

CHANGES IN MINERAL-SOIL ORGANIC MATERIAL POST WILDFIRE IN A ZERO
ORDER BASIN

By

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A Thesis Submitted to The Honors College

In Partial Fulfillment of the Bachelors degree
With Honors in

Geosciences

THE UNIVERSITY OF ARIZONA

MAY 2021

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Abstract

Carbon sequestered in soils generally exceeds that in living flora. Therefore understanding carbon dynamics and storage is critical to developing a better understanding of the global carbon balance and flux. The relationship between carbon character and the mineral-organic moieties controls short and long-term carbon cycling. Wildfire returns the above-ground carbon to the subsurface, whereby it supplies essential nutrients or remains energetically unfavorable to microbial respiration. The response of the soil post-wildfire was investigated in this study. Soil samples from nested pits were collected in a zero-order basin located within the Jemez River Basin Critical Zone Observatory, NM USA, with a >50 year fire-free history, before and after a natural fire. Sampling included 2011 samples (pre-fire), 2013 (directly post-fire), and 2015 (post-fire) at nearly identical locations and depths to compare wildfire effects on soil composition, carbon character with depth, and mineral-soil organic matter (SOM) interaction. Mineral-SOM interaction was characterized by transmission Fourier transform infrared (FTIR) spectroscopy, an essential tool for providing insight into SOM composition with the ability to observe small changes in organic complexes, especially SOM-mineral functional groups. FTIR spectroscopy exploits the response from infrared (IR) radiation active molecules in the mid-IR range ($600\text{-}4000\text{cm}^{-1}$). An absorbance of an IR active molecule is observed as energy transferred via vibrations, rotations, and bending of the molecule. This study will augment quantitative data collected on the pyrogenic carbon (PyC) (Pohlmann et al., separate study) to elucidate connections between OM-mineral interactions, short and long-term carbon storage (as biochar) and wildfire. By comparing the SOM character as a function of time, depth, and in response to a natural but significant perturbation, a better understanding can be developed on how mineral-OM interactions change when subjected to wildfire.

Introduction

Carbon is essential in all living things and can act as a building block, as in organic material, or as a necessary component of life sustaining greenhouse gasses. Both organic and inorganic processes can be beneficial or detrimental depending on the carbon balance. Soil acts as a carbon storing machine, storing more carbon in the subsurface than in the above ground flora (Ontl et al. 2012). Though there are a lot of studies on soil carbon and organic matter, there is still much to learn about the mechanisms of soil response to wildfire. With increasing drought, which promotes prolonged periods of high severity wildfires, it is vital that the responses of soil dynamics post wildfires be studied and better understood. Higher severity wildfires have negative effects on the environment, including nutrient volatilization, increased erosion rates, and major decrease in organic material (Certini 2005). Mineral-soil organic material (SOM) interactions key components in nutrient sequestration in the topsoil. By exploring the interactions between the minerals and the SOM post wildfire, more can be brought to light about the carbon cycle. This study examined soil samples from both pre and post wildfire in a zero order basin (ZOB), to determine if there are any consequential changes occurring at the SOM-mineral surface, the interface of living and nonliving components in the environment. A Fourier transform infrared (FTIR) spectrometer was used to analyze the soils at the molecular level. By investigating the molecular building blocks of the organics and inorganics in the soil, we will learn how soil responds to an imposed stress like fire, and investigate possible mechanisms for its response.

Location Description

Soil samples were collected at Redondo Peak, which is located in north-central New Mexico, USA, about 80km north of Albuquerque (Figure 1). Redondo Peak lies within the Valles Caldera National Reserve, at the Jemez River Basin Critical Zone Observatory (Figure 2). The site is a zero order basin, where there is little to no sediment deposition imported from surrounding areas. This site had not experienced a wildfire for >50 years, until the Thompson Ridge Fire in 2013. The site contains both grasslands and wooded areas, all along an elevation gradient (Figure 3).



Figure 1. Satellite image of the study site, with state boundaries superimposed. The site is approximately 80km north of Albuquerque, New Mexico. Source: Google Maps

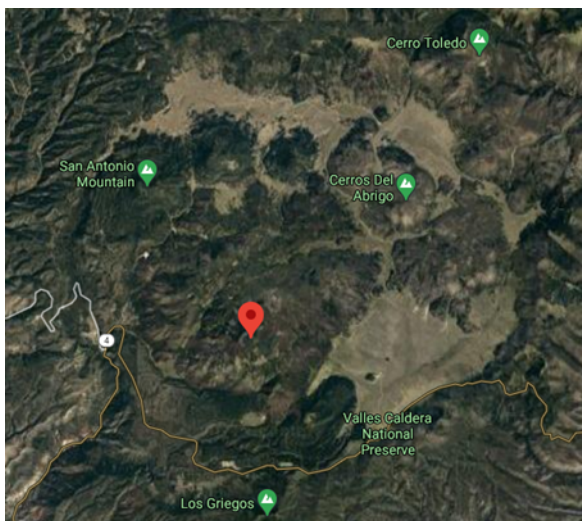


Figure 2. Satellite image of the Valles Caldera, with Redondo Peak (red marker) in the center. The caldera is roughly 21 km in diameter, with resurgence domes observable surrounding the rim of the caldera. Source: Google Maps

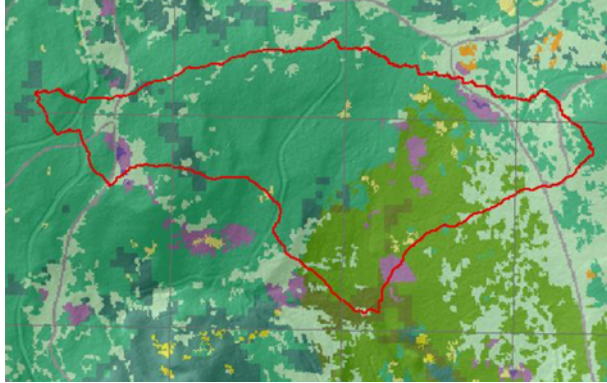


Figure 3. Vegetation map of the zero order basin in the Jemez River Basin Critical Zone Observatory. Provided by the Santa Catalina and Jemez River Basin Critical Zone Observatory.



Geology

Redondo Peak is located in the Valles Caldera, which was an active supervolcano from 1.61 to 1.47 Ma, and 1.22 to 1.12 Ma (Moravec et al. 2020). The caldera is 21 km in diameter. The region is dominated geologically by andesite, rhyolites, and tuff. The initial two eruptions filled the region with the Bandelier Tuff, which is prevalent in lower elevation of the study site.

Redondo peak itself is a resurgence dome, one of several within the larger caldera (Figure 2).

The study area consists of tuff, alluvium, siliciclastic units such as sandstone, and low temperature, silica rich igneous units from the original eruptions (Figure 4). The soil sampling location in the ZOB was selected to investigate in place soil diagenesis without imported sediments from up radiant watersheds. The lack of sediment deposition in the ZOB sampling area ensures that all soil, mineral, and rock types studied are native to the location.

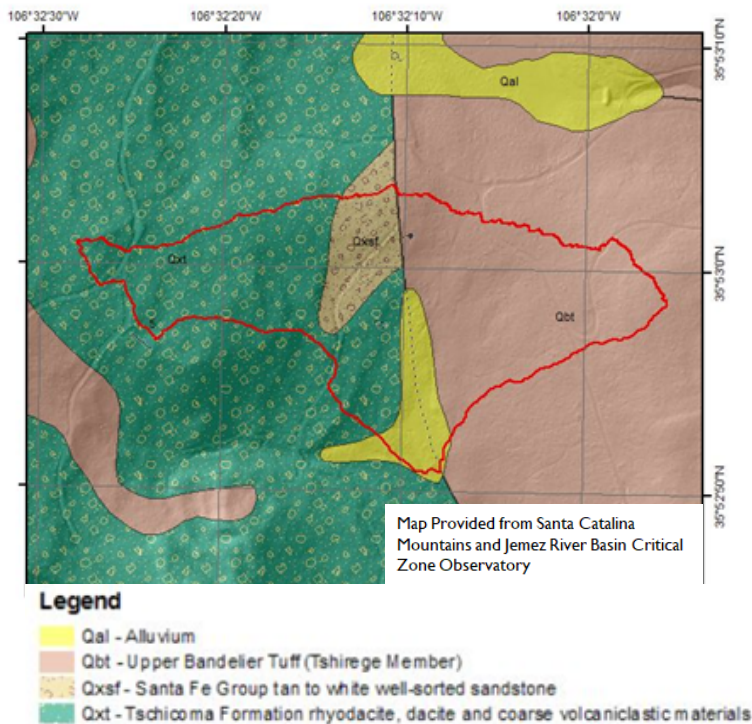


Figure 4. A geologic map of the study site.

Materials and Methods

Soil samples were collected both pre and post fire. The pre-fire samples (the fire was not part of the original sampling or investigating plan), were collected in 2011. The Thompson Ridge Fire started May 31, 2013, and burned about 30km^2 (7476 acres) in the Valles Caldera National Preserve. Immediately after the fire in 2013, a second set of soil samples were collected. Samples were collected from multiple depths across a soil profile in soil pits at the site (figure 5). For this study, only two depths were used to compare SOM pre and post fire. The first was the 0-2cm topsoil, and the second was the 2-4cm deeper soil. As SOM decreases exponentially with depth, samples below 4 cm were less likely to show measurable changes in SOM or mineral-SOM

moieties from the fire and were not investigated here. A Fourier transform infrared (FTIR) spectrometer was used to analyze the soil samples (Nicolet iS50, Thermo Fisher Scientific). In order to get full transmittance through the soil sample with the infrared energy range, the soil was pressed into pellets. A 1:50 ratio of soil to KBr was ground together with a mortar and pestle to homogenize, and subjected to nine tons of pressure in order to turn the samples into a glass pellet. KBr was specifically used to bind the soil because it is IR inactive across the wavenumbers collected and only active below the FTIR minimum range of 400 cm^{-1} . Pellets were scanned by transmission FTIR one at a time, averaging a total of sixty scans per sample. Spectra was collected in the mid-IR range from 400 to 4000 cm^{-1} using a KBr beam splitter and DTGS detector. Sample spectra were grouped together based on location, depth, and collection year. Pre and post fire spectra from proximal soil pits were compared to each other to observe any changes in the inorganic and organic compounds. Data processing including averaging, normalizing and background subtraction was via manufacturer FTIR software package OMNIC (Thermo Fisher Scientific). Normalized spectral subtractions of pre and post fire samples from the same location were performed to isolate changes in the organic compounds in the soil with the assumption that the mineralogy would be constant (one of the first changes of mineralogy would occur no less than 500°C) and any changes in the spectra would be due to changes in the soil organic fraction (Tan et al. 1986). These observed changes in the compounds of each pit were compared across the research site pits to see how the Thompson Ridge fire affected the different regions with the ZOB.

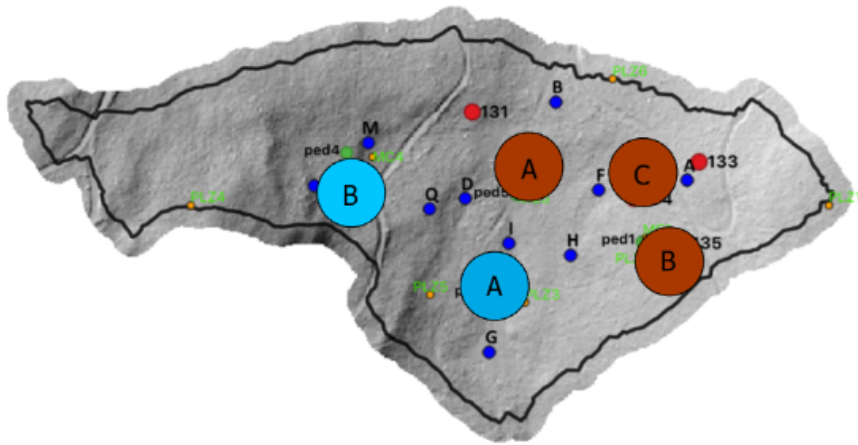


Figure 5. Location map of soil pits in the ZOB. The blue colored markers are pits at the higher elevation and lower burn severity, whereas the orange colored marker designates the lower elevation, higher burn severity pits.

Results

Samples were used from five different pits sampled each year. Three of those pits were spread out across the lower elevation region of the site, while the other two pits were located in the higher elevation area (Figure 5). The lower and higher elevation pits differ slightly in both their SOM and inorganic materials. Figure 6 explains the major spectral regions being observed in the soil samples. There are a lot of overlapping IR signals and assigning a specific peak to a specific functional group requires a comprehensive investigation, but for the purpose of this study we have designated regions as numbers. #1 is interpreted to be hydroxyl (OH) groups associated with minerals and clays, #2 is the broad O-H stretch region inclusive of alcohol O-H, carboxylic O-H, and H-O-H of water. #3 is a symmetric C-H stretch, while #4 is an asymmetric C-H stretch. #5 is a C=C peak, and #6 symmetric C-H stretch. #7 was determined to be dominated by Si-O mineral vibrations in the soil samples investigated. After examining the pre and post fire samples the operationally assigned inorganic peaks as assumed constants (i.e. assuming mineral

abundances and species would not be affected by wildfire), it was interpreted that the major peak #7 is inorganic Si-O, with a C-O peak shouldering out post burn. More needs to be performed in order to better classify the peak wavelengths in the fingerprint region ($400\text{-}1500\text{ cm}^{-1}$), however peaks in this range are currently dominated by mostly inorganics, with some notable organic molecular bends.

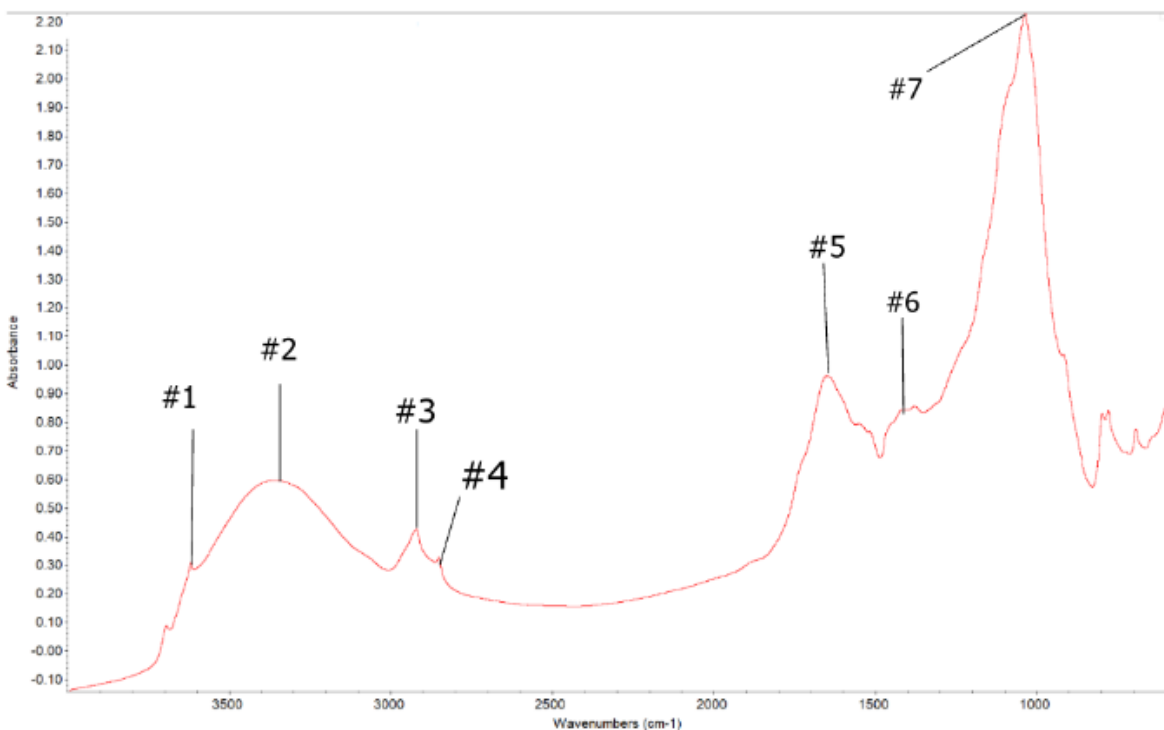
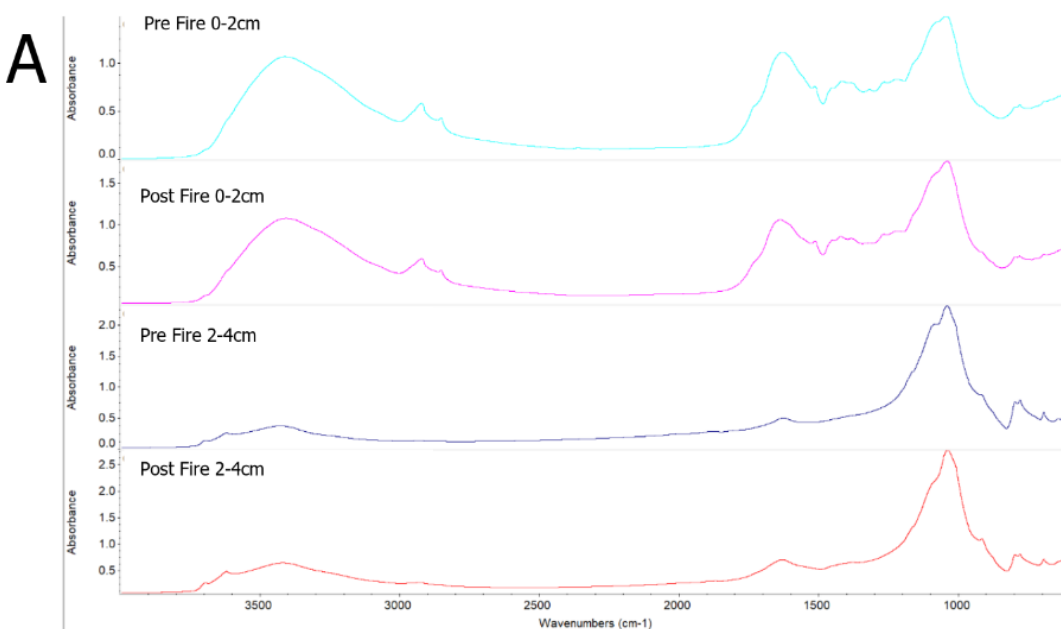


Figure 6. Delineation of the spectral regions defined for this study. See Results section for complete description of the different numbered peaks.

The first set of samples analyzed were the higher elevation, lower burn severity samples (Figure 7A, mapped in Figure 5). In the higher elevation pits, there were not pronounced clay peaks associated with the O-H stretch in the $>3500\text{ cm}^{-1}$ range. There were noticeable changes post fire; however, the largest changes in the soil organics were associated with depth, which

exhibited a relatively large decrease in all of the peaks assigned to organic groups. Post fire, the broad O-H carboxylic peak decreased, along with the symmetric and asymmetric C-H stretching at 3000-2800 cm^{-1} . The C=C aromatic peak increased relative to the other peaks, and the surrounding organic peaks decreased substantially. Also observed post fire, the Si-O developed a shoulder, which could be a C-O peak that was not identified before due to overlapping inorganic peaks. The inorganics at lower wavenumbers did not show any noticeable change (Figure 7A).



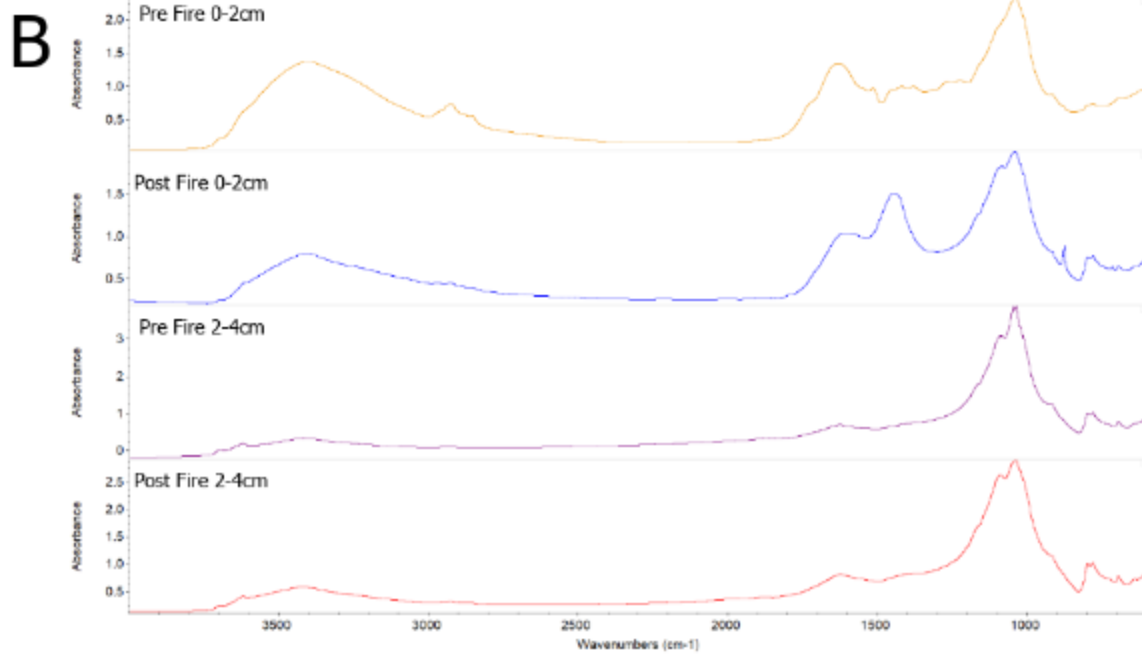
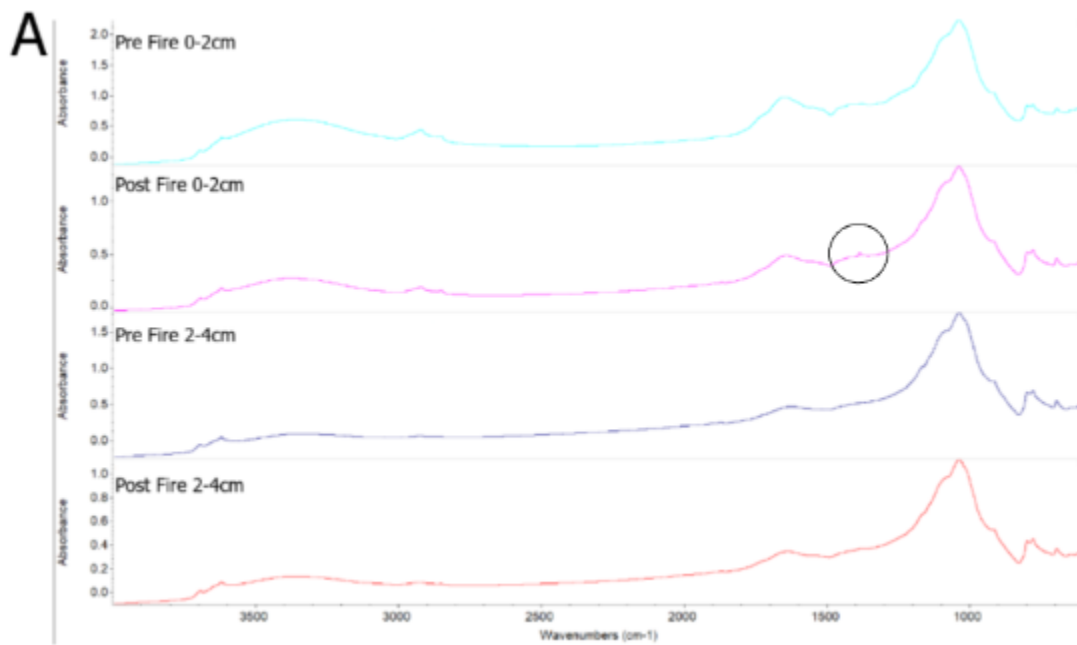


Figure 7. A and B represent the spectral data for the higher elevation, lower burn severity regions of the fire. See figure 4 for the locations of the soil pits in blue labeled A and B.

The second set of samples analyzed were from the lower elevation, higher burn severity soil pits (Figure 7B). The pits in the lower elevation regions of the ZOB site contained a more pronounced clay peak near $3650\text{-}3600\text{ cm}^{-1}$ range, which could be indicative of both the surrounding soil type and weathering. Post fire, there was again an observed decrease in the O-H carboxylic peak, along with the symmetric and asymmetric C-H peaks ($3000\text{-}2800\text{ cm}^{-1}$). In the lower elevation, severe burn regions, there was a considerable decrease in the C=C aromatic peak ($1700\text{-}1600\text{ cm}^{-1}$), which differs from the higher elevation post fire samples. Near the C=C peak, a new peak was observed post fire, which has been interpreted to be from the nitrate

v3 vibration band around 1359 cm^{-1} (Figure 8, circled to highlight). Similar to the higher elevation samples, the Si-O peak develops a shoulder post-fire around 1100 cm^{-1} .



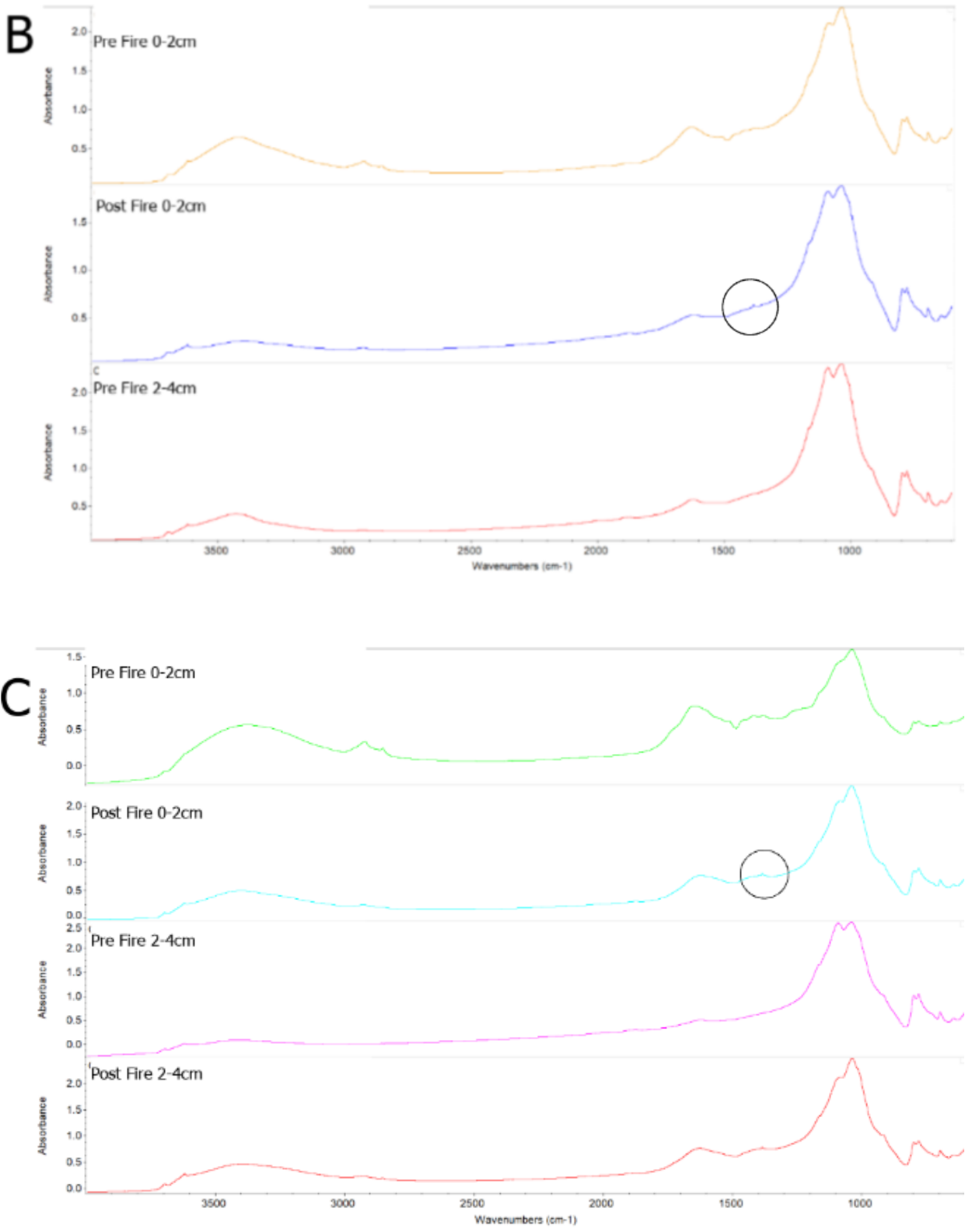


Figure 8. FTIR spectra of the three soil pits located on the lower elevation, higher burn severity region of the ZOB site. The circled peak is assigned to a ν_3 vibration band assigned nitrate, which was not present pre fire and was observed only in the lower elevation pits. See figure 4 for precise locations of the sampling for A,B and C.

Discussion

As expected, there was a clear decrease in the organic material post fire. In the higher elevation pits, a clear clay peak was lacking, as seen in the lower elevation soils. This is likely due to the parent rock material. The lower elevation soils developed over the Bandelier tuff (figure 4), which weathers to form clays, e.g. illite and smectite. The formation of the inorganic nitrate peak in the higher severity burn regions was interesting. The formation of the nitrates could indicate that the fire intensity was lower. Previous studies have found that nitrogen has a lower volatilization temperature range from around 200-375°C (Hosking 1938). It was expected that the nitrogen that was not volatilized could have broken its bonds to soil organic compounds, and would have been reworked into the soil as a more accessible fertilizer. Soils beneath the burn stand can show as much as twice the amount of nitrogen post burn, due to alteration of organic materials such as humus to inorganic nitrates (Neary 2004). The first inorganic form of nitrogen that is produced post fire is ammonium (Covington 1992). This, over time, degrades into nitrates (Covington 1992). Additional research could consist of analyzing soil samples from later years, and comparing nitrate values to test this module. A study done by (Keiluweit et al. 2009) performed a controlled burn on both wood and grass, analyzed the samples with multiple instruments including an FTIR observing the ATR-FTIR spectra. The spectra showed similar decreases in the O-H carboxylic peaks, symmetrical/asymmetrical C-H peaks, and the aromatic C=C peaks. This similar decrease occurred between the combustion temperatures of T=300°C and 400°C. This temperature was similar to the maximum nitrogen volatilization temperature of 375°C. This is consistent with a fire intensity that was lower, and could have been around 300-400°C in temperature.

More experimentation needs to be performed to better identify the changes in organic molecules post wildfire. (Margenot et al.) states that the inorganic peaks in the FTIR soil samples can interfere with the organic peaks. A solution is to oxidize out the organics using sodium hypochlorite. This will produce a more clear spectrum of the inorganics, which will then be subtracted out from the organic peaks from the earlier tested samples. This should produce a more clear picture of how the organics are being affected from the fire.

Conclusion

The two soil groups tested differed slightly in organic and inorganic composition. The higher elevation soil pits did not contain a clay peak at $3650\text{-}3600\text{ cm}^{-1}$, unlike the lower elevation, higher burn severity soil pits. The higher elevation soil samples experienced a larger decrease in organics as a function of depth rather than post fire. In the lower elevation, higher burn severity region of the ZOB, clay peaks were present around $3650\text{-}3600\text{ cm}^{-1}$. An inorganic vibrational nitrate peak was observed post fire. The presence of a nitrate post fire could be indicative of fire intensity, which would mean that fire intensity was lower, fitting between the $300\text{-}400^\circ\text{C}$ temperature range. Comparing spectra from both soil test groups, changes to the organics post wildfire ($3600\text{-}1200\text{ cm}^{-1}$ range) saw considerable decreases at the 0-2 cm depth. The 2-4 cm depth soil samples did not see much change post wildfire. In 0-2 cm depth soil samples, peak #7 (figure 6) shouldered out into two separate peaks. The second peak (around 1100 cm^{-1}) could be C-O initially covered by inorganic interference. More testing will need to be performed to discern how much inorganics are interfering with the organic peaks.

Acknowledgments

I would like to give a special thanks to everyone who has helped me conduct this study

First, I would like to thank my advisor, Dr. Jon Chorover, who helped me through the entirety of the study. Dr. Chorover presented me with the opportunity to work with him and his lab, and I was able to learn a great deal from this experience.

I would also like to thank Dr. Rob Root. Rob was in the lab helping me throughout the entire experiment. Besides that, he also was always willing to answer any questions that I may have, along with helping me edit this thesis.

I would like to thank Dr. Bryan Moravec, who was one of the first people that I got to work with in the lab. Bryan helped me jumpstart this study, answered any questions that I had, and also helped me prepare samples to run through the FTIR.

I would like to thank Michael Pohlmann, who was responsible for providing me with samples to work with in the first place. Michael also was able to answer questions about specific samples, and compare some of his research with my current project.

Lastly, I would like to thank the countless others who helped me with my project. This definitely would not have been possible without an amazing team of people constantly helping and providing insight into the study.

References

- Certini, G. Effects of fire on properties of forest soils: a review. *Oecologia* 143, 1–10 (2005). <https://doi.org/10.1007/s00442-004-1788-8>
- Coates, J. (2006). Interpretation of Infrared Spectra, A Practical Approach. In *Encyclopedia of Analytical Chemistry* (eds R.A. Meyers and M.L. McKelvy). <https://doi.org/10.1002/9780470027318.a5606>
- Covington WW, Sackett SS (1992) Soil mineral nitrogen changes following prescribed burning in ponderosa pine. *For Ecol Manage* 54:175–191
- Marco Keiluweit, Peter S. Nico, Mark G. Johnson, and Markus Kleber *Environmental Science & Technology* 2010 44 (4), 1247-1253 DOI: 10.1021/es9031419
- J.-D. Mao, R. L. Johnson, J. Lehmann, D. C. Olk, E. G. Neves, M. L. Thompson, and K. Schmidt-Rohr *Environmental Science & Technology* 2012 46 (17), 9571-9576 DOI: 10.1021/es301107c
- Moravec, B. G., White, A. M., Root, R., Sanchez, A., Olshansky, Y., Paras, B. K., et al. (2020). Resolving deep critical zone architecture in complex volcanic terrain. *Journal of Geophysical Research: Earth Surface*, 125, e2019JF005189. <https://doi.org/10.1029/2019JF005189>
- Neary, D.G. *An Overview of Fire Effects on Soils*, 2004. Southwest Hydrology Santa Catalina Mountains and Jemez River Basin Critical Zone Observatory. <https://czo-archive.criticalzone.org/catalina-jemez/infrastructure/field-area/jemez-2013-burned-zob/#czoTab6>
- Ontl, T. A. & Schulte, L. A. (2012) Soil Carbon Storage. *Nature Education Knowledge* 3(10):35
- Tan KH, Hajek BF, Barshad I (1986) Thermal analysis techniques. In: Klute A (ed) *Methods of soil analysis. 1. Physical and mineralogical methods*. American Society of Agronomy and Soil Science Society of America, Madison, WI, pp 151–18