

Geologic occurrences of erionite in the United States: an emerging national public health concern for respiratory disease

Bradley S. Van Gosen · Thomas A. Blitz ·
Geoffrey S. Plumlee · Gregory P. Meeker ·
M. Patrick Pierson

Received: 14 June 2012 / Accepted: 23 November 2012 / Published online: 12 January 2013
© Springer Science+Business Media Dordrecht(out side the USA) 2013

Abstract Erionite, a mineral series within the zeolite group, is classified as a Group 1 known respiratory carcinogen. This designation resulted from extremely high incidences of mesothelioma discovered in three small villages from the Cappadocia region of Turkey, where the disease was linked to environmental exposures to fibrous forms of erionite. Natural deposits of erionite, including fibrous forms, have been identified in the past in the western United States. Until recently, these occurrences have generally been overlooked as a potential hazard. In the last several years, concerns have emerged regarding the potential for environmental and occupational exposures to erionite in the United States, such as erionite-bearing gravels in western North Dakota mined and used to surface unpaved roads. As a result, there has been much

interest in identifying locations and geologic environments across the United States where erionite occurs naturally. A 1996 U.S. Geological Survey report describing erionite occurrences in the United States has been widely cited as a compilation of all US erionite deposits; however, this compilation only focused on one of several geologic environments in which erionite can form. Also, new occurrences of erionite have been identified in recent years. Using a detailed literature survey, this paper updates and expands the erionite occurrences database, provided in a supplemental file (*US_erionite.xls*). Epidemiology, public health, and natural hazard studies can incorporate this information on known erionite occurrences and their characteristics. By recognizing that only specific geologic settings and formations are hosts to erionite, this knowledge can be used in developing management plans designed to protect the public.

Electronic supplementary material The online version of this article (doi:10.1007/s10653-012-9504-9) contains supplementary material, which is available to authorized users.

B. S. Van Gosen (✉) · G. P. Meeker
U.S. Geological Survey, M.S. 973, Box 25046, Denver,
CO 80225, USA
e-mail: bvangose@usgs.gov

T. A. Blitz · G. S. Plumlee
U.S. Geological Survey, M.S. 964, Box 25046, Denver,
CO 80225, USA

M. P. Pierson
U.S. Forest Service, 1310 Main St., Billings, MT 59105,
USA

Keywords Erionite · Fibrous · Carcinogen ·
United States · Environmental · Occurrences

Introduction

Erionite, a zeolite mineral, holds an unfortunate distinction similar to the asbestos minerals—it is classified as a respiratory carcinogen. Inhalation of the fibrous form of erionite has been shown to cause a similar group of health effects as observed with mineral fibers classified as “asbestos,” including

malignant mesothelioma, a disease which is more typically associated with occupational and environmental exposures to asbestos (Aust et al. 2011). In fact, some studies indicate that fibrous erionite is significantly more tumorigenic than chrysotile asbestos and forms of amphibole asbestos (Wagner et al. 1985; Hill et al. 1990; Coffin et al. 1992). As a result, the International Agency for Research on Cancer (part of the World Health Organization) lists erionite as a Group 1 known carcinogen, meaning there is sufficient evidence that erionite can cause carcinogenicity in humans (International Agency for Research on Cancer 2012). The National Toxicology Program of the U.S. Department of Health and Human Services likewise designates erionite as a known carcinogen to humans.

Concerns have developed in the last several years regarding the potential for environmental and occupational exposures to erionite in North Dakota and elsewhere in the western United States (Chipera and Bish 1989; Bish and Chipera 1991; Forsman 2006; Ball 2011; Carbone et al. 2011; Weissman and Kiefer 2011). Therefore, there has been much interest in identifying locations across the United States where erionite occurs naturally. Using this information, one can examine potential correlations between these geological occurrences and epidemiological data on the distribution of diseases typically related to asbestos exposure to determine if these illnesses may have resulted from exposures to erionite rather than asbestos. To date, the compilation of erionite occurrences compiled by Sheppard (1996) has been the most widely cited. However, Sheppard's compilation only focused on one of several geological environments in which erionite can form. New occurrences of erionite have been identified in recent years. For these reasons, the U.S. Geological Survey (USGS) has undertaken an update of the Sheppard (1996) database. This paper presents the results of that update (Figs. 1 and 2), providing a database (*US_erionite.xls*) similar to those compiled by Van Gosen for natural occurrences of asbestos across the United States (Van Gosen 2005, 2006, 2007, 2008, 2010; Van Gosen and Clinkenbeard 2011).

Background

Medical studies on erionite and its designation as a Group 1 carcinogen were spawned by extremely high

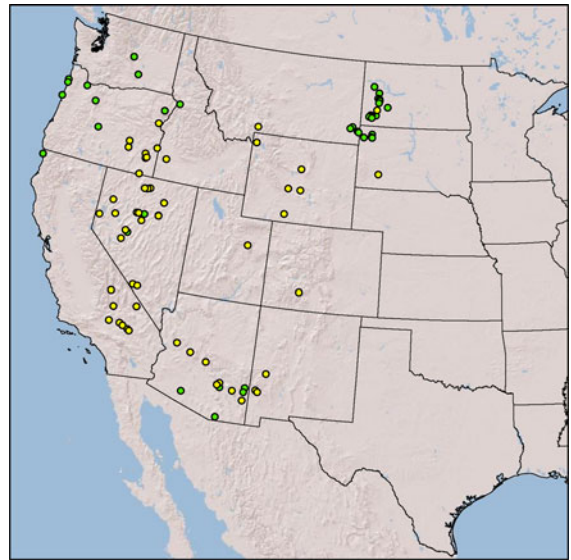


Fig. 1 Index map showing 95 documented natural occurrences of erionite in the United States. Information describing each occurrence is provided in the accompanying spreadsheet *US_erionite.xls*. *Yellow circles* ($n = 51$) indicate erionite occurrences described by Sheppard (1996); *green circles* ($n = 44$) are additional natural occurrences of erionite identified by this study

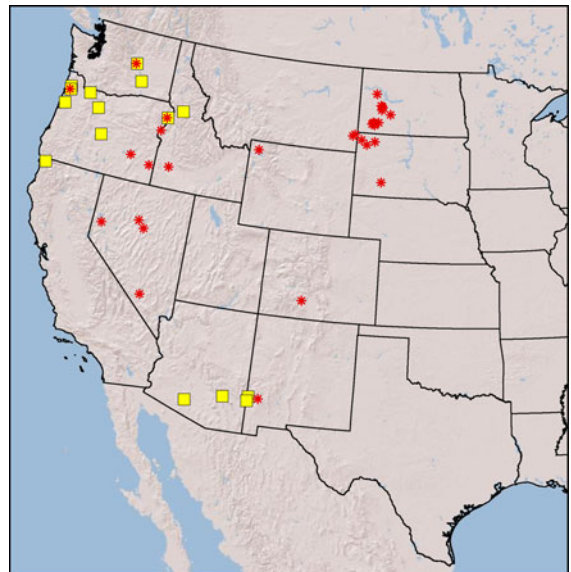
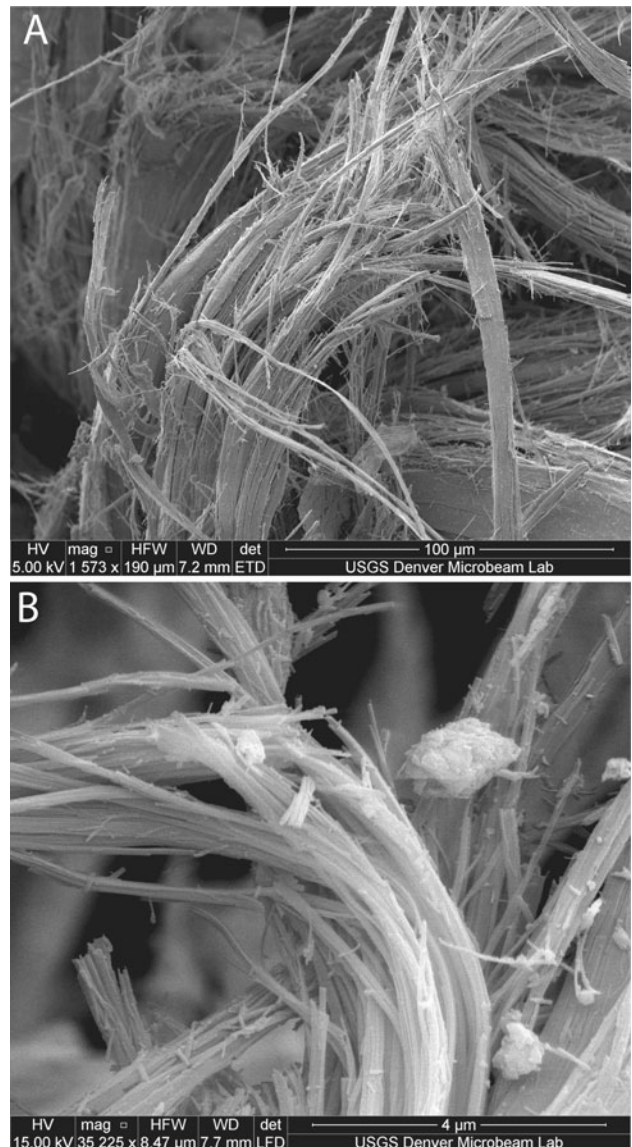


Fig. 2 Index map showing: (1) locations of 32 documented natural occurrences of fibrous erionite in the United States (*red asterisks*), based on descriptions from a variety of publications; and (2) locations of 15 documented examples where erionite lines vesicles and cavities in basalt volcanic rocks (*yellow squares*)

Fig. 3 Scanning electron microscope (SEM) images of the unusual “wooly” erionite from the type locality—the former Durkee opal mine, located along Swayze Creek near Durkee, Oregon. SEM views at **a** high magnification; and **b** even higher magnification (note the *scale bars*). Photographs by G.P. Meeker, USGS. Sample collected by R.A. Sheppard, retired, USGS



incidences of pleural and peritoneal mesothelioma discovered in three small villages located in Cappadocia, a region of Central Anatolia in Turkey. In the 1970s, it was realized that residents of these villages had epidemic-level rates of malignant mesothelioma, often resulting in death (Bariş et al. 1978). The cause of the mesotheliomas in this area was determined to be inhalation of erionite fibers from environmental exposures (Bariş et al. 1978; Artvinli and Bariş 1979; Bariş et al. 1987; Bariş and Grandjean 2006; Dogan et al. 2006; Carbone et al. 2007, 2011). The erionite in the Cappadocia region of Turkey occurs in lithified volcanic ash (tuffs), which in some areas forms cliffs. Some

of these cliffs were excavated to form caves in which residents lived. In and near the villages, fibers of erionite have been found in soils, the surfaces of unpaved roads, and within building stones (blocks cut from the tuffs) (Dogan et al. 2006).

The existence of erionite at many localities in the western United States has been known for many decades. In fact, the mineral erionite was first identified near Durkee, Oregon, by Eakle (1898), who described a “wooly” specimen at the Durkee opal mine. Eakle (1898) named the mineral *erionite* from the Greek word for wool, because at the type locality it occurs as white, woollike fibers (Fig. 3). For more than 50 years,

erionite was considered a very rare mineral until Deffeyes (1959) described several occurrences of erionite in Nevada and Wyoming. In contrast to the woolly erionite near Durkee, Oregon, which can be observed with the naked eye, most erionite is microscopic in size; this primarily explains its lack of identification for many years. Erionite occurs in many localities throughout the world; however, Sheppard (1996, p. 1) suggests that “the most voluminous deposits seem to occur in continental Cenozoic silicic tuffs of the western United States.”

Prior to 2005, the erionite occurrence in the United States that drew the most interest as a potential health hazard was at Yucca Mountain, Nevada. This occurrence of erionite in volcanic tuffs was studied extensively (Chipera and Bish 1989; Bish and Chipera 1991) because of concerns for potential occupational and environmental exposures to airborne erionite that could be released during development of the Yucca Mountain Nuclear Waste Repository. Chipera and Bish (1989) described fibrous erionite occurrences in clay–zeolite-rich layers near the top of vitrophyres (tuff layers with high volcanic glass content), and in fractures.

Elsewhere in the United States, concern for environmental exposures to erionite appeared to be limited until recently, when Dr. Nels Forsman from the University of North Dakota realized the potential for erionite exposures in the northern Great Plains region (Forsman 2006). Forsman recognized that erionite-bearing ash layers within sedimentary rocks exist in western North Dakota, specifically in the Killdeer Mountains of Dunn County within volcanic ash-bearing sedimentary layers of the Arikaree Formation of late Oligocene to early Miocene in age. He further recognized that gravel deposits, which formed from the erosion of these erionite-bearing strata, also contained erionite. Dr. Forsman also noted that over the period of two or three decades, many of these gravel deposits have been excavated and the gravel used to surface unpaved roads. As a result, the North Dakota Department of Health, in cooperation with the North Dakota Geological Survey and the University of North Dakota, designed a study to evaluate the gravel pits of the area for their erionite content. In this study, the North Dakota Department of Health sampled appropriate strata and nearby gravel pits at the Killdeer Mountains in Dunn County, analyzing the samples for the presence of erionite fibers. Erionite fibers were found in many of the

samples (North Dakota Department of Health 2012). The U.S. Geological Survey (USGS) analyzed a sample of fibrous erionite collected from the Killdeer Mountains, provided by the North Dakota Geological Survey, to examine its chemistry and morphology (Lowers et al. 2010). Using a scanning electron microscope equipped with an energy dispersive spectrometer, the USGS compared the Killdeer Mountains erionite to samples of fibrous erionite from Rome, Oregon, and samples from erionite-contaminated villages in Turkey. The USGS analyses concluded that: “The general morphology of erionite from the studied localities is similar” (North Dakota, Oregon, and Turkey) (Lowers et al. 2010, p. 2).

Erionite exposure studies in Dunn County conducted by the U.S. Environmental Protection Agency (EPA) in 2006 and 2008 found that roads, ball fields, and parking lots surfaced with erionite-containing gravels could generate high airborne levels of erionite when disturbed during various activities, such as driving, raking, and bicycling (Ryan et al. 2011, and references cited therein). A collateral study comparing the erionite exposures in Dunn County, North Dakota, to Turkish villages with elevated rates of mesothelioma found that the chemistry, morphology, and biological activity (in vitro and in vivo experiments) of the erionite were similar in both areas (Carbone et al. 2011). Also, the airborne levels of erionite in North Dakota study areas could equal or exceed those in a Turkish village that has a mesothelioma mortality rate of about 6 % (Carbone et al. 2011). Of particular concern was the elevated air concentrations of erionite in North Dakota found alongside roads at school bus stops and inside of vehicles, including school buses, even with the windows closed (Carbone et al. 2011). The study described by Carbone et al. (2011) determined that more than 300 miles of roads, including 32 miles of school bus routes, in western North Dakota are surfaced by erionite-containing gravel.

A study of residents of western North Dakota by Ryan et al. (2011) examined the rate of chest radiometric abnormalities in study participants that were potentially exposed to road gravel containing fibrous erionite. Ryan et al. (2011) found: “Interstitial, pleural, or both changes typically associated with asbestos exposure were observed by high-resolution computed tomography” in 7 of the 34 study participants. The primary pathway for 6 of the 7 affected individuals was thought to be occupational exposures from gravel pits, road maintenance, or both.

Given these findings and concerns for exposures, the North Dakota Department of Health has developed an erionite program, which includes results, public safety recommendations, and guidelines for erionite bulk sampling (see North Dakota Department of Health 2012). Additionally, the National Institute of Safety and Health (NIOSH) issued a warning to help inform and protect workers that may be exposed to erionite deposits or erionite-bearing rocks throughout North America (Weissman and Kiefer 2011).

Present study

Our study gathered information on areas within the United States where erionite has been identified and described (Figs. 1 and 2). The attached dataset *US_erionite.xls* was compiled through a systematic search of the geologic literature, with the purpose of identifying the locations and geologic settings in which erionite is known to occur in the United States. This compilation cannot be regarded as a complete inventory of the erionite that exists in the United States; rather, it represents only those erionite occurrences that have been documented in the geologic literature (as of early 2012), plus recent unpublished discoveries (described below). Also, this new inventory relies on the accurate identification of erionite by the referenced studies; erionite can be difficult to distinguish from some other zeolite minerals, such as mordenite and especially offretite.

Our paper attempts to frame the context for the geology and resulting distribution of erionite in the United States, which can then lead to site-specific detailed investigations. There was insufficient information for 32 of the 72 erionite occurrences that we found described in the literature to determine whether the erionite occurs in fibrous forms; in other words, the morphology of the erionite was not described. Clearly, in order to better understand whether potential health hazards exist at these occurrences, it would be necessary to visit each locality, sample, and examine the collected samples using electron microscopy techniques. Further, one should compare the erionite samples to examples that have been shown to cause disease (such as Turkish samples) and (or) conduct additional toxicology studies using mineralogically and geochemically well-characterized samples of the material from other localities as the dosing materials.

The dataset *US_erionite.xls* builds upon an earlier compilation by Sheppard (1996), which summarized 51 occurrences of erionite in sedimentary rocks in the western United States. The additional erionite occurrences added in our compilation are of three types:

- Recent discoveries of erionite in gravel deposits derived from the erosion of erionite-bearing, volcanic tuff-rich sedimentary units in western North Dakota (North Dakota Department of Health 2012; Pratt 2012).
- Recent discoveries of erionite-bearing, volcanic tuff-rich sedimentary units in northwestern South Dakota, western North Dakota, and southeastern Montana; this erionite was confirmed by sampling conducted by personnel of Custer National Forest and the North Dakota Geological Survey. These deposits of erionite occur in particular volcanic ash-rich strata within specific sedimentary units that are Tertiary in age.
- Erionite described at about 15 sites in which erionite lines vesicles and cavities in basalt volcanic rocks; examples are described at sites in Arizona, California, Idaho, Oregon, and Washington.

As with Sheppard's compilation (Sheppard 1996), our study includes information on the morphology of erionite (fibrous versus non-fibrous) for the locations where this information was provided by the literature sources. The mineral's morphology may be an important factor in its potential for health impacts.

Erionite geology

In earlier literature, "erionite" was described as a single mineral species (Sheppard and Gude 1969; Gude and Sheppard 1981; Armbruster and Gunter 2001; Passaglia and Sheppard 2001); now erionite is classified as a series within the zeolite mineral group. Three distinct erionite minerals are now recognized (Dogan and Dogan 2008; Dogan et al. 2008), reflecting the range in Ca, K, and Na content within the erionite series:

- (1) erionite-Ca [$\text{Ca}_4\text{K}_2(\text{Al}_{10}\text{Si}_{26}\text{O}_{72})\bullet 32\text{H}_2\text{O}$],
- (2) erionite-K [$\text{K}_4\text{Na}_2\text{Ca}(\text{Al}_8\text{Si}_{28}\text{O}_{72})\bullet 32\text{H}_2\text{O}$] (Ballirano et al. 2009), and
- (3) erionite-Na [$\text{Na}_6\text{K}_2(\text{Al}_8\text{Si}_{28}\text{O}_{72})\bullet 25\text{H}_2\text{O}$].

Because the great majority of the literature used the term erionite without a modifier, and precision mineral

analyses were rarely provided (for example, as in Ballirano et al. 2009), it is only possible to use the term “erionite” to refer to the occurrences described in this paper.

Erionite forms from the relatively low temperature (<110 °C), in-place reaction of pore waters with clays, other aluminosilicate minerals, or volcanic glass (Hay and Sheppard 2001; Langella et al. 2001).

In the United States, erionite has been found in three general geologic settings:

1. Erionite occurs within non-marine sedimentary layers, which are typically composed of altered volcanic ash (tuffs) and clays. The most common and largest erionite deposits appear to have formed in lake (lacustrine) environments, principally, where volcanic ash settled into alkaline lakes. The erionite-bearing layers in these deposits range from less than a centimeter to several meters in thickness. The erionite content can range from trace amounts (<1 %) to nearly 100 % of the rock (Sheppard 1996). The known host rocks for erionite in the United States are no older than Eocene (no more than 55 million years ago), but can be as young as a thousand years. Examples of these tuffaceous-lacustrine erionite deposits are known in all of the western States (Sheppard 1996; also this compilation), except Washington, where erionite is found in basalt (described in item 3 below).
2. Erionite is found in some silica-rich volcanic deposits that have been altered by heated (hydrothermal) fluids. Examples of fibrous erionite have been found in drill holes at depths of about 10 m in the Upper and Lower Geyer basins in Yellowstone National Park, Wyoming (Bargar and Beeson 1981; Bargar et al. 1981). At Yucca Mountain, Nevada, fibrous erionite occurs in fractures in volcanic rocks (Bish and Chipera 1991; Sheppard and Hay 2001); the erionite may have formed by groundwaters that flowed along the fractures and reacted with glassy, silica-rich volcanics.
3. Erionite forms as linings in cavities and small vesicles in some basalt volcanic rocks. The erionite-lined cavities and vesicles range from millimeters to several centimeters across. About a dozen examples of erionite in basalt are listed in the accompanying dataset; good specimens have been found (1) along the east bank of the

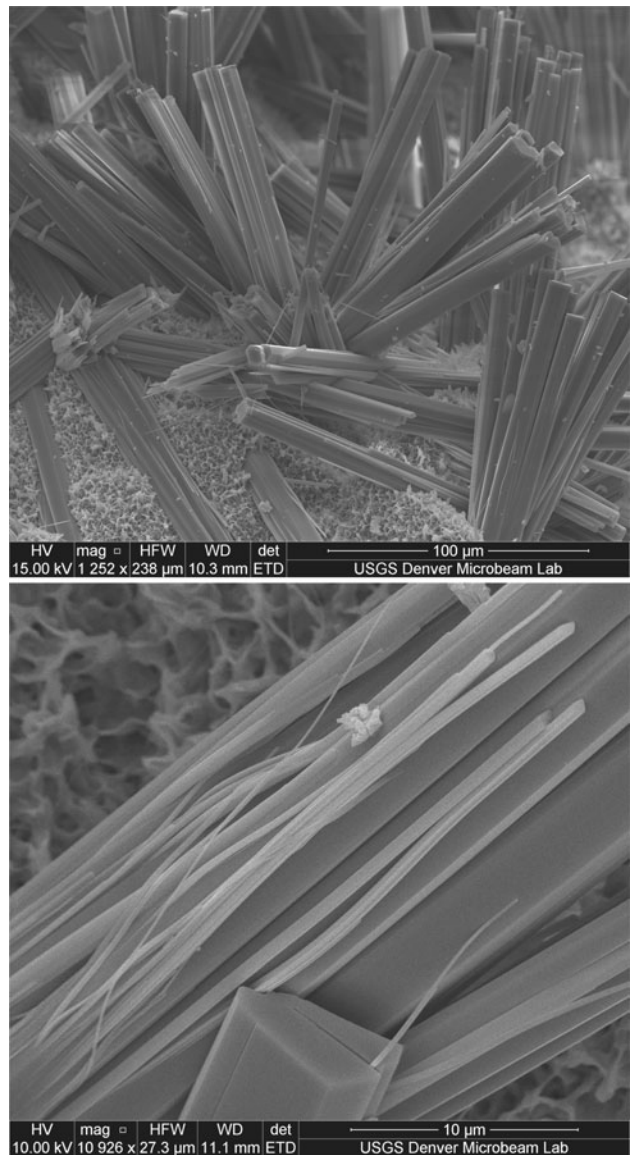
Columbia River at Rock Island Dam, near Wenatchee in Douglas County, Washington (Kamb and Oke 1960) and (2) at Yaquina Head, near Agate Beach, Oregon (Wise and Tschernich 1976; Tschernich 1992).

Erionite morphology

Erionite occurs in a variety of elongated shapes. The tiny size of most erionite crystals requires that specimens be observed with a microscope, with high-resolution scanning electron microscopy needed to examine the thinnest particles (“fibers” or “fibrils”). Terms that have been used in the literature to describe erionite crystal habits include prismatic (Fig. 4), acicular (needle like), needles, rods, rodlike crystals, fibrous, fibers, hair like, and wooly. Erionite crystals can occur individually or as “bundles of hexagonal rods,” “radiating clusters,” and “sprays” (“bundles”, “fibers”, and “fibrils”, as described by Dogan et al. 2008). Sheppard (1996, p. 1) states: “Unlike the type wooly erionite (at the Durkee, Oregon, discovery site), most erionite in sedimentary rocks is acicular, prismatic, or rod-like, and it commonly occurs in bundles or radial aggregates. The individual crystals are about 2–200 μm long and 0.1–10 μm thick.” Thus, erionite is consistently elongated, but is not always fibrous (ideally exemplified as resembling hair, as shown in Fig. 3). In fact, the morphology of the erionite can vary even within a sedimentary layer across a single outcrop or district, such as forms of erionite that range from prismatic to hair like over a distance of a few feet (for example, see Sheppard 1994).

Our review of the literature found that erionite in the United States was only occasionally described as fibrous or wooly in habit (see *US_erionite.xls* and Fig. 2). From an environmental health prospective, the relevance of this observation is that the most common forms of erionite described in the US deposits—prismatic or acicular—are typically at least 2 μm in width and would presumably be less likely to form respirable mineral particles. Respirable particles are those with widths less than 1.5 μm and would be of greater health concern (Aust et al. 2011). Another potential concern and consideration is that elongated forms of erionite greater than 2 μm in width (prismatic or rod like) may have the ability to part or cleave to

Fig. 4 Scanning electron microscope images of prismatic crystals of erionite, which were plucked from cavities in basalt found near Ajo in Pima County, Arizona. In the *bottom* image, note the fibrous particles of erionite that extend from the prismatic crystals. Photographs by G.P. Meeker, USGS. Sample collected by John Clinkenbeard, California Geological Survey

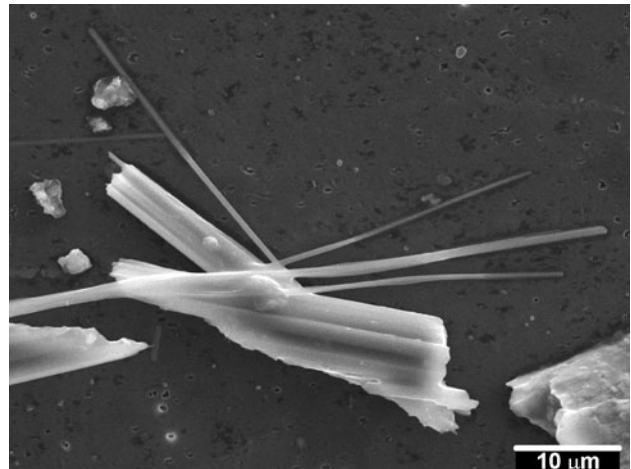


form thinner, fibrous particles of respirable size (Fig. 4). Such a study, specific to erionite, is apparently lacking in the literature.

Within the United States, our literature review found erionite described as fibrous or wooly at 15 sites:

- In the Creede Formation, near the Rio Grande River, south of Creede, Colorado (Larsen and Crossey 2000).
- In the Chalk Hills Formation, along Browns Creek, south of Oreana, Idaho (Sheppard 1991).
- Identified at depth in drill holes at Yucca Mountain, Nevada, within the Topopah Spring Member of the Paintbrush Tuff (Chipera and Bish 1989; Bish and Chipera 1991).
- Tertiary-age, volcanic ash-bearing lake deposits near Hungry Valley, Nevada (Sheppard 1996).
- The Jersey Valley zeolite deposit, Jersey Valley, Pershing County, Nevada (Shedd et al. 1982).
- The Reese River zeolite deposit near Reese River, Nevada (Sheppard 1996; Gude and Sheppard 1981).
- Tertiary-age, volcanic ash-bearing lake deposits in the upper part of the Gila Conglomerate, near Buckhorn, New Mexico (Gude and Sheppard 1988).

Fig. 5 Scanning electron microscope image of erionite in a tuffaceous sample from western North Dakota. Samples contained individual fibers, bundles of fibers, and radiating fiber bundles. Image used with permission from USGS study of Lowers et al. (2010)



- In the Miocene-age “Rome beds” near Rome, Oregon (Sheppard and Gude 1993; Dogan and Dogan 2008; Ballirano et al. 2009).
- Miocene-age, volcanic ash-bearing lake deposits near Harney Lake, Oregon (Sheppard 1994).
- At the Opal Mine quarry, on Swayze Creek, near Durkee, Oregon (Fig. 3). This is the discovery site for erionite and the type locality for “wooly” erionite (Eakle 1898; Gude and Sheppard 1986).
- Lining vesicles in Miocene-age basalt lavas near Cape Lookout, Tillamook County, Oregon (Tschernich 1992).
- Near Dollar Lake, southeast of Aneroid Lake, in Wallowa County, Oregon (Tschernich 1992).
- On Cedar Butte, south of Sheep Mountain Table, South Dakota (Sheppard 1996).
- On the east bank of the Columbia River at Rock Island Dam, near Wenatchee, Washington (Kamb and Oke 1960).
- Identified in several drill holes at depths of less than 15 m in Lower and Upper Geyser Basins, Yellowstone National Park, Wyoming (Bargar and Beeson 1981; Bargar and Keith 1995).

In addition, recent sampling and analyses of gravel pits, test gravel pits, and outcrops in southwestern North Dakota (North Dakota Department of Health 2012; Lowers et al. 2010) confirmed the presence of fibrous erionite (Fig. 5). These gravels formed from the natural erosion of nearby layered rock (volcanic ash-bearing strata) in the Arikaree Formation and the White River Group (includes the Brule and Chadron Formations), which occur in the Chalky Buttes, Little Badlands, and Killdeer Mountain areas in Slope, Stark

and Dunn counties of southwestern North Dakota. Similarly, personnel of Custer National Forest conducted reconnaissance sampling of equivalent geologic formations (Arikaree Formation and White River Formation–Chadron and Brule Members) in northwestern South Dakota and southeastern Montana (Fig. 6); they found erionite contents that ranged from trace to moderate amounts (as much as 20 %); these sites are listed in *US_erionite.xls*.

Other zeolites that can form fibrous or respirable elongated particles

In our survey of erionite, we found a number of localities in which other fibrous zeolite minerals were identified with or without erionite, most often mordenite $[(Ca,Na_2,K_2)Al_2Si_{10}O_{24}\cdot 7H_2O]$, but also thomsonite $[Ca_2Na(Al_5Si_5O_{20})\cdot 6H_2O]$ and offretite $[CaKMg(Al_5Si_{13}O_{36})\cdot 16H_2O]$. Offretite is similar to erionite in composition and can easily be confused with erionite without confirmatory x-ray diffraction and chemical analysis. Mordenite was identified in the literature at a large number of localities and was more commonly described as “fibrous” than was erionite. Toxicological studies are somewhat mixed in their conclusions about mordenite’s toxicity, but in general, these studies indicate a much lower level of toxicity than that of erionite (for example, Adamis et al. 2000; Tátrai et al. 1992; Guthrie 1992; Suzuki and Kohyama 1984). This difference has been proposed to result from differences in iron speciation on the fiber surfaces (Fach et al. 2003). However, it also appears that the different

Fig. 6 Outcrop of the Arikaree Formation in the Long Pines area of Custer National Forest, Carter County, southeastern Montana. Within this outcrop, layers rich in volcanic tuff were found to contain fibrous zeolite, most likely erionite, based on scanning electron microscopy



toxicity studies of mordenite were not consistent in their use of fibrous versus non-fibrous varieties as the test materials.

A compilation of mordenite occurrences across the United States similar to that of the current study for erionite, when compared against epidemiological data for asbestos-related diseases, may provide further insights into the relative toxicity of mordenite compared to erionite. We are currently in the process of completing such an inventory of mordenite occurrences. An inventory of mordenite could also serve as the basis for collection and characterization of mordenite-dosing materials from different sources for use in future toxicological studies.

Discussion

As noted earlier, the National Toxicology Program of the U.S. Department of Health and Human Services designates erionite as a known carcinogen to humans. However, in contrast to asbestos, at this time, there are no required established methods, guidelines, or regulations for the analyses and characterization of erionite. Dogan et al. (2005) and Dogan and Dogan (2008) have recommended specific characterization guidelines to enable the positive identification of erionite.

This study reiterates the observations that not all erionite is fibrous and that erionite may not universally occur in readily respirable forms. The presence of erionite in a sample can be determined through carefully conducted x-ray diffraction analyses, but obtaining an adequate amount of erionite for its detection is a limiting factor of the x-ray diffraction technique. Because erionite fibers are sub-microscopic

in size, their morphology (shape, length, width) must be determined using optical microscopy, or preferably, high-resolution electron microscopy with energy dispersive x-ray analysis. However, the use of x-ray microanalysis for identification of erionite, employing either energy-dispersive or wavelength-dispersive analysis, is difficult. This is due to the extreme electron beam sensitivity of erionite and related zeolites, which causes migration of cations such as Na and K, and compromises the analyst's ability to determine accurate cation ratios. This is particularly true for the analysis of small fibers. Therefore, electron beam techniques should be complimented with x-ray diffraction when possible for accurate identification of specific fibrous zeolite minerals.

It must be emphasized that while the entries in *US_erionite.xls* imply an individual site, they are in most instances representative of an erionite-bearing district. These erionite deposits are hosted by a geologic unit—a specific layer, formation, member, rock type—which experienced a geologic environment ideal for the formation of erionite. It is important to recognize that at these erionite-bearing sites, the host geologic unit can extend well away from the sampled erionite locality, often for many miles. The user should view the reported occurrence not only as a site, but also as a guide to the regional rock type, geologic conditions, and rock unit that formed and now may host erionite. Thus, the identified erionite-bearing rock units can be traced across the area, sometimes regionally, indicating the potential for other erionite occurrences that may exist in the vicinity. In addition, one should consider that wind can distribute erionite fibers, and water can also carry erionite-bearing rocks and sediments to downstream areas.

The observations of Forsman (2006) and findings of the North Dakota Department of Health (2012) and U.S. Forest Service surveys are also significant. These studies show that respirable, elongated erionite particles can be eroded from the geologic rock units in which they formed, transported by surface water runoff, and deposited in gravels, alluvium, and other sedimentary deposits up to several kilometers outside the outcrop extent of the original host rocks.

These geologic observations provide an improved basis for epidemiological investigations and assessment of occurrences of asbestos-related disease in relation to information concerning exposures to erionite. Thus, the results underscore the need for much more sampling and analysis using electron microscopy of erionite collected from localities (noted in the literature) where morphology and compositional information is not available.

The geologic observations presented in this study allow for more targeted exposure and health assessments that focus efforts and limited resources on the appropriate geologic units and geographic areas (Forsman 2006) rather than random sampling. This approach has been applied in recent years in western North Dakota by the collective efforts of U.S. Federal agencies (EPA, USGS, Agency for Toxic Substances and Disease Registry), State agencies (North Dakota Department of Health, North Dakota Geological Survey), and academic institutions (the University of North Dakota, University of Cincinnati, University of Hawaii) working together. Such efforts can serve as a guide to evaluating other erionite-bearing districts and regions in the United States and elsewhere.

Acknowledgments This paper benefited greatly from the insightful manuscript suggestions and scientific input provided by Dr. Aubrey Miller (Senior Medical Advisor for the National Institute of Environmental Health Sciences), Heather Lowers (USGS, research geologist), and two anonymous reviewers for Environmental Geochemistry and Health.

References

- Adamis, Z., Tátrai, E., Honma, K., Six, E., & Ungváry, G. (2000). In vitro and in vivo tests for determination of the pathogenicity of quartz, diatomaceous earth, mordenite and clinoptilolite. *Annals of Occupational Hygiene*, *44*(1), 67–74.
- Armbruster, T., & Gunter, M.E. (2001). Crystal structures of natural zeolites. In D.L. Bish, & D.W. Ming (Eds.), *Natural zeolites—Occurrence, properties, applications* (pp. 1–67). Washington, DC: The Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, 45.
- Artvinli, M. M., & Bariş, Y. I. (1979). Malignant mesotheliomas in a small village in the Anatolian region of Turkey—an epidemiologic study. *Journal of the National Cancer Institute*, *63*(1), 17–22.
- Aust, A. E., Cook, P. M., & Dodson, R. F. (2011). Morphological and chemical mechanisms of elongated mineral particle toxicities. *Journal of Toxicology & Environmental Health Part B: Critical Reviews*, *14*(1–4), 40–75.
- Ball, E. (2011). NIEHS workshop tackles erionite-linked disease risk. National Institute of Environmental Health Sciences, Environmental Factor, November 2011. <http://www.niehs.nih.gov/news/newsletter/2011/november/science-erionite/index.cfm>. Accessed 5 June 2012.
- Ballirano, P., Andreozzi, G. B., Dogan, M., & Dogan, A. U. (2009). Crystal structure and iron topochemistry of erionite-K from Rome, Oregon, USA. *American Mineralogist*, *94*(8–9), 1262–1270.
- Bargar, K. E., & Beeson, M. H. (1981). Hydrothermal alteration in research drill hole Y-2, Lower Geyser Basin, Yellowstone National Park Wyoming. *American Mineralogist*, *66*(5–6), 473–490.
- Bargar, K.E., & Keith, T.E.C. (1995). Calcium zeolites in rhyolitic drill cores from Yellowstone National Park, Wyoming. In D.W. Ming, & F.A. Mumpton, F.A. (Eds.), *Natural zeolites '93—Occurrence, properties, use* (pp. 69–86). Brockport, New York: International Committee on Natural Zeolites.
- Bargar, K. E., Beeson, M. H., & Keith, T. E. C. (1981). Zeolites in Yellowstone National Park. *Mineralogical Record*, *12*(1), 29–38.
- Bariş, Y. I., & Grandjean, P. P. (2006). Prospective study of mesothelioma mortality in Turkish villages with exposure to fibrous zeolite. *Journal of the National Cancer Institute*, *98*(6), 414–417.
- Bariş, Y. I., Sahin, A. A., Ozesmi, M. M., Kerse, I. I., Ozen, E. E., Kolcan, B. B., et al. (1978). An outbreak of pleural mesothelioma and chronic fibrosing pleurisy in the village of Karain/Urgüp in Anatolia. *Thorax*, *33*(2), 181–192.
- Bariş, I., Simonato, L., Artvinli, M., Pooley, F., Saracci, R., Skidmore, J., et al. (1987). Epidemiological and environmental evidence of the health effects of exposure to erionite fibers—a four-year study in the Cappadocian region of Turkey. *International Journal of Cancer*, *39*(1), 10–17.
- Bish, D. L., & Chipera, S. J. (1991). Detection of trace amounts of erionite using X-ray powder diffraction—Erionite in tuffs of Yucca Mountain, Nevada, and central Turkey. *Clays and Clay Minerals*, *39*(4), 437–445.
- Carbone, M., Emri, S., Dogan, U., Steele, I., Tuncer, M., Pass, H. I., et al. (2007). A mesothelioma epidemic in Cappadocia—scientific developments and unexpected social outcomes. *Nature Reviews Cancer*, *7*, 147–154.
- Carbone, M., Bariş, Y. I., Bertino, P., Brass, B., Comertpay, S., Dogan, A. U., et al. (2011). Erionite exposure in North Dakota and Turkish villages with mesothelioma. *Proceedings of the National Academy of Sciences of the United States of America*, *108*(33), 13618–13623.
- Chipera, S.J., & Bish, D.L. (1989). The occurrence and distribution of erionite at Yucca Mountain, Nevada. *Los Alamos National Laboratory Report LA-11663-MS*, p. 20.

- Coffin, D. L., Cook, P. M., & Creason, J. P. (1992). Relative mesothelioma induction in rats by mineral fibers—comparison with residual pulmonary mineral fiber number and epidemiology. *Inhalation Toxicology*, 4(3), 273–300.
- Deffeyes, K. S. (1959). Erionite from Cenozoic tuffaceous sediments, central Nevada. *American Mineralogist*, 44(5–6), 501–509.
- Dogan, A. U., & Dogan, M. (2008). Re-evaluation and re-classification of erionite series minerals. *Environmental Geochemistry and Health*, 30(4), 355–366.
- Dogan, A. U., Dogan, M., & Emri, S. (2005). Erionite. In P. Wexler (Ed.), *Encyclopedia of toxicology* (2nd ed., pp. 237–241). Oxford: Elsevier.
- Dogan, A. U., Baris, Y. I., Dogan, M. M., Emri, S. S., Steele, I. I., Elmishad, A. G., et al. (2006). Genetic predisposition to fiber carcinogenesis causes a mesothelioma epidemic in Turkey. *Cancer Research*, 66(10), 5063–5068.
- Dogan, A. U., Dogan, M., & Hoskins, J. A. (2008). Erionite series minerals—mineralogical and carcinogenic properties. *Environmental Geochemistry and Health*, 30(4), 367–381.
- Eakle, A. S. (1898). Erionite—a new zeolite. *American Journal of Science, Fourth Series*, 6(31), 66–68.
- Fach, E., Kristovich, R., Long, J. F., Waldman, W. J., Dutta, P. K., & Williams, M. V. (2003). The effect of iron on the biological activities of erionite and mordenite. *Environmental International*, 29(4), 451–458.
- Forsman, N. F. (2006). Erionite in tuffs of North Dakota—the need for erionite hazard maps. *Geological Society of America Abstracts with Programs*, 38(7), 366.
- Gude, A. J., 3rd, & Sheppard, R. A. (1981). Woolly erionite from the Reese River zeolite deposit, Lander County, Nevada, and its relationship to other erionites. *Clays and Clay Minerals*, 29(5), 378–384.
- Gude, A.J., 3rd, & Sheppard, R.A. (1986). Zeolitic diagenesis of tuffs in an upper Miocene lacustrine deposit near Durkee, Baker County, Oregon. In F.A. Mumpton (Ed.), *Studies in diagenesis* (pp. 301–333). *U.S. Geological Survey Bulletin* 1578.
- Gude, A.J., 3rd, & Sheppard, R.A. (1988). A zeolitic tuff in a lacustrine facies of the Gila Conglomerate near Buckhorn, Grant County, New Mexico. *U.S. Geological Survey Bulletin* 1763, p. 22.
- Guthrie, G. D. (1992). Biological effects of inhaled minerals. *American Mineralogist*, 77(3–4), 225–243.
- Hay, R.L., & Sheppard, R.A. (2001). Occurrence of zeolites in sedimentary rocks—an overview. D.L. Bish, & D.W. Ming (Eds.), *Natural zeolites—Occurrence, properties, applications* (pp. 217–234). Washington, DC: The Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, 45.
- Hill, R. J., Edwards, R. E., & Carthew, P. P. (1990). Early changes in the pleural mesothelium following intrapleural inoculation of the mineral fibre erionite and the subsequent development of mesotheliomas. *Journal of Experimental Pathology*, 71(1), 105–118.
- International Agency for Research on Cancer. (2012). Agents classified by the IARC Monographs, Volumes 1–105. <http://monographs.iarc.fr/ENG/Classification/index.php>. Accessed 12 September 2012.
- Kamb, W. B., & Oke, W. C. (1960). Paulingite—a new zeolite, in association with erionite and filiform pyrite. *American Mineralogist*, 45(1–2), 79–91.
- Langella, A., Cappelletti, P., & de Gennaro, M. (2001). Zeolites in closed hydrologic systems. In D.L. Bish, & D.W. Ming (Eds.), *Natural zeolites—Occurrence, properties, applications* (pp. 235–260). Washington, D.C.: The Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, 45.
- Larsen, D., & Crossey, L.J. (2000). Sedimentary petrology and authigenic mineral distributions in the Oligocene Creede Formation, Colorado, United States. In P.M. Bethke & R.L. Hay (Eds.), *Ancient Lake Creede—Its volcano-tectonic setting, history of sedimentation, and relation to mineralization in the Creede Mining District* (pp. 179–208). Geological Society of America Special Paper 346.
- Lowers, H.A., Adams, D.T., Meeker, G.P., & Nutt, C.J. (2010). Chemical and morphological comparison of erionite from Oregon, North Dakota, and Turkey. *U.S. Geological Survey Open-File Report 2010–1286*, 13 p. <http://pubs.usgs.gov/of/2010/1286/>. Accessed 6 June 2012.
- North Dakota Department of Health (2012). Erionite. North Dakota Department of Health. <http://www.ndhealth.gov/EHS/Erionite/>. Accessed 6 June 2012.
- Passaglia, E., & Sheppard, R.A. (2001). The crystal chemistry of zeolites. In D.L. Bish, & D.W. Ming (Eds.), *Natural zeolites—Occurrence, properties, applications* (p. 69–116). Washington, D.C.: The Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, 45.
- Pratt, S. E. (2012). Dangerous dust. *Earth*, 57(2), 36–43.
- Ryan, P. H., Dihle, M., Griffin, S., Partridge, C., Hilbert, T. J., Taylor, R., et al. (2011). Erionite in road gravel associated with interstitial and pleural changes—an occupational hazard in western United States. *Journal of Occupational and Environmental Medicine*, 53(8), 893–899.
- Shedd, K.B., Virta, R.L., & Wylie, A.G. (1982). Size and shape characterization of fibrous zeolites by electron microscopy. *U.S. Bureau of Mines Report of Investigations RI 8674*, p. 20.
- Sheppard, R.A. (1991). Zeolitic diagenesis of tuffs in the Miocene Chalk Hills Formation, western Snake River Plain, Idaho. *U.S. Geological Survey Bulletin* 1963, p. 27.
- Sheppard, R.A. (1994). Zeolitic diagenesis of tuffs in Miocene lacustrine rocks near Harney Lake, Harney County, Oregon. *U.S. Geological Survey Bulletin* 2108, p. 28.
- Sheppard, R.A. (1996). Occurrences of erionite in sedimentary rocks of the western United States. *U.S. Geological Survey Open-File Report 96–018*, p. 24.
- Sheppard, R. A., & Gude, A. J., 3rd. (1969). Chemical composition and physical properties of the related zeolites offretite and erionite. *American Mineralogist*, 54(5–6), 875–886.
- Sheppard, R. A., & Gude, A. J., 3rd. (1993). Geology and mineralogy of the Rome zeolite deposit, Rome, Oregon. In F. A. Mumpton (Ed.), *Zeo-Trip '93—An excursion to selected zeolite and clay deposits in southeastern Oregon and southwestern Idaho, June 26–28, 1993* (pp. 59–73). Brockport: International Committee on Natural Zeolites.
- Sheppard, R.A., & Hay, R.L. (2001). Formation of zeolites in open hydrologic systems. In D.L. Bish, D.L., & D.W. Ming (Eds.), *Natural zeolites—Occurrence, properties, applications* (pp. 261–275). Washington, D.C.: The Mineralogical Society of America, Reviews in Mineralogy and Geochemistry, 45.

- Suzuki, Y., & Kohyama, N. (1984). Malignant mesothelioma induced by asbestos and zeolite in the mouse peritoneal cavity. *Environmental Research*, 35(1), 277–292.
- Tátrai, E., Bácsy, E., Kárpáti, J., & Ungváry, G. (1992). On the examination of the pulmonary toxicity of mordenite in rats. *International Journal of Occupational Medicine and Environmental Health*, 5(3), 237–243.
- Tschernich, R. W. (1992). *Zeolites of the World* (p. 563). Phoenix: Geoscience Press, Inc.
- Van Gosen, B. S. (2005). Reported historic asbestos mines, historic asbestos prospects, and natural asbestos occurrences in the Eastern United States. *U.S. Geological Survey Open-File Report 2005–1189*. <http://pubs.usgs.gov/of/2005/1189/>. Accessed 6 June 2012.
- Van Gosen, B. S. (2006). Reported historic asbestos prospects and natural asbestos occurrences in the Central United States. *U.S. Geological Survey Open-File Report 2006–1211*. <http://pubs.usgs.gov/of/2006/1211/>. Accessed 6 June 2012.
- Van Gosen, B. S. (2007). Reported historic asbestos mines, historic asbestos prospects, and natural asbestos occurrences in the Rocky Mountain States of the United States (Colorado, Idaho, Montana, New Mexico, and Wyoming). *U.S. Geological Survey Open-File Report 2007–1182*. <http://pubs.usgs.gov/of/2007/1182/>. Accessed 6 June 2012.
- Van Gosen, B. S. (2008). Reported historic asbestos mines, historic asbestos prospects, and natural asbestos occurrences in the Southwestern United States (Arizona, Nevada, and Utah). *U.S. Geological Survey Open-File Report 2008–1095*. <http://pubs.usgs.gov/of/2008/1095/>. Accessed 6 June 2012.
- Van Gosen, B. S. (2010). Reported historic asbestos mines, historic asbestos prospects, and other natural occurrences of asbestos in Oregon and Washington. *U.S. Geological Survey Open-File Report 2010–1041*. <http://pubs.usgs.gov/of/2010/1041/>. Accessed 6 June 2012.
- Van Gosen, B. S., & Clinkenbeard, J. P. (2011). Reported historic asbestos mines, historic asbestos prospects, and other natural occurrences of asbestos in California. *U.S. Geological Survey Open-File Report 2011–1188*, p. 22, 1 plate. <http://pubs.usgs.gov/of/2011/1188/>. Accessed 6 June 2012.
- Wagner, J. C., Skidmore, J. W., Hill, R. J., & Griffiths, D. M. (1985). Erionite exposure and mesotheliomas in rats. *British Journal of Cancer*, 51(5), 727–730.
- Weissman, D., & Kiefer, M. (2011). Erionite—An emerging North American hazard. *NIOSH Science Blog, National Institute for Occupational Safety and Health*. <http://blogs.cdc.gov/niosh-science-blog/2011/11/erionite/>. Accessed 18 Sept 2012.
- Wise, W. S., & Tschernich, R. W. (1976). The chemical compositions and origin of the zeolites offretite, erionite, and levyne. *American Mineralogist*, 61(9–10), 853–863.