Erionite Information

What you need to Know about Erionite

Erionite is a naturally occurring zeolite typically formed by the alteration of volcanic rocks. Zeolites are a group of hydrated aluminum silicates that contain alkaline and alkaline-earth metals. Because of their inherent properties such as the ability to absorb large quantities of water, zeolites are used widely as pet litter, animal feed and other horticultural applications. Several hundred occurrences of zeolite deposits have been recorded worldwide.

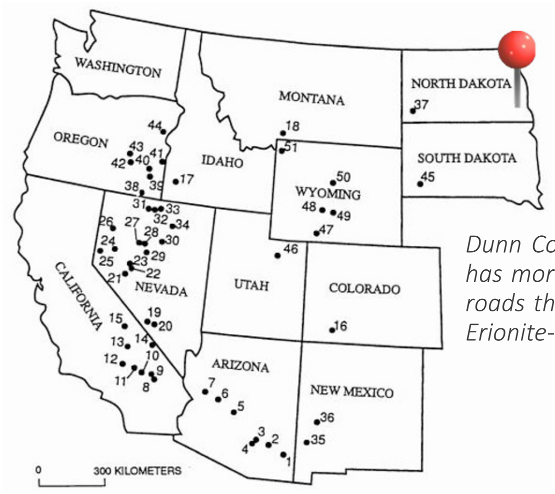
Erionite has an average formula of $K2\ (Na,Ca_{0.5})_8[Al_{10}Si_{26}O_{72}]\ 30H_2O$. However, the large chemical variability in the chemical structure of erionite can become an issue during EDS analysis. In fact, in 1997 erionite was elevated to a “series” status in an attempt to better categorize the wide chemical ranges observed for erionite. Three different species names have been created according to the most abundant extra framework cation present: **erionite- Na**, **erionite-K** and **erionite-Ca**.

Why analyze for Erionite?

Erionite has been associated with an increased risk of developing malignant mesothelioma in villages in Turkey, where people have built their homes out of erionite bearing rock. In the U.S. erionite deposits have been found in at least 13 states. A study conducted in 2011, concluded that the physical and chemical properties of erionite from Turkey and North Dakota are very similar and show identical biological activities.[1]

Erionite is classified as an IARC Class I carcinogen by the WHO and IARC but is currently not regulated by the U.S. EPA in the same way as asbestos. Currently there are no established exposure limits for erionite.

[1]2011 Carbone, M. et. al. Erionite exposure in North Dakota and Turkish Villages with Mesothelioma.



Dunn County, North Dakota has more than 300 miles of roads that were paved with Erionite-rich gravel.

EMSL utilizes the following instruments that can identify Erionite:
TEM | PLM | SEM | XRD | EBSD

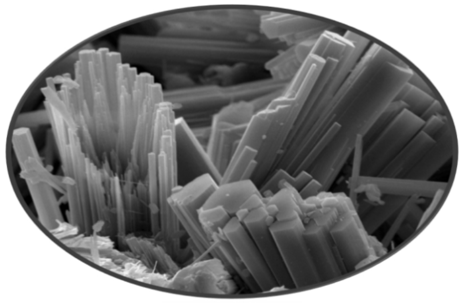
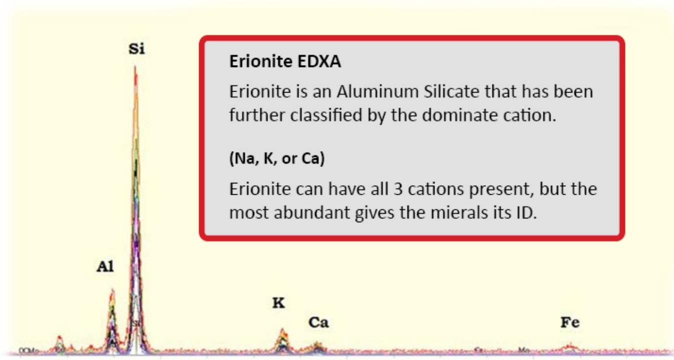


Image credit: Map by U.S. Geological Survey, R. Sheppard, Open File Report 96-018, Scanning electron microscopy (SEM) Micrographs by EMSL Analytical, Inc.

Analysis of Erionite

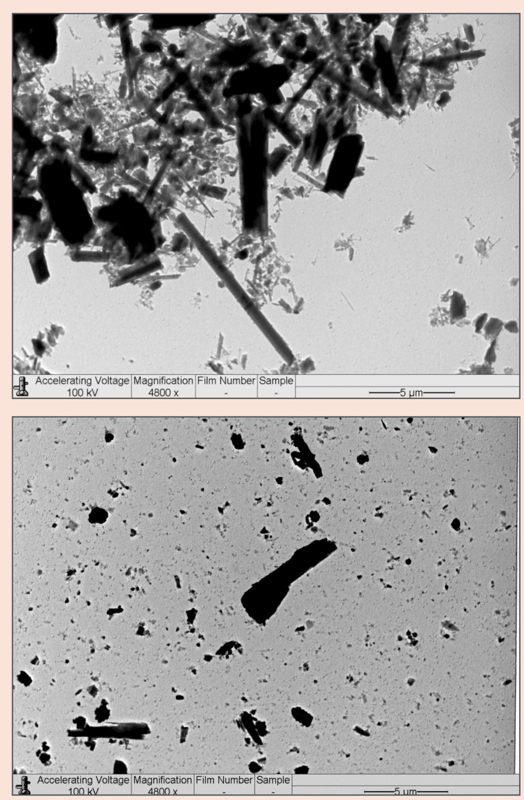
Unfortunately, there is no easy, one size fits all analytical approach to erionite. Most testing is specific to the project, so it is often customized to each unique data objective. When we talk about mineral fiber analysis in any material, there are common techniques and instruments that are relevant. The examination at each one of these instrument is for different purposes and each instrument has strengths and weakness. That is why is difficult to compare the results between the different techniques, because they measure and count a different portions of the overall picture. Erionite is much different than the asbestos and there are things that need to be adapted and considered when submitting a sample for analysis.



Most of the work EMSL has been providing for erionite has been in rock, soil dust and air matrices. Generally, existing asbestos methods are used and modified to account for the difficulties of erionite identification. Most of the modifications are to overcome:

- The variable chemistry of erionite and how to identify it from other zeolites
- Erionite's sensitivity to acids and heat,
- And it is extremely delicate and can be crushed into a non-countable, non-fibrous structure. (False Negatives)

Erionite has a very distinctive selected area electron diffraction (SAED) pattern which makes it an ideal candidate for identification by Transmission Electron Microscopy (TEM). However, unlike asbestos, it is extremely sensitive to the high energy of the electron beam. The beam's intensity has been shown to diffuse sodium and potassium and rapidly degrade the crystal lattice; which can make identification difficult. Most published erionite identification and characterization papers rely heavily on bulk sample quantitative chemistry by either ICP-MS or EPMA. However, these instruments require a larger sample size than is typically collected on the filter membrane of an air sample and chemistry alone cannot readily distinguish between offretite and erionite, unlike diffraction. With a small change to most of the TEM asbestos analysis methods, EMSL uses an approach that allow for rapid identification of erionite fibers of all sizes in air, bulk, dust, water and soil samples by TEM. This technique uses a cryogenic specimen holder to preserve the integrity of the erionite fibers for identification.



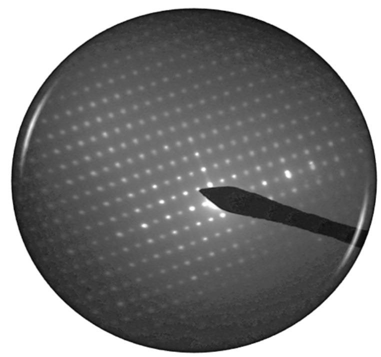
Erionite from Nevada showing fiber "loss" at different milling targets. Top -milled to 250 Bottom milled to 75 microns.

Soil and rock are particularly difficult analytically because they need to be reduced in size prior to analysis. Erionite fibers do not endure well when subjected to aggressive crushing, acid treatment or heat. Once milled the erionite fibers can break up into non-fibrous particulate and would no longer be of interest or countable as erionite fibers to an analyst – leading to the potential for false negatives.

For soil testing, EMSL recommend three approaches. First, the EPA 600/R93/116 or the ISO 22262 method for TEM Mass analysis. This approach counts all fibres greater than 0.5 um in length (min 3:1 aspect ratio) and reports erionite fibres as a mass percent. The second approach is the TEM Fluidized Bed Asbestos Segregator (FBAS). The FBAS has been developed by the US EPA to separate mineral fibres from soil and onto an air filter through elutriation. EMSL is the only commercial laboratory to be able to offer this technique. The FBAS samples for the respirable fraction of fibres in the soil and reports the respirable erionite in structures per gram. 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. For both of these, no preservation is needed and each method would require a sample of 8 oz. The last approach is the ASTM D7521 method, which does not require milling but sieves the sample into 3 size fractions for testing by PLM and optionally TEM.

For testing in air, there are three approaches that are recommend. First is counting erionite by the ISO 10312 method. This method has sampling and analysis protocols that are quite useful in these situations. It counts all fibres greater than 0.5 um (min 3:1 aspect ratio). It then reports the concentrations in various categories, such as all fibre sizes, sizes >5 um, and PCMe (PCM equivalent). It provides the most data to any air method and is commonly used by the US EPA. Results are report as structures per cc.

The second and third approach go hand in hand- the NIOSH 7400 and NIOSH 7402 methods. These methods are a tandem approach with Phase contrast microscopy (PCM) and TEM. PCM is a light microscopy method that counts all fibre >5 um. It cannot identify the fibres to any specific mineral but is used as a quick fibre index to see if you have an elevated fibre count. If the fibre count is elevated you can move onto to TEM analysis to identify mineral type of the fibres that are seen. The results for both of these tests are reported as fibre per cc. These tests are typically used for comparing occupational exposure to asbestos. That said currently there are no formally published permissible exposure limits (PEL) specific to erionite. In the absence of this information many have relied on the asbestos PEL as a place to start, with an understanding that it may not be protective enough for erionite. (Erionite seems to have a much higher potency than asbestos).



TEM SAED Diffraction pattern of erionite taken on a cryogenic sample holder.

TEM Fluidized Bed Asbestos Segregator

Another testing approach that has been used is for testing fugitive dust. In this case a TEM qualitative method is used that checks for presences of erionite. This technique does not provide quantitative results, but is useful in determining how far contamination may have spread or to pinpoint and area for investigation. This technique suspends the dust in water where it is then filtered onto a membrane filter and analyzed by TEM.

Additionally, EMSL offers erionite analysis by Scanning electron microscopy (SEM) and X-ray diffraction (XRD). Please contact your EMSL representative or contact EMSL directly at 800.220.3675 or info@emsl.com for more information on testing options.

There are many facets to erionite analysis. Regardless of your reason for testing, whether it be for quality, regulation, manufacturing or exposure rest assured that we have the experience to be your project partner. EMSL is here to help provide an approach that uses the best science and produces the most legally defensible data. Reach out to one of our industry professionals to discuss your project.