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NMED
Hazardous Waste
Bureau

Date: January 19, 2018
Refer To: ADEM-18-0004
LAUR: 18-20250

Shelley Lemon, Bureau Chief
Surface Water Quality Bureau
New Mexico Environment Department
Harold Runnels Building
1190 St. Francis Drive
Santa Fe, NM 87502

Subject: Response to November 29, 2016, Letter Regarding the Preliminary Evaluation of Los Alamos National Laboratory Aluminum Filter Study

Dear Ms. Lemon:

Los Alamos National Security, LLC (LANS) received the New Mexico Environment Department Surface Water Quality Bureau's (NMED-SWQB's) letter dated November 29, 2016, and titled "Preliminary Evaluation of LANS Aluminum Filter Study Data Aluminum Bioavailability: Implications for Ambient Water Quality Criteria and Sampling." The Los Alamos National Laboratory (LANL) Associate Directorate for Environmental Management Surface Water Program (ADEM-SWP) looks forward to continued discussions regarding the appropriate filter size needed for determining aluminum concentrations in surface and storm water for the purpose of water-quality standards and compliance. We initiated those discussions with NMED-SWQB during a meeting on August 1 and 2, 2016, which included a presentation on the subject by ADEM's consultant, Windward Environmental. In addition, ADEM-SWP and NMED-SWQB staff conducted a phone conversation on August 28, 2017, which helped ADEM-SWP to identify additional investigations needed to fill data gaps identified by NMED-SWQB in the November 29, 2016, letter.

In the November 29, 2016, letter, NMED-SWQB stated that "LANS has demonstrated that much of the Al loading on the Pajarito Plateau within LANL property and its surrounds is mostly mineral in form, and also less than 10μm in size…." In addition, NMED-SWQB encouraged LANL to perform further investigations and provided suggestions to improve the demonstration, supporting the use of a filter finer than 10 μm, which may be warranted based on the geological composition of the Pajarito Plateau and surrounding watersheds. NMED-SWQB suggestions and LANS responses are presented below.

The issue addressed by the NMED-SWQB suggestions largely concerns water-quality standards implementation whereby a new sample preparation method is needed that best represents bioavailable aluminum forms while minimizing bias from nontoxic mineral forms of aluminum. Because of the presence of nontoxic mineral forms of aluminum in particles that can pass filters as fine as 0.45 µm, preparing samples with the 10-µm filter per current NMED guidance will likely result in an unacceptably high false-positive rate when comparing the resulting filtered aluminum concentrations with current New Mexico water-quality criteria for aluminum. We plan to document our work and recommendations regarding the need for an improved sample preparation method for aluminum in surface waters in a peer-reviewed journal manuscript and invite NMED to participate and contribute to this work. In addition, we will provide recommendations for a toxicity testing program that will further investigate appropriate methods for quantifying toxicologically relevant forms of aluminum in surface waters.

NMED-SWQB Suggestion 1

An additional avenue of investigation of the mineral nature of aluminum that passes (filtrate) or is retained (retentate) by a filter might be elemental ratios of known mineral Al geology in the area. Elemental ratios of unfiltered vs. filtered samples may indicate capture of the mineral forms and passing of the amorphous and dissolved forms implicated in toxicity f with decreasing pore sizes.

LANL Response

LANL has explored the mineral nature of colloidal and particulate aluminum that passes through a 0.45-µm membrane filter with a qualitative elemental ratio approach using scanning electron microscopy and electron dispersive spectroscopy to identify the elemental composition of material collected on a 0.2-µm filter. In addition, x-ray diffraction analytical methods were used to identify bulk mineral phases of suspended sediment separated from storm water and precipitate from the same storm water aliquot at several locations on the Pajarito Plateau. Only aluminum silicate and no aluminum hydroxide phases were identified using these techniques. The attachment to this letter details this investigation and presents the results.

NMED-SWQB Suggestion 2

The Department encourages the use of toxicity tests (Whole Effluent Tests or "WET" or other appropriate test) on unfiltered and subsets of the filterable aluminum fractions to demonstrate directly the lack of toxicity of the Al retained after any proposed pre-filtration step.... Because Al toxicity has been reported for solid, precipitated, or colloidal phase aluminum, appropriate exposure testing procedures and organism(s) is encouraged.

LANL Response

LANL agrees with NMED's suggestion and will provide a proposed toxicity testing plan for NMED's review and comment. LANL will work with NMED-SWQB staff to define specific testing protocols and select an appropriate toxicity testing organism, life stage, and period of exposure.

NMED-SWQB Suggestion 3

Additional supporting information is needed to identify the watersheds or geographical/geophysical extent (e.g. Bandelier Tuff, Ecoregional boundaries, Watershed boundaries, etc.) to where this study applies, so the proposed pre-filtration step can be implemented at an appropriate scale. As discussed at the meeting, the justification to change the

Department's current approach to minimize the mineral phase may have additional merit if it is based on an appropriate geologic-based geographic boundary vs. a land management boundary.

LANS Response

The third suggestion focuses on whether the background ecoregion and associated environmental media are representative of the ecoregion and environmental media present within the Laboratory boundaries. Since the time of NMED's November 29, 2016, letter, LANS, NMED-SWQB, and the U.S. Department of Energy have identified and agreed upon collecting new storm water data sets from several undisturbed watersheds outside the Laboratory boundary as part of the Sampling and Monitoring Supplemental Environmental Project (SEP). These watersheds have ecosystems, hydrological characteristics (ephemeral/intermittent reaches and similar watershed size), precipitation regimes, and geological media similar to watersheds within and around the Laboratory. The characteristics of these background "reference watersheds" have been documented in Appendix B of the June 2017 SEP Data Quality Objective (DQO) document. Implementation of storm water sample collection, NMED hydrology protocols, and aquatic life surveys is ongoing under the SEP. All of this information has been or will be archived and will be presented in a final report to NMED-SWQB. Thus, we anticipate not only that the new background storm water data being collected as part of the SEP will be representative of the larger geologic-based area, but also that the new data will augment data sets already collected by LANL for purposes of describing and resolving the current aluminum concern.

LANS looks forward to NMED-SWQB's response to the proposals presented in this letter. Both LANS and NMED-SWQB understand the importance of determining the appropriate sample preparation and filter membrane size that would minimize the potential bias associated with nontoxic forms of minerals containing aluminum while allowing the potentially toxic forms of aluminum to pass into the filtrate and thus provide a more representative sample for water-quality standards assessment purposes. After the final agreement for the appropriate testing approach and acceptance is reached, LANL will prepare and submit a sample and analysis work plan to NMED-SWQB for review.

If you have any questions, please contact Steve Veenis at (505) 667-0013 (veenis@lanl.gov) or David Rhodes at (505) 665-5325 (david.rhodes@em.doe.gov).

Sincerely,

Bruce Robinson, Program Director
Environmental Remediation Program
Los Alamos National Laboratory

Sincerely,

David S. Rhodes, Director
Office of Quality and Regulatory Compliance
Environmental Management
Los Alamos Field Office

BR/DR/SV:sm

Attachment: Two hard copies with electronic files – Identification of Aluminum-Bearing Mineral Phases in Storm Water Collected on the Pajarito Plateau, Los Alamos County, Northern New Mexico (EP2018-0004)

Cy: (date-stamp letter hard copy)
Sarah Holcomb, NMED-SWQB,
Bryan Dail, NMED-SWQB
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Efren Ordonez, EPA Region 6
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LA-UR-18-20250
January 2018
EP2018-0004

Identification of Aluminum-Bearing Mineral Phases in Storm Water Collected on the Pajarito Plateau, Los Alamos County, Northern New Mexico

Prepared by the Associate Directorate for Environmental Management

CONTENTS

Appendixes

1.0 OBJECTIVES

This report presents x-ray diffraction (XRD) and scanning electron microscopy/electron dispersive spectroscopy (SEM/EDS) analytical results from bulk storm water suspended sediments and filter retentate collected at gage stations E240, E038, and E252. These results are presented in Appendix A. XRD and SEM/EDS analytical results from a clean cellulose nitrate filter are provided as baseline information for a background spectra and elemental reference (Figures A-1 and A-2). In addition, results from an aluminum hydroxide standard, a known toxic solid phase of aluminum, are included to compare spectra with results from the natural storm water sediments and to test the stability of freshly precipitated aluminum hydroxide. These results are presented in Appendix B. Locations E240 and E252 represent background reference locations. Gage station E038 is located downstream from the Los Alamos County townsite and monitors flow from the urban developed landscape. All locations are on Bandelier tuff, and suspended sediments collected from these locations are predominately weathered Bandelier tuff. The objective of the study is to attempt to identify toxic mineral phases of aluminum in the suspended sediment fraction of storm water. Analytical results, as well as an assessment of the data, are presented below.

2.0 MINERAL IDENTIFICATION METHODS AND MATERIALS

Crystalline phases associated with filter retentate, storm water supernatant precipitate, and suspended sediment particulates were analyzed using SEM/EDS and XRD. Samples for each analytical method were processed differently because of the nature of the material and target analytical method. Flat filter paper subsamples for retentate analysis were cut from 0.2-μm cellulose nitrate filters and mounted to a zero-background quartz plate for XRD analysis. After the suspended solids settled, 1-L aliquots of storm water supernatant were decanted and dried at 105°C in a fume hood. Precipitates from the storm water supernatant were re-dissolved and pipetted onto a zero-background quartz plate for XRD analysis. After the storm water supernatant was decanted, storm water sediment particles were collected and dried at 105°C. The particles were ground to a 1- to 5-μm particle size and mounted into a titanium-powder mount for XRD analysis. Each of these XRD samples was then scanned from 2.0 to 70.0^{o} 2θ with a scan rate of 8–20 s/step (2 s/step for the blank samples) and a step size of 0.02^{o} 2θ with Cu-Kα radiation. Mineral identification was through Jade 7.0 software.

A small portion of each filter used in the XRD analyses was cut out for SEM/EDS analyses. Dried solids from the storm water precipitates and particulates were directly analyzed without further processing. Samples were adhered to an aluminum stub using carbon tape. The edges of each filter were painted with carbon paint to present a more conductive surface. All samples were then sputter-coated with gold-palladium alloy. Imaging was performed at 5.0 kV and a 1.5 μm spot size. Chemical analyses (Energy Dispersive X-ray Spectroscopy, EDX) were performed at 30.0 kV and a 3.0 μm spot size with 10K counts collected.

3.0 SUMMARY OF RESULTS

E038 Samples. Analytical results from gage station E038 are presented in Figures A-3 through A-14. The E038 0.2-μm filter did not show a significant amount of residual solids. Most of the original filter porosity was unaltered with very little particulate accumulation on the surface. The particulate composition is similar to material on the E240 filter but is slightly more enriched in magnesium. Also, it does appear that there is a higher concentration of micaceous material on the E038 filter than on the E240 filter.

Liquid samples upon drying produced a solid phase with an amorphous morphology and a biotite-like composition (K-Fe-Mg-SiO_2). There are occurrences of calcite ($CaCO_3$) as well. Unfiltered particulate matter in the aqueous samples appears to be mostly amorphous siliceous material with varying amounts of aluminum. Honeycombed solids are present with a botryoidal morphology. These botryoidal solids were also observed on the 0.2-μm filter papers.

XRD results shown in Figure A-11indicate that the mineral composition of sediment particles is typical of what is observed in the Bandelier Formation (Kuentz 1986, 602817; Broxton et al. 2002, 072640). Orthoclase/sanidine, albite, quartz, trydimite, and cristobalite are the dominant minerals with minor amounts of mica (biotite or muscovite), smectite, and kaolinite. Storm water supernatant composition is dominated by calcite, smectite or illite (or smectite/illite mixed-layer), and halite with minor amounts of quartz, kaolinite, and feldspar. Halite and calcite most likely precipitated during storm water evaporation, whereas the silicate fractions are associated with residual small particulates (colloids) suspended in the supernatant.

E240 Samples. Figures A-15 through A-24 show images and spectra of SEM/EDS and XRD storm water sediment particulate and precipitate results from location E240. Both XRD and SEM analyses show that storm water from E240 was more turbid and contained more solid material then storm water from either E038 or E252. XRD results show that crystalline solids collected on the E240 0.2-μm filter appear to be dominated by opaline ($SiO_2 \cdot nH_2O$) materials; the amount of amorphous material is unknown (Figure A-1). Silica is the most common element in the Bandelier Formation and amorphous volcanic glass, a major component, makes up 60% to 80% of the total mass (Kuentz 1986, 602817; Broxton et al. 2002, 072640). The solids observed in the SEM imagery appear to display amorphous or subrounded morphologies suggesting particle transport effects. The silicon/aluminum elemental ratio ranges from 2 to 3; no discrete aluminum (oxy)hydroxides were observed. Most of these aluminosilicates have variable amounts of potassium, calcium, and iron. There also appears to be some type of botryoidal organic particulates bearing various amounts of phosphorous.

Liquid samples upon drying produced sodium sulfate ($NaSO_4$), potassium chloride, and sodium chloride precipitates. These precipitates suggest that the storm water had significant potassium-sodium-chlorine-sulfate concentrations compared with the other major ions. The solid phases separated from the raw water were primarily highly altered potassium-sodium feldspars (probably sanidine or orthoclase) and titanium-bearing magnetite.

E252 Samples. Analytical results for material collected at E252 are shown in Figures A-25 through A-27. Again, particulates are typical of Bandelier Formation and dominated by orthoclase/sanidine, albite, quartz, tridymite, and cristobalite with minor amounts of mica (biotite or muscovite), smectite, amphibole, hematite, and kaolinite. There is no evidence for the presence of aluminum hydroxides. Storm water supernatent precipitate shown in Figures A-26 and A-27 is dominated by calcite, amorphous matter (broad hump at 20–30° 2θ), and halite with minor amounts of quartz and feldspar, typical of Bandelier Formation mineralogy. The broad XRD spectra hump at low 2-Θ angles could be a poorly crystalline smectite but is inconclusive. The amorphous hump (coupled with SEM/EDS) appears to be aluminosilicate in composition. Halite and calcite are primarily from precipication during storm water evaporation, whereas the silicate fractions are associated with unsettled particulates. Residue from evaporated storm water produced a mixed K-Na-Mg-SO_4-Cl salt, fibrous $CaCO_3$, and amorphous silica, suggesting storm water with a similar composition.

4.0 ALUMINUM PHASE IDENTIFICATION

The purpose of this project was to evaluate the nature of the toxic aluminum mineral phases and determine if aluminum oxyhydroxides or hydroxides are present in the storm water samples collected in the Los Alamos area. Amorphous aluminosilicates collected on the 0.2-μm filters and in the settled particulates suggest that aluminum is associated with aluminosilicates ranging from colloidal- to micrometer-sized solids. Sediment particles are typical of the Bandelier Formation and are dominated by orthoclase/sanidine, albite, quartz, trydimite, and cristobalite with minor amounts of mica (biotite or muscovite), smectite, and kaolinite (Kuentz 1986, 602817; Broxton et al. 2002, 072640). All of these mineral phases contain various amounts of aluminum in their crystal structure as verified by SEM/EDS results.

Note that precipitates associated with the dried storm water (total dissolved solids) provide a good approximation of the storm water compositions but do not yield data on the formation of aluminum hydroxide phases that may have formed by forced precipitation during evaporation of the liquid phase. This may suggest that free aqueous aluminum was not available during precipitation given the low solubility of aluminum in the neutral pH range (Stumm and Morgan 1981, 059079). Smaller colloidal-sized particles are included in the precipitant as observed by the quartz and feldspar (albite/sanidine) spectra.

5.0 DISCUSSION

Results from the aluminum hydroxide syntheses, presented in Appendix B, provide a spectra and elemental standard to compare results from natural storm water sediment samples. Aluminum hydroxide [$Al(OH)_3$] clearly is not stable and was observed to transition into pseudoboehmite [Al_2O_3 x H_2O] within a short period of time. See Coelho et al. (Coelho Vieira et al. 2008, 602818), Tettenhorst and Hofmann (Tettenhorst and Hofmann 1980, 602819), and Brown and Hem (Brown and Hem 1975, 602820) for more information on poorly crystalline aluminum clay minerals and stability of hydrated $Al(OH)_x$ gels. Simple clay minerals, i.e., pseudoboehmite, are not toxic forms of aluminum because aluminum is locked in the crystal structure and is not bioavailable. In addition, the SEM/EDS spectra of the $Al(OH)_x$ material show a predominant aluminum peak and lower oxygen peak, with an aluminum/oxygen ratio of approximately 3/1, indicating abundant aluminum was observed. The EDS spectra for oxygen is not reliable, as with the lighter elements, so it is difficult to access the ratio quantitatively. The SEM/EDS pattern, spectra, and ratio observed from the storm water sediment particles are very different from the $Al(OH)_x$ spectra, with an aluminum to oxygen ratio of 1/2 to 1/3, showing dominant silica and less abundant aluminum. Whole-rock analysis of Bandelier tuff indicates that the predominant elements are oxygen, silica, and aluminum. Aluminum ranges from 5.7 to 7 weight percent; silica ranges from 33 to 37 weight percent (Broxton et al. 2002, 072640). Although it is not possible to calculate elemental mass from the SEM/EDS spectra, there is qualitative agreement of the relative abundance of oxygen, silica, and aluminum between the SEM/EDS spectra and whole-rock analysis.

Comparing the XRD 2-Ө position of the peaks observed from the synthetic aluminum standard (Figure B-3) with natural storm water sediment XRD 2-Ө positions (Figures A-11, A-21, A-25) makes clear that the minerals' assemblage spectra do not match the $Al(OH)_x$ standard spectra. Sediment XRD spectra in the region of the five dominant synthetic aluminum standard peaks (2-Ө positions 14, 28, 38, 50, and 66 degrees) are dominated by feldspars and quartz; the $Al(OH)_x$ peaks are not visible. There may be several explanations, including (1) the information is masked by the baseline noise or (2) the concentration of $Al(OH)_x$ phases is absent or so low as not to be detected. However, thermodynamic data suggests that aluminum hydroxide species may exist in the circumneutral pH range in low concentrations but under a scenario where highly acidic or basic waters are neutralized; i.e., mixing of acid mine drainage in a stream or lake (Stumm and Morgan 1981, 059079; Sposito 1989, 058685). The thermodynamically derived solubility stability diagram in Figure B-2 shows this as well. Surface water pH values observed on the Pajarito Plateau are within the circumneutral range and do not possess the chemical conditions (highly acidic or basic) to dissolve or much less maintain stable aqueous forms of aluminum. Aqueous aluminum species are required for the formation of polymeric aluminum hydroxides. A semi-quantitative evaluation of the SEM/EDS spectra from the three suspended sediment sample locations shows a predominant silica-to-aluminum elemental ratio of 2/1, indicating the presence of aluminum silicates and amorphous material (most likely volcanic glass). Volcanic glass, a dominant component of Bandelier tuff, is largely composed of silica but contains various amounts of trace elements, including aluminum (Kuentz 1986, 602817; Broxton and Eller 1995, 058207). Volcanic glass is amorphous (poorly crystalline) and metastable and devitrifies, and breaks down into small silica particles, many smaller than 1 µm; see SEM/EDS images. Because of the poor crystallinity, trace elements, including aluminum, are weakly bound and are released during acidification (preservation and pre-analytical digestion) and are thus detected in the subsequent analysis. This process would not normally occur under environmental conditions observed on the Pajarito Plateau indicating trace constituents, including aluminum, are not bioavailable in surface water.

6.0 CONCLUSIONS

XRD and SEM results did not identify any aluminum hydroxide phases from suspended sediment samples collected at gage stations E038, E240, and E252. Three lines of evidence include (1) comparison of the XRD 2-ϴ peaks from the $Al(OH)_x$ standard with the XRD 2-ϴ peaks from the storm water sediment particulate spectra, (2) qualitative elemental ratios of the SEM/EDS spectra, and (3) aluminum solubility constraints (supporting evidence from thermodynamic aluminum solubility calculations and references). Finally, the terrain, hydrology, and geology found on the Pajarito Plateau are not conducive to acid mine drainage or production of acidic bog waters, environments where aluminum could potentially be soluble and bioavailable. The Laboratory believes that aluminum is a common constituent of geologic formations on the Pajarito Plateau as shown by numerous studies, is mineral bound, and is thus not bioavailable. However, aluminum is released to an aqueous phase when storm/surface water samples are subjected to aggressive acidification during preservation and the pre-analytical digestion step mandated by the recoverable aluminum analytical method. These factors contribute to elevated aluminum concentrations observed in aqueous analytical results. These conclusions indicate that aluminum is not present in a bioavailable form in surface waters on the Pajarito Plateau.

7.0 REFERENCES

The following reference list includes documents cited in this report. Parenthetical information following each reference provides the author(s), publication date, and ERID or ESHID. This information is also included in text citations. ERIDs were assigned by the Associate Directorate for Environmental Management's (ADEM's) Records Processing Facility (IDs through 599999), and ESHIDs are assigned by the Environment, Safety, and Health Directorate (IDs 600000 and above). IDs are used to locate documents in the Laboratory's Electronic Document Management System and in the Master Reference Set. The NMED Hazardous Waste Bureau and ADEM maintain copies of the Master Reference Set. The set ensures that NMED has the references to review documents. The set is updated when new references are cited in documents.

Brown, D.W., and J.D. Hem, 1975. "Reactions of Aqueous Aluminum Species at Mineral Surfaces," Chemistry of Aluminum in Natural Water, Geological Survey Water-Supply Paper 1827-F, United States Government Printing Office, Washington, D.C. (Brown 1975, 602820)

Broxton, D., R. Warren, P. Longmire, R. Gilkeson, S. Johnson, D. Rogers, W. Stone, B. Newman, M. Everett, D. Vaniman, S. McLin, J. Skalski, and D. Larssen, March 2002. "Characterization Well R-25 Completion Report," Los Alamos National Laboratory report LA-13909-MS, Los Alamos, New Mexico. (Broxton et al. 2002, 072640)

Broxton, D.E., and P.G. Eller (Eds.), June 1995. "Earth Science Investigations for Environmental Restoration—Los Alamos National Laboratory, Technical Area 21," Los Alamos National Laboratory report LA-12934-MS, Los Alamos, New Mexico. (Broxton and Eller 1995, 058207)

Coelho Vieira, A.C., G.A. Rocha, P. Souza Santos, S.S. H, and P.K. Kiyohara, 2008. "Specific Surface Area and Structures of Aluminas from Fibrillar Pseudoboehmite," *Revista Materia,* Vol. 13, No. 2, pp. 329-341. (Coelho 2008, 602818)

Kuentz, D.C., December 1986. "The Otowi Member of the Bandelier Tuff: A study of the petrology, petrography, and geochemistry of an explosive silicic eruption, Jemez Mountains, New Mexico," Master's Thesis, University of Texas at Arlington. (Kuentz 1986, 602817)

Sposito, G., 1989. *The Chemistry of Soils*, Oxford University Press, New York, New York. (Sposito 1989, 058685)

Stumm, W., and J.J. Morgan, 1981. "Metal Ions and Ligands," in *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, Wiley-Interscience Publication, New York, New York, p. 341. (Stumm and Morgan 1981, 059079)

Tettenhorst, R., and D.A. Hofmann, 1980. "Crystal Chemistry of Boehmite," *Clays and Clay Minerals,* Vol. 28, No. 5, pp. 373-380. (Tettenhorst 1980, 602819)

Appendix A

Analytical Results from Storm Water and Sediments Collected at Gage Stations E038, E240, and E252

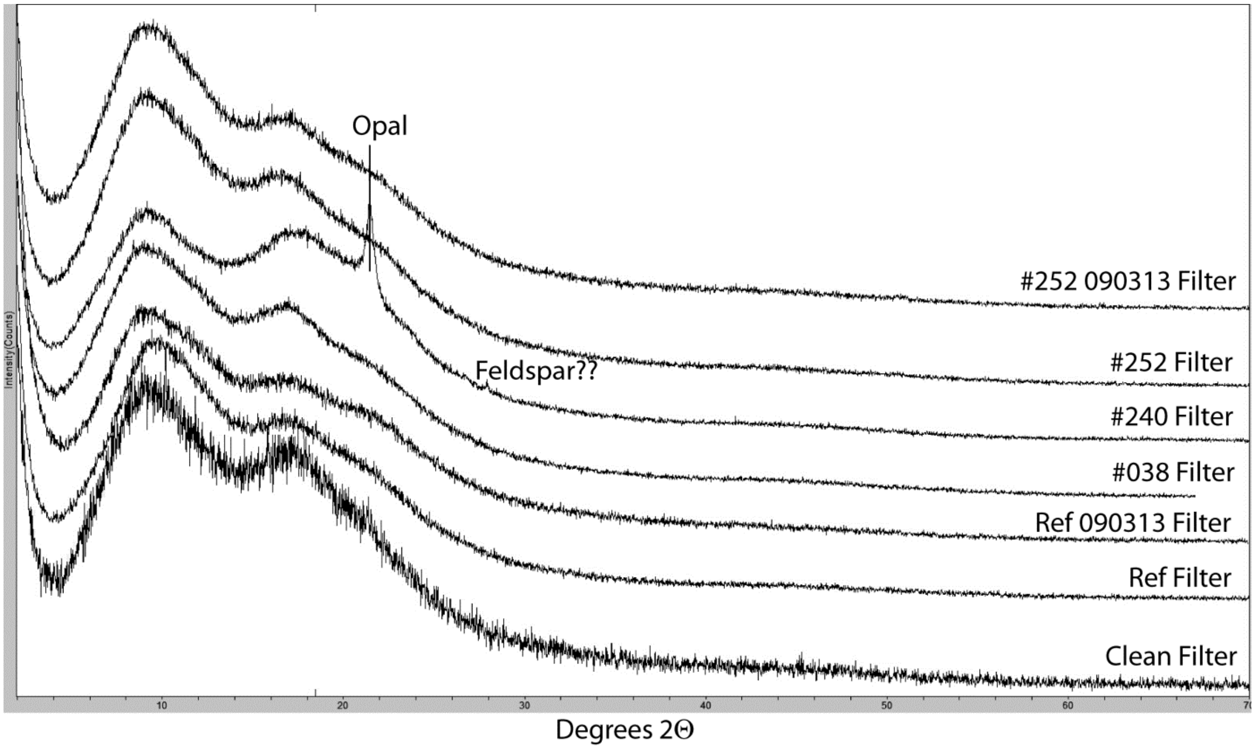

Figure A-1 **Diffraction patterns of the E240, E038, and E252 retentate; reference filters; and a clean cellulose nitrate filter. Because of the high background associated with filter papers, it is difficult to discern amorphous materials within the filtrate. Storm water retentate from E240 is the only sample that contains detectible crystalline materials, i.e., opal and feldspars.**

Blank 0.2-µm Filter

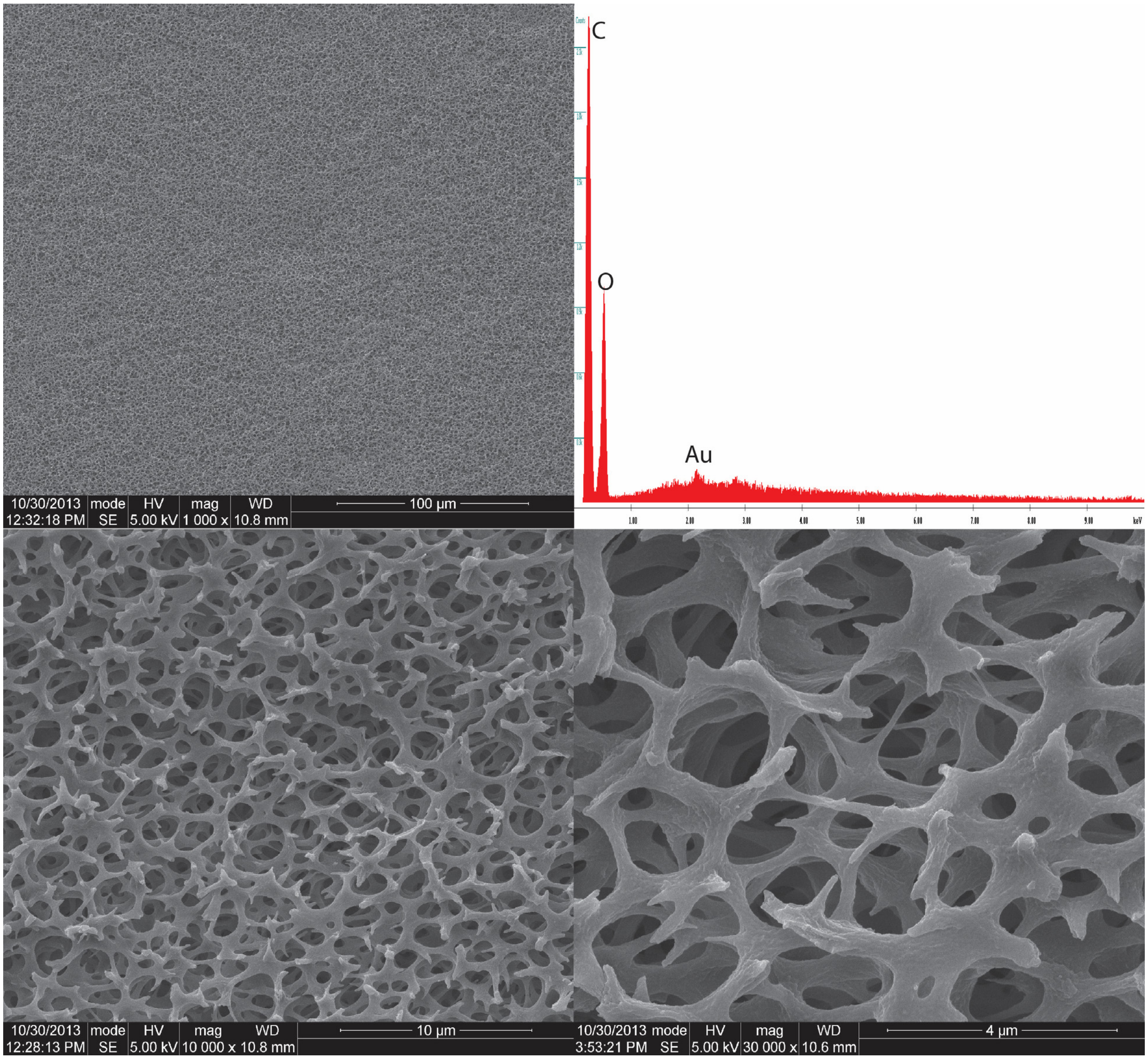

Figure A-2 **Clean cellulose nitrate 0.2-µm filter showing a open pore network with pore sizes typically no larger than 1–2 µm in diameter. The network of the pores restricts particles greater than 0.2 µm from emerging from the filter. The spectra represents an elemental baseline for scanning electron microscopy/electron dispersive spectroscopy (SEM/EDS) and x-ray diffraction (XRD) results. Three images show different magnifications (1k, 10k, and 30k) of the same filter. Filters contain carbon and oxygen with no evidence of nitrogen silica or aluminum.**

E038 Storm Water Suspended-Sediment Analysis

0.2-µm Cellulose Nitrate Filter

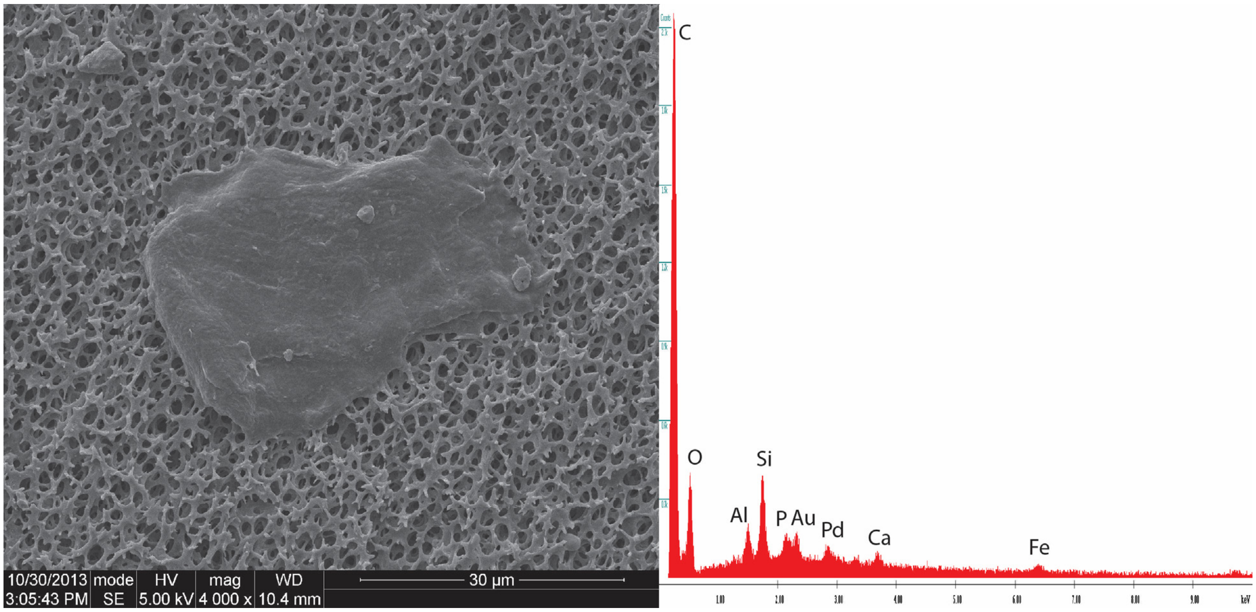

Figure A-3 **Material collected on the E038 0.2-µm filter displaying an amorphous texture. Chemical composition is carbon rich with minor amounts of phosphorus. This composition is simialar to the botryoidal particles observed on location E240 filters.**

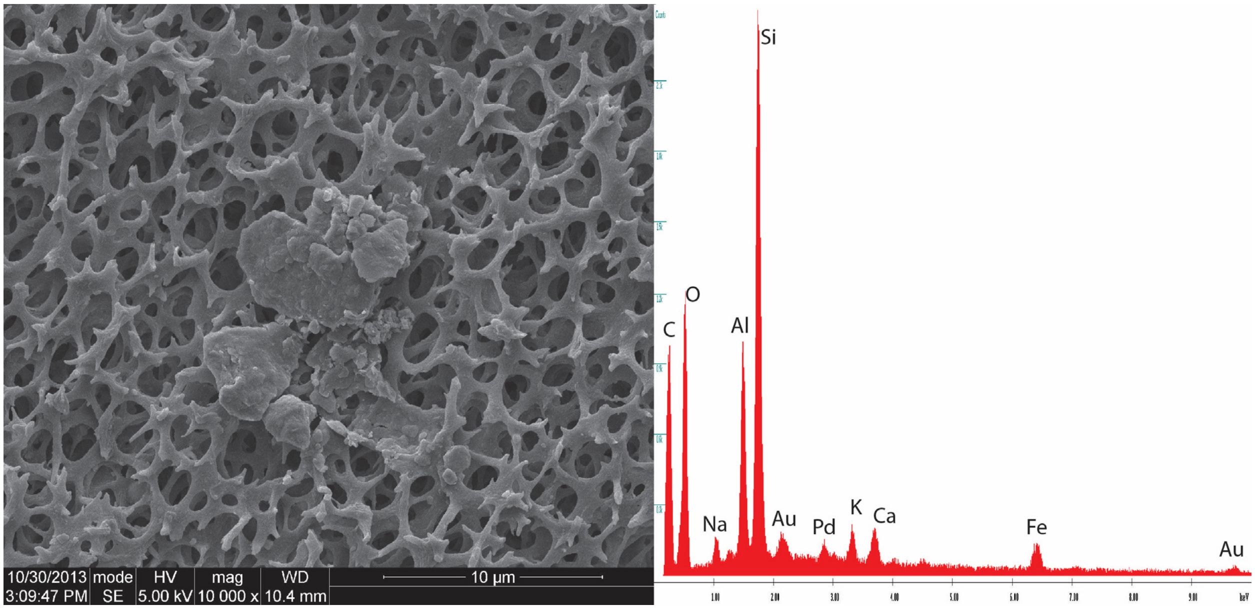

Figure A-4 **Aluminosilicate particles collected on the filter paper displaying granular texture**

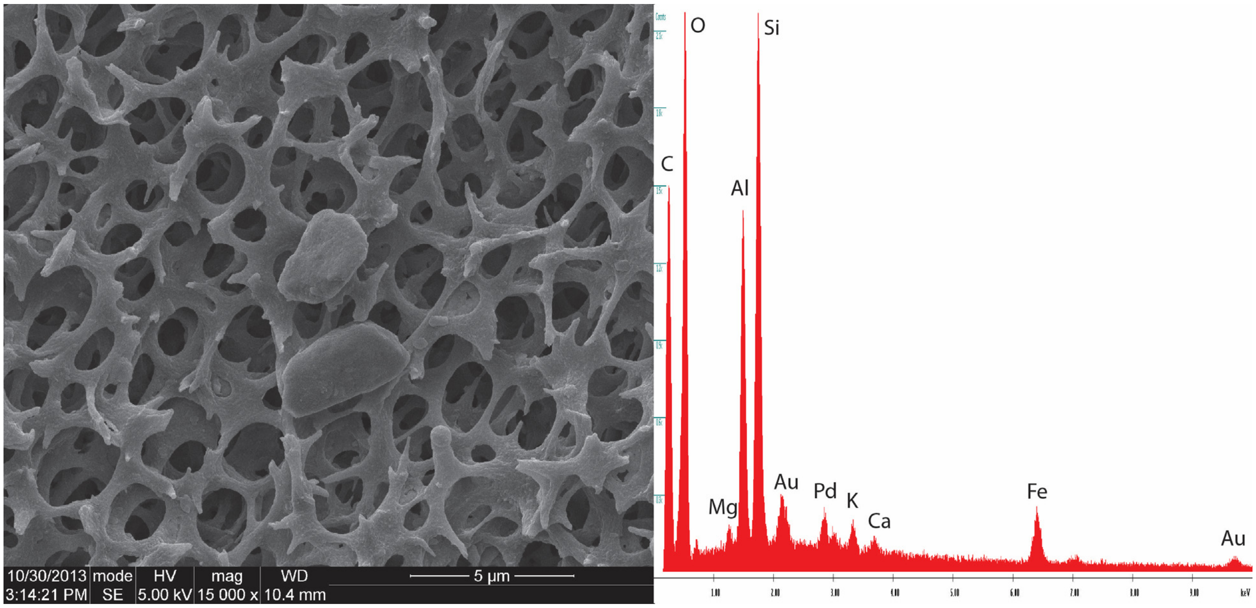

Figure A-5 **Subrounded, aluminosilicate particles collected on a E038 0.2-µm filter. These particles are slightly more aluminum rich compared with other particles on this filter.**

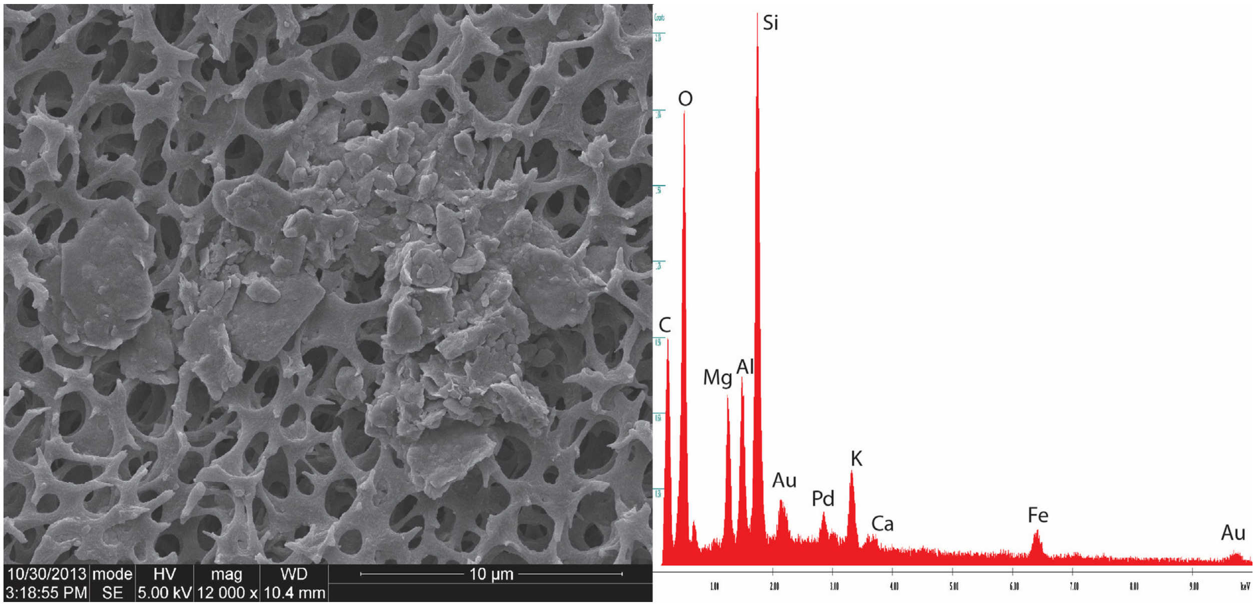

Figure A-6 **Aluminosilicate aggregates collected on the E038 0.2-µm filter. The platey particles tended to be more enriched in magnesium compared with other particles. They appear to be micas (most likely biotite).**

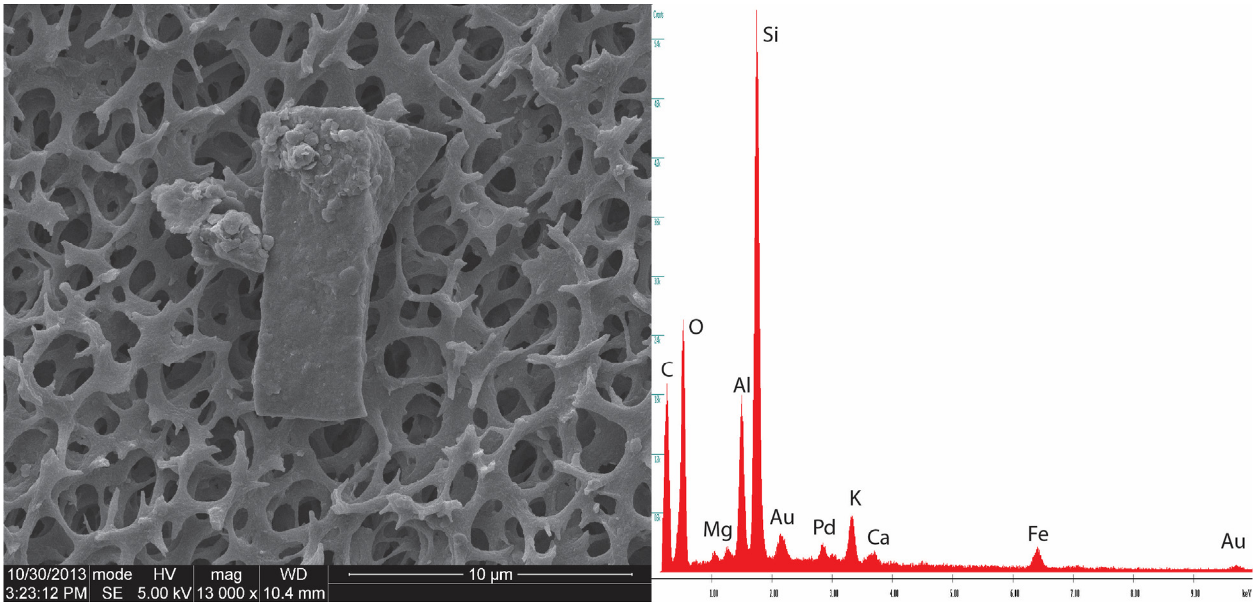

Figure A-7 Bladed, aluminosilicate particle, most likely a mica, but unknown

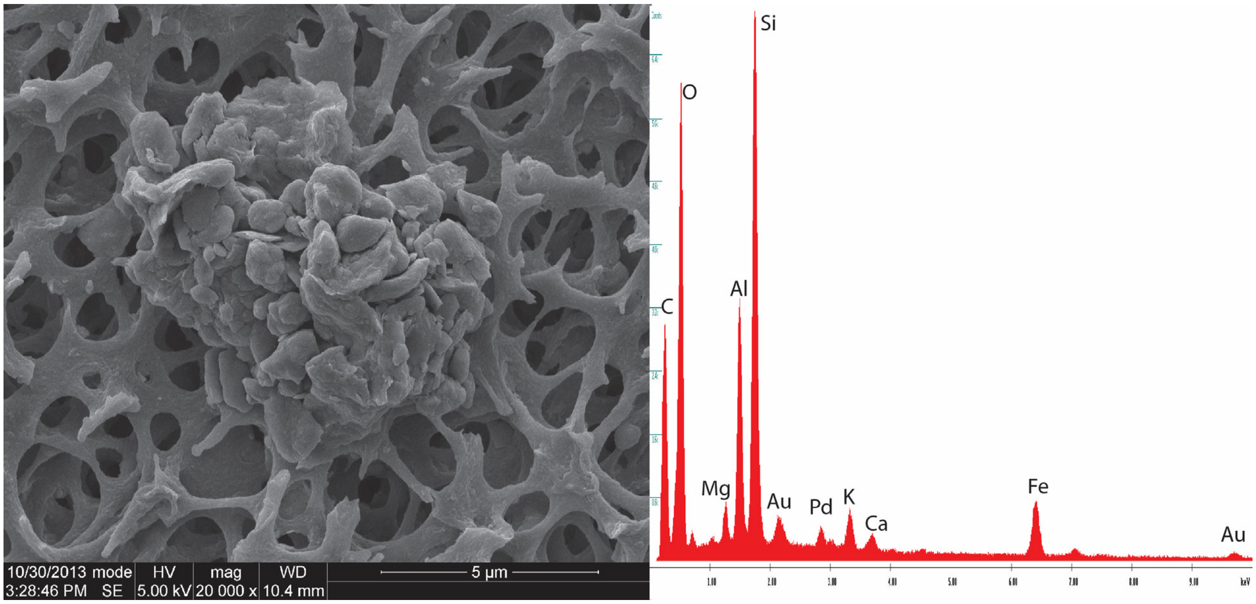

Figure A-8 Unusual aluminosilicate aggregate

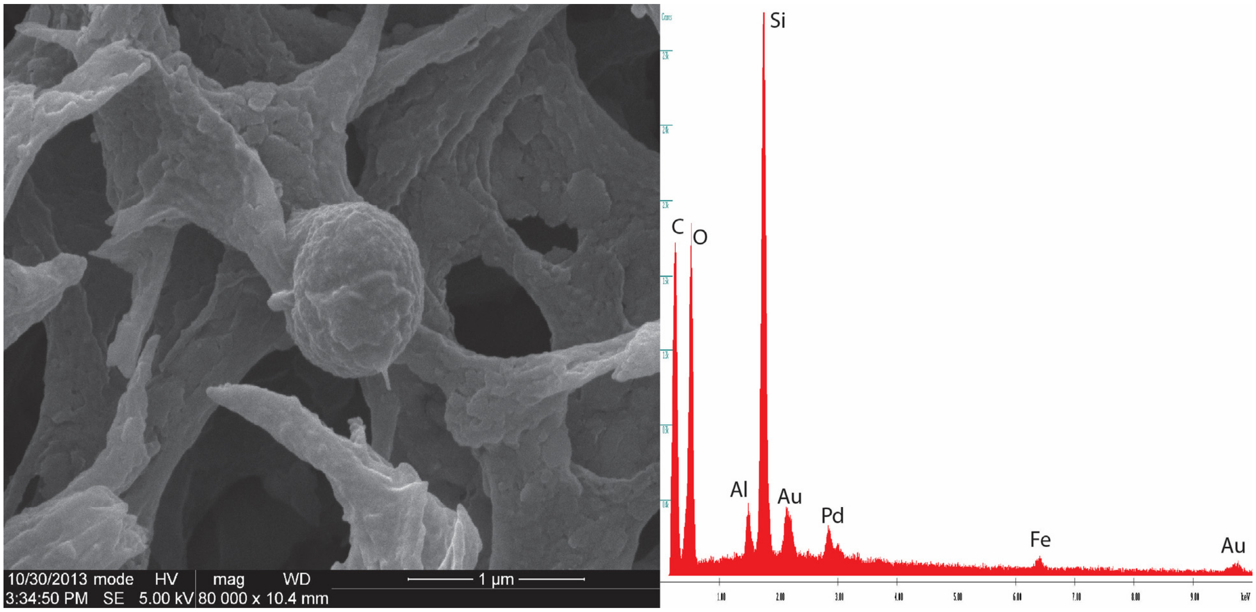

Figure A-9 **The EDS results show low aluminum. The material is most likely amorphous silica glass coating the filter.**

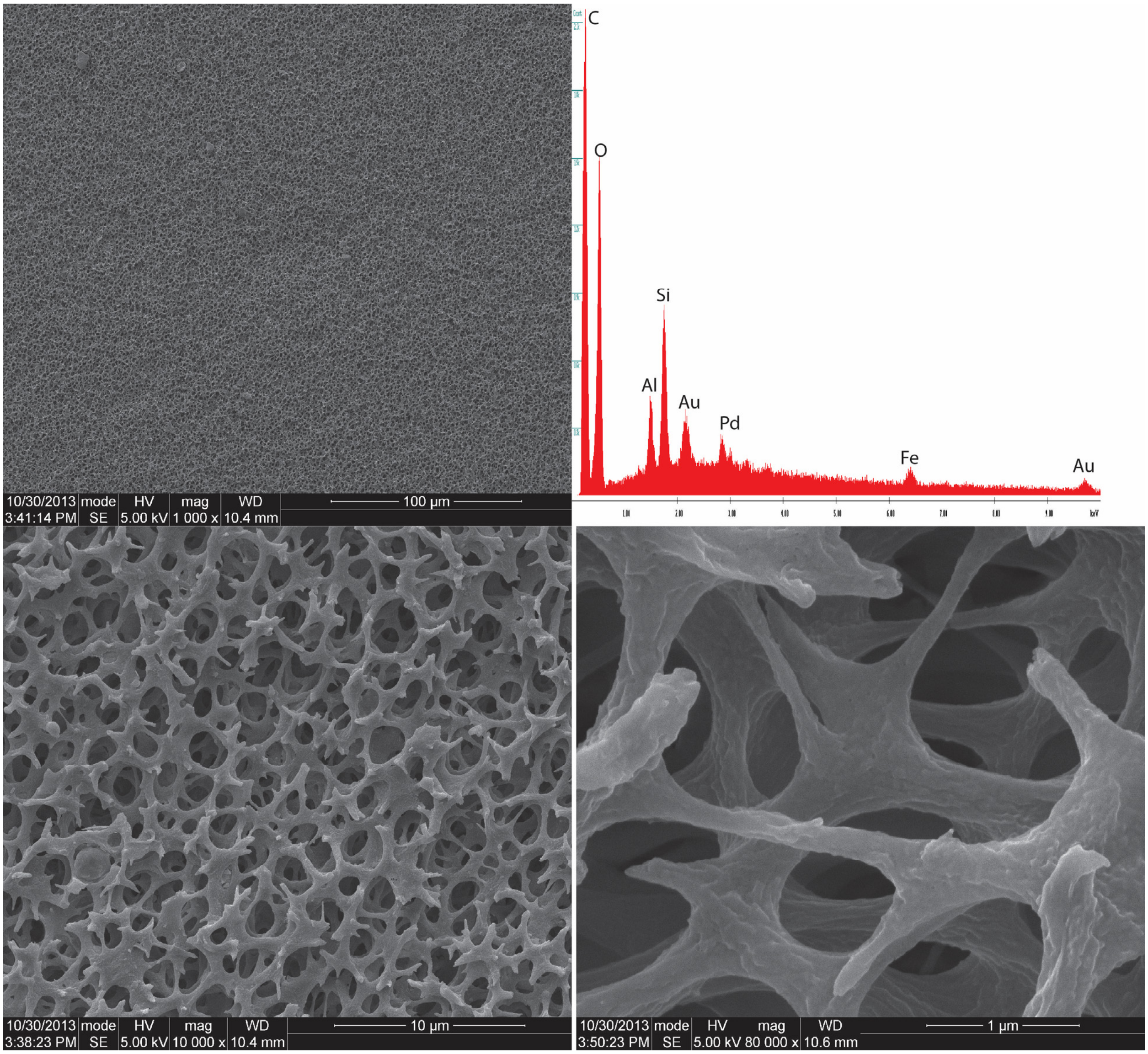

Figure A-10 **E038 filter imaged at three different magnifications (1k, 10k, and 80k). There is no noticible porosity loss and extensive particulate collection. The average composition (collected on the 10k image) shows some aluminosilciate materials but lower concentration compared with the filter from E240. Material from E038 and E240 have similar aluminum/silicon elemental ratios.**

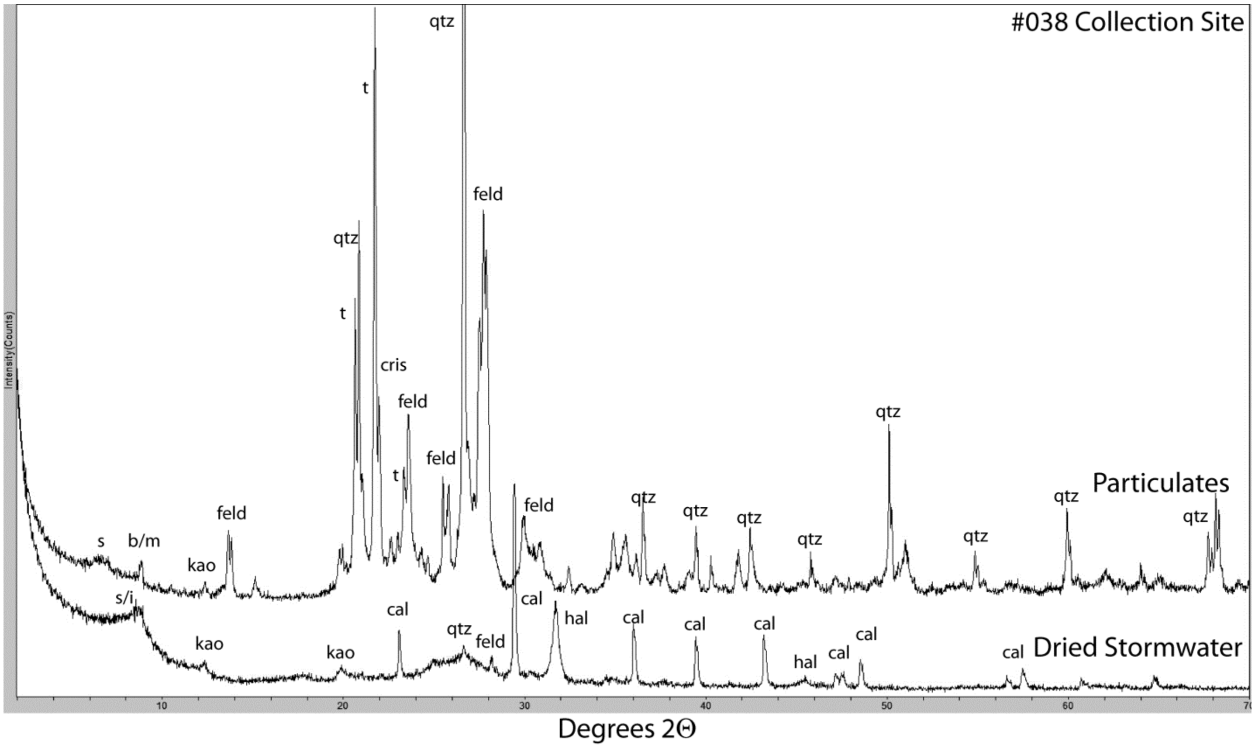

Figure A-11 **XRD mineral identification patterns from E038 dried storm water precipitant and sediment particulates from the same storm water sample. The dried stormwater precipitate is dominated by calcite (cal), smectite (s) or illite (i) (or smectite/illite mixed-layer [s/i]), and halite (hal) with minor amounts of quartz (qtz), kaolinite (kao), and feldspar (feld). Halite and calcite are primarily from precipication during storm water evaporation, whereas the silicate fractions are associated with unsettled particulates. Suspended sediment particulates are typical of Bandelier Formation minerology and dominated by orthoclase/sanidine (feld), albite (feld), quartz (qtz), trydimite (t), and cristobalite (c) with minor amounts of mica (biotite or muscovite [b/m]), smectite, and kaolinite.**

Dried Storm Water Precipitate from E038

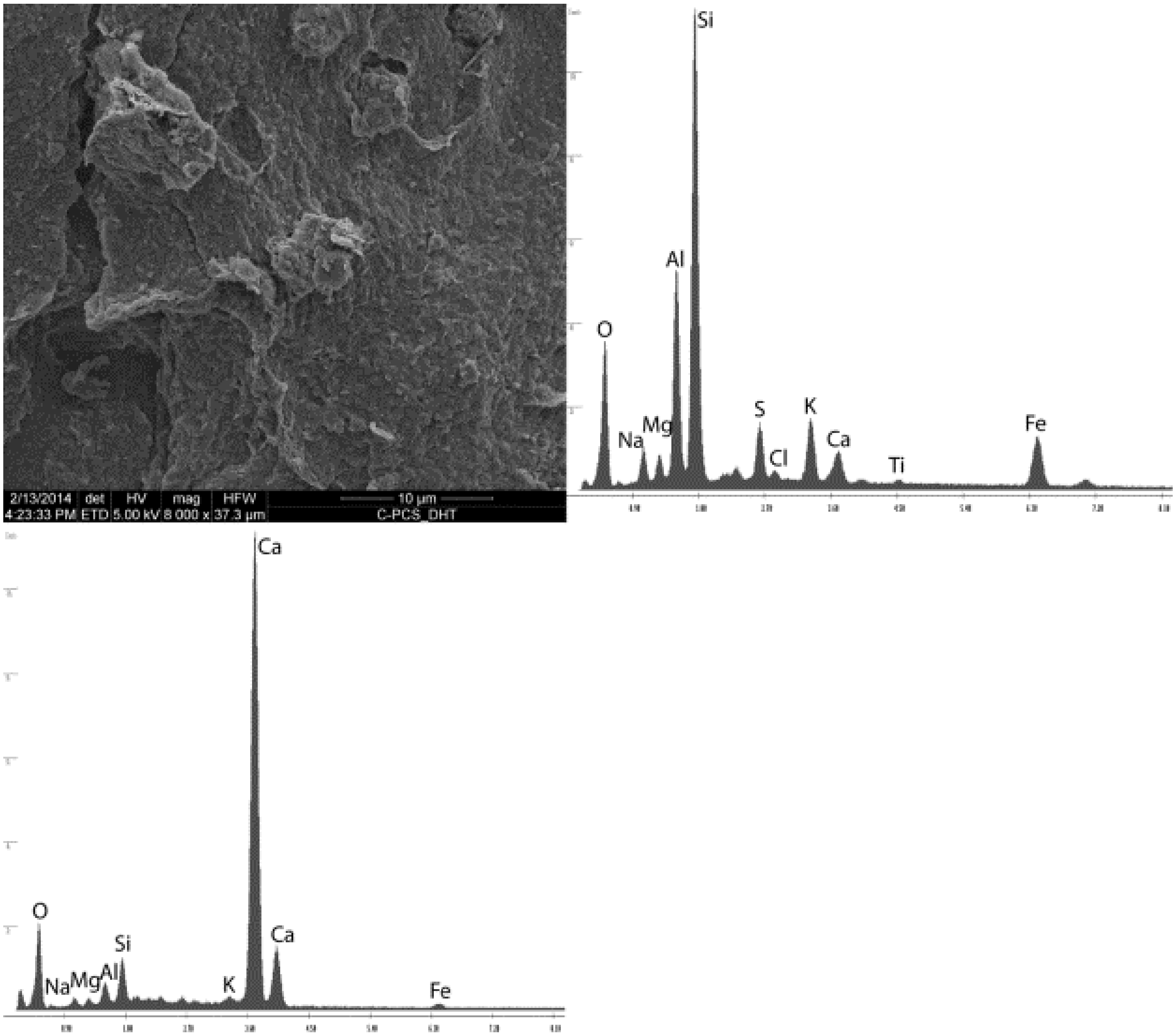

Figure A-12 **SEM/EDS spectra from the dried storm water precipitate collected from E038. The precipitate displays an amorphous texture and elemental chemistry similar to biotite or iron-rich smectite. The calcium-dominated energy-dispersive x-ray spectroscopy (EDS) analysis was from a fiber bundle typical of $CaCO_3$. Sulfate solids are present throughout the sample yielding the sulfur peak.**

Storm Water Sediment Particulates

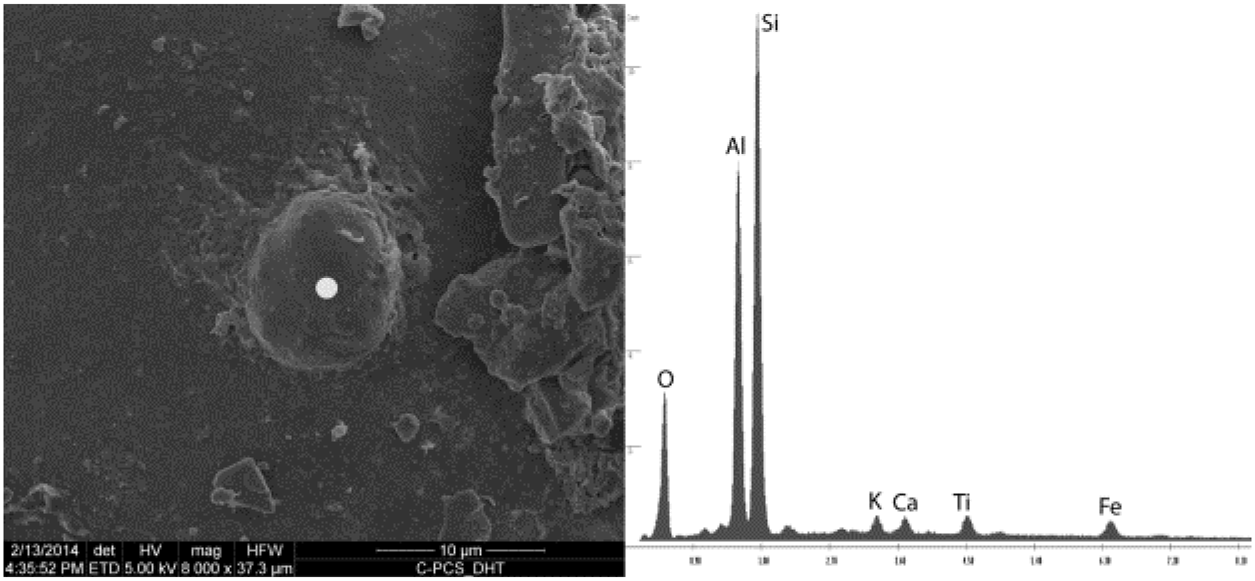

Figure A-13 Spheriodal aluminosilicate particulate with minor amounts of potassium, calcium, titanium, and iron. The particle is most likely amorphous material that precipitated from storm water during desiccation. Area for EDS analysis is noted by the bright spot.

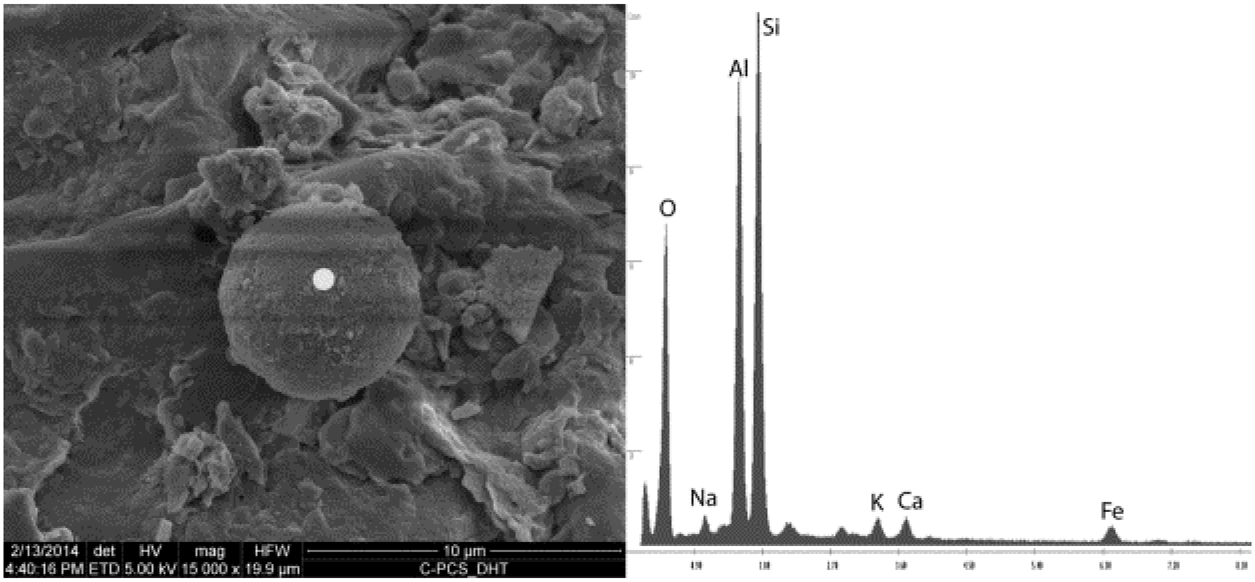

Figure A-14 Spheriodal aluminosilicate particulate with minor amounts of potassium, calcium, and iron. The particle is probably amorphous material precipitated from the storm water. Area for EDS analysis is noted by the spot. Aluminum is notibly higher in this spectra, with an aluminum to oxygen ratio of almost 1/1.

E240 Storm Water Suspended-Sediment Analysis

0.2-µm Cellulose Nitrate Filter

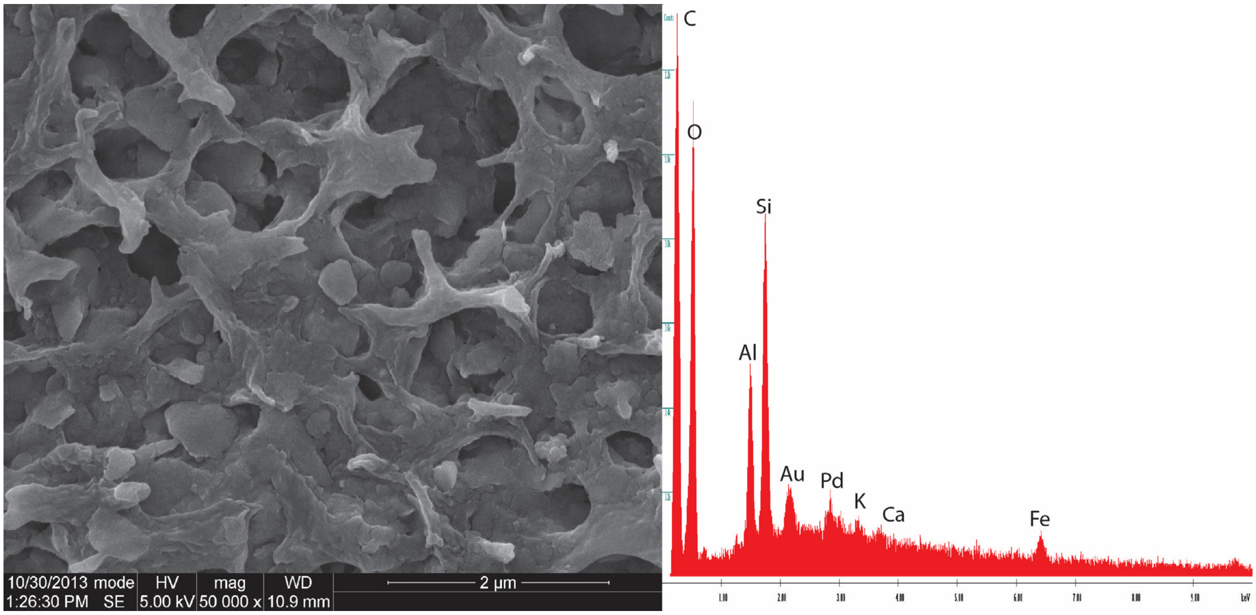

Figure A-15 Retentate exhibiting an amorphous morphology dominated by aluminum and silicon; aluminum/silicon ratio of 1/2. There are minor amounts of potassium, calcium, and iron. The particles appear to have filled most of the porosity opposed to residing on the filter surface. Particulates on the surface typically are well rounded.

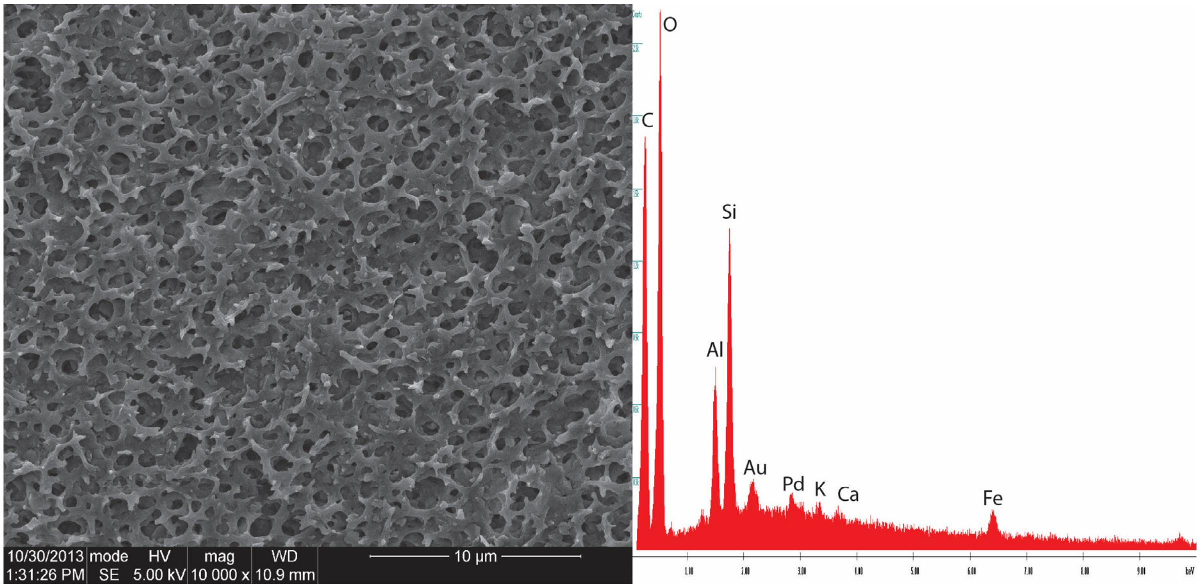

Figure A-16 10k magnification image showing reduced porosity and low concentration of particulates collected on filter surface. EDS spectra collected on the entire area shown in image shows the average chemical composition of solids collected on the filter.

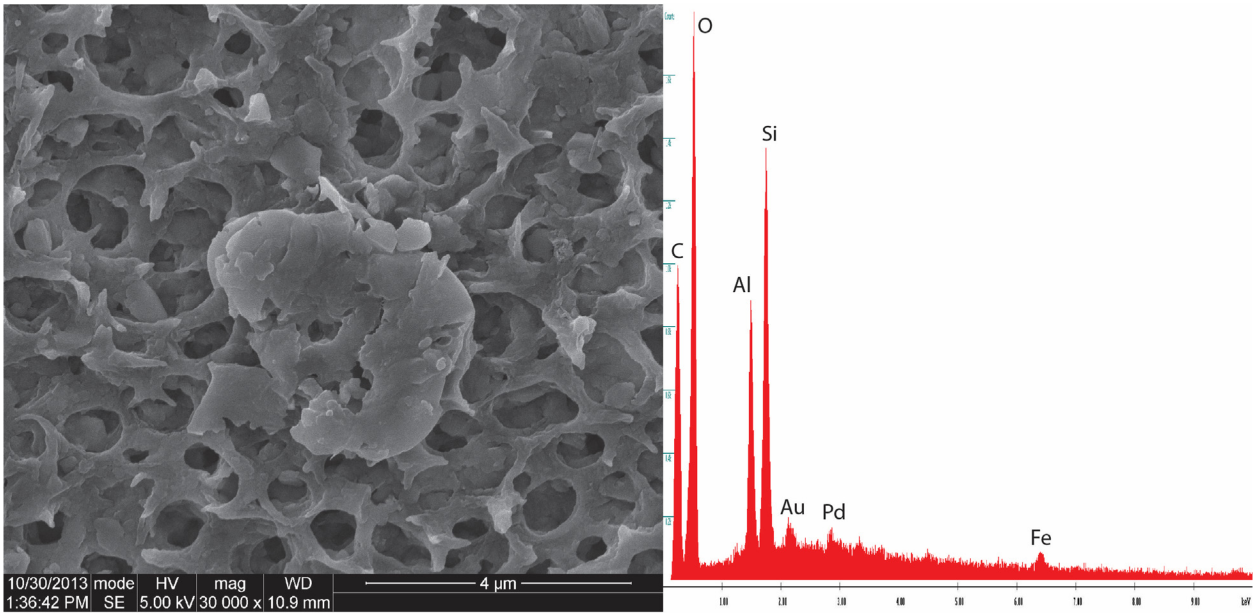

Figure A-17 **Silicon-aluminum-rich particle with a subrounded morphology displaying either dissolution or mechanical abrasion features.**

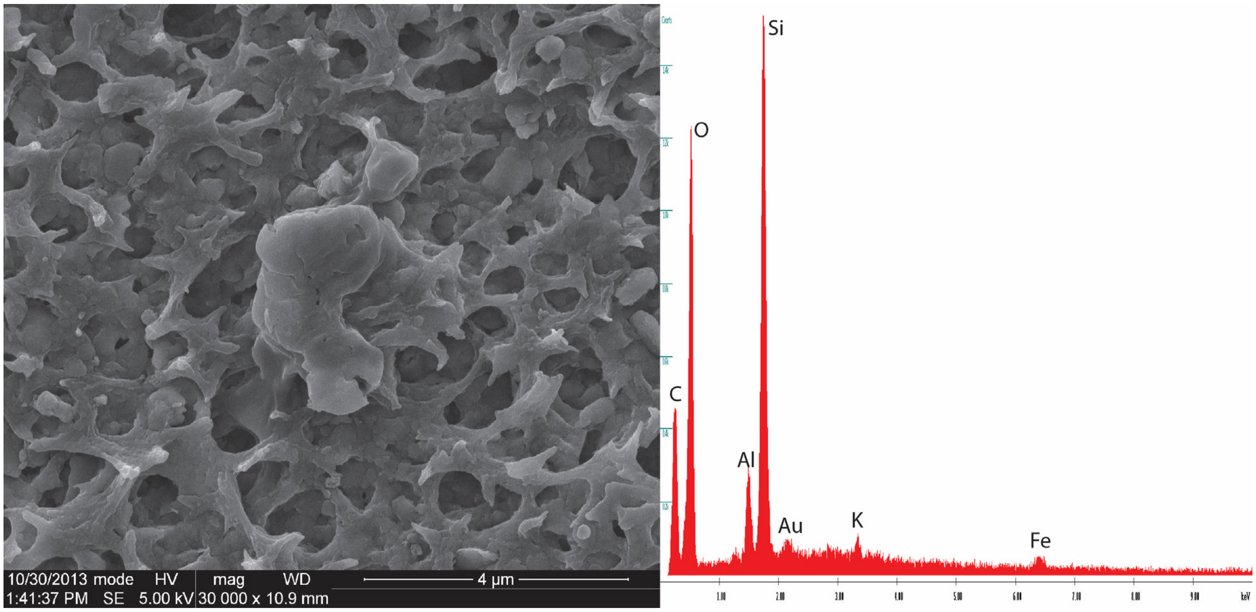

Figure A-18 **Subrounded particulate that is silicon enriched compared with the average chemical composition; most likely volcanic glass.**

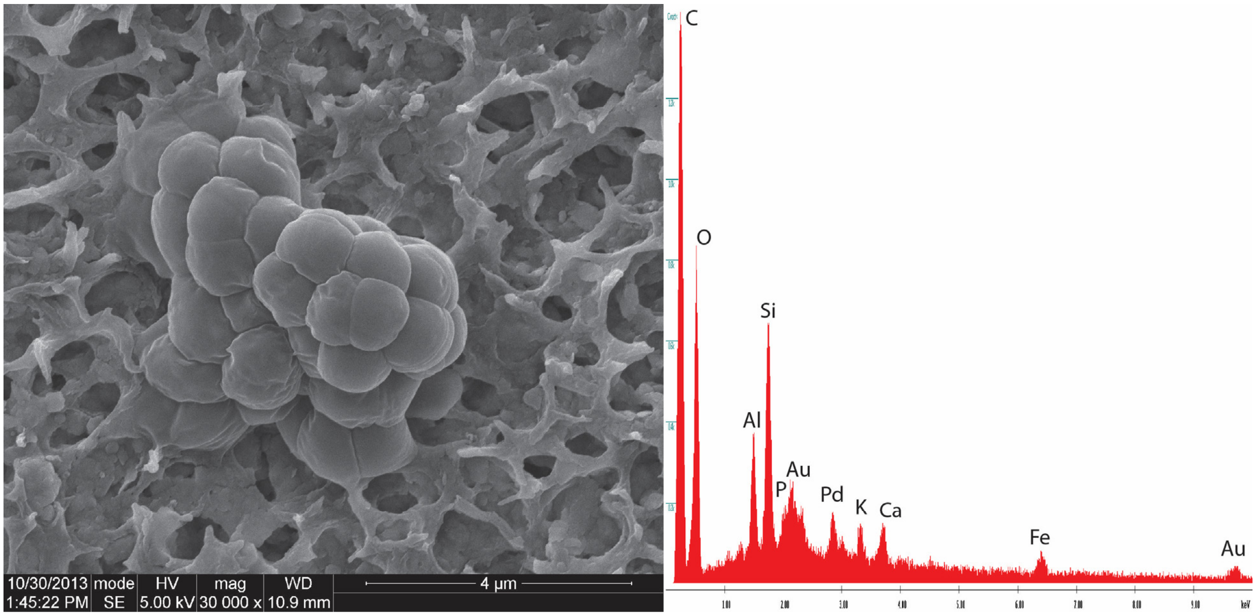

Figure A-19 **Particle displaying a botryoidal morphology with a carbon-enriched chemical composition. These particles also contain various amounts of phosphorus along with aluminum, silicon, potassium, calcium, and iron. It would appear that carbon,potassium-bearing particulate has grown on an aluminosilicate particle, or the aluminosilicate composition is from the underlaying substrate. The particle's origin is not known.**

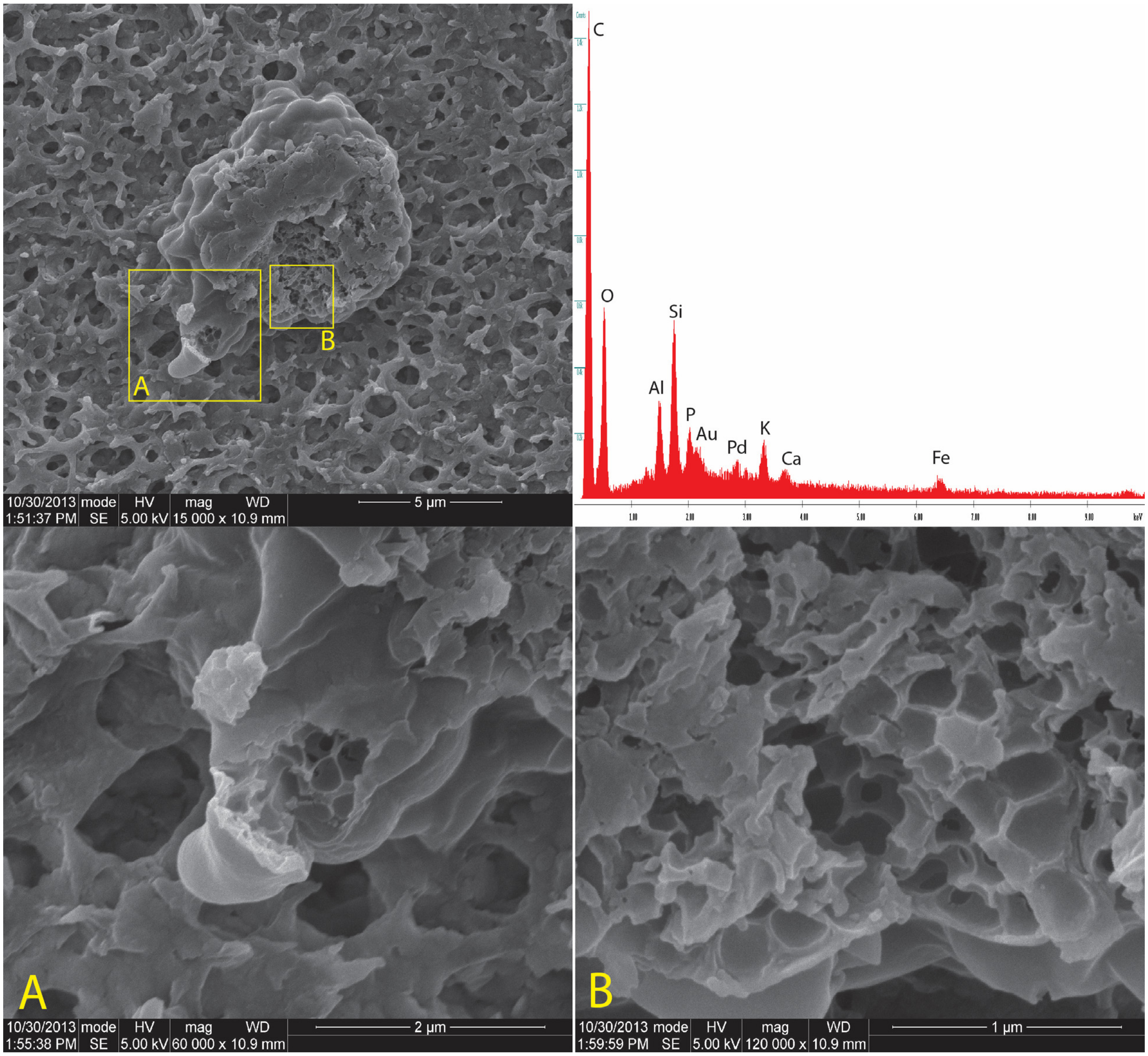

Figure A-20 **Particle with a similar botryoidal morphology and chemical composition to the particle displayed in Figure A-19. A honeycombed internal structure is evident in the magnified images (A and B). This is unusual considering the honeycombed structure is not expressed on the external surfaces.**

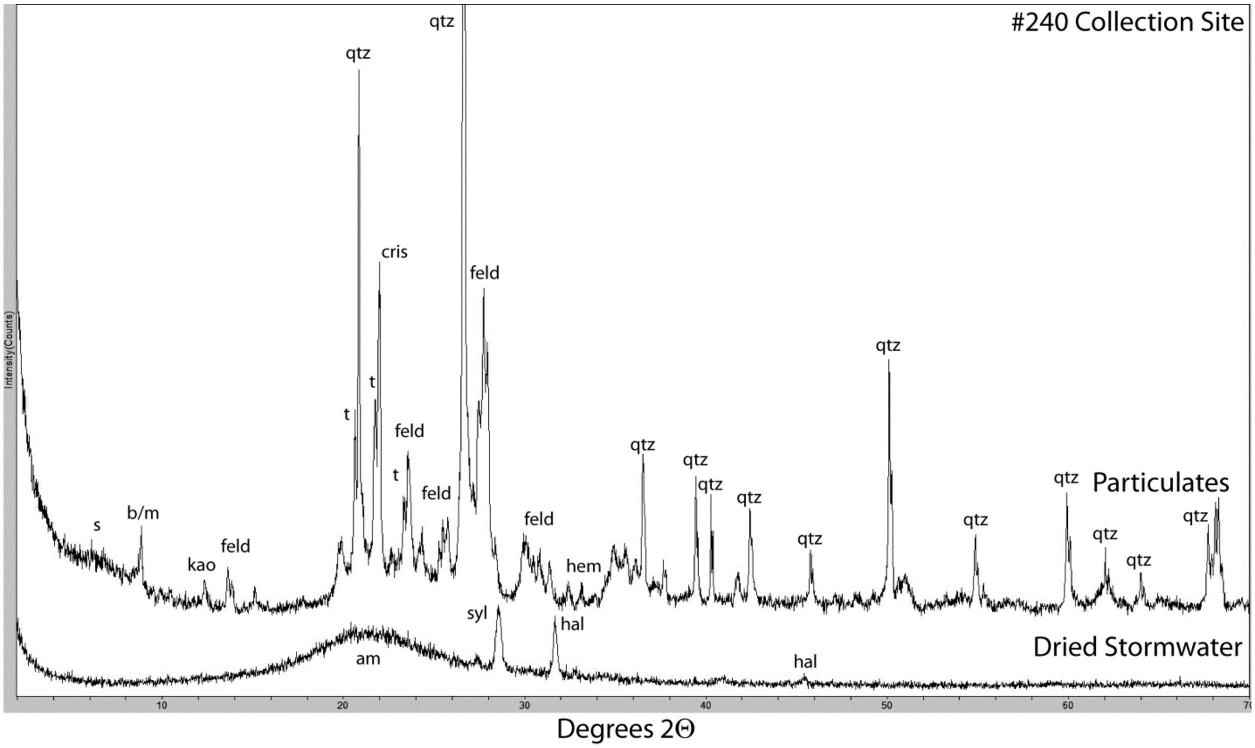

Figure A-21 **XRD patterns from dried storm water and suspended sediment particulates from the same storm water sample (E240). The dried storm water was dominated by amorphous matter (broad hump at 20–30°2θ), sylvite (syl), and halite (hal). The amorphous hump (coupled with SEM/EDS) appears to be aluminosilicate. Sylvite and halite are primarily from precipication during storm water evaporation. Suspended sediment particulates are typical of the Bandelier Formation and dominated by orthoclase/sanidine (feld), albite (feld), quartz (qtz), trydimite (t), and cristobalite (c) with minor amounts of mica (biotite or muscovite [b/m]), smectite, hematite (hem), and kaolinite (kao).**

Dried Storm Water Precipitate

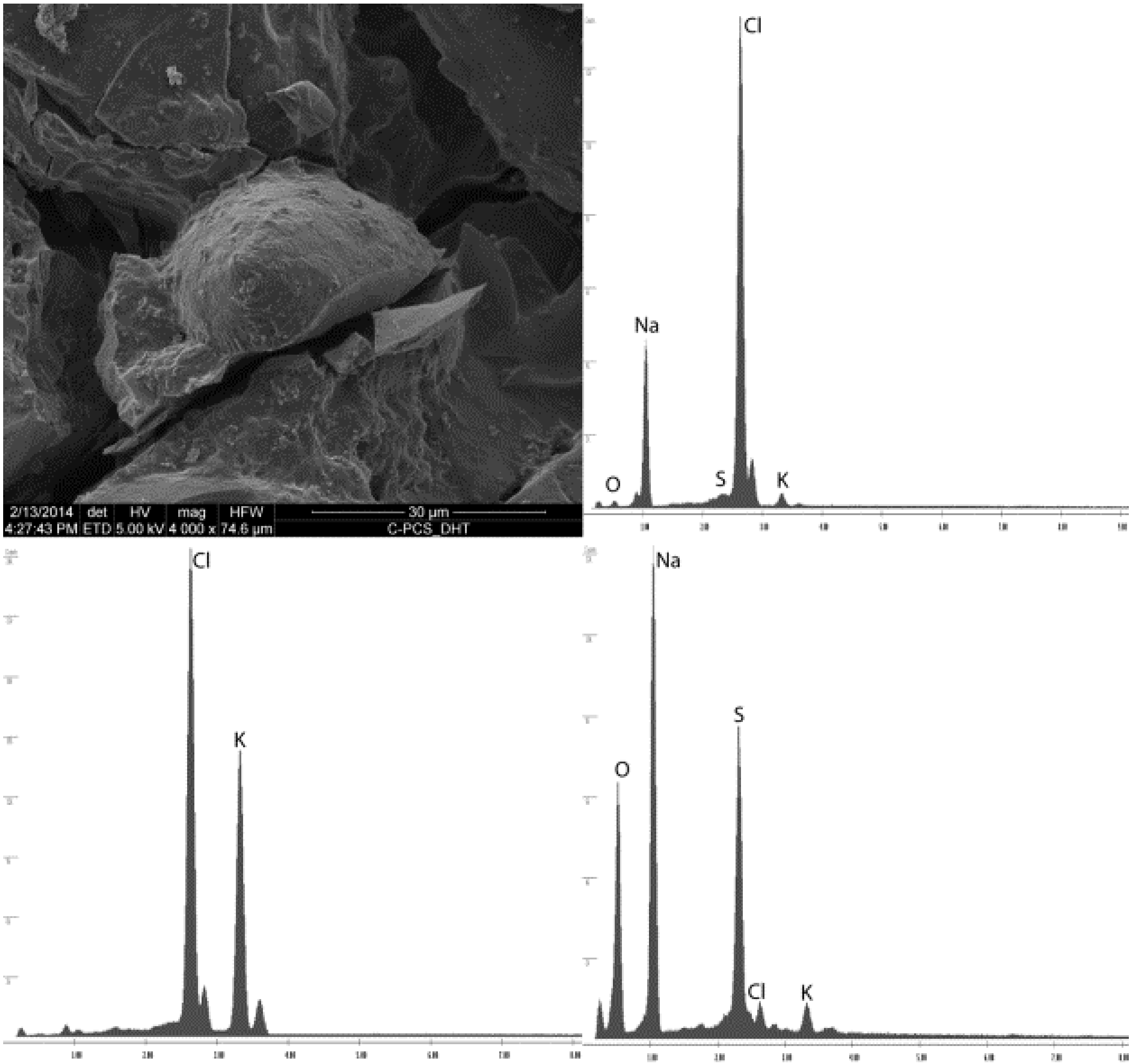

Figure A-22 **SEM image of precipitates from storm water collected at location E240. EDS indicates NaCl, KCl, and (Na,K)$_2$SO$_4$ were the dominate salts to precipitate, suggesting a Na-K-Cl-SO$_4$ dominated fluid.**

Storm Water Sediment Particulates

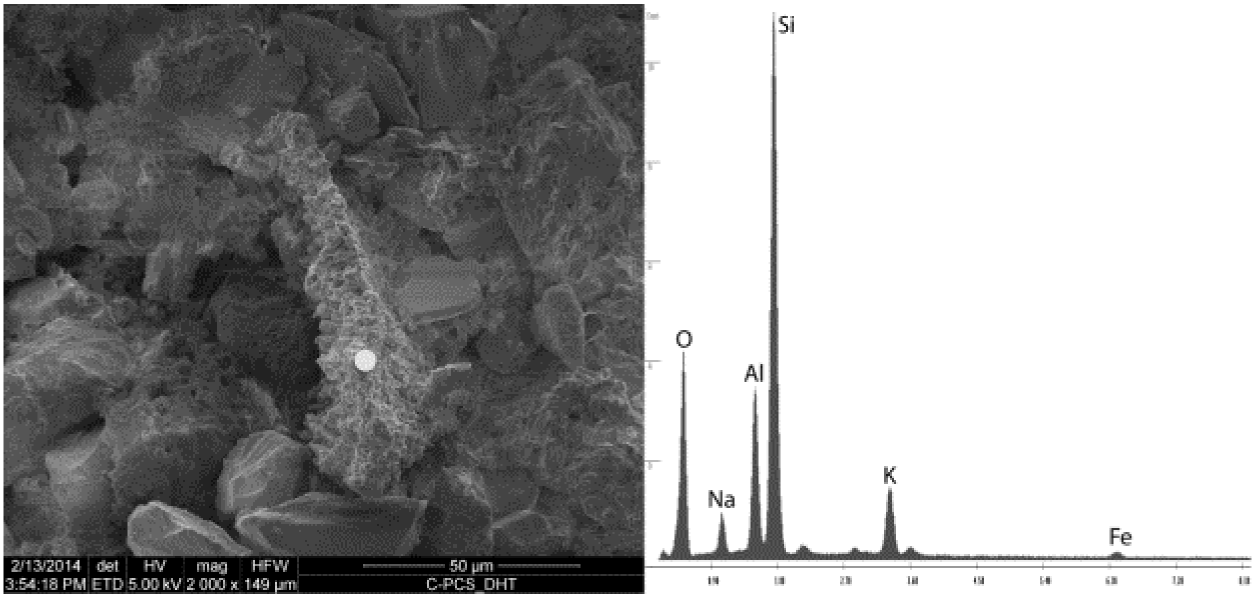

Figure A-23 **Extensively altered sodium,potassium-feldspar with minor amount of iron. This feldspar is probably either orthoclase or sanidine. These feldspars are typical of Bandelier Formation volcanic tuffs. Area for EDS analysis is noted by the bright spot.**

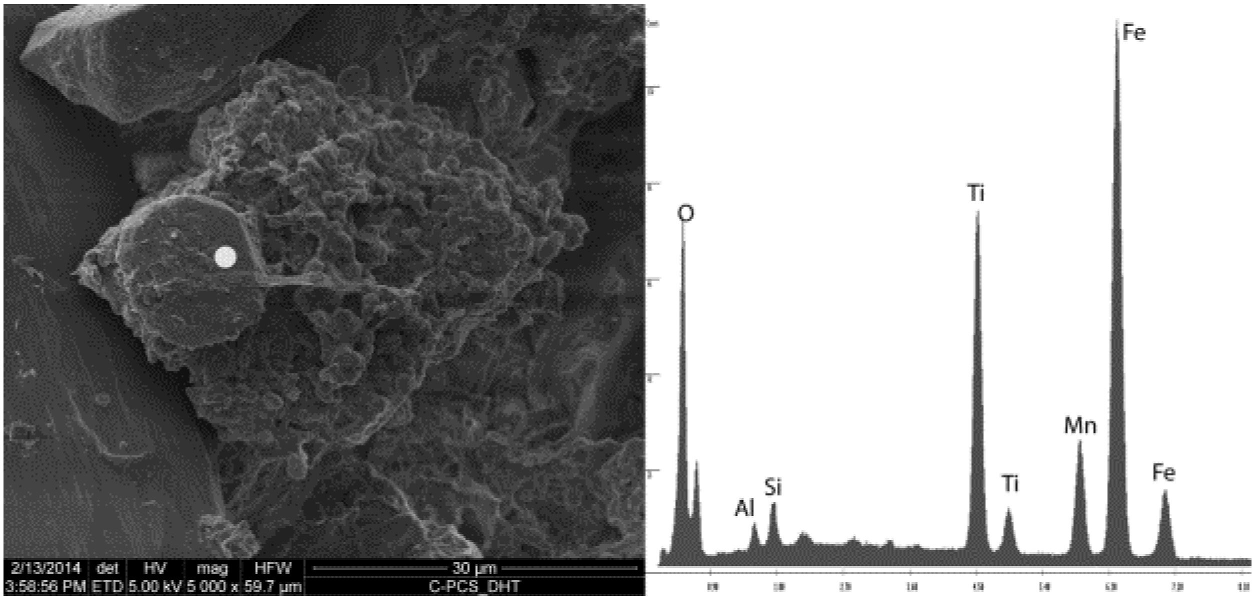

Figure A-24 **Subangular titanium,manganese-bearing magnetite (or ilmenite) sitting on an aluminosilicate substrate; note aluminum/silicon ratio of 1/2. The magnetites or ilmenites are most likely associated with the Tshicoma Formation sediments sourced higher up the western boundary Jemez Mountains front.**

E252 Storm Water Suspended Sediment Analysis

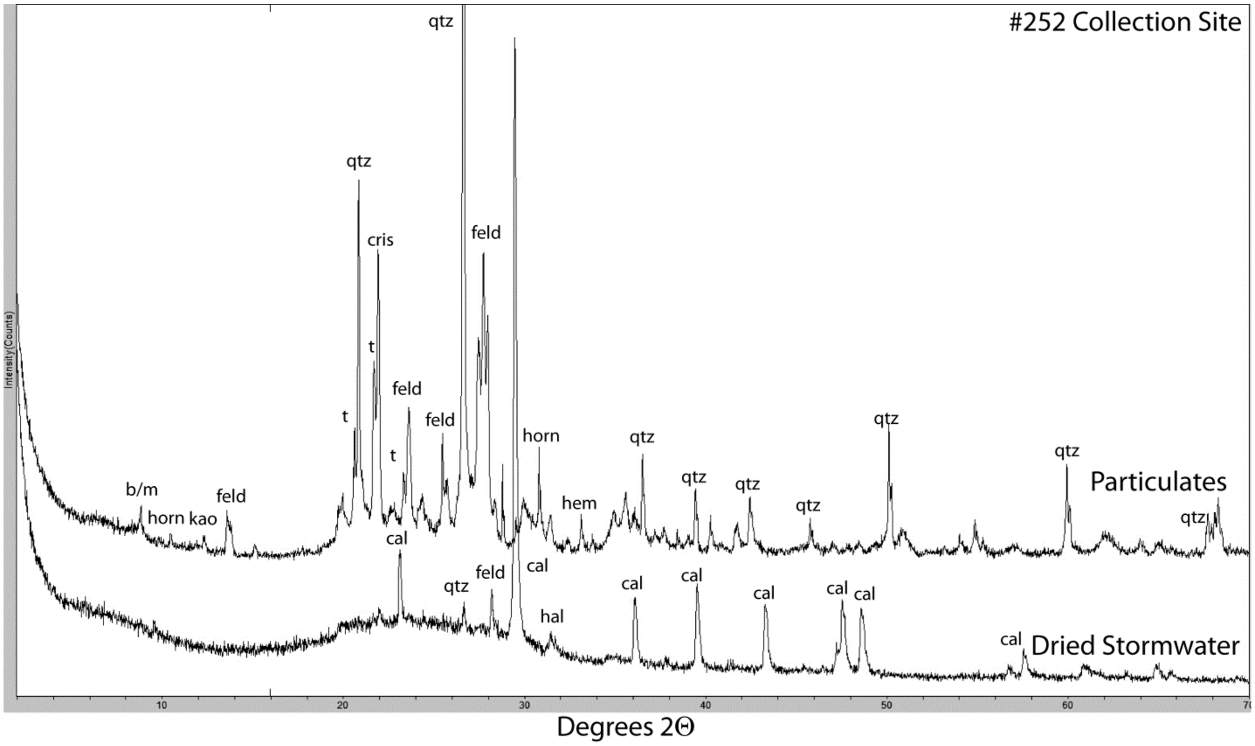

Figure A-25 **XRD patterns from dried storm water and suspended sediment particulates from the same storm water sample (E252). The dried storm water is dominated by calcite (cal), amorphous matter (broad hump at 20–30°2θ), and halite (hal) with minor amounts of quartz (qtz) and feldspar (feld). There is a broad hump at low angles that could be a poorly crystalline smectite but is inconclusive. The amorphous hump (coupled with SEM/EDS) appears to be aluminosilicate in composition. Halite and calcite are primarily from precipication during storm water evaporation, whereas the silicate fractions are associated with unsettled particulates. Suspended sediment particulates are typical of the Bandelier Formation and dominated by orthoclase/sanidine (feld), albite (feld), quartz, tridymite (t), and cristobalite (c) with minor amounts of mica (biotite or muscovite [b/m]), smectite, amphibole (horn), hematite (hem), and kaolinite (kao).**

Dried Storm Water Supernatant Precipitate

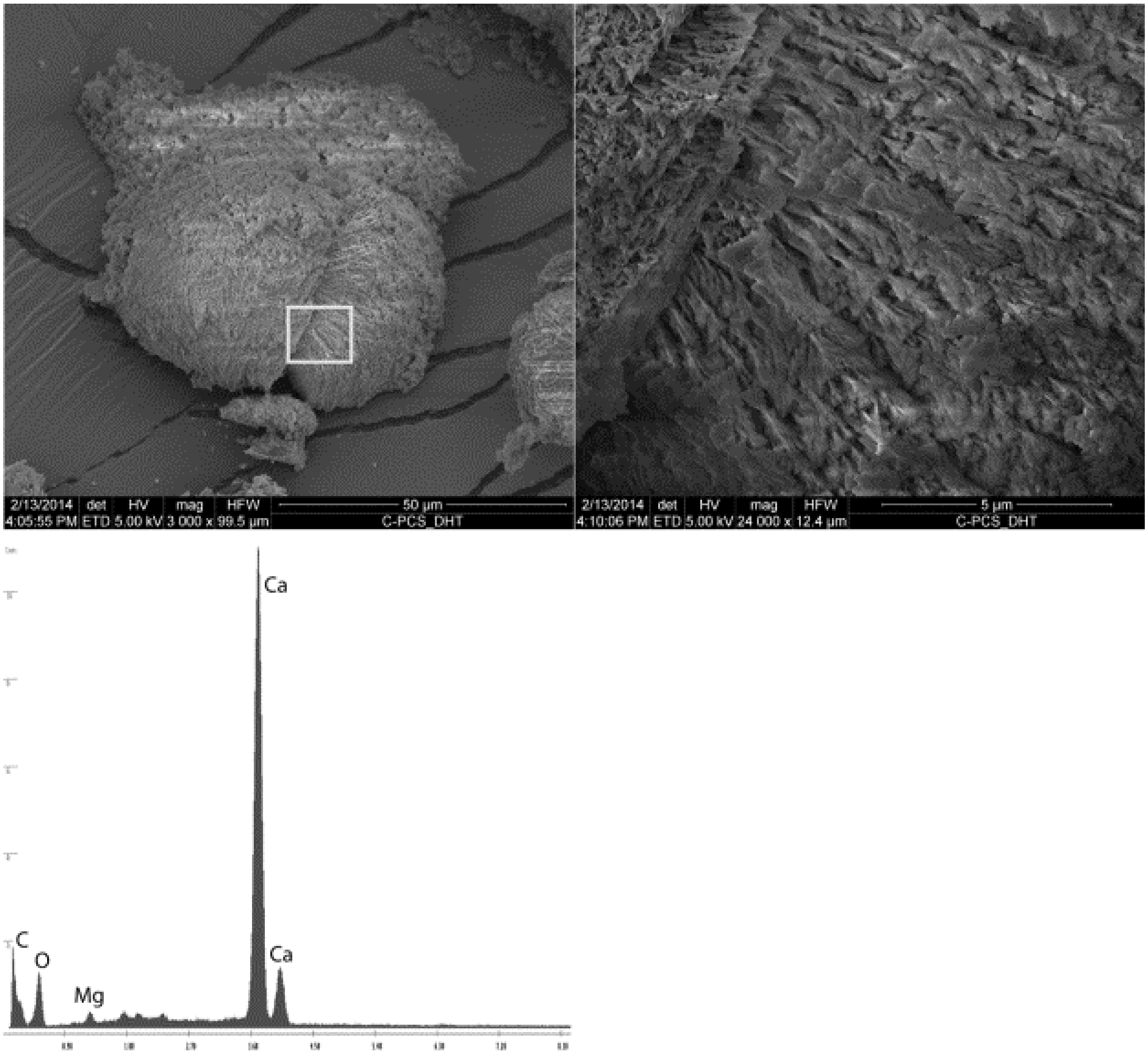

Figure A-26 **Typical $CaCO_3$ bundle associated with dried E252 storm water precipitate. Image on the right is a higher magnification of the boxed area in left-hand image. These bundles are typical of calcites observed in the storm water precipitate from all locations. The EDS spectra is dominated by calcium, suggesting calcite as a predominant phase.**

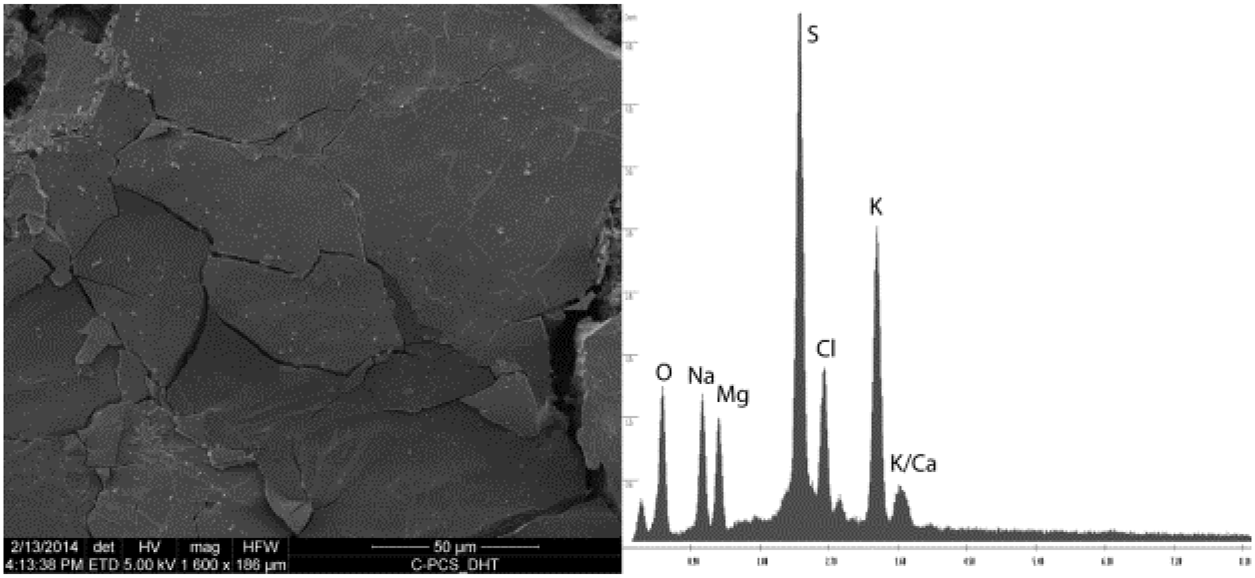

Figure A-27 Mixed Cl-SO_4 salt-phase crusts from the dried E252 storm water precipitate.

Appendix B

Amorphous $Al(OH)_3$ *Synthesis*

B-1.0 OBJECTIVE

Prepare an aluminum hydroxide [Al(OH)3] standard to use as a reference, or standard, in order to compare $Al(OH)_x$ spectra and elemental analytical results with those of entrained storm water sediments. An additional objective is to test the stability of freshly precipitated aluminum hydroxide, knowing that it quickly transforms to a more stable and ordered phyllosilicate phase.

B-2.0 METHOD

Aluminum hydroxide was precipitated following a modified method described by Prodromou and Pavlatou-Ve (Prodromou and Pavlatou-Ve 1995, 602821) to create an $Al(OH)_3$ standard for comparison with x-ray diffraction (XRD) and scanning electron microscopy (SEM) results from storm water–suspended sediments collected at gage locations E038, E240, and E252. In order to produce amorphous $Al(OH)_3$, 100 mL of 0.11 M $Al_2(SO4)_3$ was titrated with 1.5 M potassium hydroxide (KOH). Potassium hydroxide was added in 2-mL increments as shown in the top of Figure B-1. A white precipitate started to form immediately during the KOH titrations and became more persistent around a pH of 4. In the process, the batch became over-titrated causing the $Al(OH)_3$ solid to dissolve around a pH of 10.90 (38 ml KOH). The titration continued and was terminated at an endpoint pH of 12.83 (64 mL KOH). The solution was then back titrated with 110 mM $Al_2(SO_4)_3$ in order to drive the pH down, increase Al^{3+} hydrolysis activity, and force precipitation of $Al(OH)_3$ at a pH between 11 and 10. Final solution pH was around 9.90 after the addition of 114 mL of 110 mM $Al_2(SO_4)_3$. During titrations, the solution was kept at room temperature and continuously stirred. The resulting gel (solid) was washed three times with deionized water to remove excess salts and then freeze-dried and prepped for XRD and SEM analyses.

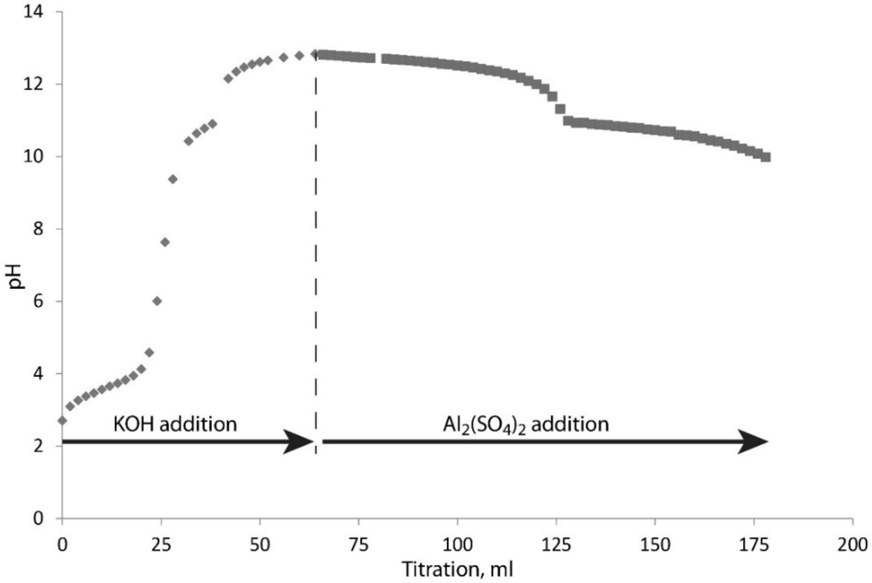

Figure B-1 Titration curve showing pH changed and volume of KOH or $Al_2(SO_4)_3$ addition

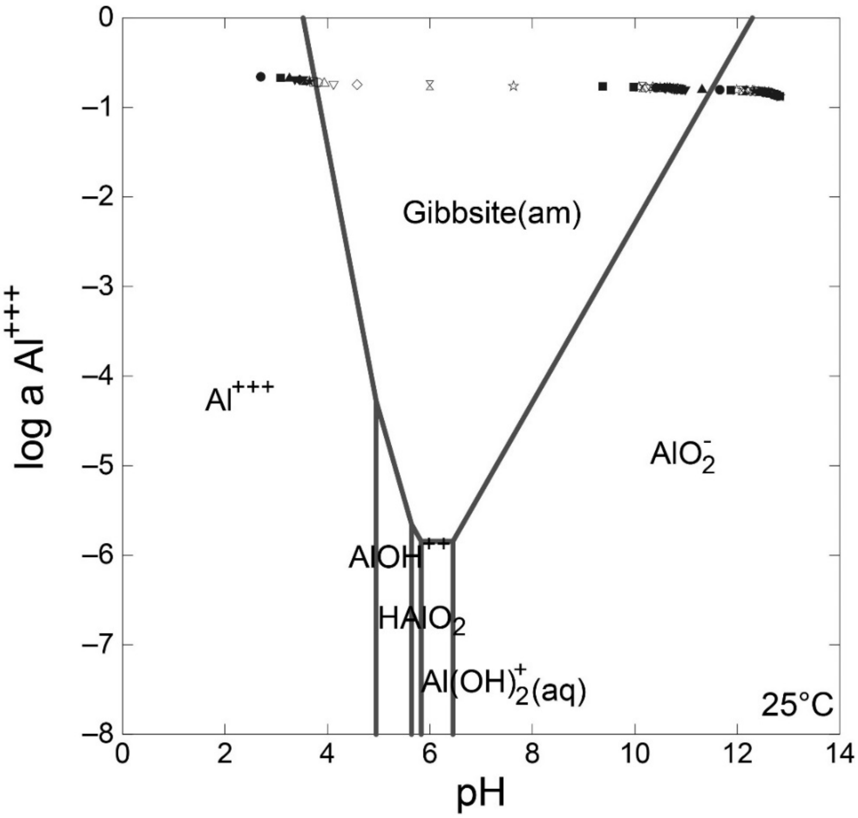

Figure B-2 Phase diagram showing soluble aluminum-species and solid amorphous (am) $Al(OH)_3$, as amorphous gibbsite. Points along the top of the diagram show the titration pathway running though soluble Al^{3+} into the solid amorphous $Al(OH)_3$ region and into the soluble AlO_2^- region. Back titrating with 0.11 M $Al_2(SO_4)_3$ forced the solution composition back into the solid amorphous $Al(OH)_3$ region along the same pathway.

B-3.0 X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPY RESULTS

X-ray results show that amorphous $Al(OH)_3$ may have initially formed but transformed to pseudoboehmite [AlO(OH)] during precipitated or drying before XRD analysis.

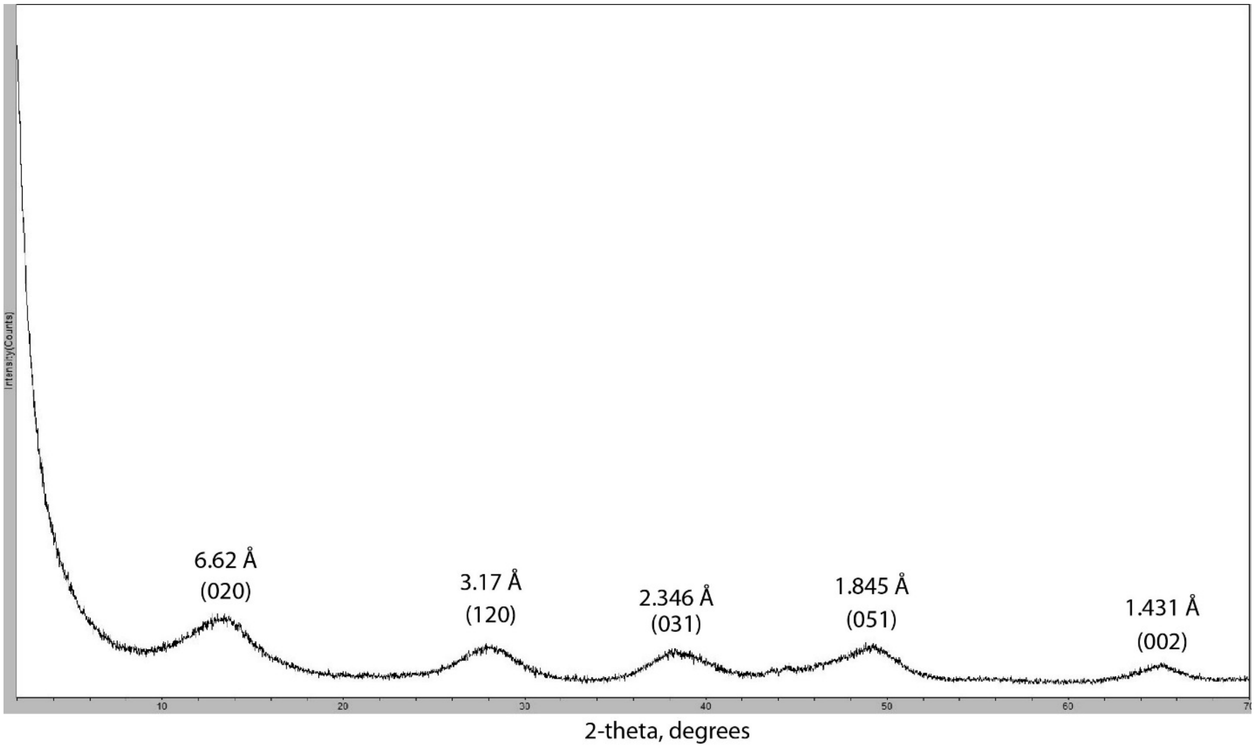

Figure B-3 XRD pattern of aluminum oxyhydroxide reaction products. Predominate phase associated with the precipitates is identified as pseudoboehmite [AlO(OH)].

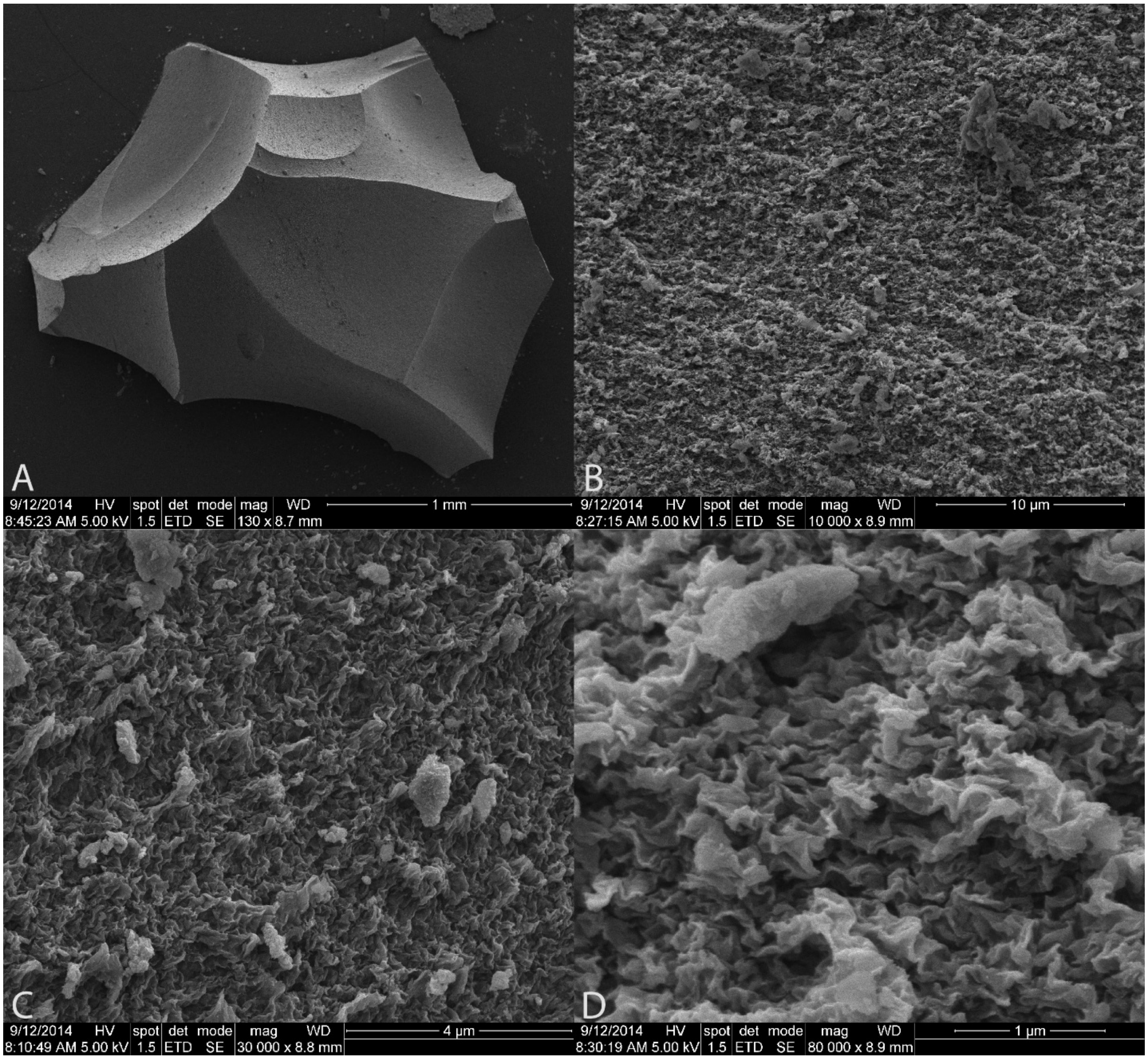

Figure B-4 **Images from freeze-dried particles from Al(OH)$_3$ synthesis. (A) Overview image of an individual solid particle; conchoidal fracture is prevalent. Plates B, C, and D are sequential close-up images showing the foily morphology that is typical of pseudoboehmite.**

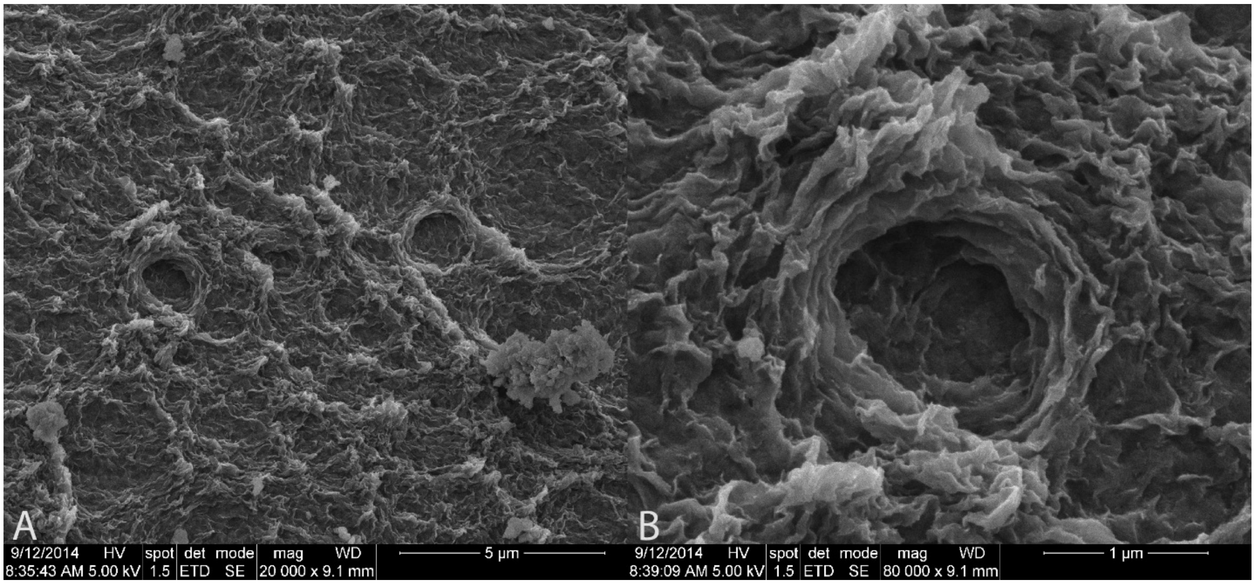

Figure B-5 **Images from freeze-dried particles from $Al(OH)_3$ synthesis. (A) Overview image of an individual solid particle showing dimpled surfaces. (B) Close-up image showing the dimpled surface that probably developed during freeze-drying.**

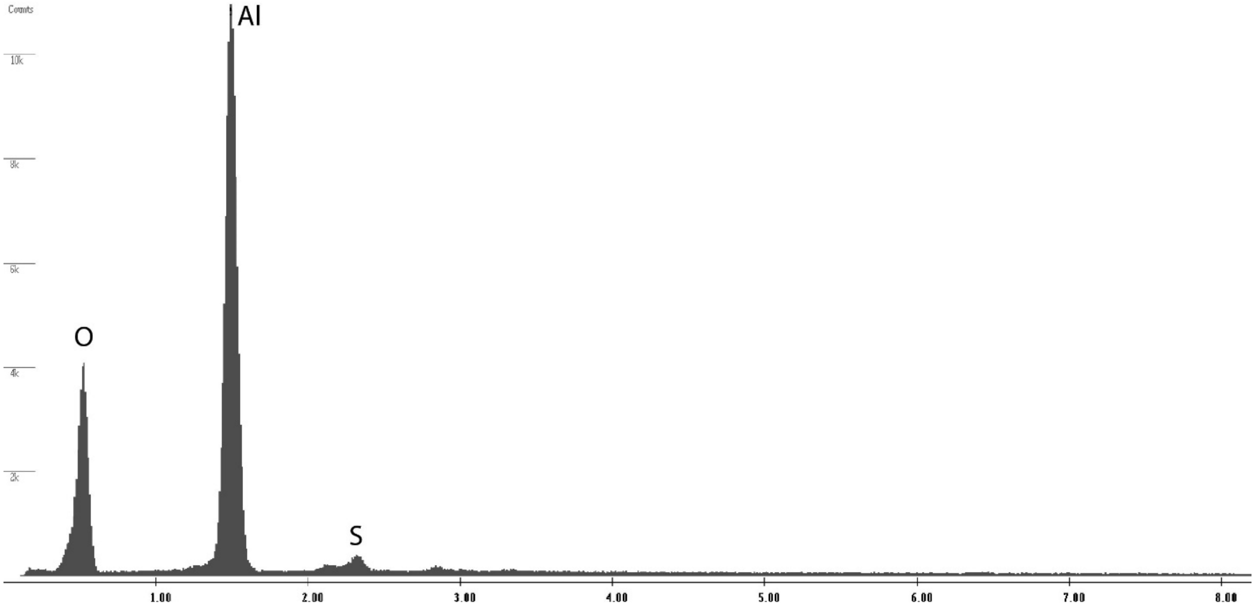

Figure B-6 **Electron dispersive spectroscopy (EDS) analysis from particles in Figure B-5. Aluminum and oxygen are dominant as is expected; aluminum/oxygen elemental ratio is approximately 3/1. There is residual sulfur from the back titration feed of $Al(SO_4)_3$.**

B.4.0 REFERENCES

The following reference list includes documents cited in this report. Parenthetical information following each reference provides the author(s), publication date, and ERID or ESHID. This information is also included in text citations. ERIDs were assigned by the Associate Directorate for Environmental Management's (ADEM's) Records Processing Facility (IDs through 599999), and ESHIDs are assigned by the Environment, Safety, and Health Directorate (IDs 600000 and above). IDs are used to locate documents in the Laboratory's Electronic Document Management System and in the Master Reference Set. The NMED Hazardous Waste Bureau and ADEM maintain copies of the Master Reference Set. The set ensures that NMED has the references to review documents. The set is updated when new references are cited in documents.

Prodromou, K.P., and A.S. Pavlatou-Ve, 1995. "Formation of Aluminum Hydroxides as Influenced by Aluminum Salts and Bases," *Clays and Clay Minerals,* Vol. 43, No. 1, pp. 111-115. (Prodromou 1995, 602821)