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Erionite and offretite from the Killdeer Mountains, Dunn County, North Dakota, USA

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ABSTRACT

The carcinogenic potential of erionite has sparked concern about human exposure in areas where it is present in regional bedrock. The Arikaree Formation in western North Dakota contains altered tuffaceous units with authigenic zeolites. We sampled stratigraphic profiles in the Killdeer Mountains, Dunn County, North Dakota to determine the distribution and chemical composition of zeolites. Powder X-ray diffraction, SEM/EDS and electron microprobe analyses were carried out on sample concentrates. Only samples stratigraphically in or below the distinctive Burrowed Marker Unit were found to contain zeolites. Erionite and offretite were the most common zeolites identified, with offretite being more abundant based on frequency of measured Mg/(Ca+Na) ratios. Intermediate chemical compositions could be natural or due to intimate intergrowths of the two minerals. A better understanding is needed of the potential toxicity across the range of erionite and offretite compositions.

Keywords: erionite, offretite, zeolite, Killdeer Mountains, North Dakota, Arikaree

INTRODUCTION

During the late 1970's, an epidemic of mesothelioma was discovered in three villages in the Cappadocian region of central Turkey (Baris et al., 1978; Artvinli and Baris, 1979). Subsequent studies investigated the link between the high incidence of deaths within the group caused by malignant pleural mesothelioma (MPM) and the occurrence of erionite in the region's bedrock (Baris et al., 1987). Emigrants from the region were found to have increased risk of MPM and 49% or more of the deaths in the Cappadocian region of Turkey due to MPM had a potential link to erionite exposure (Metintas et al., 1999). It was reported that 78% of the deaths that had occurred in the study group were due to malignant mesothelioma and it is estimated that 50% of the total deaths in the area can be attributed to mesothelioma (Metintas et al., 1999; Emri et al., 2002).

Experimental studies show erionite has up to 300-800 times more carcinogenic potency and may be 20-40 times more active than some asbestos forms (U.S. EPA, 2010). It has been classified as a Group I carcinogen by the International Agency for Research on Cancer (IARC, 1987). Physical and chemical differences between the minerals could explain these differences (Kleymenova et al., 1999; Emri et al., 2002). Supporting studies on rats have shown that inhaled erionite fibers resulted in increased incidence of mesothelioma in those animals (Wagner et al., 1985). A North American case of mesothelioma attributed to erionite exposure was reported by Kliment et al. (2009), however the mineral identification did not include a crystallographic tool such as XRD or TEM. Increasing interest in the subject prompted many more studies on the health effects of erionite, as well as new investigations into its carcinogenic potential, mechanisms of carcinogenesis and potential genetic predispositions (Carbone and Yang, 2012), its identification and classification (Dogan and Dogan, 2008), erionite mineral structure, and the similarities between the mineral erionite and other closely related zeolites. A summary is provided by Carbone et al. (2007).

The concern with the carcinogenic potential of erionite has sparked an interest within North Dakota and other areas containing erionite in regional bedrock or sediments. These areas include other high butte formations scattered across western North Dakota as well as the badland formations of North Dakota, South Dakota, and Montana (Goodman and Pierson, 2010). There is concern with exposure and transmission of airborne dusts and particulates possibly containing erionite fibers from gravel pits, roads, parking lots, playgrounds, feed lots, building and construction, mining operations, oil extraction, and farming/ranching operations (Carbone et al., 2011; Maher, 2010). The study reported here was undertaken to characterize the distribution and chemical composition of erionite and related zeolites in rocks exposed in the Killdeer Mountains of Dunn County, North Dakota.

GEOLOGIC SETTING AND PREVIOUS WORK

Bluemle (2000), Murphy (2001), Murphy et al. (1993) and Hoganson et al. (1998) provide descriptions of the general geology, the geologic time setting, and the past geologic processes that resulted in the formations and stratigraphy found in the study area.

The majority of the bedrock in the area surrounding the Killdeer Mountains consists of the sandstones, siltstones, claystones, and lignites of the Paleocene Fort Union Group. During Eocene time, rivers and streams cut into the Fort Union sediments, ultimately depositing coarse gravel and sand beds which would become a part of the Chalky Buttes Member of the Chadron Formation of the White River Group. Presently, river and stream erosion along with mass wasting is still the primary form of erosion affecting the southwestern North Dakota landscape (Bluemle, 2000). These processes contribute to redistribution of any zeolite bearing sediments that are present.

The Killdeer Mountains consist of two predominant mesas located in northern Dunn County of western North Dakota (Fig. 1). The two mesas rise about 200 m above the surrounding landscape and cover an area of approximately 2000 hectares. They are composed of, from top to bottom, rock units from the Arikaree Formation, Chadron Formation (Chalky Buttes Member) and the Golden Valley Formation (Bear Den Member and Camel Buttes Member). No Brule Formation appears to be present in this location (Denson and Gill, 1965; Murphy et al., 1993).

The mesas are located in an area once covered by a large lake or a series of many smaller lakes during Miocene time. The Arikaree Formation, which constitutes the caprock of the Killdeer Mountain complex, is the most well-recognized erionite bearing unit. It consists of approximately 100 m of tuffaceous siltstones, sandstones, and carbonates, with the sandstones and siltstones being calcareous (Denson and Gill, 1965). Most units contain some volcanic glass (Delimata, 1975; Forsman, 1986), which characterizes them as slightly to highly tuffaceous. Volcanic ash in these units is believed to have originated from volcanic eruptions westward of the Killdeer Mountains (Delimata, 1975). The ash would have been deposited across western North Dakota by eolian processes and then transported to the lake systems by fluvial processes, eventually accumulating to approximately 30 m thickness in locations. The ash-rich, tuffaceous sediment eventually lithified into tuffaceous limestone beds. Since the Pliocene, the erosional cycle in the area removed large amounts of surrounding sediment. The geologic setting of the area has been described as an inverted lake basin (Delimata, 1975). Diagenetic processes resulted in glass shards being altered to a clay and zeolite assemblage (Delimata, 1975; Forsman, 1986).

A predominant cliff-forming unit of the Killdeer Mountain caprock contains interbedded tuffaceous sandstone and siltstone layers with carbonate lenses (Fig. 2). This unit, dated using fission track analysis to 25.1 +/- 2.2 Ma, was termed the “burrowed marker unit” (BMU) by Forsman (1986) for the presence of an abundance of what has been classified as fossilized burrows of unknown origins (Murphy et al., 1993).

Delimata (1975) carried out XRD analysis on samples from the Killdeer Mountains and reported the occurrence of clinoptilolite, offretite (which he considered identical to erionite following Hey and Fejer (1962)), and chabazite. He described the habits as radiating acicular and columnar void fillings, along with fibrous habits found in matrix pores. Forsman (1986) reported on zeolites within the pores and vugs of tuffaceous ash units. Based on standard powder X-ray diffraction (XRD) and electron microprobe (EMP) analysis on single mineral crystals, he concluded that erionite composed the majority of the zeolite content in the samples collected. Due to the possible health risks associated with erionite, hazard mapping (Forsman, 2006) was undertaken by the North Dakota Department of Health (NDDoH), in cooperation with the North Dakota Geological Survey (NDGS) and the Environmental Protection Agency (EPA). These investigations led to gravel quarry restrictions, gravel use restrictions, dust control measures, and guidance plans to control and reduce the overall exposure by businesses and private landowners working in close proximity to the bedrock formations and/or gravel quarries which potentially contain erionite (NDDoH, 2005).

Lowers and Meeker (2007) conducted a study by the USGS on 20 soil and roadbed samples collected from western North Dakota for zeolite identification. The SEM/EDS analysis determined the zeolite composition as intermediate between erionite and offretite as determined by Passaglia et al. (1998), and as similar to zeolites associated with high incidences of malignant diseases in Turkey (Dogan et al., 2006). Their EMP data plot within the offretite field on a Mg – Ca+Na – K diagram, and agree with the EMP data collected by Forsman (1986). XRD data supported the presence of erionite, but because both minerals have similar diffraction patterns, the presence of offretite could not be ruled out (Lowers and Meeker, 2007). Eylands et al. (2009) studied sandstones and siltstones from buttes in Dunn, Stark, and Slope Counties of North Dakota and identified erionite using XRD and SEM. Lowers et al. (2010) and Carbone et al. (2011) found erionite from the Killdeer Mountains with that from villages in Turkey to have similar physical and chemical characteristics. However, the EMP data from Lowers et al. (2010) plot in the offretite field. Steele (2011) carried out single crystal studies on zeolite from North Dakota and Turkey and confirmed the presence of erionite in both areas.

The U.S. EPA carried out chest X-rays and sensitive high resolution computed tomography (HRCT) scans to detect pleural and interstitial changes associated with fiber exposure in current or past residents of western North Dakota with exposure to road gravels and erionite containing rock units (U.S. EPA, October, 2010; Ryan et al., 2011). Chest X-ray results did not indicate a significant increase in interstitial or localized pleural changes. The HRCT scans did indicate an increase in interstitial changes. Results of that study suggested that exposure to erionite containing rock units and road gravels could increase the risk of pleural and interstitial changes in humans that are commonly associated with asbestos exposure.

SAMPLING AND ANALYSIS

Field work and sampling for this study was carried out during 2008 at North and South Killdeer Mountains (Fig. 1). At South Killdeer Mountain (SKDM), samples were taken along the southeast edge of the mesa in the region of Medicine Hole Plateau (approximately 47°26"38' N;

102°53"40' W). The measured geologic section of Murphy et al. (1993) is used here as a basis for locating samples (Fig. 1). At North Killdeer Mountain (NKDM), samples were taken on both sides of the entry to a former quarry at the top of the mesa (47°29"53' N, 102°53"36' W). Sampling was also conducted at West and East Rainy Buttes and at White Butte (Chalky Butte complex) in southwest North Dakota; these results and analyses of Killdeer Mountain samples provided by Forsman from his 1986 collection are presented in Triplett (2012). Sample locations and descriptions are provided in the supplemental materials file.

Small portions of samples were disaggregated into a coarse powder to liberate any zeolite minerals. Some samples were well enough cemented that an agate mortar and pestle was used, but the majority were friable enough to disaggregate easily without grinding. This disaggregated material was considered as "unprocessed" and used for SEM/EDS analysis, before further processing for powder XRD and EMP analysis.

Initial sample preparation for SEM/EDS was removal of small portions of the rock by pressing carbon tape onto the sample surface. Visual inspection and qualitative SEM/EDS analyses were carried out on unprocessed samples to identify any zeolite minerals.

Samples that showed apparent zeolite minerals in initial screening were subjected to a simple floatation process. Disaggregated material was placed into distilled water in a 1000 ml graduated cylinder and allowed to settle. A ball pipette was used to transfer all of the suspension, the water and fine suspended particles, into a vacuum filter system. Filtered material was used for powder XRD, SEM/EDS, and EMP analysis.

Filtered material was pulverized for XRD using an agate mortar and pestle. Powder XRD mounts were prepared using ethanol on glass slides and were analyzed at the NDSU Department of Chemistry and Biochemistry on a Phillips X'Pert MPD X-Ray Powder Diffractometer. Search match was carried out using Jade + and X'Pert Highscore software.

Samples were prepared for SEM/EDS and EMP analysis by placing concentrated sample material onto carbon tape and then carbon coated. SEM/EDS analysis was carried out at the North Dakota State University Electron Microscopy Center on a JEOL JSM -7600F with a field-emission source. EMP analysis was conducted at the University of Minnesota Electron Microprobe Lab, Department of Earth Sciences using a JXA-8900 SuperProbe. Microprobe analysis was carried out using the standards: Na, amelia albite; Ba, barite; K, Asbestos microcline; Mg, Si, Al, Ca and Fe, Kakanui hornblende. H_2O was calculated by difference in ZAF correction. Analytical conditions were 15kV with a beam current of 10 nA; the beam diameter was nominally 5 μm, although it was modified for particular grains from 2 to 10 μm. Counting times were 10 sec on-peak and 10 sec off-peak. Experimental error was assessed by analyzing 8 spots on Kakanui hornblende. The measured average and standard deviations are: 40.92 (0.31) wt.% SiO_2, 15.14 (0.21) wt.% Al_2O_3, 11.08 (0.20) wt.% FeO, 12.99 (0.13) wt.% MgO, 10.33 (0.18) wt.% CaO, 2.84 (0.08) wt.% Na_2O, 2.22 (0.05) wt.% K_2O. Depending on the zeolite concentration and the accessibility of the mineral grains within the surrounding matrix, 1 to 6 grains were analyzed by EMP from each of the nine samples. We analyzed 27 grains on 77 different points.

RESULTS AND DISCUSSION

Powder XRD analysis identified some type of zeolite in ten of the fourteen SKDM samples and seven of the nine NKDM samples (Table 1, Fig. 1). The processed material often contained calcite, quartz or other minerals, and these are noted. Erionite and offretite were the most common zeolites, but chabazite, heulandite, and clinoptilolite were also identified. XRD identification of zeolites in one of the samples, 080603-05 is questionable.

SEM/EDS and EMP analyses were carried out on samples with detectable zeolite based on the XRD analyses. Additional SEM/EDS analyses were carried out on samples provided by Forsman from his 1986 study. Some grains measured using EMP were the identical ones measured by SEM/EDS. EMP analyses are presented in Table 2 and Fig. 3 is a plot of the compositions as measured by both EMP and SEM/EDS.

Figs. 4 and 5 are micrographs of representative grains. As discussed in Gunter et al. (2007) relating to amphiboles, terms such as "fibers" and "fibrous" are applied differently by different groups. Gunter et al. (2007) also discuss use of the terms "particle," "cleavage-fragment" and "fragment." To mineralogists, the morphological term "fiber" is a textural description for flexible thin partings. The grain shown in Fig. 5 exhibits such fibrous morphology. The grains in Fig. 4 could be single crystals, or based on aspect-ratio criteria, could be considered as fibers by the regulatory community. In zeolite nomenclature, however, the term "fibrous zeolite" is used as part of a crystal-chemical classification scheme referring to zeolites containing T_5O_{10} chains of tetrahedra (Gottardi and Galli, 1985; Armbruster and Gunter, 2001), with no implication on a particular mineral fragment's flexibility.

Identification of and distinction between erionite and offretite can be difficult because of their structural and chemical similarities (Passaglia et al., 1998), and because of the possibility of intergrowth of the two species within each crystal (Tschernich, 1992; Coombs et al., 1997). The erionite general formula is $(K_2\,Na_2\,Ca_3)\,[Al_{10}\,Si_{26}\,O_{72}]\cdot 30H_2O$ (Passaglia et al., 1998) with a hexagonal space group symmetry $P6_3/mmc$ and unit cell parameters $a \approx 13.15$ and $c \approx 15.05$ Å (Passaglia et al., 1998). Three erionite species have been identified, erionite-Ca, -Na, and -K

(Coombs et al., 1997). The offretite general formula is (Ca K Mg) $[Al_5\,Si_{13}\,O_{36}]\cdot 16H_2O$ (Passaglia et al., 1998) with a hexagonal space group symmetry P6m2 and unit cell parameters a ≈ 13.30 and c ≈ 7.60 Å (Gualtieri et al., 1998). In erionite, Si + Al $[+Fe^{3+}]$ should be equal to 36 atoms based on 72 oxygen atoms, while in offretite, Si + Al $[+Fe^{3+}]$ should be equal to 18 atoms based on 36 oxygen atoms. Here, all data are calculated on the basis of 72 oxygen atoms.

The reliability of a chemical analysis used to determine the zeolite species (or any framework silicate) can be evaluated by using a balance error formula (Passaglia, 1970):

$$E\% = [(Al+Fe^{3+}) - Al_{th}] / Al_{th} \times 100$$

where $Al_{th} = Na + K + 2(Ca+Mg+Sr+Ba)$.

An extended balance formula is presented in Coombs et al. (1997). Chemical analyses for zeolites are considered to be reliable if the balance error (E%) is equal to or less than +/-10% (Passaglia, 1998). If the E% falls within the set conditions, then the mineral may be erionite or may be another closely related zeolite with similar chemical composition. While some EMP analyses in Table 2 fall outside the +/-10% range, all are presented here for completeness.

A chemical attribute relevant to distinguishing erionite from offretite is the ratio of Mg to (Ca+Na). Passaglia et al. (1998) defined the ratio Mg/(Ca+Na) = 0.30 as the boundary between the two minerals. As seen on the fields depicted on Fig. 3 and discussed in Gualtieri et al. (1998), erionite is generally magnesium poor due to crystal structural limitations, whereas offretite is more magnesium rich with a Ca/Mg ratio close to 1.0. However, Rinaldi (1976) as cited in Tschernich (1992) reported a magnesium rich erionite from Sasbach, Germany. It should be noted, that the structural and chemical conclusions of Gualtieri et al. (1998) and Passaglia et al. (1998) were based on zeolites that were not collected from tuffs such as in Turkey or North Dakota and so may not be directly applicable to zeolites formed in other geologic environments

(Steele, pers. comm., 2013). Fig. 5 is a histogram of Mg/(Ca + Na) ratio for zeolite grains analyzed in this study. The dataset includes SEM/EDS and EMP analyses of samples collected for this study, and of samples provided to us by Forsman from his 1986 study. The relative frequency of Mg/(Ca + Na) > 0.3 is approximately 80%. Following Passaglia et al. (1998), these high ratios indicate compositions consistent with offretite occur more frequently than those consistent with erionite. The apparent lack of a compositional gap could be the result of analytical error, grain scale intergrowth of erionite with offretite, or real compositional variation.

The study by Lowers and Meeker (2007) of zeolite grains from 20 soil and roadbed samples from the Killdeer Mountain region showed comparable results. SEM/EDS analyses overlap the erionite and offretite fields of Passaglia et al. (1998), and EMP analyses indicate the presence of offretite. XRD analysis showed the presence of erionite but offretite could not be ruled out. For the South Killdeer Mountain profile studied here, all samples except those stratigraphically above the BMU contained erionite or offretite, while six of the nine samples collected from NKDM contained erionite or offretite. At SKDM, erionite or offretite containing rock units were identified down to the base unit of the Arikaree Formation, which at that location is described as a 7.6 m (25 ft) thick moderately cemented siltstone with sand lenses and concretions approximately 94 m (308 ft) from the top of the mesa (Murphy et al., 1993). Zeolite was not found in samples above the BMU: from the entrance to Medicine Hole, from the massive sandstone unit in the middle of the Arikaree Formation (unit 10 of Murphy et al., 1993), from the calcareous portion of the burrowed marker unit, nor from the sandstone near the top of the mesa (unit 13 of Murphy et al., 1993). Because this was the extent of the sampling for this study, it is possible that the zeolite bearing rock units extend below the Arikaree Formation into the Chadron and Golden Valley Formations.

At North Killdeer Mountain, erionite or offretite were identified in six of nine samples taken (Fig. 1; Tables 1, 3). Zeolites were present in rock units from just below the uppermost weathered horizon of NKDM down to the massive sandstone unit in the middle of the Arikaree Formation, and additionally from the base of the massive unit down to the stratigraphically lowest exposed outcrop of the NKDM east quarry wall. That unit is interpreted to be the bottom of the burrowed marker unit, the stratigraphically lowest sampling for this project at North Killdeer Mountain. One of the samples without zeolite (080604-04) was from weathered surficial material, and another (080604-05) was a lithic fragment. Because this was the extent of sampling at NKDM, it is possible that stratigraphically lower rock units may contain zeolite minerals.

In this study, we have documented the extent and composition of erionite and offretite in sampled profiles of exposed Killdeer Mountain rock units. It is unclear whether the mineralogic distinction between erionite and offretite has any health implications. However, as has been seen for the case of asbestos minerals (Gunter et al., 2007; Berndt and Brice, 2008; Thompson et al., 2011), codification of nomenclature such as specific mineral names or habits into laws or regulations may have consequences in the application of health and legal policy. An area of research to be explored in environmental health may be to better understand any differences in potential toxicity between erionite and offretite including the varieties and intergrowths of these minerals.

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REFERENCES CITED

Armbruster, T. and Gunter, M.E. (2001) Crystal structures of natural zeolites. In D.L. Bish and D.W. Ming, Eds., Natural zeolites; occurrence, properties, applications. Reviews in Mineralogy and Geochemistry, 45, 1-67.

Artvinli, M., and Baris, Y.I. (1979) Malignant mesothelioma in a small village in the Anatolian region of Turkey: An epidemiologic study. Journal of the National Cancer Institute, 63, 17-22.

Baris, Y.I., Sahin, A.A., Ozesmi, M., Kerse, I., Ozen, E., Kolacan, B., Altinörs, M., and Göktepeli, A. (1978) An outbreak of pleural mesothelioma and chronic fibrosing pleurisy in the village of Karain/Ürgüp in Anatolia. Thorax, 33, 181-192.

Baris, I., Artvinli, M., Saracci, R., Simonato, L., Pooley, F., Skidmore, J., and Wagner, C. (1987) Epidemiological and environmental evidence of the health effects of exposure to erionite fibres: A four-year study in the Cappadocian region of Turkey. International Journal of Cancer, 39(1), 10-17.

Berndt, M.E., and Brice, W.C. (2008) The origins of public concern with taconite and human health: Reserve Mining and the asbestos case. Regulatory Toxicology and Pharmacology, 52, S31–S39.

Bluemle, J.P. (2000) The Face of North Dakota (3rd ed). North Dakota Geological Survey Educational Series 26, 206 p.

Carbone, M., and Yang, H. (2012) Molecular pathways: Targeting mechanisms of asbestos and erionite carcinogenesis in mesothelioma. Clinical Cancer Research, 18, 598-604.

Carbone, M., Emri, S., Dogan, A.E., Steele, I., Tuncer, M., Pass, H.I., and Baris, Y.I. (2007) A mesothelioma epidemic in Cappadocia: scientific developments and unexpected social outcomes. Nature Reviews Cancer, 7, 147-154.

Carbone, M., Baris, Y.I., Bertino, P., Brass, B., Comertpay, S., Dogan, A.U., Gaudino, G., Jube, S., Kanodia, S., Partridge, C.R., Pass, H.I., Rivera, Z.S., Steele, I., Tuncer, M., Way, S., Yang, H., and Miller, A. (2011) Erionite exposure in North Dakota and Turkish villages with mesothelioma. Proceedings of the National Academy of Sciences of the USA, 108(33), 13618-13623.

Coombs, D.S., Alberti, A., Armbruster, T., Artioli, G., Colella, C., Galli, E., Grice, J.D., Liebau, F., Mandarino, J.A., Minato, H., Nickel, E.H., Passaglia, E., Peacor, D.R., Quartieri, S., Rinaldi, R., Ross, M., Sheppard, R.A., Tillmanns, E., and Vezzalini, G. (1997), Recommended nomenclature for zeolite minerals: Report of the Subcommittee on Zeolites of the International Mineralogical Association, Commission on New Minerals and Mineral Names. Canadian Mineralogist, 35, 1571-1606.

Delimata, J.J. (1975) Petrology and geochemistry of the Killdeer carbonates, Ph.D. thesis, University of North Dakota, Grand Forks. 256 p.

Denson, N.M., and Gill, J.R. (1965) Uranium-Bearing Lignite and Carbonaceous Shale in the Southwestern Part of the Williston Basin-A Regional Study: United States Geological Survey Professional Paper 463, 75 p.

Dogan, A.U. and Dogan, M. (2008) Re-evaluation and re-classification of erionite series minerals. Environmental Geochemistry and Health, 30(4), 355-366. doi: 10.1007/s10653-008-9163-z

Dogan, A.U., Baris, Y. I., Dogan, M., Emri, S., Steele, I., Elmishad, A.G. and Carbone, M. (2006) Genetic predisposition to fiber carcinogenesis causes a mesothelioma epidemic in Turkey, Cancer Research, 66, 5063-5068. doi:10.115 8/0008-5472.CAN-05-4642

Emri, S., Demir, A., Dogan, M., Akay, H., Bozkurt, B., Carbone, M., Baris, I. (2002) Lung diseases due to environmental exposures to erionite and asbestos in Turkey. Toxicology Letters, 127, 251-257.

Eylands, K.E., Azenkeng, A., Mibeck, B.A., and Raymond, L.J. (2009) Subtask 1.1 – Characterization of Erionite. Report 2009-EERC-12-06. www.osti.gov/bridge/purl.cover.jsp?purl=/971247-9B7QwY/Subtask1.1-CharacterizationofErionite.pdf

Forsman N.F. (1986) Documentation and diagenesis of tuffs in the Killdeer Mountains, Dunn County, North Dakota. Report of Investigation No. 87, North Dakota Geological Survey, 13 p.

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.

Gottardi G. and Galli, E. (1985) Natural Zeolites. Springer-Verlag, Berlin, 409 p.

Goodman, B.S. and Pierson, M.P. (2010) Erionite, a naturally occurring fibrous mineral hazard in the tri-state area of North Dakota, South Dakota, and Montana. Geological Society of America Abstracts with Programs, 42(3), 5.

Gualtieri, A., Artioli, G., Passaglia, E., Bigi, S., Viani, A., and Hanson, J.C. (1998) Crystal structure-crystal chemistry relationships in the zeolites erionite and offretite, American Mineralogist, 83, 590-606.

Gunter, M.E., Belluso, E., and Mottana, A. (2007) Amphiboles: Environmental and Health Concerns. In F.C. Hawthorne, R.Oberti, G. Della Verntura and A. Mottana, Eds., Amphiboles: Crystal Chemistry, Occurrence, and Health Issues. Reviews in Mineralogy and Geochemistry, 67, 453-516.

Hey, M.H. and Fejer, E.E. (1962) The identity of erionite and offretite. Mineralogical Magazine, 33, 66-67.

Hoganson, J.W., Murphy, E.C., and Forsman, N.F. (1998) Lithostratigraphy, paleontology, and biochronology of the Chadron, Brule, and Arikaree Formations in North Dakota. In D.O. Terry, Jr., H.E. LaGarry, and R.M. Hunt, Eds. Geological Society of America Special Paper 325, 185-196.

IARC (1987) Overall evaluations of carcinogenicity: an updating of IARC Monographs volume 42. IARC Monographs on the evaluation of carcinogenic risks to humans, Suppl. 7: p. 203.

Kliment, C.R., Clemens, K. and Oury, T.D. (2009) North American erionite-associated mesothelioma with pleural plaques and pulmonary fibrosis: A case report. International Journal of Clinical and Experimental Pathology, 2, 407-410.

Lowers, H.A., and Meeker, G.P. (2007) Denver microbeam laboratory administrative report 14012007: U.S. Geological Survey Administrative Report, 11 p.

Lowers, H.A., Adams, D.T., Meeker, G.P., and 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.

Maher, B. (2010) Epidemiology: Fear in the Dust. Nature, 468, 884–885.

Metintas, M., Hillerdal, G., and Metintas, S. (1999) Malignant mesothelioma due to environmental exposure to erionite: follow-up of a Turkish emigrant cohort. European Respiratory Journal, 13(3), 523-526.

Murphy, E.C. (2001) Geology of Dunn County. North Dakota Geological Survey Bulletin 68 Part 1, Bismarck, ND, 36 p.

Murphy, E.C., Hoganson, J.W., and Forsman, N.F. (1993) The Chadron, Brule, and Arikaree Formations in North Dakota. North Dakota Geological Survey Report of Investigation No. 96, Bismarck, ND, 144 p.

North Dakota Department of Health (2005) www.health.state.nd.us/EHS/Erionite/. Accessed Aug. 17, 2009.

Passaglia, E. (1970) The crystal chemistry of chabazites. American Mineralogist, 55, 1278-1301.

Passaglia, E., Artioli, G., and Gualtieri, A. (1998) Crystal chemistry of the zeolites erionite and offretite. American Mineralogist, 83, 577–589.

Ryan, P.H., Dihle, M., Griffin, S., Partridge, C., Hillbert, T.J., Taylor, R., Adjei, S. and Lockey, J.E. (2011) Erionite in road gravel associated with interstitial and pleural changes - an occupational hazard in western United States. Journal of Occupational Environmental Medicine, 53, 892-898.

Steele, I.M. (2011) Comparison of erionite from N. Dakota and central Turkey. Geological Society of America Abstracts with Programs, 43(5), 138.

Thompson, B.D., Gunter, M.E., and Wilson, M.A. (2011) Amphibole asbestos soil contamination in the USA: A matter of definition. American Mineralogist, 96, 690-693.

Tschernich, R.W. (1992) Zeolites of the World, Geoscience Press, Pheonix, AZ, 563 p.

Triplett, J.W. (2012) Identification and characterization of zeolites in western North Dakota, M.S. Thesis, North Dakota State University, Fargo, ND, 112 p.

U.S. EPA (2010) Radiographic changes associated with exposure to erionite in road gravel in North Dakota. Report EP-R8-06-02/TO#0804, 2010. 90 p.

Wagner, J.C., Skidmore, J.W., Hill, R.J., and Griffiths, D.M. (1985) Erionite exposure and mesotheliomas in rats. British Journal of Cancer, 51, 727-730.

FIGURE CAPTIONS

Figure 1. Topography, stratigraphic profiles, and sample identifications in the study area. SKDM: South Killdeer Mountain. NKDM: North Killdeer Mountain. BMU: "burrowed marker unit". Inset shows general location of study area. SKDM stratigraphy from Murphy et al. (1993). Base map from google.com.

Figure 2. Photo of "burrowed marker unit" (BMU) of Forsman, 1986 on South Killdeer Mountain. Sample 080603-08 is from the more weathered, friable material between harder calcareous layers; sample 080603-09 is from the more resistant calcareous material.

Figure 3. Ternary compositional plot of zeolite minerals. This study squares: SEM/EDS (filled square is mineral pictured in Fig. 5); circles: EMPA. Triangles: Forsman (1986). Eri (erionite) and Off (offretite) fields after Gualtieri et al. (1998).

Figure 4. Electron micrographs of zeolite minerals. a: 080603-06 grain 1, b: 080603-06 grain 2, c: 080603-07, d: 080603-08. Scale bar 10 micrometer.

Figure 5. Electron micrograph of a zeolite mineral separated from a North Killdeer Mountain sample provided by N. Forsman. Scale bar 10 micrometer.

Figure 6. Histogram of Mg/(Ca + Na) ratios for zeolite fibers analyzed in this study. Note: one measured value of 3.40 not included.

TABLE 1. Powder XRD identification of minerals in processed samples, Killdeer Mountains, North Dakota

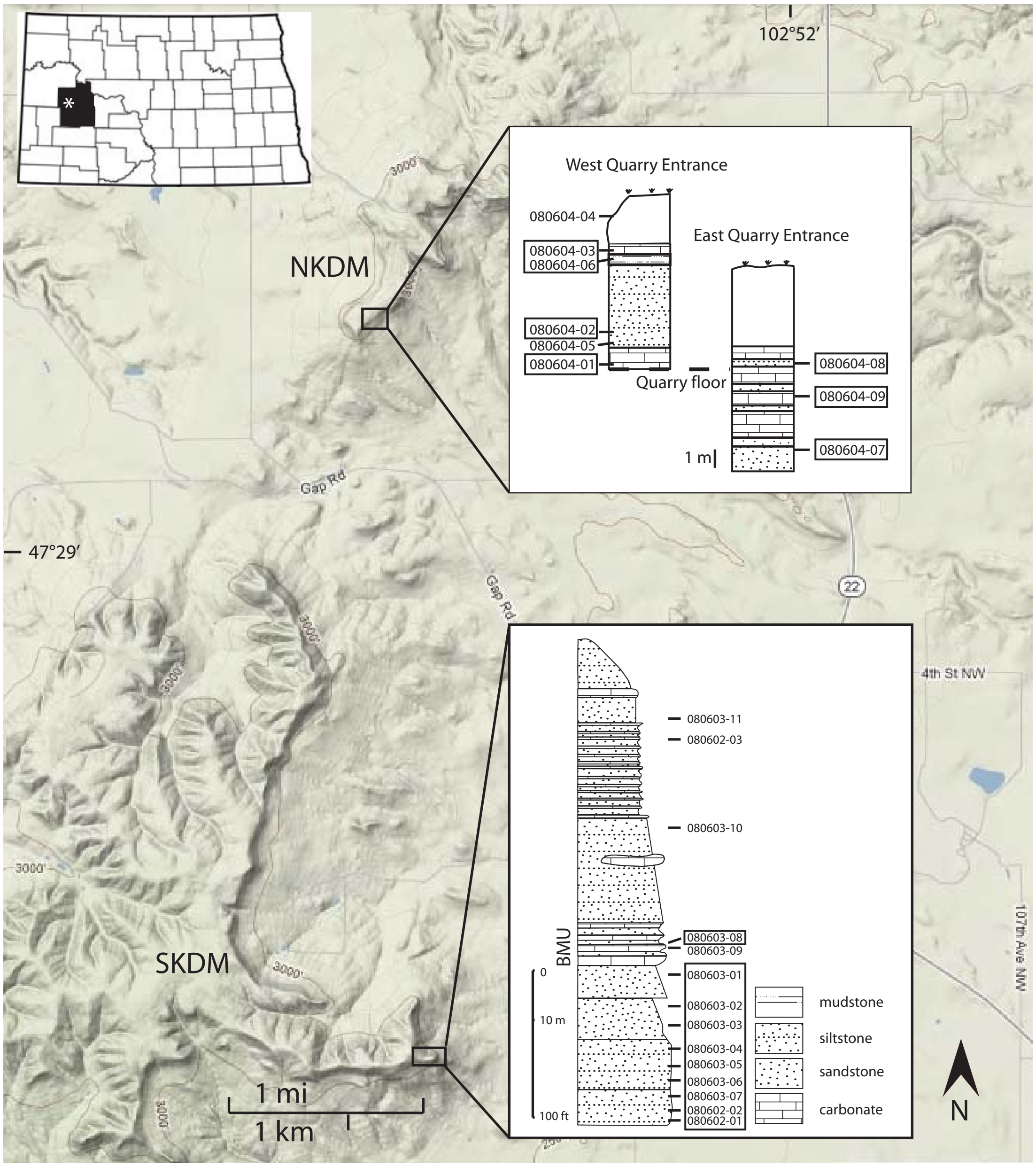
sample	minerals
080602-01*	Eri, Qz
080602-02*	Off, Eri, Cal
080602-03	Cal, Ank
080603-01	Eri, Cal
080603-02	Eri, Off
080603-03	Off, Eri, Cal
080603-04	Eri, Cal
080603-05	Eri?, Off?
080603-06	Eri, Cal, Qz
080603-07*	Off, Cal
080603-08	Eri, Qz
080603-09	Cal, Qz
080603-10	Dol, Qz
080603-11	Cal, Qz
080604-01	Off, Cal
080604-02	Cal, Qz
080604-03	Eri, Chab, Cal, Qz
080604-04	Eri, Hul, Cal, Qz
080604-05	Cal, Qz
080604-06	Cpt, Eri, Off, Cal, Qz
080604-07	Off
080604-08	Eri, Off, Cal
080604-09	Off, Cal, Qz

Notes: Eri – erionite, Off – offretite, Chab – chabazite, Hul – heulandite, Cpt – clinoptilolite, Cal – calcite, Dol – dolomite, Ank – ankerite, Qz – quartz
*sample location possibly slumped
? - tentative identification

Table 2. Chemical compositions of erionite and offretite from the Killdeer Mountains

Sample No./Grai	080603-08/1	080603-08/2	080603-08/3	080603-07/1	080603-07/2	080603-07/3	080603-07/4	080604-09/3	080604-08/1	080604-07/2	080603-01/1	080603-01/2	080602-03/1	080602-03/2	080604-01/1	080604-01/3
SiO2	44.86	53.54	43.49	61.82	48.06	54.70	48.72	64.87	67.52	62.45	58.89	48.20	61.46	59.53	45.10	64.51
Al2O3	12.03	13.90	12.03	15.74	12.03	14.31	12.97	16.36	17.27	15.14	12.90	10.98	14.93	14.33	14.44	16.24
Fe_2O_3	1.99	0.28	0.05	0.66	0.17	6.53	0.31	0.12	0.32	0.57	0.08	0.21	0.24	0.29	0.17	0.03
MgO	1.78	1.04	0.74	1.62	1.35	4.73	1.08	0.37	0.77	0.69	1.29	2.35	2.52	2.61	1.95	1.99
CaO	2.77	3.85	2.85	3.59	2.63	1.68	3.66	6.00	5.95	4.57	3.14	2.73	3.08	3.35	2.92	3.42
Na2O	0.16	0.22	0.23	0.16	0.09	0.14	0.17	0.03	0.03	0.05	0.11	0.29	0.02	0.05	0.08	0.05
K2O	2.41	3.22	3.65	3.02	2.13	2.51	2.71	2.35	2.33	3.20	2.62	1.28	1.57	1.30	2.35	2.79
H_2O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Si	26.79	27.54	26.60	27.73	27.94	25.80	27.35	27.92	27.78	28.05	28.70	28.08	28.06	27.99	26.29	27.94
Al	8.47	8.43	9.37	8.32	8.23	7.96	8.61	8.30	8.38	8.01	7.39	7.54	8.04	7.95	9.92	8.29
Fe^{3+}	0.90	0.11	0.03	0.22	0.07	2.32	0.13	0.04	0.10	0.19	0.03	0.09	0.08	0.10	0.07	0.01
Mg	1.58	0.80	0.73	1.08	1.17	3.33	0.90	0.24	0.47	0.46	0.92	2.04	1.72	1.83	1.70	1.28
Ca	1.78	2.13	2.14	1.72	1.64	0.85	2.21	2.77	2.62	2.20	1.65	1.70	1.51	1.69	1.82	1.59
Na	0.18	0.22	0.35	0.14	0.11	0.13	0.18	0.02	0.03	0.04	0.11	0.32	0.02	0.05	0.09	0.04
K	1.84	2.12	3.21	1.73	1.58	1.51	1.94	1.29	1.22	1.84	1.69	0.95	0.92	0.78	1.75	1.54
Number of point	1	3	2	2	2	1	3	1	1	1	3	1	1	2	1	1
Al_{th}	8.73	8.19	9.30	7.48	7.29	9.99	8.35	7.33	7.44	7.20	6.94	8.76	7.39	7.86	8.88	7.32
E%	7.19	4.25	1.06	14.03	13.89	2.89	4.64	13.82	13.95	13.95	6.91	-12.91	9.89	2.35	12.46	13.39
Si+Al	35.26	35.97	35.97	36.04	36.17	33.76	35.97	36.22	36.15	36.06	36.08	35.62	36.10	35.94	36.20	36.23
Mg/(Ca+Na)	0.81	0.34	0.31	0.58	0.68	3.40	0.38	0.09	0.18	0.21	0.55	1.01	1.12	1.06	0.89	0.79

Note: Atomic ratios based on 72 O. The balance error E% = [(Al+Fe^{3+}) – Alth] / Alth x 100 where Alth = Na + K + 2(Ca+Mg+Sr+Ba) (Passaglia, 1970)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47°29′
West Quarry Entrance
080604-04
080604-03
080604-06
080604-02
080604-05
080604-01
Quarry floor
East Quarry Entrance
080604-08
080604-09
080604-07
1 m
NKDM
3000′
Gap Rd
22
4th St NW
107th Ave NW
080603-11
080602-03
080603-10
BMU
080603-08
080603-09
0
10 m
100 ft
080603-01
080603-02
080603-03
080603-04
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mudstone
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carbonate
SKDM
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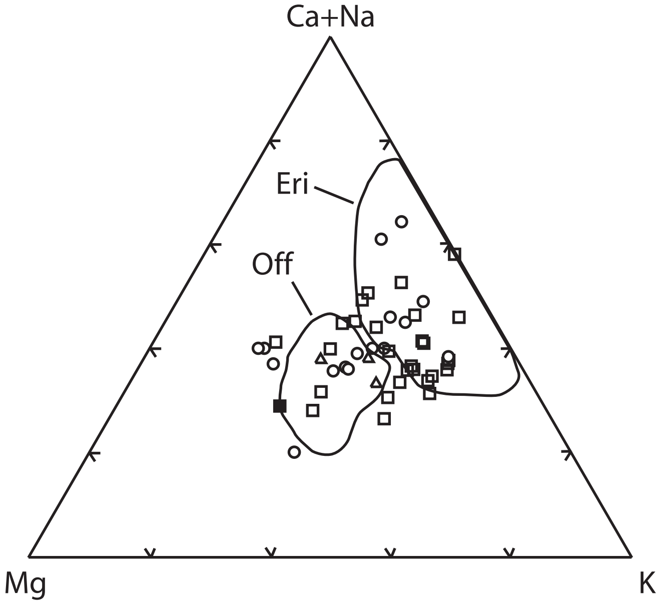
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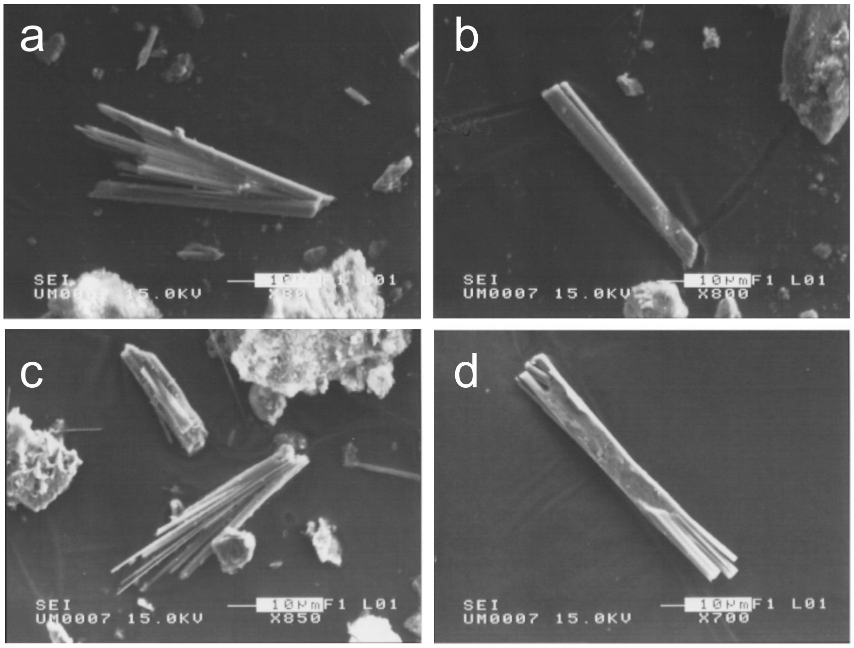
Eri
Off
Mg
K


a
SEI
L01
15.0KV
b
SEI
10µm F1 L01
UM0007 15.0KV
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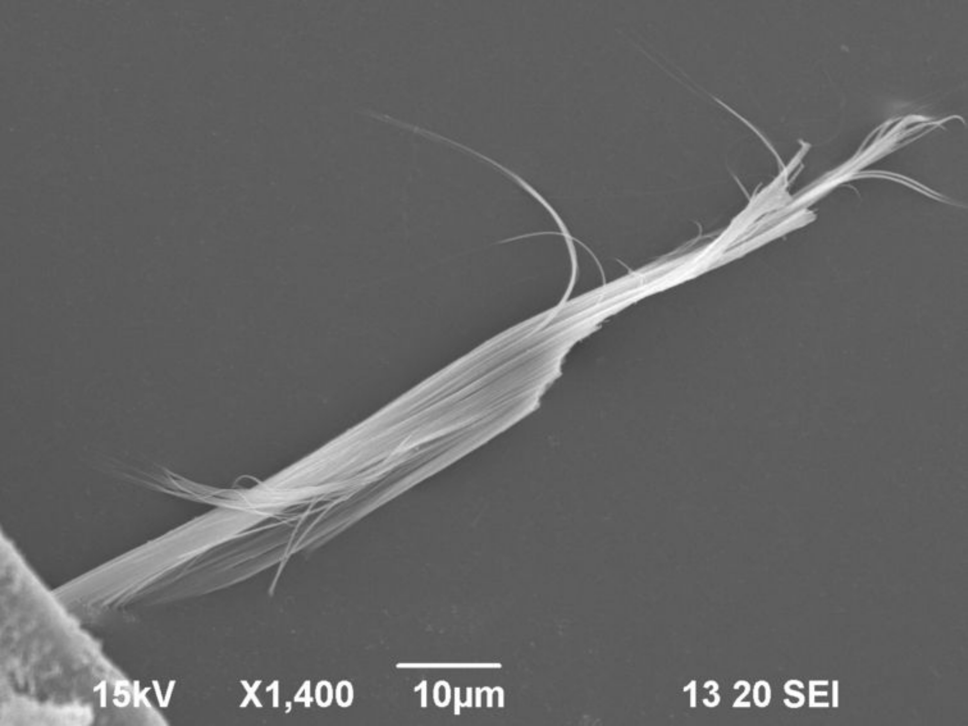
X700


15kV
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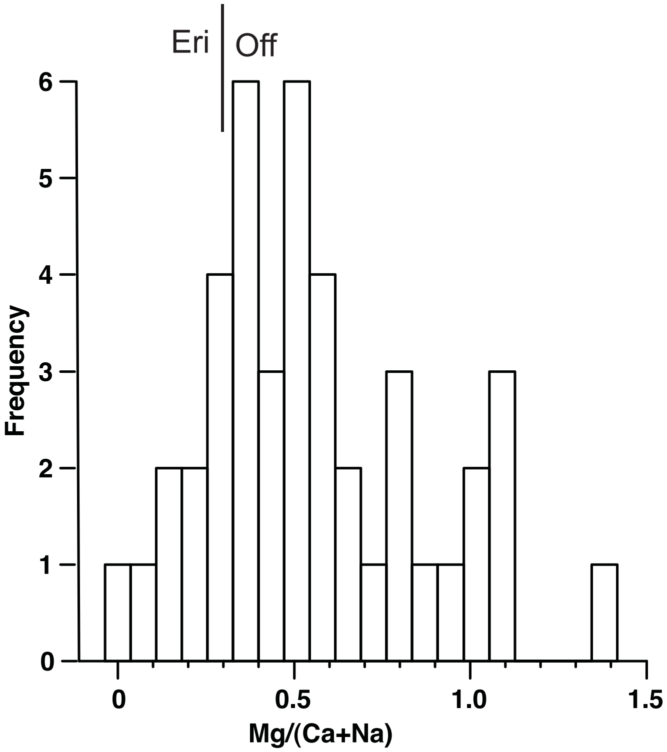

Figure 5