SEM-EDX Analysis of
Aerosol Samples

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Abstract

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One of the important environmental issues in upstate New York is the acid rain problem in the Adirondack Mountains, which is associated with atmospheric aerosols. As a part of a systematic study to understand the transport, transformation, and effects of airborne pollutants in the Adirondack Mountains, we are performing an analysis of atmospheric aerosols collected at Piseco Lake. In previous work, we used proton induced X-ray emission (PIXE) [1] spectrometry to measure the concentrations of elements in aerosol samples as a function of the size of the particulate matter. The results of the PIXE analysis indicate significant concentrations of sulfur in small particles that can travel great distances and may contribute to acid rain. Here we report on the investigation of the small-particle aerosol samples using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) to obtain elemental information on individual particles. Many of the particles contain large concentrations of sulfur and oxygen that may indicate the presence of sulfur oxides from industry and coal combustion that are known contributors to acid rain, but they are not always in the same ratio. There are also many particles that contain significant concentrations of elements commonly found in soil (Al, Si, K, and Ca).

1 Introduction

1.1 Previous Research and Motivation

One of the current research projects in the Union College Ion-Beam Analysis Laboratory has focused on the study of atmospheric aerosols in the Adirondack Mountains. An important environmental issues in upstate New York is the acid rain problem in the Adirondack Mountains, which is associated with atmospheric aerosols. We did this research to better understand the atmospheric aerosol pollution around the Adirondacks. The issue was first discovered about thirty years ago, but according to data from Department of Environmental Conservation (DEC) the situation is getting a little bit better. By 2007, the pH value of the rain at Piseco Lake in the Adirondacks was measured to be 4.77, which makes the rain no longer classified as acid rain, but still the pH value is pretty low and may produce chronic acidification of lakes and soils. The best way to solve the problem of acid rain is to identify the atmospheric aerosol pollution around the Adirondacks and using the data, to trace back to the source of pollution. Therefore, we did our research on airborne particulate pollution with different particle sizes near Piseco Lake, located in the Adirondack Mountains.

As part of a systematic study to understand the transport, transformation, and effects of airborne pollutants in the Adirondack Mountains, in 2012 we obtained air samples from Piseco Lake and analyzed particulate depositions with proton induced X-ray emission spectrometry (PIXE) [1]. In the PIXE experiments, samples were bombarded with 2.2-MeV proton beams from the Union College Pelletron Accelerator and the energy spectra of the X-rays were measured with a silicon drift detector. The X-ray energy spectra were analyzed using GUPIX software to extract the elemental concentrations of the particulate matter (PM). We found significant concentrations of sulfur for PM 0.25-2 μm, characteristic of coal combustion and industry, and large concentrations of Fe and K, Si, Ca at larger particle sizes ($\frac{1}{2}$-8 μm) that are most likely due to soil.

Now we are analyzing the samples using a scanning electron microscope (SEM), along with energy dispersive X-ray spectroscopy (EDX) to identify the particular elements in individual particles and their relative proportions instead of the concentration for each element contained in the whole sample. By doing this, we can have a better clue on the sources that contribute the most to the significant concentrations of sulfur.

1.2 SEM

A scanning electron microscope (SEM) is an instrument that produces a magnified image of a sample by scanning it with a focused beam of electrons [2]. In SEM, an electron gun fitted with a tungsten filament cathode and placed at the top the microscope thermionically emits a beam of electrons. The emitted electrons are focused along a vertical path by an anode. Then electromagnetic fields and lenses are set along the vertical path of the beam to focus the beam down toward the sample. Shown in Figure 1 is a schematic diagram of the scanning electron microscope.

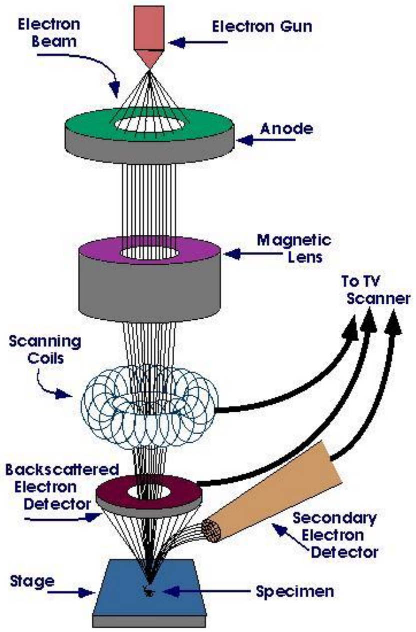

Figure 1. A schematic diagram of the scanning electron microscope [3].

When the electrons strike the sample, they interact with atoms in the sample both elastically and inelastically. During an elastic interaction, the trajectory of the electron is changed without energy loss, where most of the backscattering electrons are created. In inelastic scattering, signals can be detected; the most common are due to secondary electrons and characteristic X-rays. Secondary electrons and backscattered electrons are the two major types of signals commonly used for imaging. The secondary electrons are the most common imaging signal used for demonstrating the morphology and topography of the sample, while the backscattered electrons are more useful when imaging multiphase samples. Secondary electrons are ejected from the K-shell of the atoms in samples by inelastic scattering. These electrons have relatively low energy (< 50 eV) and are emitted within a few nanometers from the sample surface, so they are best for imaging the outer surfaces of samples and are usually collected by an Everhart-Thorley detector. After being collected, the electrons are accelerated to activate a scintillator or phosphor to emit flashes of light. These emitted signals are then amplified and transformed into electrical signal outputs used for producing digital images.

1.3 EDX

Energy dispersive X-ray spectroscopy is a non-destructive method of examining samples for their elemental makeup using X-ray emitted by bombarding a solid sample with a focused beam of electrons. This process involves an electron interaction with an atom causing the inner shell electron from the atom to be ejected. Then a vacancy is created that is filled by an electron from a higher electron orbit. To fill this vacancy, the electron with higher order needs to de-excite. During this process, an X-ray will be emitted to conserve energy. Shown in Figure 2 is a schematic diagram of this process. The energy of this X-ray generated from each element is unique, so we can determine what element the X-ray is emitted from. The intensity of the X-ray line is proportional to the concentration of the element.

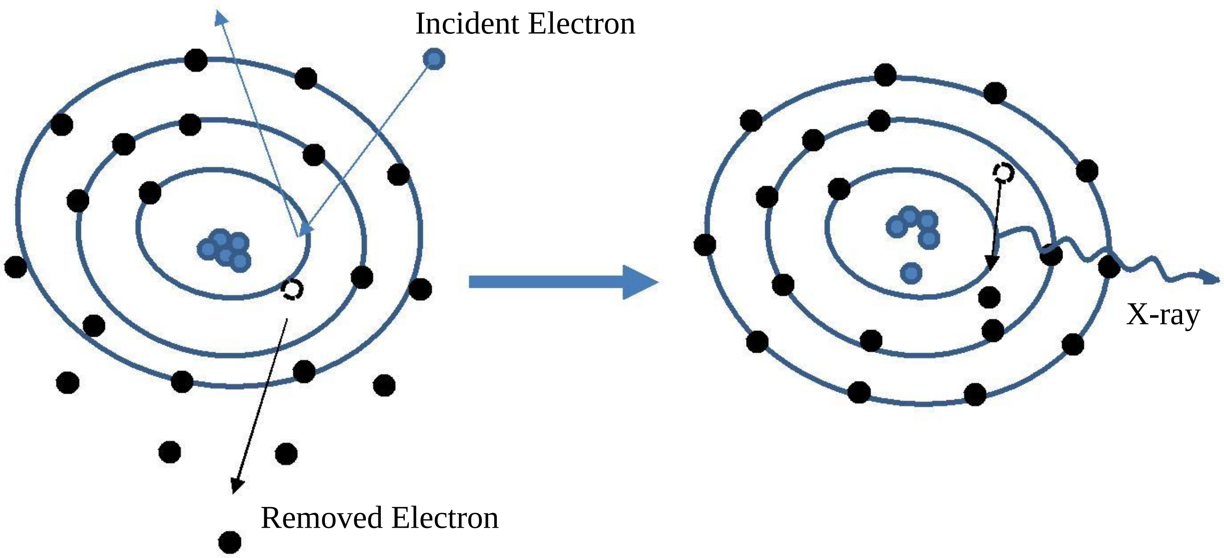

Figure 2. A schematic diagram of showing the process in which an X-ray is emitted from an atom when an inner-shell electron is ejected [4].

2 Procedure

2.1 Collection and Preparation of Samples

We collected aerosol samples near Piseco Lake in the Adirondack Mountains. We did this to test the composition of the pollution in the air samples in order to try to identify the source of aerosol pollution. To collect our aerosol samples we used a PIXE International [*3*] nine

stage cascade impactor shown in Figure 3. The impactor works by pulling air, at a rate of 1L/min, through 9 stages that separate particles based on their aerodynamic size. The aerodynamic cutoff size of the collected particles ranges from 0.06µm (stage L1) to 16µm (stage 7). The collected particles in each stage are deposited onto 7.5µm thick Kapton foils. Shown in Figure 4 is a microscope image of the deposit on one of the Kapton foils.

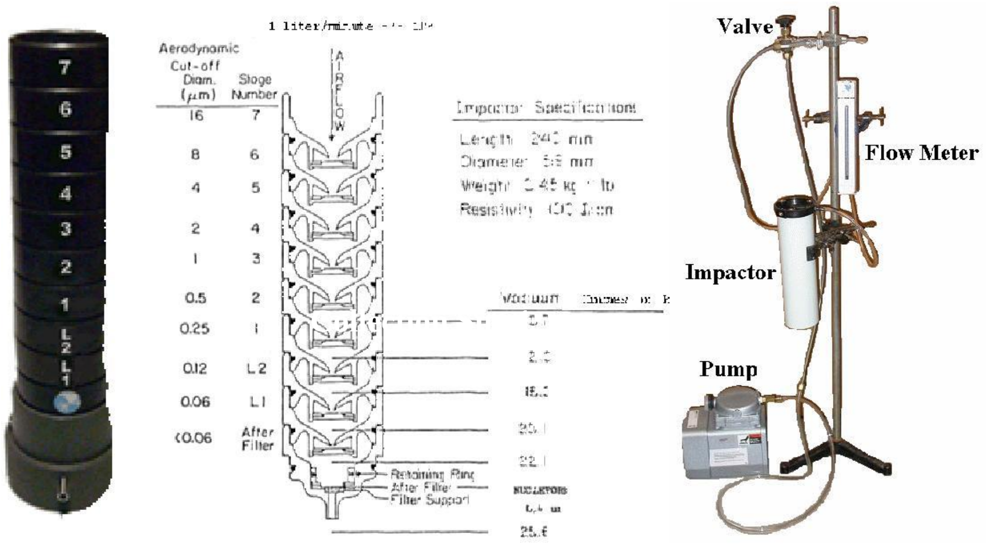

Figure 3. On the left is a picture of the nine stage cascade impactor which works by drawing air from the top and pulls the air through the 9 stages. The middle is a schematic diagram showing the cross-section of the impactor along with aerodynamic cutoff particle size for each stage. The picture on the right shows the impactor installed in the sampling system [5].

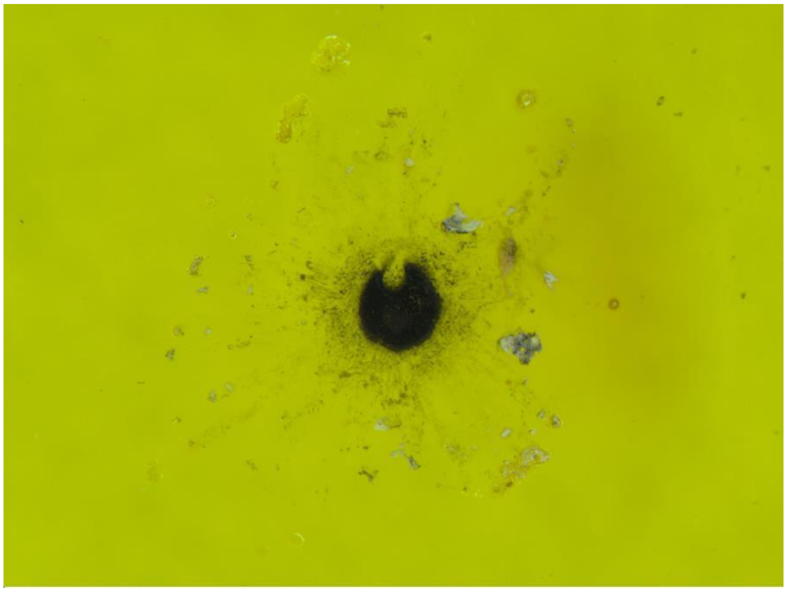

Figure 4. A microscope image of the deposit on one of the Kapton foils.

2.2 SEM Image Acquisition

For this experiment, we used a scanning electron microscope (SEM), shown in Figure 5, to produce images of the sample by scanning it with a focused beam of electrons. The SEM has a Bruker Quantax 200 EDX system with a Peltier-cooled XFlash silicon drift detector for X-rays. The detector has an active area of 10 mm^2. It has an energy resolution of better than 125 eV at count rates up to 60,000 cps. A photograph of the inside structure of the SEM is shown in Figure 6. As shown in Figure 6, the secondary-electron (SE) detector is located behind and to the left of the electron lens pole piece. Secondary electrons have relatively low energy and are emitted from the upper several nanometers of the material under the electron beam, so the wire cage around the end of the detector is usually set to a positive "bias voltage" of hundreds of volts to collect the secondary electrons even if they exit the sample traveling away from the detector. This also makes the SE detector able to produce images at very low probe currents which has a positive effect on the resolution. However, the image result is a gray scale due to the fact that the detector only measures the number of electrons hitting it.

Figure 5. A photo of the SEM/EDX [6].

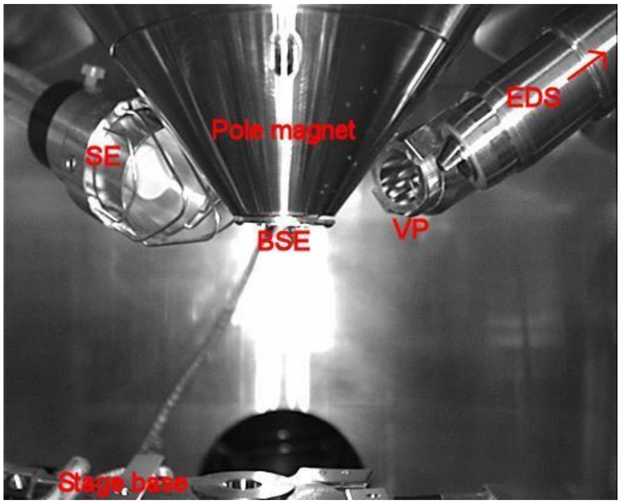

Figure 6. A photo of the inside structure of the SEM/EDX [6].

To find the optimum input parameters used during SEM/EDX imaging, we first tried to image a copper tape. In setting up the instrument for best imaging, we need to adjust a couple of parameters. The very first thing to adjust is the probe current. The lower the probe current the better the resolution will be. Therefore, we usually start around 100 pA and a detector bias voltage of +420 V.

Second, we need to adjust the beam voltage to suite the sample. High voltages can give better resolution, since high voltage means the electrons have shorter wavelength, but they can also penetrate the surface and provide electrons from material behind the sample, especially for the aerosol samples we collected, which are thin and have low average atomic number. Therefore, in most cases the accelerating voltage for a particular X-ray line should be about three times the critical excitation voltage for that line. However, since we are dealing with samples containing more than one single type of element, it is obviously impossible to have the optimum voltage for every element, so compromises must be made. In general, 20-30 kV is used for metals, 15 kV for oxides and silicates, and 5-10 kV for analysis of light elements. Some adjustments were made within the range during the experiments based on experience.

The third thing that we need to adjust is the contrast. Unlike voltage and current, the contrast cannot be adjusted directly, but it can be increased by increasing the current. Therefore, it is always increased at the expense of maximum resolution. For a given amount of contrast inherent in the signal, a certain minimum beam current is required to distinguish features from random background noise. This threshold current can be calculated as

$$I_b > \frac{4 \times\ 10^{-18}\ coulomb}{C^2 \varepsilon t}$$

where C is the contrast value, t is dwell time per pixel and ε is the electron collection efficiency.

Once we find the minimum current required by contrast, we can tune to optimize resolution. Since features smaller than the beam spot size cannot be resolved, the voltage needs to be adjusted to decrease the minimum spot size at constant current until the voltage is too large and might penetrate the sample.

2.3 Sample Preparation

Since our sample is non-conducting, a thin conductive coating is required. One of the most often used coatings is carbon, but for this experiment, we chose another common coating, gold-palladium, because carbon coatings are usually too thick for high resolution imaging and works better with polished spheres. Another reason is that gold-palladium alloy coating has a high atomic number which generates a lot of secondary electrons. To coat the samples, we used a Denton Vacuum deck IV standard sputter coater, and we coated the samples for 20s under 20V. The sputter coater is shown in Figure 7.

Figure 7. The Denton Vacuum deck IV standard Sputter Coater at Union college [7].

3. Results

Shown in Figure 8 is a graph of the measured concentrations in mass per unit area for each element as a function of particle size determined from the PIXE analysis for the samples collected in July of 2012 [6]. In the graph, we can see that the sulfur concentration peaks at aerodynamic cutoff diameter between ¼ and 2 μm. To investigate the morphology of these aerosol particles, we used SEM-EDX to analyze the samples collected on stage 2 and stage 3 which have aerodynamic cutoff diameter of ½ and 1μm respectively. The goal is to try to get a better understanding of the chemical composition of the sulfur containing particles and maybe even identify the sources. However, due to the fact that the samples are thin films which can be penetrated easily by high current, we chose to do SEM-EDX imaging with low current. Thus, the heavy elements with high atomic numbers greater than Ca might not be shown in EDX spectra.

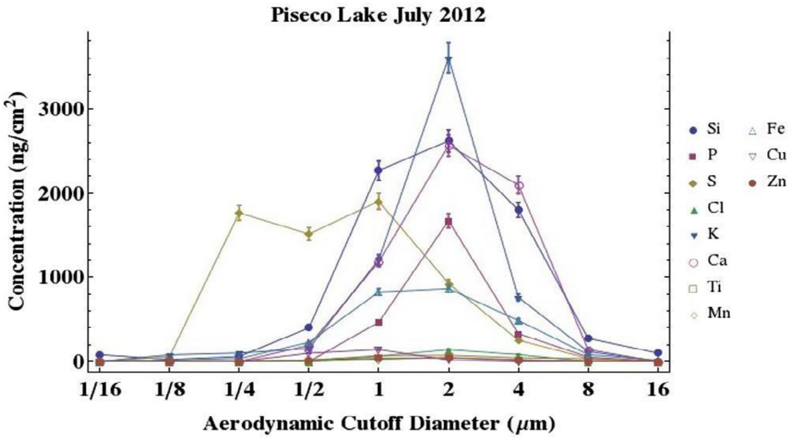

Figure 8. A graph of the measured concentrations in mass per unit area as a function of particle size for each element in the samples collected in July of 2012[1].

Shown in Figure 9 is an SEM micrograph of the sample collected on stage 2 which contains particles with an aerodynamic cut off diameter of ½ µm. We chose 6 particles and collected one EDX-spectrum of 500,000 total counts for each particle. The spectra are shown in Figures 10-15 in the order they are labeled in Figure 9.

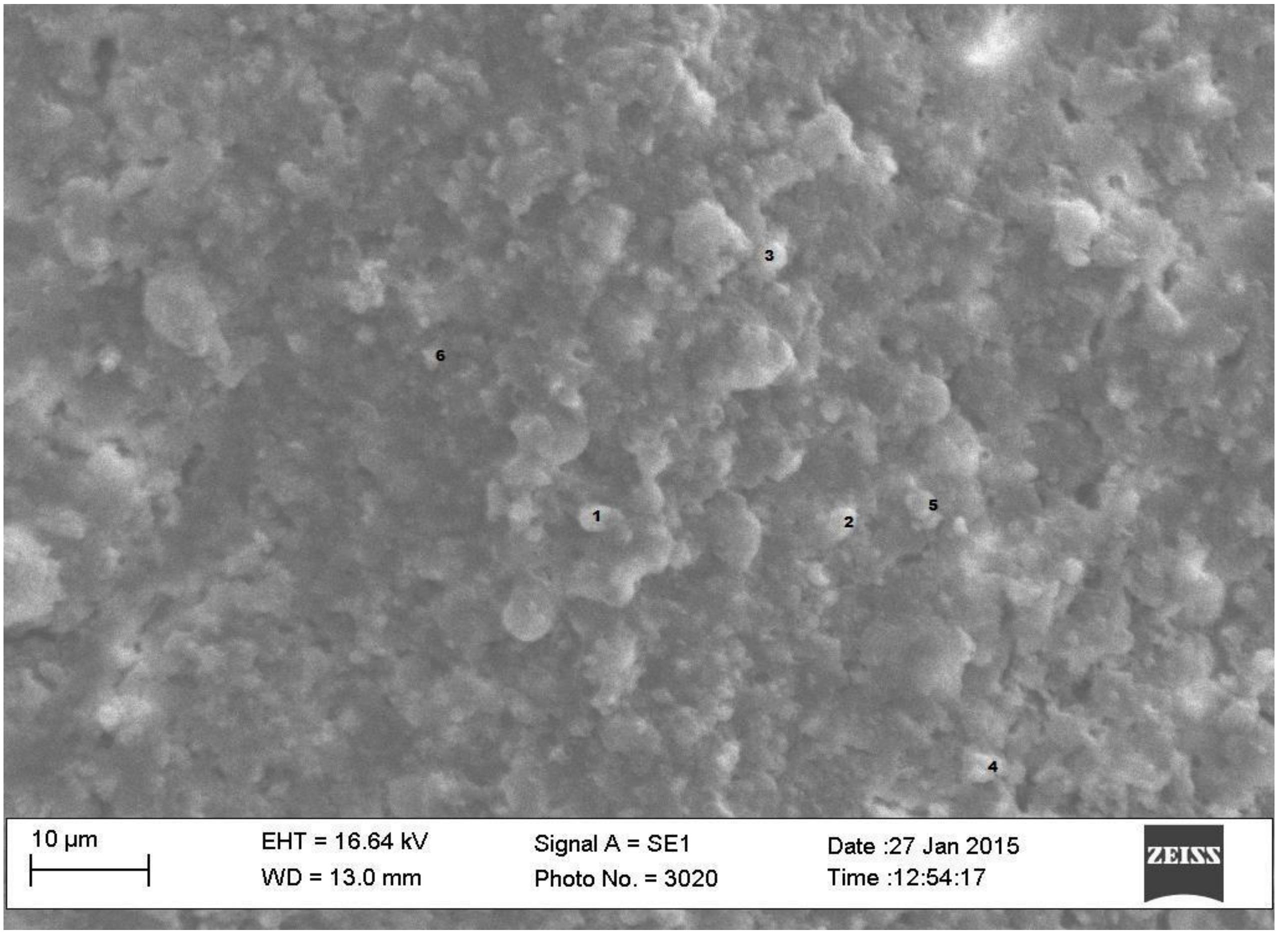

Figure 9. An SEM micrograph of the stage 2 sample with six individual particles labeled.

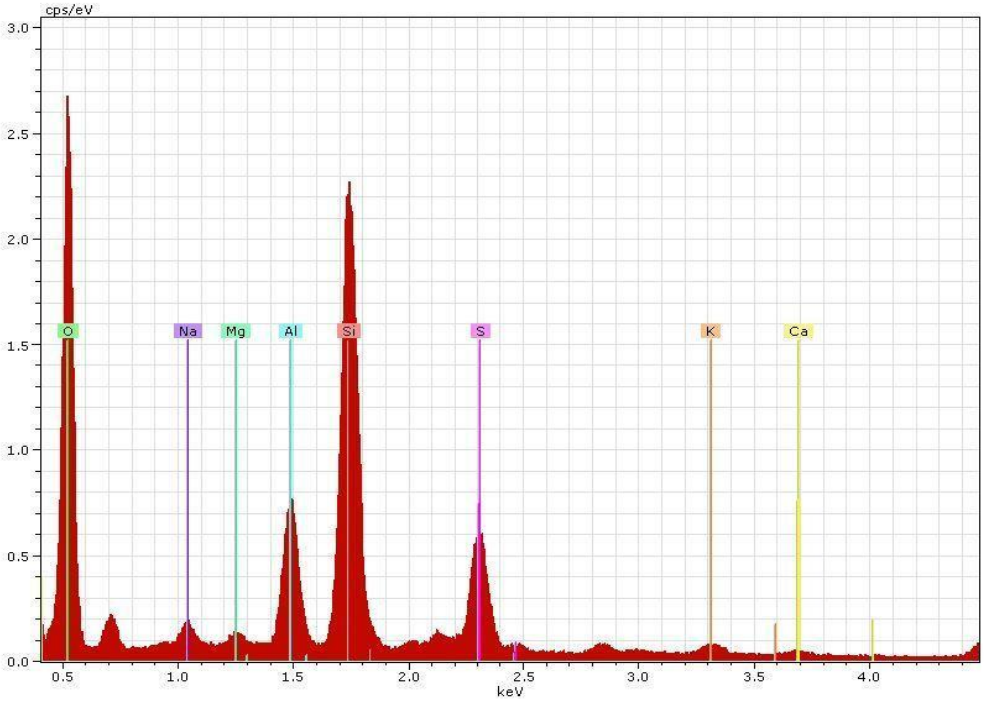

Figure 10. An EDX-spectrum taken on particle 1 in the SEM image shown in Figure 9.

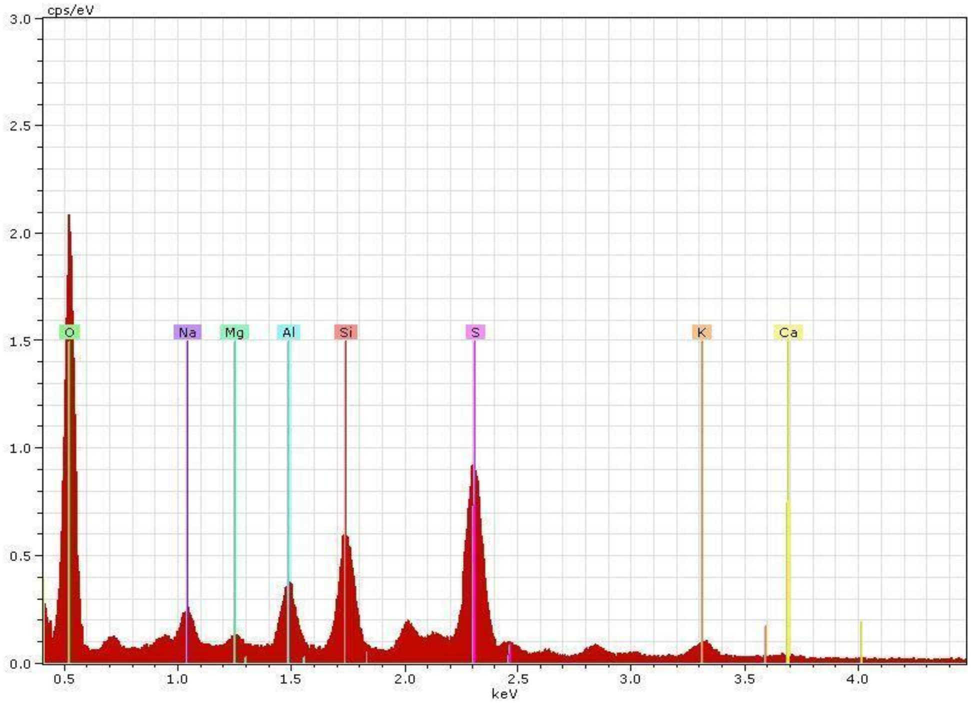

Figure 11. An EDX-spectrum taken on particle 2 in the SEM image shown in Figure 9.

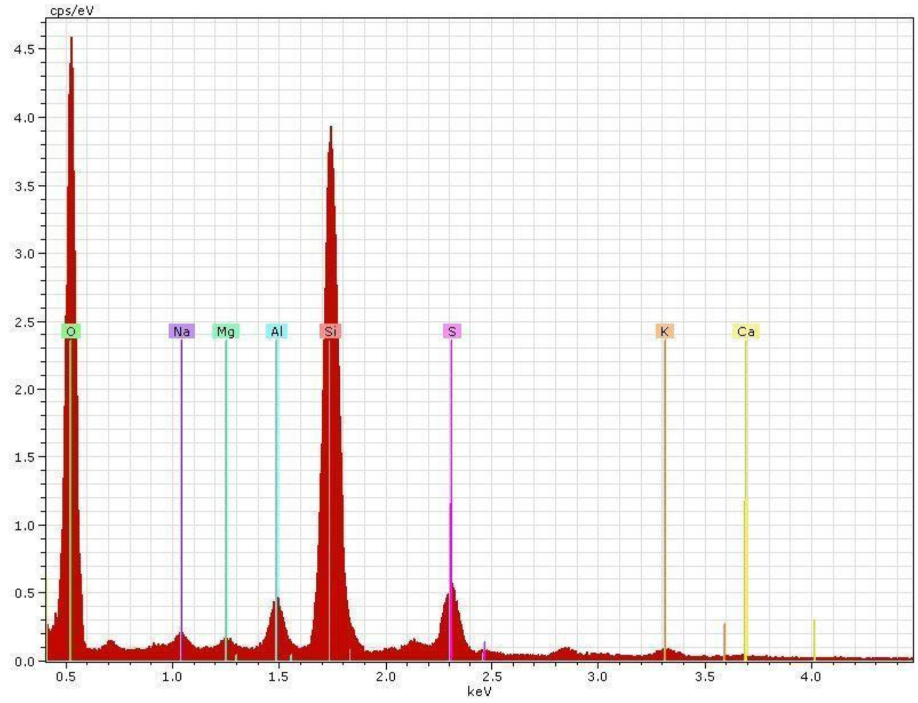

Figure 12. An EDX-spectrum taken on particle 3 in the SEM image shown in Figure 9.

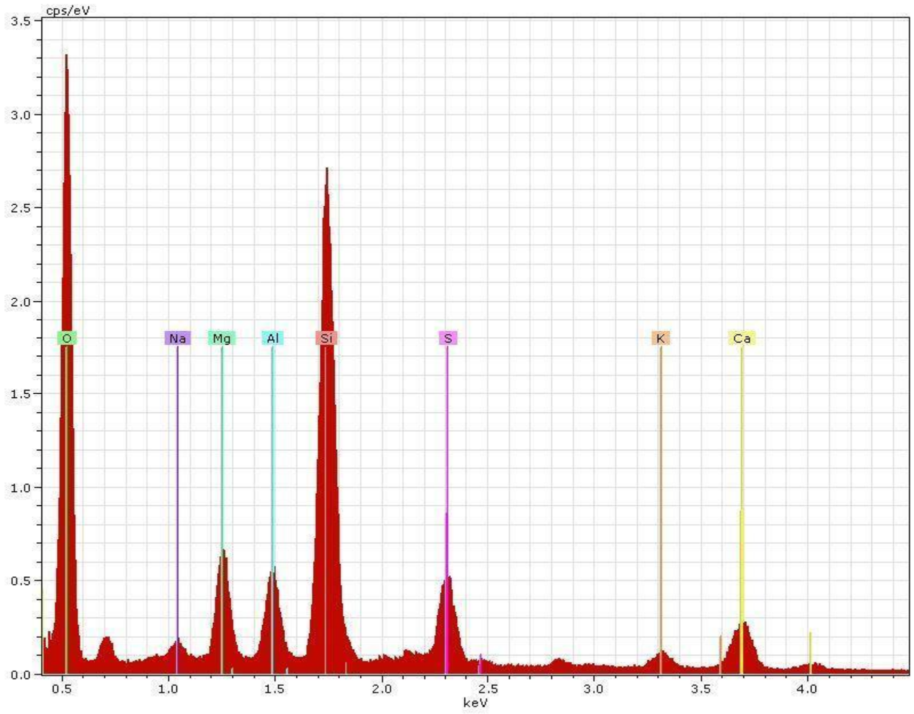

Figure 13. An EDX-spectrum taken on particle 4 in the SEM image shown in Figure 9.

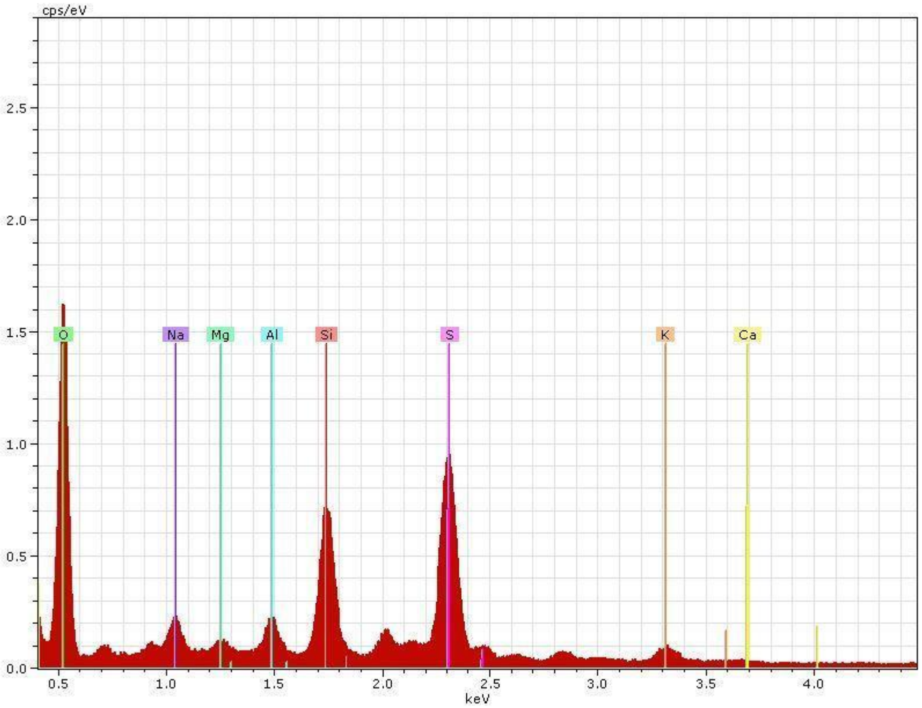

Figure 14. An EDX-spectrum taken on particle 5 in the SEM image shown in Figure 9.

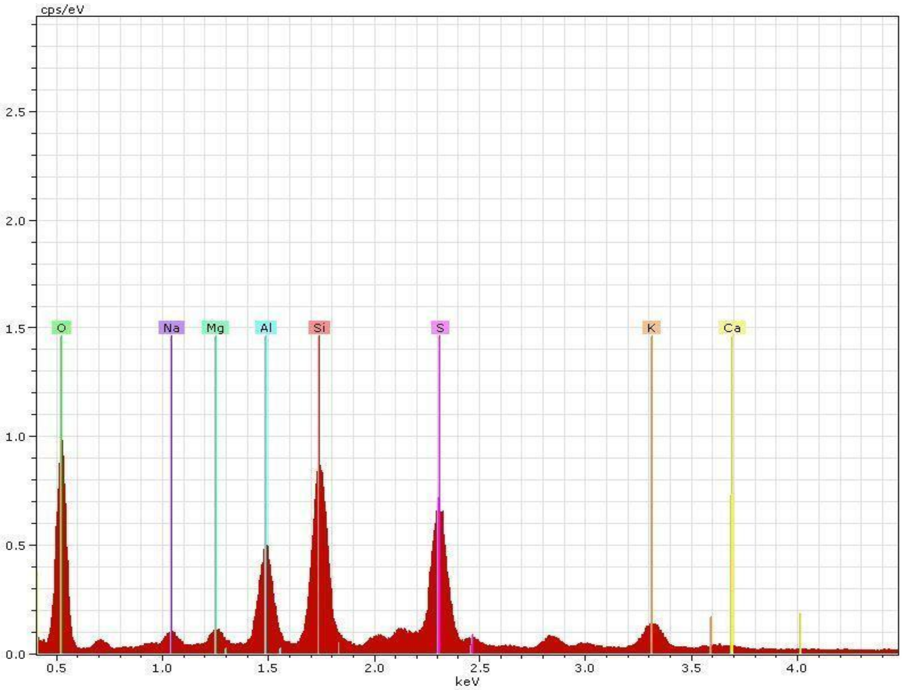

Figure 15. An EDX-spectrum taken on particle 6 in the SEM image shown in Figure 9.

Significant concentrations of S and Si are observed in the SEM/EDX spectra taken on all 6 particles in the stage 2 sample consistent with the results from the PIXE analysis. Large O peaks are also present in all 6 spectra, but the ratio of O to S is not constant in each spectrum suggesting that the sulfur is not bound in one particular sulfur-oxide. In all six spectra, there exist strong silicon peaks along with Al, K and Ca peaks suggests the presence of airborne soil particles. Based on the PIXE graph shown in Figure 8, there should also be iron and copper in the sample, so we can make a wide guess that the sulfur might be correlated to iron which might due to iron sulfate which is a indication of fly ash produced by industrial burning.

Shown in Figure 16 is an SEM micrograph taken on the stage 3 sample which contains particles with an aerodynamic cutoff of 1µm. Again we also chose 6 particles and collected one EDX-spectrum of 500000 total counts for each particle. The spectra are shown in Figures 17-22 in the order they are labeled in Figure 16.

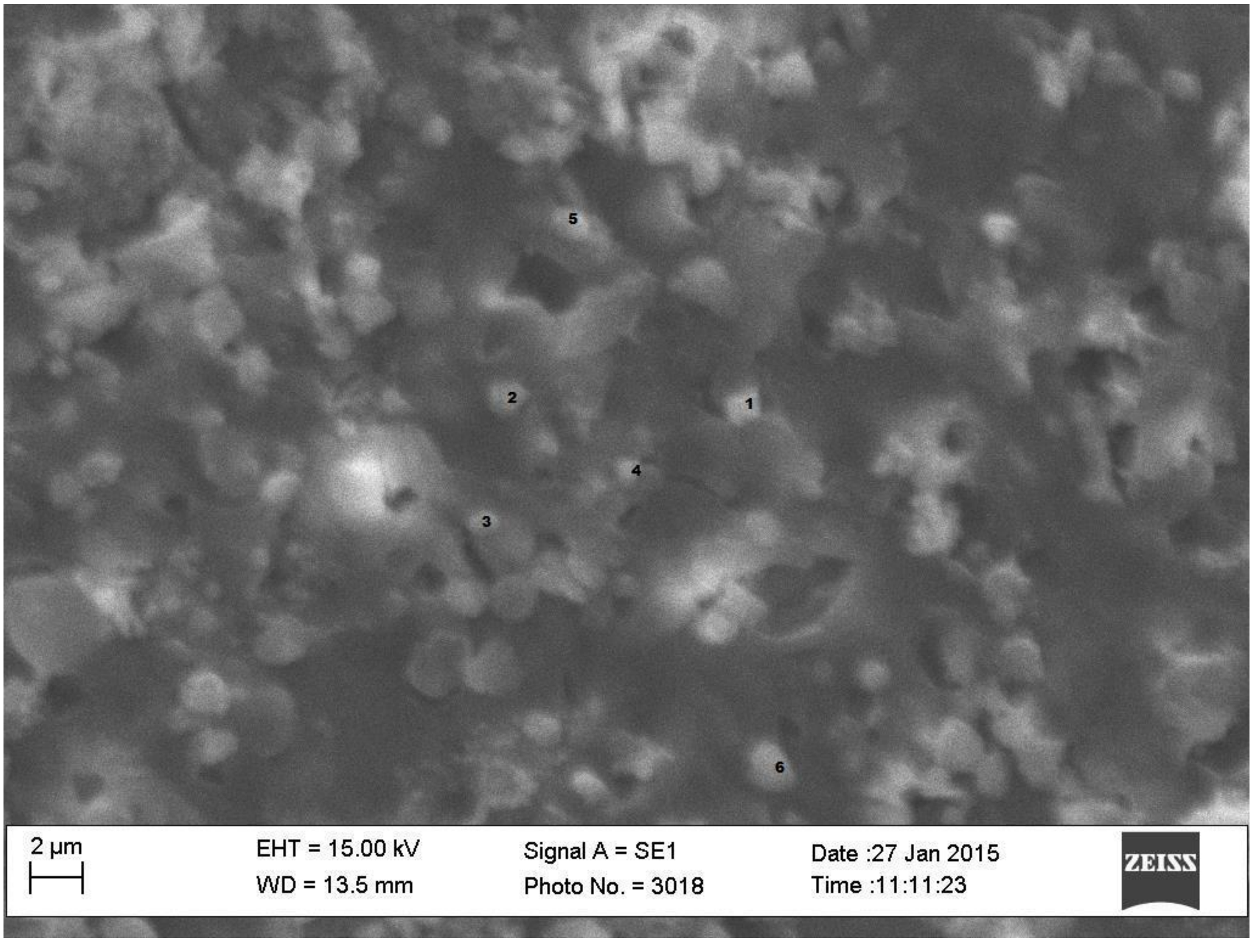

Figure 16. An SEM micrograph of the stage 3 sample with six individual particles labeled.

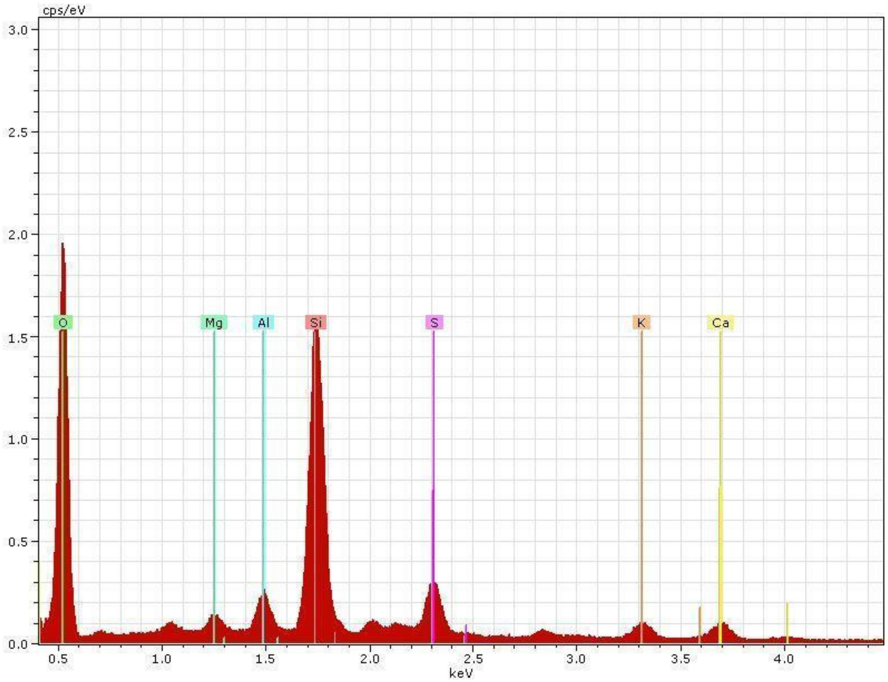

Figure 17. An EDX-spectrum taken on particle 1 in the SEM image shown in Figure 16.

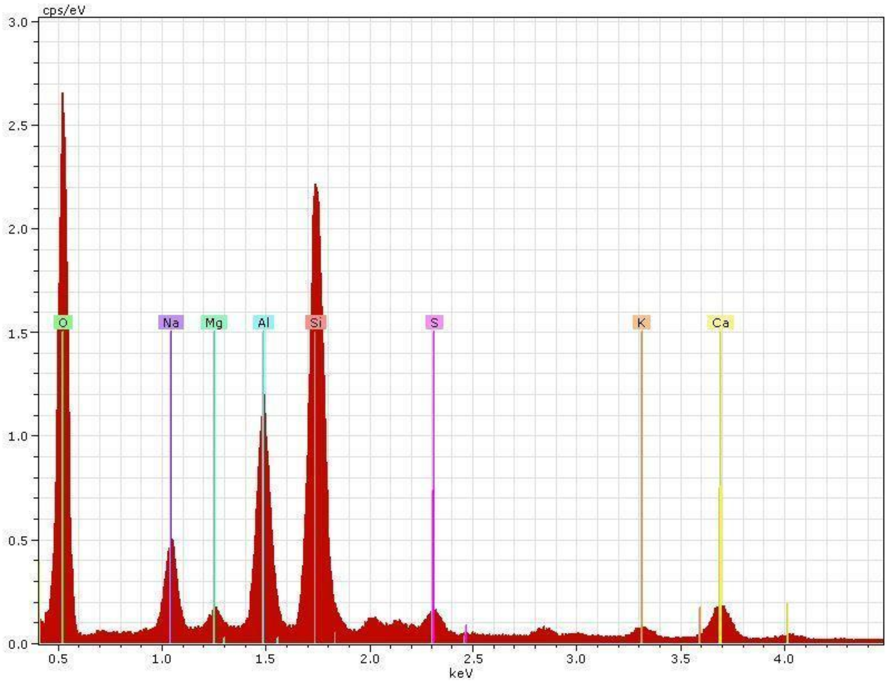

Figure 18. An EDX-spectrum taken on particle 2 in the SEM image shown in Figure 16.

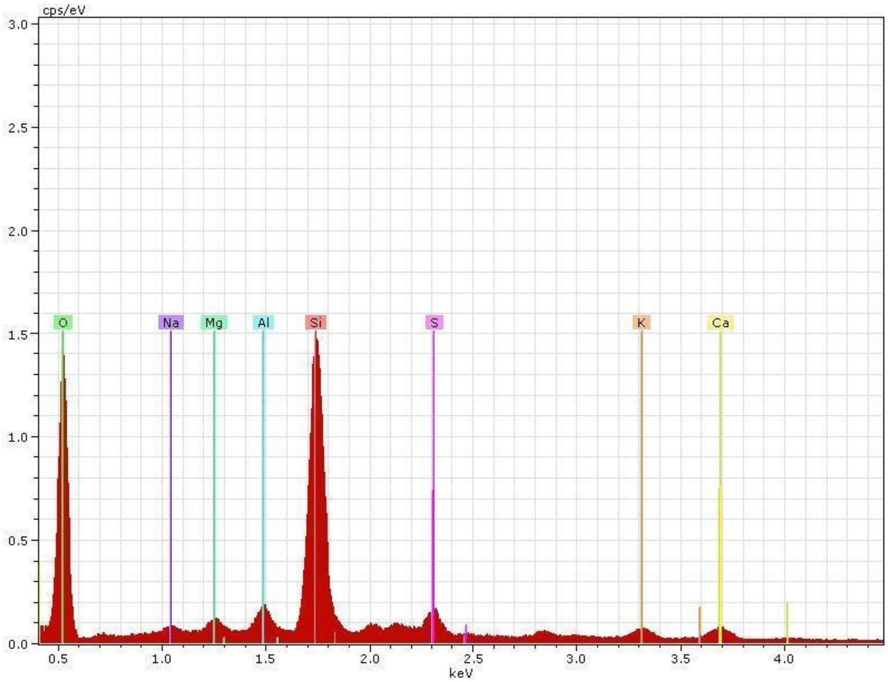

Figure 19. An EDX-spectrum taken on particle 3 in the SEM image shown in Figure 16.

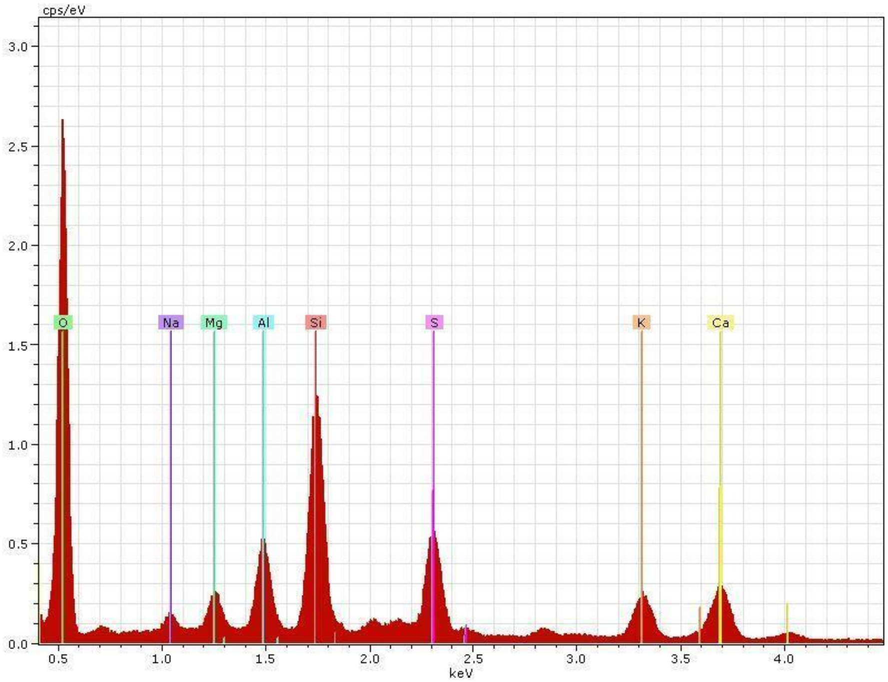

Figure 20. An EDX-spectrum taken on particle 4 in the SEM image shown in Figure 16.

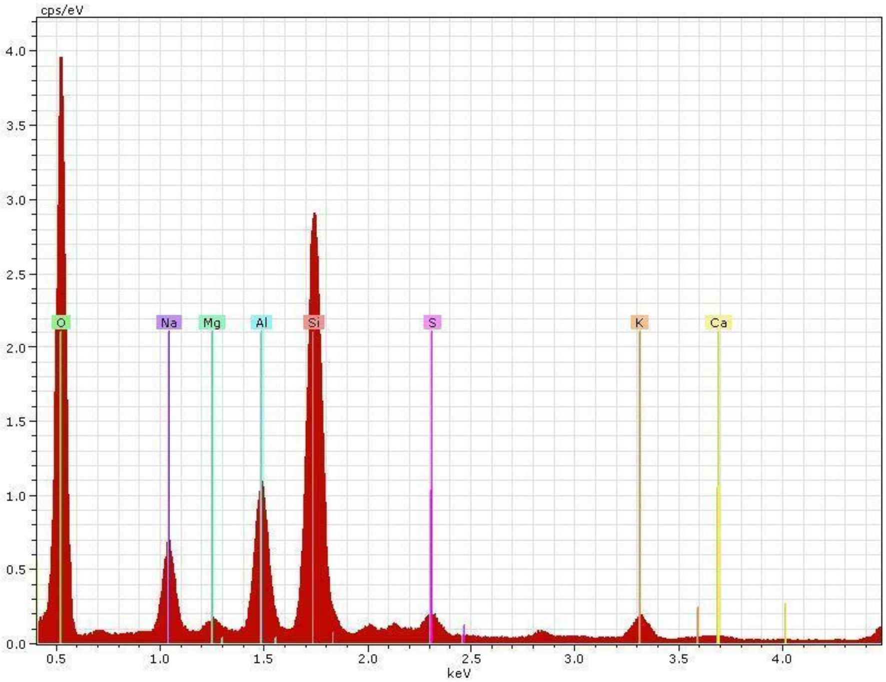

Figure 21. An EDX-spectrum taken on particle 5 in the SEM image shown in Figure 16.

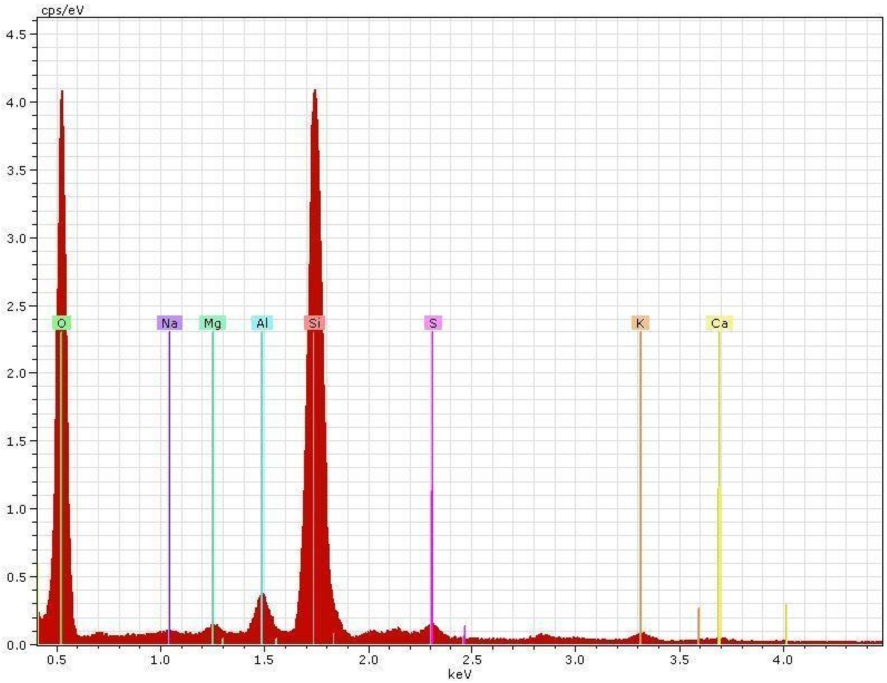

Figure 22. An EDX-spectrum taken on particle 6 in the SEM image shown in Figure 16.

As in the case of the spectra taken on the stage 2 sample, the spectra taken on all 6 particles in the stage 3 sample are consistent with the result from the PIXE analysis. In each of the spectra, Si is the most abundant element besides O. there are also significant concentration of Al, K, and Ca, suggesting the presence of airborne soil. While there are s peaks in most of the spectra, they are much smaller than the Si and O peaks in every case.

4. Summary and Conclusions

One of the important environmental issues in upstate New York is the acid rain problem in the Adirondack Mountains, which is associated with atmospheric aerosols, so we did this research to better understand the atmospheric aerosol pollution around the Adirondacks. As part of a systematic study to understand the transport, transformation, and effects of airborne pollutants in the Adirondack Mountains, in 2012 we obtained air samples from Piseco Lake and analyzed particulate depositions with proton induced X-ray emission spectrometry. In this work we analyzed some of the samples using a scanning electron microscope (SEM), along with energy dispersive spectroscopy (EDX) to identify the particular elements in individual particles and their relative proportions instead of the concentration for each element contained in the whole sample.

In this study, we are focused on the particles with aerodynamic cutoff diameter of ½ and 1 µm. The results from SEM-EDX are consistent with the previous results from PIXE in the general overall element concentrations in the sample. The results from the SEM-EDX analysis suggest that the sources are some combination of industry and airborne soil. The results also support the conclusion from the PIXE analysis that there are large concentrations of S in small particles that can be suspended in the air for long periods of time and travel great distances. However, the observed ratios of S to O are not consistent for different particles, suggesting that the S is not bound in one Particular Oxide.

References:

[1]. M.F. Vineyard, S.M. LaBrake, S.F. Ali, B.J. Nadareski, A.D. Safiq, J.W. Smith, J.T. Yoskowitz. *Characterization of atmospheric aerosols in the Adirondack Mountains using PIXE, SEM/EDX, and Micro-Raman spectroscopies*. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 29 January 2015. ISSN 0168-583X.

[2]. D. Morata, M. Polve, A. Valdes, M. Belmar, M. I. Dinator, M. Silva, M. A. Leiva, T. Aigouy, J. R. Morales. *Characterisation of aerosol from Santiago, Chile: an integrated PIXE-SEM-EDX study.* Environmental Geology. 01 November 2008.

[3]. Purdue University. *Scanning Electron Microscope*. http://www.purdue.edu/ehps/rem/rs/sem.htm

[4]. S.A.E. Johansson, J.L. Campbell, K.G. Malmqvist. *Particle-Induced X-Ray Emission Spectrometry (PIXE)*. Wiley, New York (1995)

[5]. PIXE International Corporation, P.O. Box 2744, Tallahassee, FL 32316 USA.

[6]. Kurt Hollocher. *Secondary Electron (SE) Imaging*. Geology Department Union College Schenectady, NY 12308 U.S.A.

[7]. Kurt Hollocher. *Coating Sample*. Geology Department Union College Schenectady, NY 12308 U.S.A.