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ORIGINAL ARTICLE

# Evaluation of fluidized bed asbestos segregator to determine erionite in soil

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**Abstract** Three sets of soil samples were collected by the National Institute for Occupational Safety and Health and one set by South Dakota School of Mines & Technology from in and around the Slim Buttes Land Unit of the Sioux Ranger District of the Custer–Gallatin National Forest in the northwest of South Dakota. The rocks forming the Slim Buttes are sedimentary clays, sands and gravels including re-worked volcanic ash-falls in which the zeolite mineral erionite has crystallized during diagenesis in a fibrous form or morphology similar to that of asbestos. The samples were prepared using the fluidized bed asbestos segregator (FBAS) and analyzed by phase contrast microscopy (PCM) or transmission electron microscopy to detect the presence of mineral fibers. FBAS–PCM results compared to semi-quantitative polarized light microscopy (PLM) and X-ray diffraction analysis indicated a recovery of approximately 1% and a linear relationship that likely can be extrapolated to concentrations well below the 1% detection limit of PLM. There were small variations between a PCM count of 10 fibers to a count of 100 fibers (or a maximum of 200 microscopic fields of view), which indicates the possibility of rapid turnaround of results. Although the four sets of samples examined in this work were collected by slightly different techniques, some tentative conclusions can be drawn about the distribution of erionite in soils. Erionite was detected in almost every soil sample, even those taken several miles from the outcrop, but without any distribution indicating recent transportation from the current volcaniclastic sediment outcrops. Removal of more extensive volcaniclastic sediments through erosion may have resulted in remnant material in soils, including erionite crystals, but

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this possibility requires further study. Although we have demonstrated that erionite in soils can be detected through FBAS–PCM, we have not attempted to correlate those results with human inhalation exposure through activity-based sampling, and thus, any risk inherent in working these soils is unknown.

**Keywords** Erionite · Soil analysis · South Dakota · Fluidized bed asbestos segregator · FBAS · Microscopy

## Introduction

Erionite is a naturally occurring mineral that belongs to a group of silicate minerals called zeolites. It was originally described and named in 1898 by Eakle (Eakle 1898), who gave it the name erionite, derived from a Greek word meaning wool, because at the type locality erionite occurs as white, wool-like fibers. However, the wooly habit of erionite is unusual and erionite was considered extremely rare, with no additional occurrences listed until Deffeyes (Deffeyes 1959) described material from Nevada and Wyoming. These subsequent occurrences were either crystals formed in the vesicles of (mainly) basaltic lavas, or microscopic, acicular to fibrous crystals found in diagenetically altered, silicic, vitric tuffs of Cenozoic lacustrine deposits (Mumpton and Ormsby 1978). Numerous additional discoveries of erionite have been reported since including many localities within the western USA (Van Gosen et al. 2013). Erionite occurring in the "sedimentary" formations crystallizes as needle-like fibers of nanometer- to micrometer-size widths. Larger bundles of these crystals are also common, often with a splayed appearance (Fig. 1). Disturbance of the friable rocks containing these microscopic crystals can generate airborne fibers with physical dimensions similar to asbestos fibers. These particles may further resemble particles of asbestos by exhibiting similar toxicity. For example, it has long been known that residents of some Turkish villages where erionite-containing rock was used to construct homes have a remarkably high risk for development of malignant mesothelioma (Baris 1991). Exposures in the USA have been related to those in Turkey (Carbone et al. 2011). A comparison of erionites from Turkey and localities within the USA, such as in North Dakota, did not find obvious large differences in chemistry or morphology (Lowers et al. 2010). Therefore, it is necessary to exercise prudence with respect to exposure to erionite elsewhere.

In North Dakota, concern has been raised about the use of erionite-containing sediments as road-base, as exposures to airborne fibers have been associated with activities (USEPA 2010a), and pleural changes have been detected in a number of workers engaged in digging gravels and laying roads (Ryan et al. 2011). Potential health concerns led to recommendations not to use erionite-containing gravels (Campbell 2010). The Killdeer Mountains in Dunn County, ND, contain the largest outcrops of erionite-containing rocks (Forsman 1986). The rocks in the Killdeer Mountains are mostly limestones, in some cases dolomitized, interspersed with poorly indurated tuffaceous strata containing variable quantities of explosive volcanic materials. Silicification in some horizons has occurred as highly alkaline groundwaters have dissolved silica from volcanic glass, including pore-filling crystallization of zeolites (Saini-Eidukat and Triplett 2014). These isolated erosional remnants are of Middle Cenozoic (Oligocene or Miocene) age, probably correlatable with strata of the White River (Eocene–Oligocene) and Arikaree (Oligocene–Miocene) Groups in NW South Dakota and NE Montana. These other outcrops in South Dakota and Montana are not as well-studied as the formations in Dunn County, ND. In the Ekalaka Hills of MT, the Arikaree has been described as containing 45% quartz, 10–15% feldspars and 35–40% lithic fragments, floating in a matrix of abundant calcite (Roy 1993). The lithic fragments are believed to be of volcanic origin. In the Slim Buttes area of the Sioux Ranger District of the Custer–Gallatin National Forest (CGNF), which is the area under study here, the White River Group (Chadron and Brule formations) consists of basal coarse-grained arkoses and conglomerates overlain

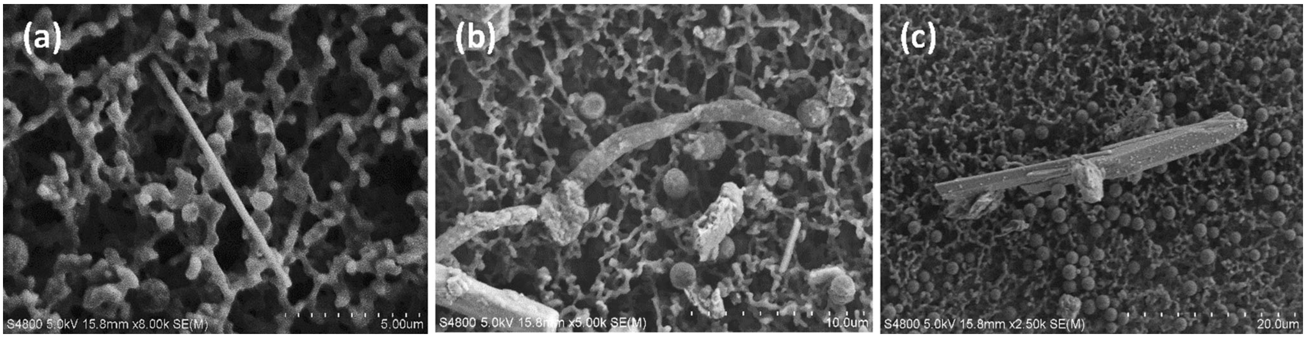


**Fig. 1** Example SEM images of **a** erionite fiber, **b** cellulose fiber and **c** gypsum crystal deposited on a MCE filter from FBAS

by claystone, siltstone and tuffaceous sandstones intercalated with bentonitic claystones. Brule Formation rocks are typically coarser-grained allowing steep-sided buttes to develop. The overlying Arikaree Group rocks are mainly pink to greenish gray and light gray siltstones and sandstones that contain abundant reworked volcanic ash deposits. Whitish-pink cross-bedded sandstone typically occurs as a resistant cap-rock at the top (Martin et al. 2004). At this location, the rocks are considered to be fluvial or lacustrine sediments incorporating re-worked or contemporaneous volcanic ash-falls. XRD analysis of bulk samples identifies calcite, quartz, gypsum, mica, feldspars and amphiboles, as well as erionite. As in ND, later diagenetic alteration processes cause dissolution of volcanic glass and the growth of erionite crystals in pores.

The presence of zeolites in the formations in the CGNF in SD and MT has only recently been noted and has not been as extensively investigated as in ND (Goodman 2010). A recent analysis of a sample from the Arikaree Group from Reva Gap in the Slim Buttes (SD) unit indicated the presence of "~50%" erionite, although the method of analysis is not noted (Earney and Baran 2016). One of the authors of the current publication collected a sample which was analyzed to contain approximately 45–63% (average 51%) erionite by visual area estimation (1200 point count) under polarized light microscopy (PLM). However, when the sizes and densities of other particles (assumed to be quartz) are accounted for, the mass contribution is closer to 1%. Further analyses of the bulk rocks should be undertaken to confirm these results.

In 2013, the National Institute for Occupational Safety and Health (NIOSH) Health Hazard Evaluation (HHE) Program received a request from a government agency to investigate the potential exposure of forest workers and wildland firefighters to erionite mineral fibers (Beaucham et al. 2015). The agency was concerned that employees could inhale airborne erionite fibers during routine maintenance activities in the forest as well as during firefighting. Disturbance of soils directly overlaying the erionite-containing rocks clearly gave rise to airborne erionite. Soils at a distance from the outcrops could also contain minerals through outwash or wind erosion, and there was a question as to how far away from the outcrops erionite could be detected in soils. In addition, it was noted that the existing outcrops of the White River and Arikaree Formations in ND, SD, MT and WY became separated from each other as regional erosion exposed older Palaeocene Ludlow and Upper Cretaceous Hell Creek Formation rocks on the surrounding lower plains. Isolated occurrences of these Formations are likely remnants of a once conterminous outcrop. Thus, it may be possible for relict minerals, including erionite, to be retained in soils formed during erosion of the overlying bedrock. The soils in the Slim Buttes unit of the CGNF are classified (USDA 2004) mainly as the Reva–Rockoa Association (Unit 12). This association is described as well-drained calcareous gravelly very fine sandy loam (Reva soils) or very channery (gravelly) loam overlaying calcareous, channery loam (Rockoa soils). Outside of the Slim Buttes unit the largest areas of soils are classified as Bullock–Parchin Association (Unit 7), Twilight–Parchin–Cabbart Association (Unit 8) or Reeder–Rhoades Association (Unit 9). These are also described as loams, either sandy or clayey, with the lower parts often described as calcareous and with gypsum.

The Fluidized Bed Asbestos Segregator (FBAS) has been developed to separate mineral fibers from soil onto an air filter through elutriation, and it can be used to determine trace amounts of releasable fibers from soil. Research conducted by US Environmental Protection Agency (EPA) has shown that the FBAS technique is able to detect asbestos in soil at very low levels ranging from 0.002 to 0.005% by weight (Januch et al. 2013). Recovery is a linear function of spiked quantity, although the absolute recovery from spiked samples is quite low (around 1%). The EPA continues to work on determining a relationship between FBAS soil content of asbestos and characterization of inhalation exposure resulting from human activities (activity-based sampling). While erionite is not asbestos, the fibers are of similar size and shape and may behave in a similar fashion. In this study, we evaluate the performance of the FBAS preparation method along with particle estimation through phase contrast microscopy (PCM) to determine low levels of the erionite in soil. The FBAS is potentially a useful tool for preparation of samples for analysis by PCM, which is a well-known method for counting fibers on filters. PCM may be preferable to PLM as erionite fibers are easy to detect and measure under PCM. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) can also be used to analyze these types of samples; however, PCM offers advantages in terms of reduced preparation and analytical costs and a more rapid turnaround time. PCM cannot equivocally determine the nature of a fiber, although erionite fibers have a quite distinctive morphology and high contrast which makes them easy to see and count. SEM and TEM can make use of energy-dispersive spectroscopy and selected area X-ray diffraction to characterize mineral particles further, but these techniques are difficult to apply to fine zeolite crystals.

## Methods

### Soil sampling

Soil samples from 63 locations in the CGNF and surrounding areas were collected in various field surveys by

**Table 1** Analyses performed for each sample collection

| Sample collection | NIOSH | | | | EPA | BVNA | | |
|---|---|---|---|---|---|---|---|---|
| | FBAS–PCM | | | | | | | |
| | 0.0425 | | 0.0125 | | | | | |
| | 10 counts | 100 counts | 10 counts | 100 counts | FBAS–PCM | FBAS-TEM | XRD | PLM |
| Health hazard evaluation[a] | ✔ | ✔ | X | X | X | X | ✔ | ✔ |
| Camp ground (single sample) | ✔ | ✔ | X | ✔ | X | X | ✔ | ✔ |
| NIOSH first collection (I)[b] | ✔ | ✔ | ✔ | ✔ | ✔ | ✔ | X | X |
| NIOSH first collection (II)[c] | ✔ | X | X | X | ✔ | ✔ | X | X |
| NIOSH second collection (I)[d] | ✔ | ✔ | ✔ | ✔ | X | X | ✔ | ✔ |
| NIOSH second collection (II)[e] | ✔ | X | ✔ | X | X | X | ✔ | ✔ |
| SDSMT[f] | ✔ | X | X | X | X | X | X | X |

[a] Health hazard evaluation contains samples: HHE 1, HHE 4, HHE 11, HHE 12, HHE 13, HHE 16, HHE 17, HHE 19, HHE 21 and HHE 22

[b] NIOSH first collection (I): NIOSH 1/5, NIOSH 1/6, NIOSH 1/11, NIOSH 1/12, NIOSH 1/14 and NIOSH 1/17

[c] NIOSH first collection (II): NIOSH 1/4, NIOSH 1/7, NIOSH 1/8, NIOSH 1/9, NIOSH 1/10, NIOSH 1/13, NIOSH 1/15 and NIOSH 1/16

[d] NIOSH second collection (I): NIOSH 2/1, NIOSH 2/8, NIOSH 2/10, NIOSH 2/11, NIOSH 2/13 and NIOSH 2/14

[e] NIOSH second collection (II): NIOSH 2/2, NIOSH 2/3, NIOSH 2/4, NIOSH 2/5, NIOSH 2/6, NIOSH 2/7, NIOSH 2/9 and NIOSH 2/12

[f] SDSMT: All samples

the National Institute for Occupational Safety and Health (NIOSH) and the South Dakota School of Mines & Technology (SDSMT). All the sample locations were identified by global positioning system (GPS). In total, there are four sample sets, which have been combined as far as possible to give the most comprehensive areal coverage. However, the sets were collected at different times by different personnel and for different purposes. As a result, not all analyses were conducted on all samples. The four sets are labeled SDMT, NIOSH Health Hazard Evaluation (HHE) and NIOSH-1 and NIOSH-2, and the analyses performed on each are given in Table 1. In addition, a soil intended as a reference was collected from the Reva Gap campground as described below and it is included in the table.

SDSMT collected samples on September 19–20, 2008, in the areas adjacent to the Slim Buttes Land Unit with the goal to evaluate materials that might have contaminated soils through atmospheric deposition as part of a separate study on uranium (Stone and Stetler 2009). The handle of a stainless steel soil scoop used for collection was held at an angle to the surface such that the scoop tip was the only part of the scoop touching the surface, slight downward pressure was applied, and the scoop was slowly pulled backward across the surface. This motion “fluffed” the surface and broke any surface crust that may have existed. The soil was skimmed off by a forward motion of the scoop and placed into a clean sample jar. Splits of the dust powder (approximately 25 g each) were sent to the NIOSH laboratory for FBAS preparation and analysis by PCM.

NIOSH personnel conducted sampling first for the purposes of the HHE on September 9–10, 2014, according to a modification of a bulk sampling method developed by the EPA (USEPA 2013). Soil samples were collected as composites consisting of a total of 50 grams (g) of soil from 30 individual sampling points equidistant to each other, to be representative of a 1500-square-foot area.

NIOSH conducted two further surveys on non-private lands, firstly from locations outside the boundary of the CGNF on September 9, 2014, and, secondly, additional samples from within the boundary of the CGNF August 11–12, 2015. Sampling during these campaigns used a metal scoop to obtain a single sample of about 50 g at a generally deeper level (3–5 cm) than the SDSMT samples. Also a composite soil sample of about 400 g was collected from the Reva Gap campground site down to 5 cm depth. This sample was sent to another contract laboratory, Asbestos TEM Laboratories, Inc., in Berkeley, California, where it was dried at 40 °C for 2 h, passed through a ¼ in. (6.35 mm) sieve to remove plant material and to identify soil clods for break-up and further screening. The sieved fraction was passed through a #60 sieve (0.25 mm) sieve and mixed using a 3-D Turbula® mixer for 5 min. This additional mixing was done to create a homogenous sample that could be used as a reference material for inter-laboratory comparisons.

## Analysis

All samples were analyzed by FBAS–PCM at the NIOSH laboratory in Morgantown, WV. In addition, 10-g splits of the soil samples from the NIOSH-2 collection (outside the

CGNF boundary) were sent for FBAS preparation and analysis by PCM at the USEPA Region 10 laboratory in Port Orchard, Washington, to test between-laboratory precision. The FBAS procedure is known from prior studies of asbestos-spiked soils not to give 100% recovery. Thus, it was necessary to calibrate the FBAS–PCM to the extent possible against alternative techniques. One such technique is calibrated visual area estimation under PLM. Another is X-ray diffraction also calibrated against known standards. Both methods require a certain amount of sample and both methods cannot produce useful results below about 1% by weight. Thus, not all samples were analyzed by all techniques (see Table 1). The preferred technique for the FBAS analysis of asbestos by the EPA is TEM, and thus, some samples were analyzed by FBAS-TEM to compare with FBAS–PCM. PCM is known to be dependent on analyst skill in seeking and identifying fibers, and so, this aspect of the technique was also evaluated. Finally, aliquots of the "reference" Reva Gap campground soil were analyzed at NIOSH, Morgantown, and at the EPA Port Orchard laboratory and by another laboratory with FBAS equipment (EMSL, Cinnaminson, NJ) for FBAS–PCM comparison. Table 1 lists the methods used for analysis of each sample collection.

### Fluidized bed asbestos segregator separation

NIOSH and SDSMT soil samples were prepared at NIOSH for processing according to the ASTM D7521-13 method (ASTM 2013), which consisted of drying samples in a laboratory oven at 60 °C for 12 h, followed by sieving on a shaker with 3 sieving levels (19, 2 mm, 106 μm) for 5 min to remove large particles or debris. The soil samples were analyzed in triplicates, except the NIOSH-HHE samples as noted below, and a random aliquot of 1 g of soil material was extracted from each sample container using a clean stainless steel spatula and mixed with 19 g of sand and placed into the FBAS glass vessel. The FBAS apparatus operates by flowing air through the soil sample/sand mixture at a rate equal to the soil particulate fluidization velocity, when the soil material begins to circulate and act as a fluid. Small mass particles elutriate from the fluidized air/soil sample/sand mixture and are drawn into the air toward the top of the FBAS glass vessel. An isokinetic splitter is used to split the air flow, and a fraction of the air is further drawn through a mixed cellulose ester (MCE) filter. Each soil sample/sand mixture was fluidized for 3 min. Mechanical vibration of the glass vessel is also used to prevent larger particles from adhering to the inside walls of the vessel. The FBAS unit was decontaminated after each sample by removing and cleaning the glass vessel. Throughout the FBAS preparation process, lot blanks, laboratory blanks and sand blanks were collected according to the FBAS standard operation protocol (SOP) to ensure decontamination methods were effective and cross-contamination did not occur during processing (USEPA 2010b).

The FBAS SOP as used by EPA calls for 16 L/min total flow rate and 0.2 L/min filter flow rate, the ratio of the filter:total flow rate is defined as $Q_r$ ($Q_r = 0.2/16 = 0.0125$). The NIOSH laboratory observed that the preparation using a $Q_r$ of 0.0125 led to an accumulation of large particles on the filter and caused a rapid build-up of carry-over soil in the waste-trap, leading to problems with flow maintenance. Therefore, an adjusted $Q_r$ of 0.0425 (14.1 L/min total flow rate and 0.6 L/min filter flow rate) was used by the NIOSH laboratory. Some samples were analyzed using both flow regimes at NIOSH, including the campground soil. EMSL used a $Q_r$ of 0.0155, the difference from EPA being a result of the precision in setting the flow rates. All samples in this study were analyzed by FBAS in triplicate (i.e., three samples providing three filters) with the exception of the NIOSH samples collected for the HHE, for which only a single FBAS filter was prepared due to the small quantity of the samples received.

### SEM

SEM and PCM analyses were performed on different portions of the same filter. Samples for SEM analysis were prepared through a procedure which retained the particles in the similar position during SEM analysis as they were on the sampling filter. After coating with gold-palladium, the morphology of the fibers in the samples was examined with a Hitachi S-4800 Field Emission Scanning Electron Microscope operated at 5 kilovolts and equipped with a Bruker Quantax Esprit EDS package. Each sample was scanned at 500× for the presence of fibers, and photographs were taken at 20,000× magnification. The morphology of the erionite fibers was first observed under SEM at NIOSH, and this information provided the possibility to discriminate between the smooth parallel longitudinal faces of erionite fibers (Figs. 1a, 2), irregular, flattened and wavy plant cellulose fibers (Fig. 1b) or rectangular-like structure gypsum crystals (Fig. 1c). Thus, a heuristic was derived for a similar discrimination under PCM at the NIOSH laboratory. The EPA laboratory did not apply this heuristic in their analysis.

### PCM

MCE filters from the FBAS separation were prepared for PCM analysis in all laboratories using the acetone vapor/triacetin method according to NIOSH Manual of Analytical Methods 7400 (NIOSH 1994a). Analysis was conducted using a 40× phase objective resulting in a total magnification of 400× in all laboratories. At NIOSH, a

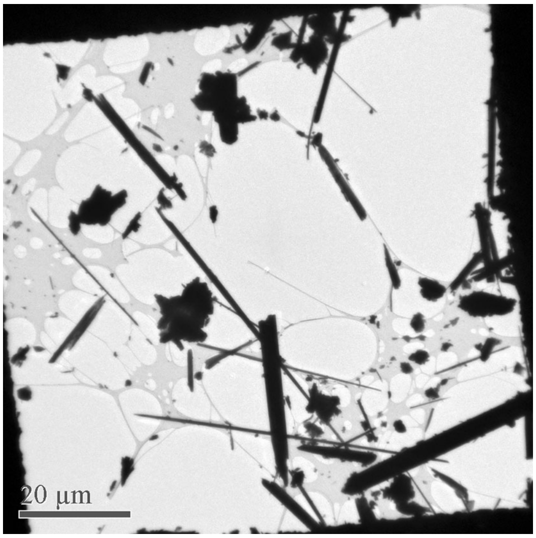


**Fig. 2** Example image of erionite on a lacy carbon grid (Courtesy Alan Dozier, NIOSH Division of Applied Research and Technology, Cincinnati, OH)

Nikon Eclipse 50i microscope was used with Nikon's CFI60 400× optical magnification and a Nikon Digital Sight Series HD 5-megapixel camera DS-Fi2 with image resolution of 2560 × 1920 pixels. For each fiber included in the count, the length and width (without regard to upper limit of width) were recorded using the measurement function of the standalone control unit DS-L2 calibrated with a Nikon 100-µm calibration slide. The EPA Region 10 laboratory performed the analysis by PCM with a Carl Zeiss Axioskop 40 PCM. The images were captured with a Carl Zeiss AxioCam and processed with Carl Zeiss Axiovision digital imaging software where the measurements were made using a scaler function calibrated to a Graticules Ltd stage micrometer. EMSL used a Meiji MT6520 Positive Phase Contrast Microscope outfitted with a Leica ICC50HD Camera.

Erionite fibers were defined for this analysis as any width particle longer than 5 µm with an aspect ratio (length:width) equal to or greater than 3:1 (NIOSH 7400 "A" counting rules). Then the fibers meeting the geometric definition of a fiber were further examined, in the NIOSH laboratory only, to see whether they were likely to be erionite rather than vegetable material or gypsum based on comparison of their appearance to particles observed under SEM. However, this subjective discrimination under PCM is difficult to apply consistently by all analysts. Six analysts were asked to perform fiber counting of six randomly selected slides on the same NIOSH PCM unit (to minimize instrument error) to calculate the analyst variability in this procedure. Two of these analysts had experience in discriminating particles for asbestos analysis, and the other four had little or no experience.

The concentration of erionite in soil was reported from the PCM analysis as soil mass percent. The mass of each fiber observed was calculated from its dimensions, assuming the fiber shape as a rod-like cylinder (Matassa et al. 2015), with a density of 2.1 g/cc as follows:

$$m_{\mathrm{i}} = V_{\mathrm{f}} \cdot \delta \cdot 10^{-12}$$

where $m_{\mathrm{i}}$ = mass percentage of erionite in soil, $V_{\mathrm{f}}$ = volume of the fiber (cm$^3$), $\delta$ = density of erionite (2.1 g cm$^{-3}$), and $10^{-12}$ = unit conversion factor (from cm$^3$ to µm$^3$).

The concentration (grams of erionite per 100 g of soil) is calculated as follows:

$$C_{\mathrm{soil}} = \sum m_{\mathrm{i}} \cdot S \cdot 100$$

where $S$ = analytical sensitivity (g$^{-1}$) and calculated as:

$$S = \mathrm{EFA}/(\mathrm{GO_x} \cdot \mathrm{Ago} \cdot M \cdot Q_{\mathrm{R}})$$

where EFA = effective filter area (385 mm$^2$), $\mathrm{GO_x}$ = number of grid openings (TEM) evaluated or fields of view (PCM), Ago = area of one grid opening or PCM (Walton–Beckett graticule = 0.00785 mm$^2$), $M$ = mass of the erionite-containing soil (g), $Q_{\mathrm{R}}$ = flow ratio of the air passed through the soil to that passing through the MCE filter.

The stopping rule used for counting fibers was defined as 200 fields or 10 fibers, including the count of all the fibers in the field of view in which the 10th fiber appeared for all analyzed slides. A second stopping rule of 200 fields or 100 fibers including the count of all the fibers in the field of view in which the 100th fiber appeared was used for several selected slides to determine whether additional counting would affect the result.

## PLM confirmation

The NIOSH-HHE and NIOSH-2 samples and the campground sample were analyzed by PLM at Bureau Veritas North America, Novi, Michigan (BVNA). BVNA is a laboratory accredited by the American Industrial Hygienist Association, Laboratory Accreditation Programs, LLC, for analyses of asbestos in building materials by PLM (EPA 600/R-93-116), and it also participates in the National Voluntary Laboratory Accreditation Program which is administered by the National Institute of Standards and Technology. Samples were analyzed for erionite based on calibrated visual area estimation as described in test method EPA/600/R-93/116 (USEPA 1993) modified for identification of erionite, rather than asbestos. Specifically, the samples were dried (80 °C) and lightly ground. Microscopic analysis was performed using an Olympus BX53 polarizing microscope based on the unique optical properties of erionite including birefringence, sign of elongation, dispersion staining and shape/color. Becke line technique was used to estimate and compare the refractive index (RI) of fibers from each sample against a liquid of known RI for comparison to the RI of reference material of erionite from Rome, Oregon (~1.472 Parallel and 1.474 Perpendicular). The oil used was Cargille RI 1.48. The analysis results were reported as mass percentage based on comparison against prepared standard mixtures in accordance with the method protocol. However, in the absence of an erionite reference the comparison was made against standards containing asbestos, and thus, the results should be considered to have greater uncertainty than when the procedure is used to quantify asbestos content.

## XRD confirmation

The NIOSH-HHE and NIOSH-2 samples and the campground sample were analyzed by BVNA (which is also accredited for bulk materials by XRD (NIOSH 7500)), using a Rigaku Ultima III diffractometer with acquisition range 5–80 two-theta degrees and Cu radiation source. Approximately 1 g from each sample was added to a mortar and ground to a fine powder using a pestle. The ground powder was wet sieved through a 45-µm sieve using 2-propanol. The alcohol was evaporated in a drying oven for 2 h, and then, the dried samples were stored in a sealed test tube. Approximately half a gram of each sieved-dried sample powder was placed into an aluminum sample plate and then in the automated sample changer for analysis by XRD. A high purity, 80–85% erionite (checked by a second laboratory) reference material from Rome, Oregon, was used as standard and the reference material diffraction pattern was in good agreement with erionite-K as described in “The American Mineralogist Crystal Structure Database” (http://rruff.geo.arizona.edu/AMS/amcsd.php). A nominal 5% concentration of erionite reference sample was prepared in a borosilicate glass which served as non-crystalline dilution matrix. The sample peak identifications were assigned referencing known material data found in “The American Mineralogist Crystal Structure Database” and Jade 8.0 software. A 2 degrees/min, full range XRD scan of the powder was acquired to determine the primary sample constituents. A 0.02 degrees/min scan was performed for selected XRD regions to confirm the erionite presence and identity. Fully quantitative analysis was not possible because the exact purity of the erionite in the reference material is not known. Rudimentary estimates for the erionite in each sample were calculated as ratio relative to the approximatively 5% erionite-K of the diluted reference sample based on the peak area at 7.7 two-theta degrees.

## TEM

FBAS filter samples from NIOSH-1 collection were analyzed by BVNA (also accredited for asbestos in air samples by TEM by ISO Method 10312) using a Philips CM-12 electron microscope and iXRF EDS according to NIOSH Method 7402 for asbestos modified to include a differential filter count (NIOSH 1994b) and quantified according to FBAS SOP soil mass percent formula. Four grids were placed consecutively in the TEM for examination. The stopping rules were defined as 200 grid openings, or 50 fibers, including the count in the grid opening in which the 50th fiber appeared. For field blank samples, 40 grid openings were analyzed. Fibers meeting the NIOSH Manual of Analytical Methods 7400 counting rule A size parameters criteria (without regard to width) underwent examination by EDS to identify the chemical composition of the fiber. Only fibers with strong peaks for Si and Al and minor peaks for at least one of the elements Na, Ca or K were counted as erionite. Selected area electron diffraction (SAED) patterns are difficult to acquire from zeolite minerals, and so, this was not possible in every case.

## Geographical information system (GIS)

Slim Buttes land unit border layer “S_USA.AdministrativeForest” was extracted from the USDA Forest Service data server, and the “NR_L_SD_Geology” layer of South Dakota Geological Survey (SDGS) was extracted from the South Dakota GIS data server. The acquired data had been organized as thematic layers using ArcGIS 10.2 (Redlands, CA: Environmental Systems Research Institute, Inc., 2010), in order to analyze erionite sample locations relative to the erionite-bearing layers lithology (Arikaree and White River Groups) and the CGNF Slim Buttes Land Unit border. To achieve this aim, the tabular data for the erionite samples were imported into ArcMap, and the x,y coordinate data were displayed with the World Geodetic System (WGS) 1984 projection. The x,y event layer was exported to create a point feature layer to symbolize the erionite concentration percentages and to overlay on the geologic base layers for mapping purposes. Selection by location produced another layer with only those soil samples outside of the outcrop of the Arikaree and White River Groups, and further selection by attribute produced two layers: soil samples collected by SDSMT and soil samples collected by NIOSH. The concentration percentages were then represented by graduated symbols and mapped. The wind rose was created using the average daily wind speed (meters per second) and direction of fastest 2-min wind (degrees) from the meteorological data furnished by National Oceanic and Atmospheric Administration for the

Station Buffalo of South Dakota between October 01, 2010, and October 21, 2016.

### Data analysis

Data were analyzed using SAS 9.3 (SAS Institute Inc., Cary, NC). All statistical methods used in this paper assume level of significance at $\alpha = 0.05$. Two-sided $p$ value was used when performing $t$ test. Regression coefficient and R-squared were derived from linear regression. In some instances, if data did not satisfy assumptions for common parametric methods, nonparametric methods were used to analyze data.

## Results

### FBAS–PCM versus PLM

To compare PLM and FBAS–PCM methods, 22 pairs of results presented in Table 2 were analyzed as statistically dependent variables. PLM concentrations reported as less than 1% by PLM method were considered as 0.5% in the statistical analysis; PLM concentrations reported as non-detect were not included in the analysis. A paired $t$ test was carried out using log-transformed variables indicating no significant difference ($p$ value 0.672). As shown in Fig. 3, with intercept = 0 the regression coefficient is 1.041, R-squared is 0.959, and $p$ value of the regression is <0.0001. FBAS–PCM measured mean concentrations are consistently about 100 times lower than the nominal PLM levels (i.e., 1% recovery). Thus, the reported FBAS–PCM concentrations were multiplied by a factor of 100 to align with the PLM results.

### FBAS–PCM versus XRD

The 14 paired XRD and FBAS–PCM concentrations presented in Table 2 were log-transformed to satisfy the normality assumption (XRD values reported as non-detect were not included in the analysis). There is evidence of a statistically significant correlation between them with regression coefficient 0.718, R-squared 0.795 and $p$ value of <0.0001. Paired $t$ test did not find a statistically significant difference between the two groups ($p$ value 0.132). XRD had a poorer correlation with FBAS–PCM results adjusted for 1% recovery, and XRD concentrations were most often higher than PLM concentrations for the NIOSH-HHE samples and lower than the PLM concentrations for NIOSH-2 samples. Although the analyses were performed at different times, no obvious factor to explain this difference was apparent.

**Table 2** Mass concentration results of NIOSH samples collected for the HHE and NIOSH second collection (on-outcrop)

| Sample (collection/number) | Mass concentration (%) | | |
|---|---|---|---|
| | NIOSH/FBAS–PCM[c] | PLM | XRD |
| HHE 1[a] | 5.1 | 5 | 10 |
| HHE 4[a] | 3.9 | 3 | 10 |
| HHE 11[a] | 1.0 | <1 | 5 |
| HHE 12[a] | 1.3 | <1 | 1 |
| HHE 13[a] | 1.4 | <1 | 2 |
| HHE 16 | 2.5 | 2 | 6 |
| HHE 17 | 4.2 | 3 | 6 |
| HHE 19[b] | 0.10 | ND | 4 |
| HHE 21[b] | 0.10 | ND | 7 |
| HHE 22[b] | 0.00 | ND | 4 |
| NIOSH 2/1 | 12 | 12 | 10 |
| NIOSH 2/2 | 1.3 | 2 | 5 |
| NIOSH 2/3 | 1.5 | 2 | 2 |
| NIOSH 2/4 | 1.3 | 3 | 1 |
| NIOSH 2/5 | 2.7 | 4 | 1 |
| NIOSH 2/6 | 2.6 | 3 | 3 |
| NIOSH 2/7 | 4.6 | 3 | 4 |
| NIOSH 2/8 | 6.9 | 5 | 4 |
| NIOSH 2/9 | 2.7 | 3 | 1 |
| NIOSH 2/10 | 4.1 | 7 | 5 |
| NIOSH 2/11 | 2.3 | 2 | ND |
| NIOSH 2/12 | 3.9 | 4 | 2 |
| NIOSH 2/13 | 8.5 | 13 | 3 |
| NIOSH 2/14 | 23 | 23 | 5 |
| Campground | 8.3 | 10 | 8 |

[a] Sample not used in Fig. 6

[b] Sample not used in Figs. 5 and 6

[c] Based on analysis of 10 countable fibers/200 fields of view, $Q_r$ of 0.0425 and adjusted for recovery of 1%

### FBAS–PCM versus FBAS-TEM

The 13 paired NIOSH-2 FBAS–PCM and FBAS-TEM concentrations presented in Table 3 were log-transformed to satisfy the normality assumptions. There is evidence of a statistically significant correlation between them with regression coefficient 1.49, R-squared 0.65 and $p$ value of 0.0004. However, paired $t$ test did find a statistical difference between the two groups ($p$ value 0.0007). Some fibers that displayed faint or short-lived diffraction patterns under the electron beam that could not be timely verified were not counted.

### FBAS–PCM between-laboratory precision

The results of the paired $t$ test between the 14 FBAS–PCM samples analyzed at both the NIOSH Morgantown and

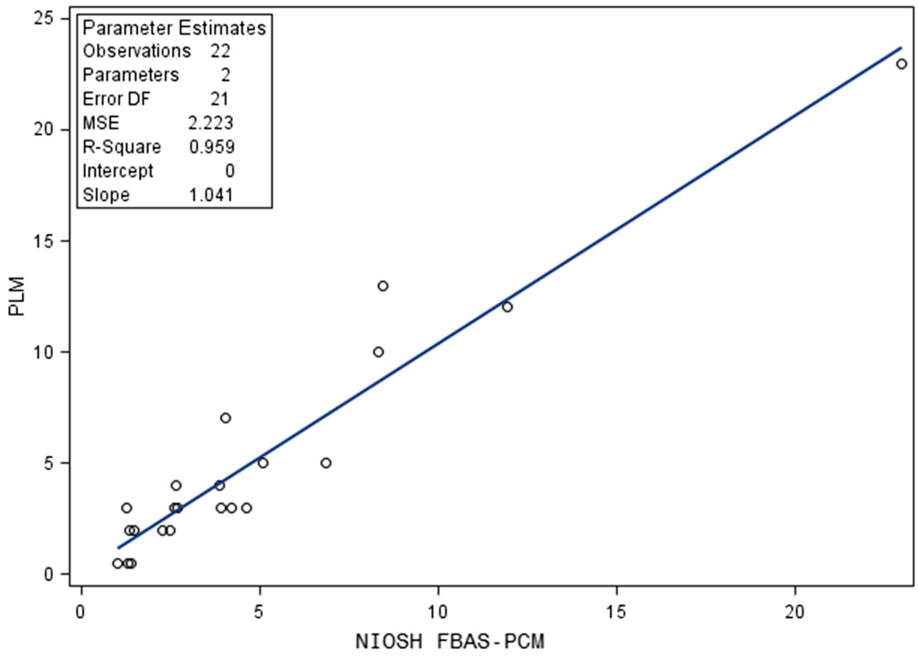


**Fig. 3** NIOSH FBAS–PCM (adjusted × 100) versus PLM

EPA Port Orchard laboratory are presented in Table 3 and showed no significant difference by *t* test (*p* value 0.60). There is also evidence of a statistically significant correlation between laboratories as shown in Fig. 4 with regression coefficient 0.84, R-squared 0.66 and *p* value of 0.0002.

### $Q_r$ of 0.0425 versus 0.0125

The UNIVARIATE Procedure in SAS was used to compare the two different air flow ratios for the 15 FBAS–PCM results from Table 4. The nonparametric “Sign test” was used since data did not satisfy requirements of symmetric distribution and the observed *p* value was $<0.0001$. The two groups are statistically significantly different with median difference $-0.523$. A $Q_r$ of 0.0125 yields, on average, 17% higher results than a $Q_r$ of 0.0425.

### 10 versus 100 fibers counting

A *t* test indicated that there is no significant difference in results between 10 versus 100 fibers counts when using either the 0.0425 $Q_r$ fraction ($p = 0.69$, $N = 22$) or the 0.0125 fraction ($p = 0.23$, $N = 13$) is used as given in Tables 5 and 6.

**Table 3** Mass concentration results of NIOSH sample collection (off-outcrop)

| Sample (collection/number) | Mass concentration (%) | | |
|---|---|---|---|
| | FBAS–PCM | | BVNA FBAS-TEM[c] |
| | NIOSH[a] | EPA[b] | |
| NIOSH 1/4 | 0.06 | 0.18 | 0.01 |
| NIOSH 1/5 | 0.03 | 0.04 | 0.06 |
| NIOSH 1/6 | 0.11 | 0.40 | 0.06 |
| NIOSH 1/7 | 0.11 | 0.10 | 0.00 |
| NIOSH 1/8 | 0.67 | 0.50 | 0.83 |
| NIOSH 1/9 | 0.31 | 0.35 | 0.02 |
| NIOSH 1/10 | 0.33 | 0.19 | 0.04 |
| NIOSH 1/11 | 0.86 | 0.16 | 0.39 |
| NIOSH 1/12 | 0.84 | 1.1 | 0.33 |
| NIOSH 1/13 | 0.57 | 0.12 | 0.09 |
| NIOSH 1/14 | 0.74 | 1.4 | 0.03 |
| NIOSH 1/15 | 0.70 | 0.31 | 0.23 |
| NIOSH 1/16 | 0.71 | 0.49 | 0.10 |
| NIOSH 1/17 | 0.50 | 0.46 | 0.06 |

[a] Based on analysis of 10 countable fibers/200 fields of view, $Q_r$ of 0.0425 and adjusted for recovery of 1%

[b] Based on analysis of 100 countable fibers/200 fields of view, $Q_r$ of 0.0125 and adjusted for recovery of 1%

[c] Based on analysis of 50 countable structures/200 grid openings, $Q_r$ of 0.0425 and adjusted for recovery of 1%

### Campground soil FBAS–PCM versus other methods

The NIOSH FBAS–PCM analysis of the campground sample, counted by the strict 7400 Method geometric rules with no adjustments for morphology, yielded a concentration of 40% ($Q_r = 0.0125$, 100 fiber counts, adjusted for 1% recovery), which agreed well with the EPA Region 10 FBAS–PCM concentration of 39% counted based on the same methodology. A second PCM analysis

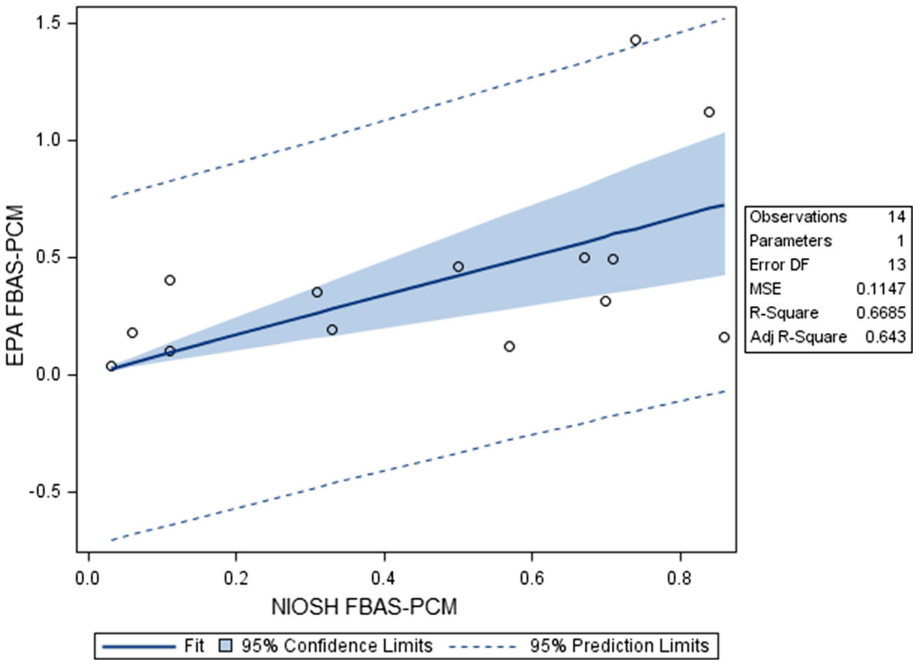


**Fig. 4** NIOSH FBAS–PCM versus EPA FBAS–PCM

**Table 4** Comparison of mass concentration between 0.0125 versus 0.0425 FBAS flow ratios

| Sample (collection/number) | Mass concentration (%) | | |
|---|---|---|---|
| | $Q_r = 0.0425$[a] | $Q_r = 0.0125$[a] | % Increase |
| NIOSH 2/1 | 12 | 15 | 24 |
| NIOSH 2/2 | 1.3 | 1.5 | 15 |
| NIOSH 2/3 | 1.5 | 1.6 | 11 |
| NIOSH 2/4 | 1.3 | 1.3 | 6.9 |
| NIOSH 2/5 | 2.7 | 3.0 | 12 |
| NIOSH 2/6 | 2.6 | 3.0 | 16 |
| NIOSH 2/7 | 4.6 | 4.9 | 6.8 |
| NIOSH 2/8 | 6.9 | 7.9 | 15 |
| NIOSH 2/9 | 2.7 | 3.2 | 19 |
| NIOSH 2/10 | 4.1 | 4.7 | 15 |
| NIOSH 2/11 | 2.3 | 2.8 | 21 |
| NIOSH 2/12 | 3.9 | 4.5 | 15 |
| NIOSH 2/13 | 8.5 | 10 | 19 |
| NIOSH 2/14 | 23 | 29 | 26 |
| Campground | 8.3 | 12 | 40 |

[a] Based on analysis of 10 countable fibers/200 fields of view and adjusted for recovery of 1%

of the same slide by NIOSH, which employed the same 100 fiber count stopping rule, excluding the particles displaying non-erionite fiber characteristics, was also performed and yielded a concentration of 10%. This result was in close agreement with the concentration of 10% reported by EMSL and the analysis of the bulk soil by PLM (10%) and XRD (8%). A recount on the microscope captured images of the Port Orchard FBAS–PCM using the same counting heuristic also led to a lower result (16%).

## Variation by analysts

As given in Table 7, among the six analysts used in this study, the average coefficient of variation (CV) was 0.65.

## GIS analysis

Five of the samples used in the comparative microscopic analysis were not used in the GIS analysis as they were taken from outside of the area of interest. There are two distinct distributions of erionite concentrations (based on FBAS–PCM expressed as mass percent and adjusted for 1% recovery) within the soil samples, the first distribution has a range from 0.009 to 0.39% for samples outside the erionite-containing geological layers, and the second distribution has a range from 1.0 to 23% for samples inside the erionite-containing geological layers as observed in Fig. 5. The coefficient of variation (CV) of triplicate samples by FBAS–PCM is a function of the absolute level of erionite in the samples. The samples taken from outside the erionite-containing geologic formations have a higher average CV (0.38) than the samples taken inside the erionite-containing geologic formations (average 0.05). Figure 6 shows all samples, and the higher levels of soils on or just off the outcrops are already defined, but the scale does not allow evaluation of the distribution of the values off-outcrop. In Fig. 7, only the values off-outcrop are displayed with a scale that allows an evaluation of the distribution.

Table 5 Comparison of mass concentration between FBAS–PCM 10 versus 100 counts at 0.0425 FBAS flow ratio

| Sample (collection/number) | Mass concentration (%) | |
|---|---|---|
| | 10 counts | 100 counts |
| NIOSH 1/5 | 0.03 | 0.01 |
| HHE 19 | 0.10 | 0.23 |
| HHE 21 | 0.10 | 0.33 |
| NIOSH 1/6 | 0.11 | 0.13 |
| NIOSH 1/17 | 0.50 | 0.45 |
| NIOSH 1/14 | 0.74 | 0.52 |
| NIOSH 1/12 | 0.84 | 0.61 |
| NIOSH 1/11 | 0.86 | 0.29 |
| HHE 11 | 1.0 | 1.3 |
| HHE 12 | 1.3 | 1.5 |
| HHE 13 | 1.4 | 1.6 |
| NIOSH 2/11 | 2.3 | 2.4 |
| HHE 16 | 2.5 | 2.6 |
| HHE 4 | 3.9 | 3.9 |
| NIOSH 2/10 | 4.1 | 4.0 |
| HHE 17 | 4.2 | 4.6 |
| HHE 1 | 5.1 | 4.8 |
| NIOSH 2/8 | 6.9 | 6.3 |
| Campground | 8.3 | 8.1 |
| NIOSH 2/13 | 8.5 | 8.1 |
| NIOSH 2/1 | 12 | 12 |
| NIOSH 2/14 | 23 | 24 |

Reported concentration adjusted for recovery of 1%

Table 6 Comparison of mass concentration between FBAS–PCM 10 versus 100 counts at 0.0125 FBAS flow ratio

| Sample (collection/number) | Mass concentration (%) | |
|---|---|---|
| | 10 counts | 100 counts |
| NIOSH 1/5 | 0.05 | 0.05 |
| NIOSH 1/17 | 0.06 | 0.12 |
| NIOSH 1/6 | 0.17 | 0.10 |
| NIOSH 1/14 | 0.37 | 0.77 |
| NIOSH 1/12 | 0.40 | 0.33 |
| NIOSH 1/11 | 0.53 | 0.44 |
| NIOSH 2/11 | 2.8 | 3.0 |
| NIOSH 2/10 | 4.7 | 4.9 |
| NIOSH 2/8 | 7.9 | 7.9 |
| NIOSH 2/13 | 10 | 10 |
| Campground | 12 | 10 |
| NIOSH 2/1 | 15 | 16 |
| NIOSH 2/14 | 29 | 29 |

Reported concentration adjusted for recovery of 1%

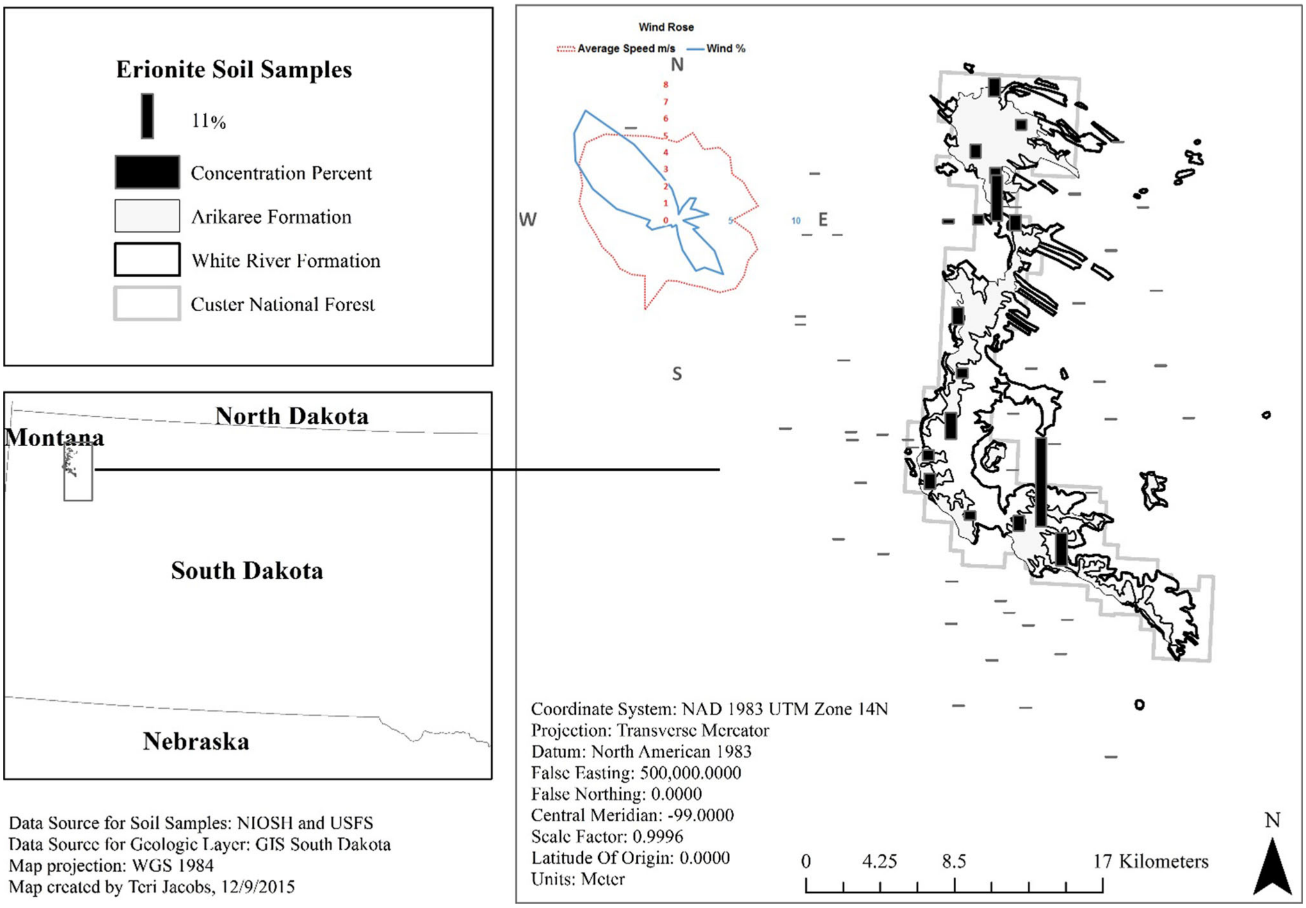
## Discussion

The FBAS was used with PCM to detect the presence of erionite in soil samples collected in and around the Slim Buttes Land Unit of the CGNF in South Dakota. The results were compared with those obtained from PLM and XRD analyses for samples with a significant content of erionite and where sufficient sample was available for analysis. Pure erionite for calibration purposes is not available; erionite from basaltic vesicles or “wooly” erionite is relatively pure, but with a different morphology from volcaniclastic erionite. Thus, in the absence of a pure erionite standard in which to calibrate methods, none of these methods can be considered fully quantitative. Comparison of results to PLM and XRD indicated a FBAS–PCM recovery of approximately 1%. While this is a low recovery, it is similar to what was observed in prior FBAS studies of asbestos in soil. FBAS-TEM results for soils spiked with nominal levels of Libby Amphibole asbestos reported recoveries of 0.1–4.2% (Januch et al. 2013). The comparison with PLM results was also linear, indicating a high likelihood that the relationship can be extrapolated to concentrations below the 1% limit of PLM. Thus, the FBAS–PCM technique can be used to determine erionite concentrations in these soils down to at least 0.03% (after adjustment for 1% recovery). In addition, results using a single microscopist varied little from a count of 10 fibers to a count of 100 fibers (or a maximum of 200 microscopic fields of view), indicating the possibility of rapid turnaround of results. However, results between microscopists within the same laboratory varied considerably, based on their ability to observe, recognize and measure fibers, and this must be accounted for in the evaluation of method uncertainty. Results obtained using different $Q_r$ flow ratio differed slightly (17%). A comparison of results between two different PCM laboratories may have been biased because of differences in counting heuristic, one laboratory used judgment in determining the nature of fibrous particles while the other used only a simple geometric definition. However, a *t* test found no significant difference. XRD analyses based on dilution of a reference erionite sample gave higher results than PLM for the first set of data (HHE samples) but lower than expected for the later samples (NIOSH-2). This may be due to an error in the calculation of the XRD reference sample concentration, but lower than expected results may also be a result of more intensive grinding in the preparation of the samples for XRD analysis, leading to a loss of crystallinity (Occella 1994). Under- or overestimation by PLM is also possible, especially since exact calibration standards are not available. FBAS-TEM results are generally lower than FBAS–PCM results from the same sample. This is most likely due

**Table 7** FBAS–PCM results by six different individual microscopists at NIOSH

| Sample (collection/number) | Mass concentration (%)[a] | | | | | | SD | Average | CV |
|---|---|---|---|---|---|---|---|---|---|
| | Analyst 1 | Analyst 2 | Analyst 3 | Analyst 4 | Analyst 5 | Analyst 6 | | | |
| NIOSH 1/6 | 0.03 | 0.14 | 0.16 | 0.04 | 0.04 | 0.11 | 0.06 | 0.09 | 0.62 |
| NIOSH 1/12 | 0.26 | 0.57 | 0.30 | 0.21 | 0.14 | 0.84 | 0.27 | 0.39 | 0.69 |
| NIOSH 1/17 | 0.07 | 0.10 | 0.31 | 0.74 | 0.01 | 0.50 | 0.29 | 0.29 | 0.99 |
| NIOSH 2/1 | 12 | 17 | 23 | 14 | 20 | 12 | 4.5 | 16 | 0.28 |
| NIOSH 2/8 | 3.2 | 2.0 | 2.2 | 2.0 | 2.1 | 6.9 | 2.1 | 3.3 | 0.63 |
| NIOSH 2/11 | 1.2 | 0.74 | 1.5 | 0.33 | 0.38 | 2.3 | 0.74 | 1.2 | 0.70 |

[a] Based on analysis of 100 countable fibers/200 fields of view, $Q_r$ of 0.0425 and adjusted for recovery of 1%



Data Source for Soil Samples: NIOSH and USFS
Data Source for Geologic Layer: GIS South Dakota
Map projection: WGS 1984
Map created by Teri Jacobs, 12/9/2015

Coordinate System: NAD 1983 UTM Zone 14N
Projection: Transverse Mercator
Datum: North American 1983
False Easting: 500,000.0000
False Northing: 0.0000
Central Meridian: -99.0000
Scale Factor: 0.9996
Latitude Of Origin: 0.0000
Units: Meter

**Fig. 5** Map of study area depicting locations and concentrations of erionite soil samples within and outside the formations. The number next to the *bar symbol* in the legend represents the data value for the symbol value of that size on the map. Thus, bars taller than the legend scale equate to values greater than 11% and *smaller bars* indicate values less than 11%. The data values range from 0 to 22.98%. Values less than 1% appear as *dashes*

to a more accurate exclusion of non-erionite particles by TEM, although there is also a possibility of low bias due to the smaller area of filter examined (NIOSH 1994b).

Even though the four sets of samples examined in this work were collected by slightly different techniques, it is possible to map them and draw some tentative conclusions about the distribution of erionite in soils. Firstly, the erionite in soils developed above the outcrops is highly concentrated compared to the erionite content of the parent rock, which rarely is greater than 1–2%. Some of the other components of the rock such as gypsum, calcite or clay minerals therefore must be removed faster than the erionite

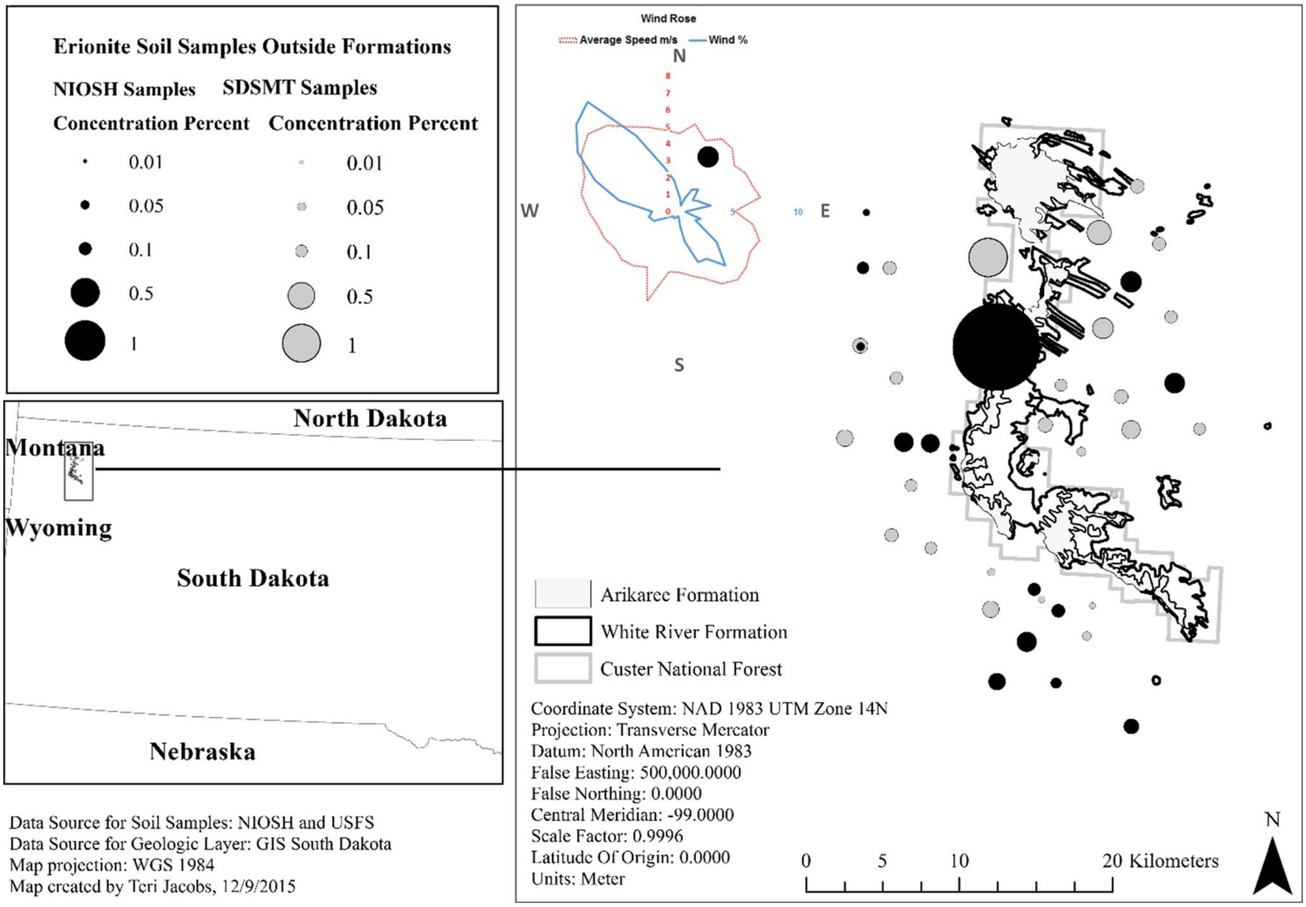
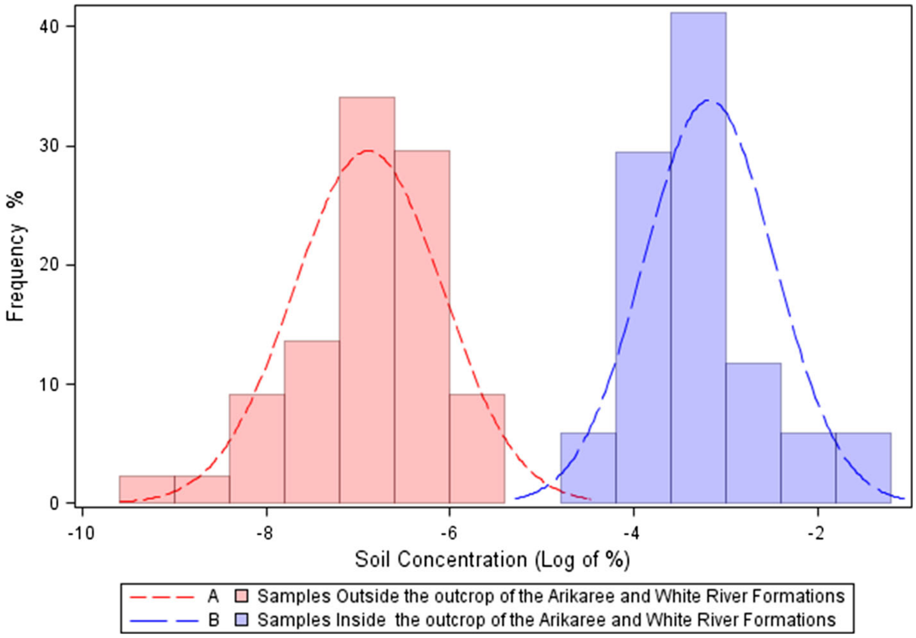


**Fig. 6** Map of study area depicting only the concentration and location of soil samples outside the formations. Concentrations were symbolized with *proportional symbols*, and the size of the symbol reflects the actual data value

**Fig. 7** Histograms of erionite soil concentration data



through weathering. Secondly, erionite was found in nearly every soil sample, even those taken several miles from the outcrop. This attests to the stability of erionite under weathering, but it may also be due to a continuous replenishment, perhaps through wind-blown dust accumulation in soils. Wind erosion of soils in this area is well-documented. However, if wind erosion was the major transport route of erionite to soils outside of the outcrop, then enhanced erionite concentration might be expected along a prevailing wind direction, and the concentrations in the more “surface” samples collected by the South Dakota School of Mines and Technology should be higher than the deeper “sub-surface” samples collected by NIOSH (Fig. 6). However, neither factor is obvious from the Figure. Nor is there any evidence of fluvial or other transportation; the area was not glaciated, there is no obvious diminution of concentration with distance from outcrop, and there are topographic highs present between the outcrop and some sample locations. A possible reason for the presence of erionite in off-outcrop soils that is consistent with these observations is that they are relict minerals after erosion of a once more extensive outcrop (older rocks make up the underlying geology between outcrops). However, we have not researched this possibility in the detail necessary to establish a complete model of the situation.

## Conclusions

Erionite is a potentially hazardous mineral, which occurs naturally in volcaniclastic sedimentary rocks found in the western USA. In addition to its presence in rocks, erionite remains in soils after weathering and disturbance of those soils can lead to inhalation exposures as documented in prior studies. FBAS is a sample preparation technique that when used in conjunction with microscopic analysis of filters can detect the presence of erionite in soils. If a 1% recovery is assumed by comparison with PLM analyses of soils with high concentrations, the technique can be considered a semi-quantitative estimate, which can likely be extrapolated to concentrations almost two orders of magnitude below the limit of PLM quantitation. No overall significant difference was found between FBAS–PCM concentrations in 14 low-concentration (below 1%) soil samples analyzed by two different laboratories. However, large differences in the counting and sizing of particles by different microscopists can add a large level of uncertainty to the concentration estimates. FBAS-TEM can be used to avoid such differences but at larger cost and with longer sample turnaround times. Mapping of erionite concentrations in soil could lead to a greater understanding of the geological processes which have led to its presence. Although we have demonstrated that erionite in soils can be detected through FBAS–PCM, we have not attempted to correlate those results with human inhalation exposure through activity-based sampling, and thus, any risk inherent in working these soils is unknown.

## Disclaimer

The findings and conclusion in this report are those of the author(s) and do not necessarily represent the views or official position or policy of NIOSH/USFS/EPA/SDSMT. Mention of trades names and or commercial products does not constitute endorsements or recommendations for use. The authors have no known conflicts of interest in conducting and reporting this research. This project was supported in part by an appointment to the Research Participation Program at the Centers for Disease Control and Prevention administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the US Department of Energy and the Centers for Disease Control and Prevention.

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