Prepared for U.S. Environmental Protection Agency, Region 8

Denver Microbeam Laboratory Administrative Report 14012007

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U.S. Department of the Interior
U.S. Geological Survey

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U.S. Geological Survey, Reston, Virginia 2007

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

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Introduction

The U.S. Environmental Protection Agency (USEPA), Region 8, requested the U.S. Geological Survey (USGS) Denver Microbeam Laboratory conduct a study of the zeolite mineral in 20 soil and roadbed samples collected from North Dakota. This report summarizes the morphology and chemistry of the zeolite mineral observed in the fine fraction of the samples provided by USEPA.

Analytical Techniques

A random aliquot of material was removed from each sample bag using a stainless steel spatula. The material was placed into a separate glass vial with approximately 1 milliliter of isopropanol and shaken to suspend the material in solution. The suspension was pipetted immediately (to prevent fractionation by settling) onto a polycarbonate filter adhered to an aluminum sample stub. After coating with carbon, samples were examined with a JEOL 5800-LV scanning electron microscope (SEM) operated at 15 kilovolts and 0.1-1.0 nanoamperes current and equipped with an Oxford ISIS energy dispersive spectroscopy (EDS) package. Each sample was scanned at 500 times magnification for the presence of fibrous zeolite minerals. An image and semiquantitative chemical data were acquired for each of the individual fibers.

A polished grain mount of sample KM-13, the zeolite source material, was prepared for electron probe microanalysis. A JEOL 8900 electron probe microanalyzer (EPMA) with a spot beam, operating at 10 kilovolts and 20 nanoamperes, was used to get as precise chemical data of the zeolite as possible. The water content of the zeolite was determined by difference assuming a 100 percent total. Correction procedures were implemented to account for the volatilization of sodium and potassium.

Material from sample KM-13 was suspended in isopropanol and decanted into a Millepore filter apparatus to concentrate the zeolite material for x-ray diffraction. The filter was adhered to an x-ray transparent glass slide and analyzed with a Scintag X-1 automated diffractometer fitted with a spinning sample holder using copper (Cu) K-alpha radiation. The sample was run at a power setting of 45 kilovolts and 35 milliamps with a step size of 0.02 degrees 2-theta from 4 to 60 degrees 2-theta with a 1 second per step count time.

Results and Conclusions

The following results apply only to the suspended material and are meant as a qualitative, not quantitative, assement of the fibrous zeolite present. All samples contained zeolite in the suspension with the exception of KM-6 in which no fibrous zeolite minerals were observed. Qualitatively, samples KM-1, KM-9, KM-10, KM-13, and KM-16 contain more fibrous zeolite than the remaining samples.

The morphology of the zeolite is acicular to asbestiform (fig. 1). The average length, width, and aspect ratio of the zeolite from all samples is 24 micrometers, 2 micrometers, and 15, respectively (fig. 2). Approximately 40 percent of the suspended material falls into the respirable size range of less than 1.5 micrometers in width (fig. 2) as

per USEPA health consultation. Forsman (1986) reported size and content differences of the erionite in Killdeer, North Dakota, rock samples in which some samples contained many needle-shaped crystals that were about 30 micrometers long whereas other samples contained crystals that were about 160 micrometers long. No difference was observed in the size distribution of the samples examined for this study. This may be due to analyzing only the fine fraction or the original collection procedure.

The SEM/EDS composition of the zeolite is intermediate between the erionite and offretite fields described by Passaglia and others (1998) (fig. 3). The SEM/EDS data also overlap compositionally with zeolites that are associated with high incidences of malignant diseases in Turkey (Dogan and others, 2006). However, confirmation of the chemical analyses acquired by Dogan and others (2006) is needed prior to a risk evaluation of the North Dakota samples. The EPMA data fall in the offretite field and agree with the EPMA data collected by Forsman (1986). X-ray diffraction data confirm erionite is present (fig. 4) but cannot preclude the presence of offretite because both minerals have similar diffraction patterns (Passaglia and others, 1998).

References Cited

Dogan, U.A., 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, v. 66, no. 10, p. 5063-5068.

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

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

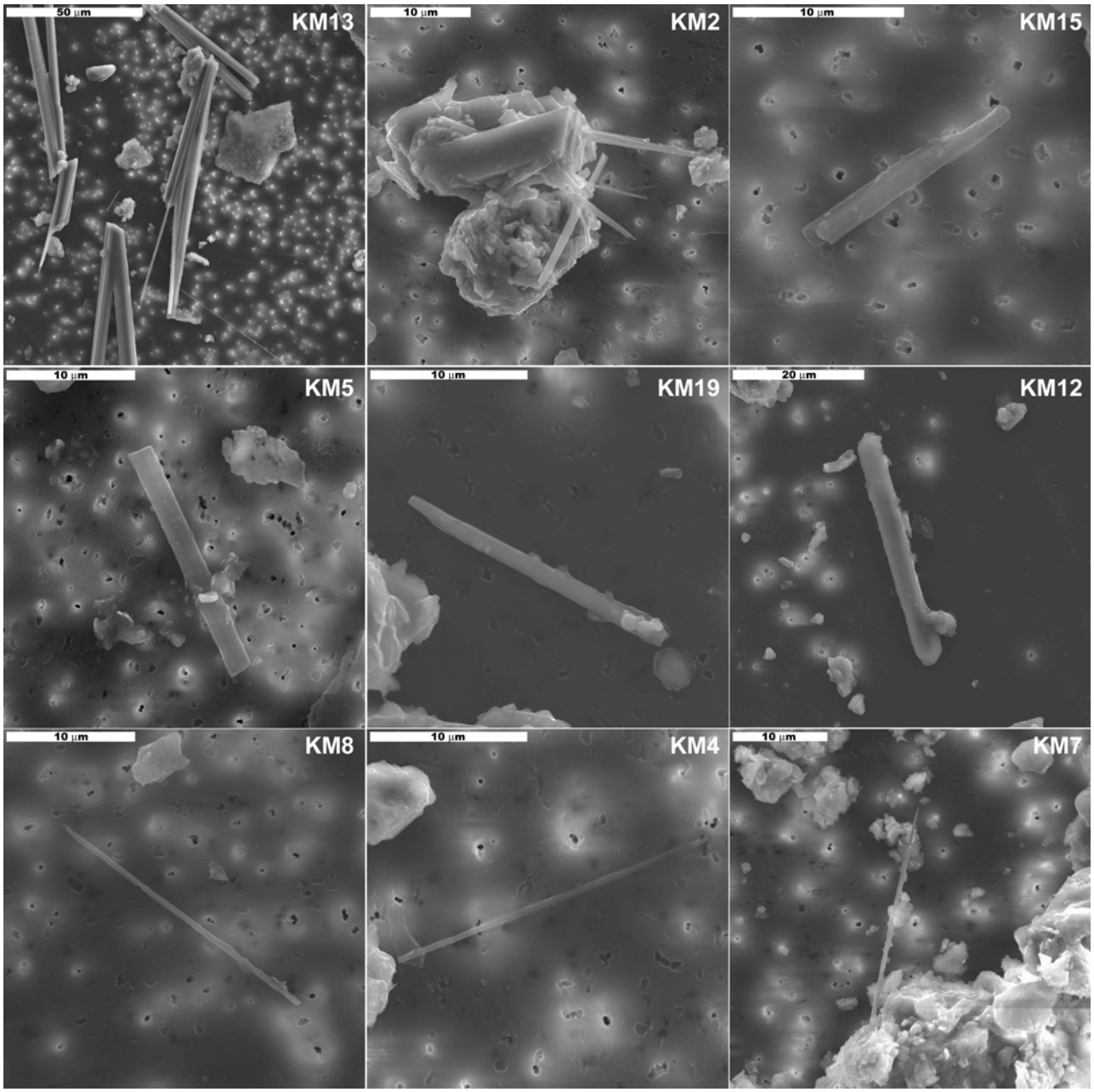

Figure 1. Typical zeolite morphologies of the fine fraction of the source rock (KM13) and remaining samples.

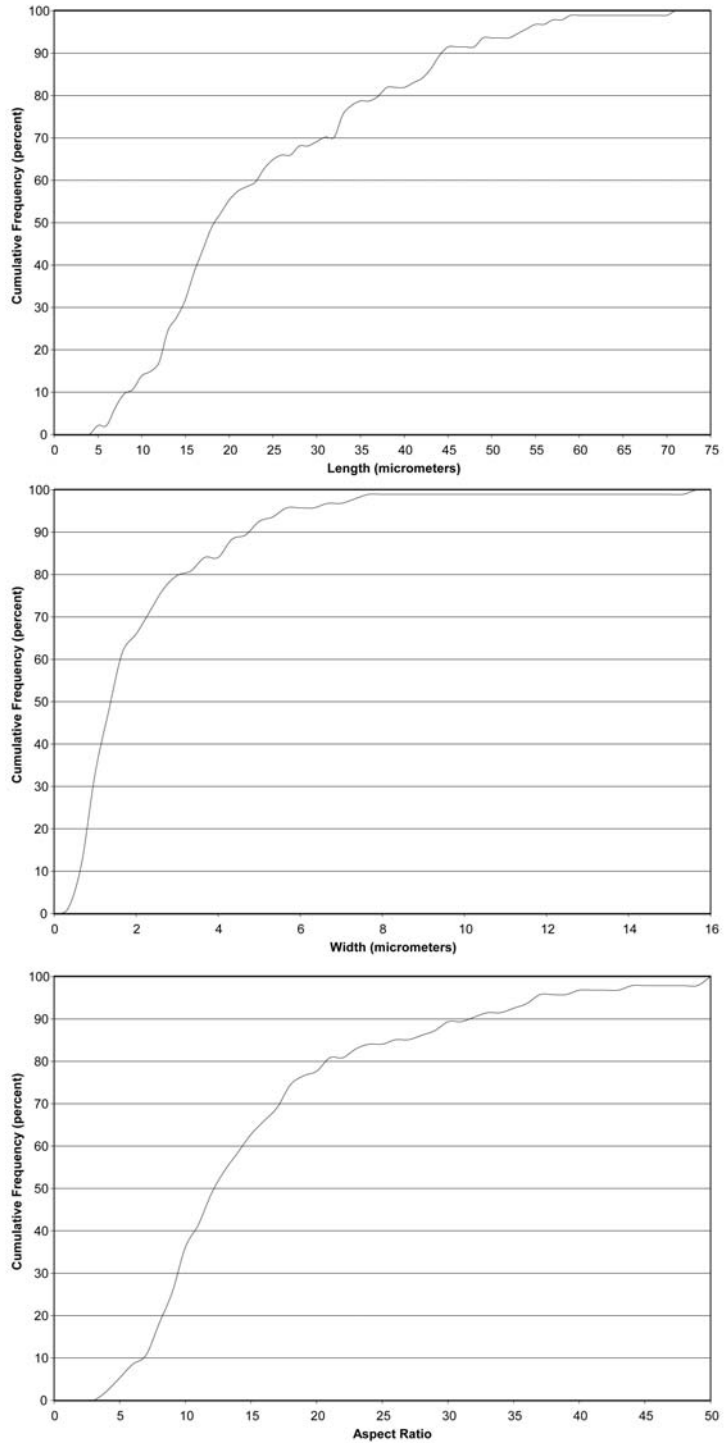

Figure 2. Cumulative frequency (n=94) plots of zeolite size distribution show the average (50 percent) width of the zeolite in the fine fraction is less than 2 micrometers and 40 percent of the particles have widths less than 1.5 micrometers, which is of respirable size.

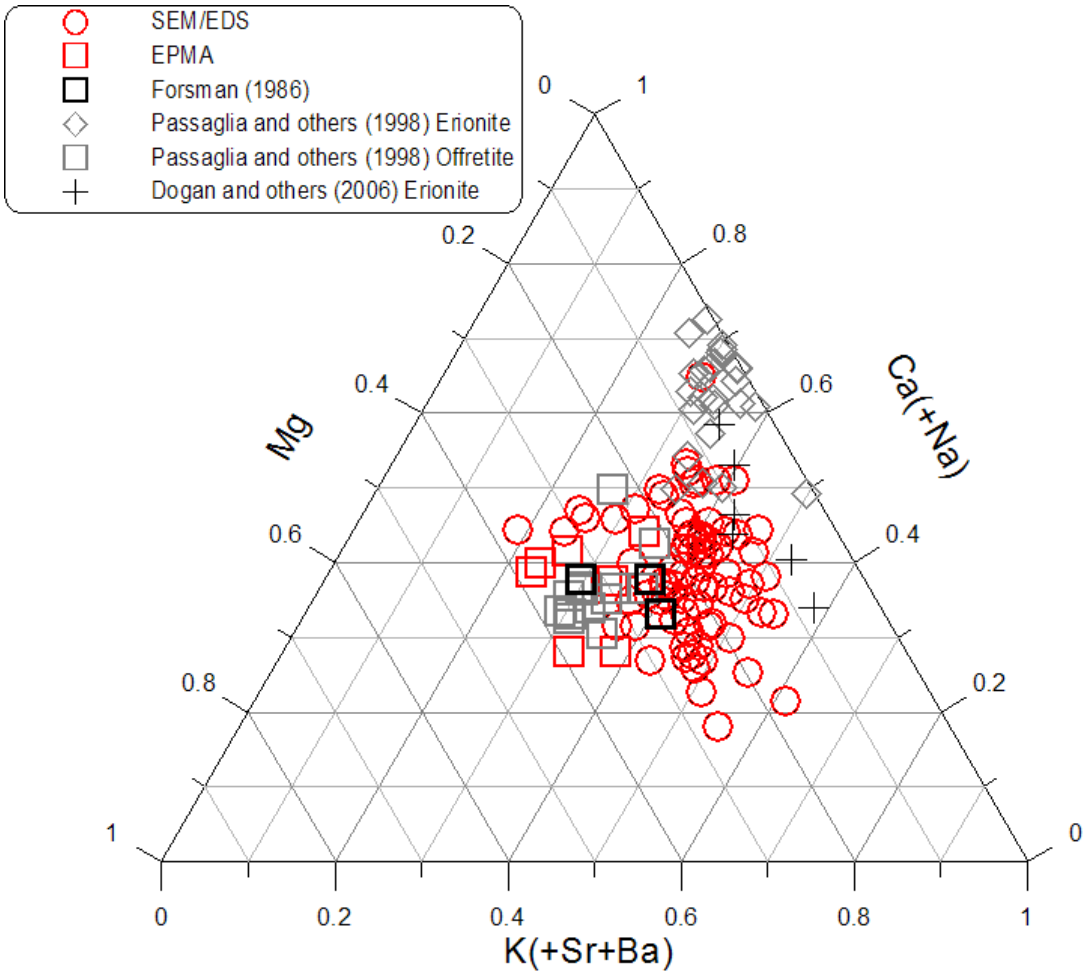

Figure 3. The scanning electron microscope-energy dispersive semiquantitative chemical composition (SEM/EDS) of the zeolite falls between the Ca(+Na)-Mg-K erionite and offretite fields described by Passaglia and others (1998). The electron microprobe data (EPMA) fall in the offretite field. However, the best structural match is to erionite based on x-ray diffraction data. The SEM/EDS data overlap compositionally with zeolite compositions that are associated with malignant diseases (Dogan and others, 2006).

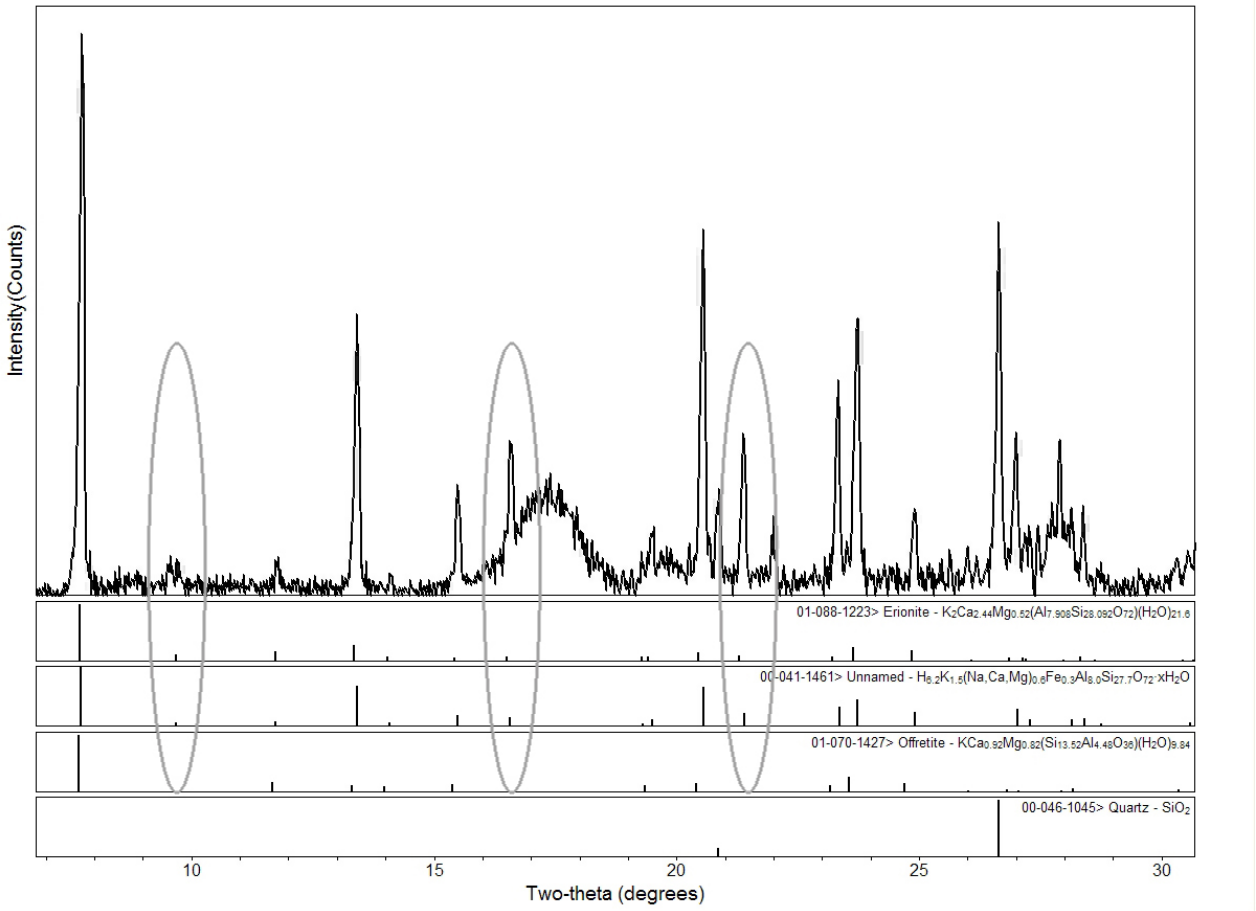

Figure 4. The two-theta regions marked with circles on the diffractogram indicate differences between erionite (01-088-1223 and 00-041-1461) and offretite (01-070-1427) diffraction patterns. This pattern confirms the presence of erionite but does not preclude the presence of offretite. The broad peak at 17 degrees two-theta is due to the filter substrate.