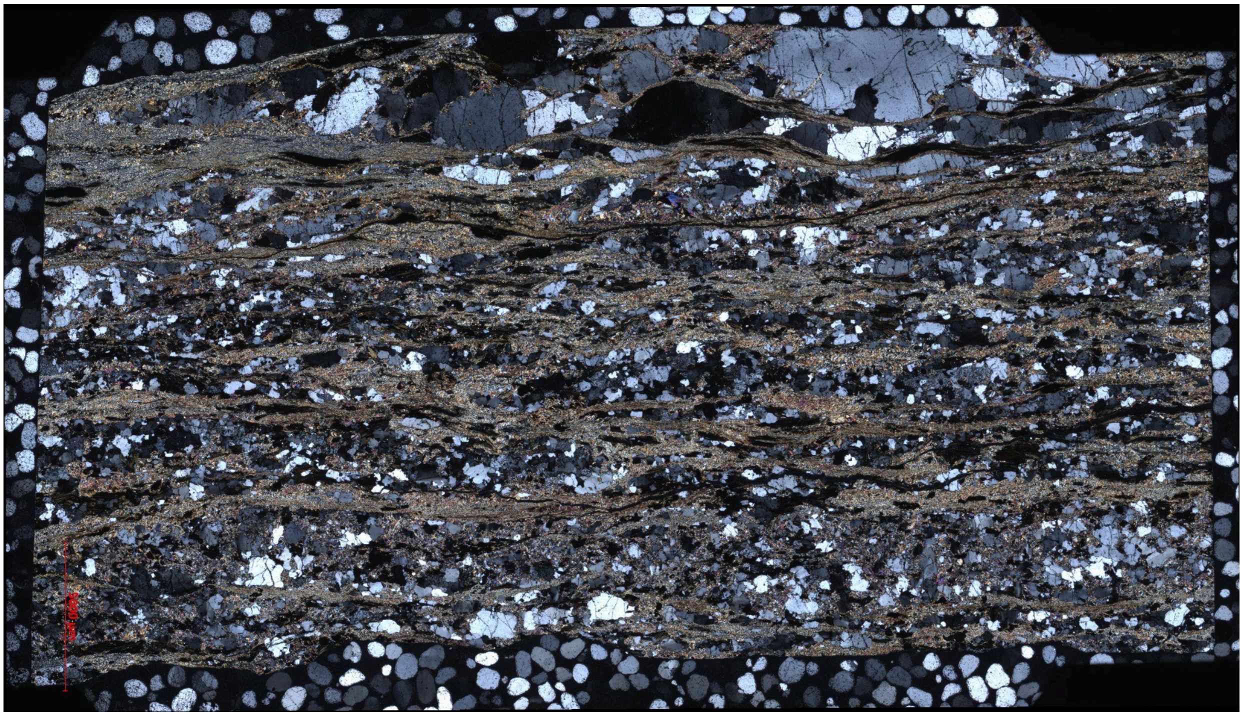
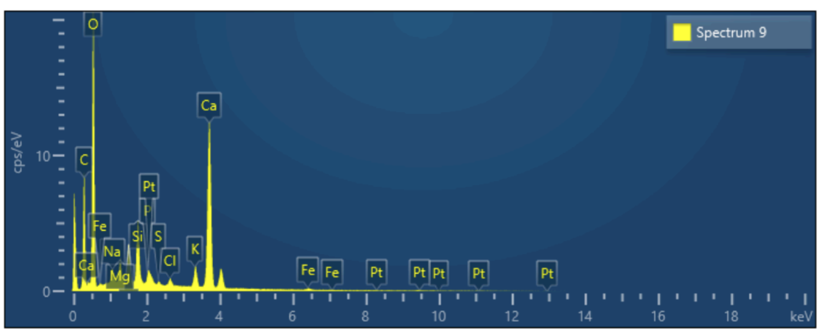


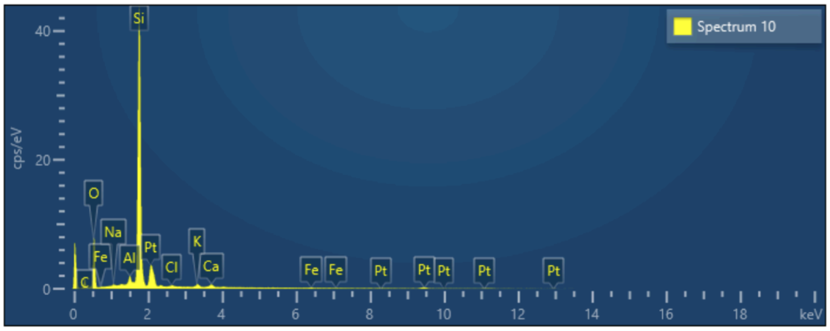
Image 9: Mosaic of rock sample seen as a thin section under cross polarized light (XPL). XPL was used to help determine the mineralogical composition of the rock.



Spectrum 9

Element	Line Type	Weight %	Weight % Sigma	Atomic %
C	K series	32.34	0.43	42.97
O	K series	48.35	0.35	48.24
Mg	K series	0.92	0.03	0.60
Al	K series	1.34	0.03	0.79
Si	K series	2.11	0.04	1.20
K	K series	1.23	0.03	0.50
Ca	K series	11.95	0.11	4.76
Na	K series	0.73	0.04	0.51
Cl	K series	0.30	0.02	0.14
Fe	K series	0.36	0.05	0.10
P	K series	0.24	0.02	0.12
S	K series	0.12	0.02	0.06
Total		100.00		100.00

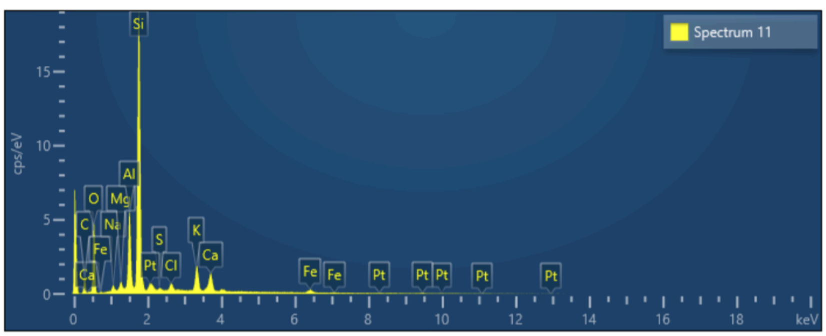
Image 10: SEM graph taken in SE showing the range of elemental composition in the pika urine powder.



Spectrum 10

Element	Line Type	Weight %	Weight % Sigma	Atomic %
C	K series	30.23	1.07	42.93
O	K series	32.77	0.57	34.94
Si	K series	33.86	0.54	20.57
Al	K series	0.91	0.05	0.57
K	K series	0.72	0.05	0.31
Ca	K series	0.76	0.05	0.32
Cl	K series	0.23	0.04	0.11
Fe	K series	0.33	0.10	0.10
Na	K series	0.20	0.04	0.15
Total		100.00		100.00

Image 11: SEM graph taken in SE showing the range of elemental composition in the unweathered center of the rock.



Spectrum 11

Element	Line Type	Weight %	Weight % Sigma	Atomic %
O	K series	30.88	0.48	33.93
Al	K series	5.86	0.10	3.82
Si	K series	22.68	0.32	14.20
K	K series	3.97	0.09	1.79
Ca	K series	3.24	0.08	1.42
C	K series	29.24	0.92	42.80
Cl	K series	0.86	0.04	0.43
Na	K series	0.62	0.04	0.47
Mg	K series	0.62	0.04	0.45
Fe	K series	1.81	0.12	0.57
S	K series	0.21	0.04	0.12
Total		100.00		100.00

Image 12: SEM graph taken in SE showing the range of elemental composition at the boundary of the pika urine and the rock surface.

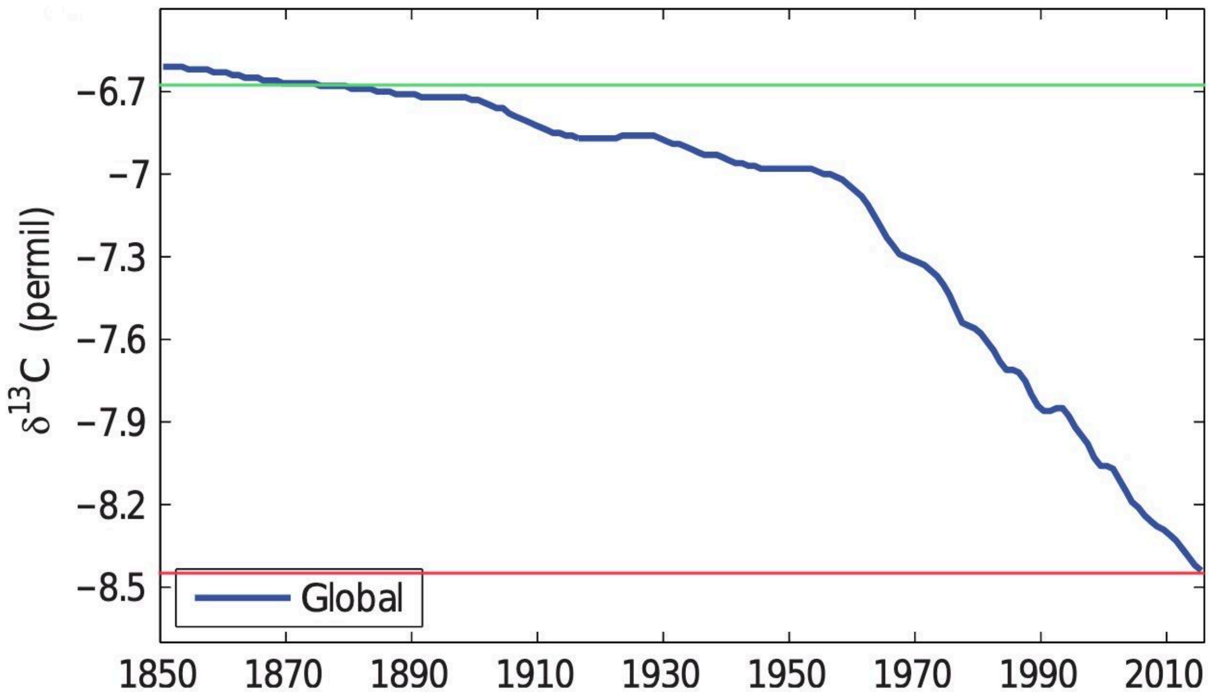


Image 13: Graph of the annual global mean $\delta^{13}C$ repurposed from Graven et al, showing the change in $\delta^{13}C$ over time. The green line represents the value at NWT-23-PPB and the red line represents the value at NWT-23-PPS.

<u>Postliminary Results</u>

Data was received regarding the $\delta^{15}N$ values after the defense date. The results, as well as comparative data from Yi, 2006 are listed below.

Tested Area	**$\delta^{15}N$**
Pika Fur (Yi 2006)	2.68‰

Pika Bone Collagen (Yi 2006)	2.6‰
Atmosphere (Yi 2006)	Around 0‰
Plants (Yi 2006)	<0‰
Our Data	0.38-1.5‰

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