

Differentiation of Erionite From Other Fibrous Zeolites by Central Stop Dispersion Staining: A Preliminary PLM Investigation¹

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KEYWORDS

Asbestos, asbestiform, cancer, carcinogens, central stop dispersion staining (CSDS), energy dispersive X-ray spectroscopy (EDS), Environmental Protection Agency (EPA), erionite, fibrous minerals, high dispersion (HD), International Agency for Research on Cancer (IARC), mineral identification, polarized light microscopy (PLM), transmission electron microscopy (TEM), X-ray diffractometers (XRD), zeolites

ABSTRACT

Erionite is a fibrous zeolite often difficult to differentiate from other fibrous zeolites by polarized light microscopy (PLM) and other techniques. It is associated with increased risks of mesothelioma-like cancers documented from population studies conducted in the Cappadocian region of Turkey during the 1970s. The studies are important because they initiated a growing awareness that fibrous mineral carcinogenicity is a function of asbestiform habit not restricted to the six minerals currently classified as asbestos. Erionite is an IARC Group 1 carcinogen that includes asbestos, but it is currently not regulated by the U.S. Environmental Protection (EPA) in the same manner as asbestos. The EPA has stated that erionite causes lung cancer in lab rats, and it is currently conducting studies with the North Dakota Department of Health, which may lead to the inclusion of erionite into the asbestos mineral classification. This paper discusses analyses performed on eight fibrous zeolite

specimens for documented localities, causes for potential misclassification errors based on traditional methods of analysis, and an investigation of the possibility of using central stop dispersion staining with a 1.48 high dispersion (HD) refractive index liquid for differentiation of erionite from some other fibrous zeolites.

INTRODUCTION

Zeolites are interesting minerals belonging to the tectosilicate group of complex aluminosilicates. The term zeolite is derived from the Greek words *zeo* (to boil) and *lithos* (stone) and was coined in 1756 by Swedish mineralogist Axel F. Cronstedt, who observed a release of steam while heating stilbite (1). Zeolites differ from other aluminosilicates by the presence of water molecules in a microporous structure often referred to as "molecular sieves." Zeolitic microporosity provides the ability to selectively sort molecules based primarily on a size exclusion process. This property lends zeolites to high cation exchange capacity for use as petrochemical catalysts, solar thermal collectors, detergents, Portland cements and sorbents (kitty litter, medical applications). It is also used by the nuclear industry to trap fission products, and in agriculture to the slow release of nitrogen (2).

A total of 175 zeolites (mined and synthesized) have been identified. More than 40 of these are naturally occurring and approximately a dozen crystallize in a fibrous habit (3). Natural zeolites typically form through diagenetic processes when alkaline ground water interacts with volcanic rocks and ash deposits. They can

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Table 1. Comparison of Some Optical Properties of Some Fibrous Zeolites

Zeolite	Formula	Refractive Indexes	Birefringence	Morphology
Erionite	$K_2(Na, Ca_{0.5/8})[Al_{10}Si_{26}O_{72}] \cdot 30H_2O$	1.455-1.483 (ω) 1.457-1.485 (ϵ)	Low first order	Hexagonal prisms/ pinacoid terminations
Mazzite	$K_2(Na_2, Mg, Ca)_8[Al_{10}Si_{26}O_{72}] \cdot 28H_2O$	1.506 (ω) 1.499 (ϵ)	Low first order	Hexagonal prisms needles
Mesolite	$Na_{16}Ca_{16}[Al_{48}Si_{72}O_{240}] \cdot 64H_2O$	1.504-1.505 (α) 1.505-1.506 (β) 1.505-1.507 (γ)	Very low first order	Monoclinic prisms, needles
Mordenite	$(Na_2, Ca, K_2)_4[Al_8Si_{40}O_{96}] \cdot 28H_2O$	1.471-1.483 (α) 1.475-1.485 (β) 1.476-1.487 (γ)	Low first order	Orthorhombic and monoclinic prisms, needles
Natrolite	$Na_2[Al_2Si_3O_{10}] \cdot 2H_2O$	1.473-1.483 (α) 1.476-1.486 (β) 1.485-1.496 (γ)	Low first order	Orthorhombic and monoclinic prisms, needles
Offretite	$(Ca, K_2, Mg)_{2.5} \cdot [AlSi_{13}O_{36}] \cdot 16H_2O$	1.489-1.493 (ω) 1.486-1.491 (ϵ)	Low first order	Hexagonal prisms/ pinacoid terminations
Perlielite	$(K_9, NaCa, Sr)[Al_{12}Si_{24}O_{72}] \cdot 15H_2O$	1.479-1.483 (ω) 1.488-1.489 (ϵ)	Low first order	Hexagonal needles
Thomsonite	$Ca_2Na[Al_5Si_5O_{20}] \cdot 6H_2O$	1.497-1.530 (α) 1.513-1.536 (β) 1.518-1.544 (γ)	Low first order	Orthorhombic monoclinic blocky and acicular prisms

also crystallize in shallow marine basins over periods ranging from thousands to millions of years (1).

Erionite is a hexagonal fibrous zeolite of a general composition $K_2(Na, Ca_{0.5/8})[Al_{10}Si_{26}O_{72}] \cdot 30H_2O$ and has three recognized varieties based on the predominant exchangeable framework cation (K, Na, Ca). A.S. Eakle first described erionite in 1898, as white woolly fibrous masses in rhyolite lava vugs of the type locality, near Durkee, Baker County, Oregon (4). It was considered a relatively rare zeolite until the 1960s, but since then it has been found in many volcanic and sedimentary deposits around the world. Occurrences of erionite can be found in Turkey, Germany, France, Italy, Japan, Norway, Iceland and the United States (Nevada, Oregon, Arizona, California) (1). A prevalence of mesothelioma cases in the Cappadocian region of Turkey resulted in this mineral being classified as an IARC Group 1 carcinogen, along with asbestos in the 1980s (5).

Once used as a petroleum cracking catalyst, commercial use of erionite has been banned. Potential risk of erionite exposure can arise from the mining of commercial zeolite deposits with erionite contamination, or from disturbance of soils containing volcanic erosion products. Exposure risk has prompted some states

to issue public notices regarding the health hazards associated with erionite (6).

ZEOLITE ANALYSIS CONUNDRUM

Erionite was considered to be a relatively rare zeolite mineral prior to the 1960s. This is largely due to the inherent difficulty of distinguishing zeolite species from each other by early or traditional methods of identification. Mineralogy really began to evolve as a science in the 18th century, when identifications were made primarily on the basis of hand-specimen examination and blow pipe tests for predominant cation identification. Unfortunately, most fibrous zeolites have similar morphologies and cationic compositions, and could not be adequately differentiated using light microscopes of the day. With the invention of the polarized light microscope by William Nicol in the 19th century, more precise mineral characterization became possible. Zeolite identification by PLM, however, can be difficult due to intergrowths of species, epitaxial overgrowth of species and pseudomorphism. PLM identification is further complicated because the refractive indices of many zeolites are similar, and subtle differences in refractive

Table 2. Comparison of Specimens Procured for Study

Stated Zeolite Specimen	Formula From Source	XRD Library Results	EDS Percentage						RI by PLM*	
			Si	Al	Mg	Ca	Na	K		⊥
Erionite: Rome, Oregon	$K_2(Na, Ca_{0.5})_8 [Al_{10}Si_{26}O_{72}] \cdot 30H_2O$	Erionite: best match with Erionite-Ca	78.83	8.97	0	0	0	12.09	1.476	1.478
Erionite-K: Chase Creek, Oregon	$K_2(Na, Ca_{0.5})_8 [Al_{10}Si_{26}O_{72}] \cdot 30H_2O$	Offretite (Ca, K ₂ , Mg) _{2.5} [Al Si ₁₃ O ₃₆] · 16H ₂ O	73.70	12.94	0	2.28	0	10.28	1.476	1.482
Erionite-Ca: Beech Creek, Oregon	$K_2(Na, Ca_{0.5})_8 [Al_{10}Si_{26}O_{72}] \cdot 30H_2O$	Chabazite (Ca, Na ₂ , K ₂ , Sr, Mg) [Al ₂ Si ₄ O ₁₂] · 6H ₂ O and Thomsonite	57.62	24.68	1.96	14.39	1.34	0	1.518	1.52
Erionite-Na: Nagasaki, Japan	$K_2(Na, Ca_{0.5})_8 [Al_{10}Si_{26}O_{72}] \cdot 30H_2O$	Not confirmed. See EDS RI PLM.	64.38	16.97	0	7.04	2.92	7.60	1.471	1.474
Mordenite: Goble, Oregon	$(Na_2, Ca, K_2)_4 [Al_9Si_{40}O_{96}] \cdot 28H_2O$	Mordenite	88.24	1.82	0	9.93	0	0	1.476	1.478
Thomsonite: Sagasen, Norway	$Ca_2Na [Al_5Si_5O_{20}] \cdot 6H_2O$	Natrolite	75.89	22.36	0	0.55	1.19	0	1.51	1.53
Mesolite: Skookumchuck Dam, Wash.	$Na_{16}Ca_{16} [Al_{48}Si_{72}O_{240}] \cdot 64H_2O$	Mesolite	64.91	21.35	0	13.74	0	0	1.50	1.51
Natrolite: Lane City, Oregon	$Na_2[Al_2Si_3O_{10}] \cdot 2H_2O$	Natrolite	60.60	21.75	0	1.06	16.67	0	1.486	1.478

*Obtained with Becke line technique. || = parallel; ⊥ = perpendicular

index can be difficult to establish using the Becke line technique. A comparison of the similarity of optical properties for some fibrous zeolites and their chemical formulae is provided in Table 1. Accurate zeolite speciation became possible and relatively routine in 1945, when Norelco produced the first commercial X-ray diffractometers (XRD). Structural analysis by XRD has become the standard for most mineral identifications and is usually required for definitive zeolite speciation. Unfortunately, misclassifications still occur due to outdated optical data in literature for type locality specimens, which may not have been validated for structural identification by XRD. As a result, most mineralogists recognize a need for an integrated approach to accurate zeolite identification because of their complexity, and frequently use classification diagrams to assist in species delineation.

ZEOLITES OF PRELIMINARY INVESTIGATION

Specimens of six zeolite species from documented localities were procured from mineral dealers for the investigation (Table 2). The species procured as identified by supplier sources were one each of mordenite, mesolite, natrolite and thomsonite, and three specimens of erionite (Ca, K, Na). In addition, a specimen of erionite (typically erionite-K) from Rome, Oregon, was provided by Dr. Umran Dogan of the University of Ankara, Turkey, and University of Iowa. Complementary methods of mineralogic analysis were used for this study due to the inherent difficulty of zeolite identification that can arise as a result of pseudomorphism, intergrowth of species and epitaxial overgrowth. X-ray diffraction analysis is the definitive means of zeolite identification, but unfortunately it is not in the rep-

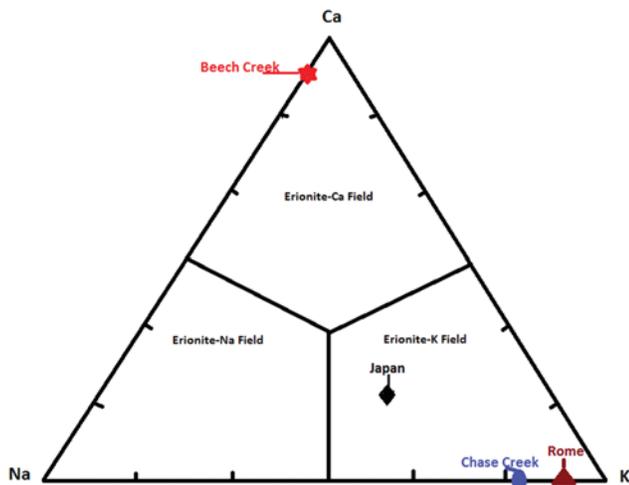


Figure 1. A Ca-Na-K ternary diagram shows potential misclassification of four "erionite" varieties without XRD analysis (7).

ertoire of many environmental laboratories. XRD analysis was performed on the specimens at Minerals Technologies, Inc. (Easton, PA) in order to determine if the mineral species procured were in fact erionite as reported by suppliers. Transmission electron microscopy (TEM) using energy dispersive X-ray spectroscopy (EDS) and PLM are common analytical techniques in environmental laboratories that may encounter samples requiring erionite identification. Therefore, TEM/EDS analysis was performed on the specimens for comparison of predominant cation content as a species discriminator. Refractive index measurement by the PLM Becke line technique, combined with central stop dispersion staining (CSDS), was performed to assess the feasibility of differentiating erionite from other fibrous zeolites. TEM and PLM analyses were performed by International Asbestos Testing Laboratories, Inc.

COMPLEMENTARY ANALYSIS SUMMARY

A summary of the analyses performed is provided in Table 2. The refractive index (RI) data presented in Table 2 was obtained using the Becke line technique. Review of the acquired data provided some revealing indications, which are summarized by the following points:

1. The only erionite specimen procured for this study, which was confirmed to be erionite by XRD, was from Rome, Oregon. Elemental and RI data for this specimen is consistent for erionite as compared to literature values. A discrepancy exists, however, for its varietal identification by XRD compared to its predominant cat-

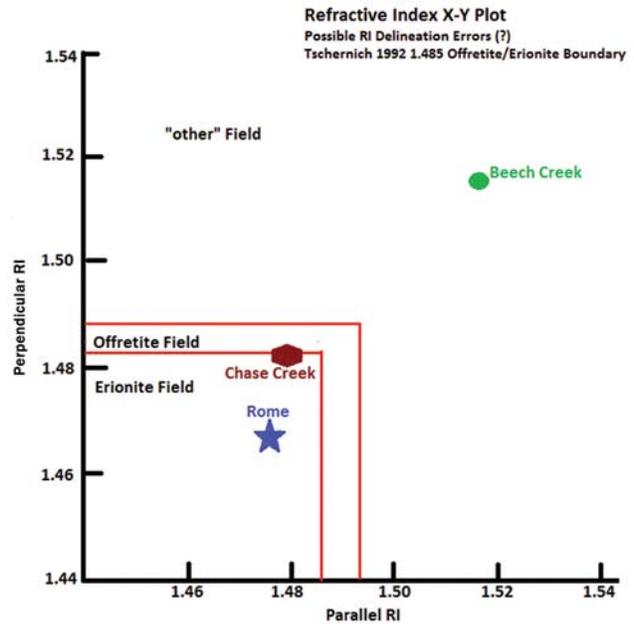


Figure 2. A refractive index plot shows distinctions of erionite and offretite based on refractive index and cation content (1).

ion content determination by TEM/EDS. The best match obtained for this specimen by XRD was with an erionite-Ca reference card. EDS obtained on the specimen indicates K as the predominant cation, which is consistent for erionite-K from this well-documented (and analyzed) locality. This suggests that the XRD card may not be accurate for erionite-Ca, or the compositional-structural variation in the sample is only evident on the XRD level, and many more fibers would have to be analyzed by TEM/EDS in order to determine if erionite-Ca and erionite-K are both present. XRD data in the literature on the Rome, Oregon, erionite specimen is limited, and further evaluation could not be made on the best match reference card.

2. The Chase Creek specimen was identified structurally as offretite, not erionite, by XRD. This fibrous zeolite is notoriously difficult to distinguish from erionite by optical microscopy because of common epitaxial overgrowth of offretite-erionite. Elemental analysis of the specimen by EDS ($K > Ca$), however, suggests that the specimen is not offretite. Becke line RI data obtained on the specimen is consistent for the range of reported literature values for erionite and offretite and is, therefore, of no value for differentiation. K as the predominant cation by EDS suggests heterogeneity in the sample and that offretite-erionite coexist (not unusual) and together cannot be resolved by XRD.

3. "Erionite-Na" from Japan was not analyzed by

XRD. EDS elemental data suggests this specimen is not erionite-Na due to predominance of Ca (7.04%) and K (7.60%) over Na (2.92%). Refractive index measurements (RIM) are consistent for erionite.

4. The mordenite, mesolite and natrolite specimens were confirmed by XRD with fair agreement from RI and EDS data.

5. XRD analysis indicated that the "thomsonite" specimen is actually natrolite, which is consistent with RI and EDS data, suggesting possible hand specimen misclassification.

6. The Beech Creek specimen was identified by XRD as a mixture of chabazite and thomsonite, not erionite, as reported by the supplier.

DISCUSSION OF MISCLASSIFICATION ERRORS

Based on the data acquired for the study specimens, there appear to be several possible causes contributing to misclassification. This misclassification error is most likely due to hand specimen misidentification on the basis of morphology (habit). The first, and perhaps most prevalent, is multiple species occurrence at a given locality. This possible cause is exemplified by the Beech Creek "erionite," which is actually a mixture of thomsonite and chabazite. Both species, along with offretite and erionite, have been documented to occur at this locale (1).

Another cause of misclassification could be hand lens misidentification without adequate knowledge of occurrence heterogeneity or additional confirmatory analysis (8). This error may be most prevalent in historical collection specimens and specimens for sale at the hobbyist level that have not been validated by XRD.

A third means of misclassification can arise from inadequate refractive index determination by Becke line measurement without XRD validation or elemental analysis. This means of misidentification can be partly due to changes in refractive index as a result of elemental variation along fibrous zeolite crystals (9). The fourth means of misclassification can arise as a result of relying on cationic elemental analysis without XRD validation. The last consideration to contemplate is the possibility of outdated reference diffraction cards, which may not adequately reflect updates to zeolite species classification by the Commission on New Minerals, Nomenclature and Classification (CNMNC).

Figure 1 provides an example of potential misclassification if elemental composition and refractive index is used for classification without XRD validation. Cationic ternary diagrams are frequently used for mineralogic and whole rock geochemical classifi-

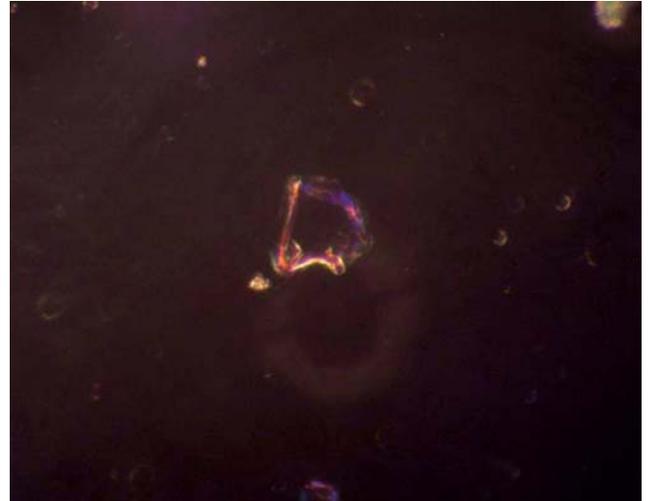


Figure 3. CSDS image of a glass particle in formulated Cargille 1.48 HD liquid at 100X magnification.

cations. If the four "erionite" specimens of this initial study were identified as erionite on the basis of refractive index and plotted on the Ca-Na-K ternary, they would be erroneously classified.

Figure 2 serves as another example of potential misclassification based on refractive index combined with cation analysis. The figure is based on work done by Tschernich (1) for differentiation of erionite from offretite based on refractive index measurement and cation content. If the maximum refractive index is greater than 1.485 and $Ca+Mg > K+Na$, the mineral is offretite. If the maximum refractive index is less than 1.485 and $Ca+Mg < K+Na$, it is erionite. The classification diagram is modified from the principles of Tschernich and includes an upper refractive index limit for the offretite domain. Applying these principles, the Chase Creek specimen (structurally identified by XRD as offretite) would be misclassified as erionite if cation and refractive index data were used for identification of this specimen without performing XRD analysis. In addition, the Beech Creek specimen would also be misclassified as erionite if refractive index and cation data were used for identification if an upper limit was not used for the offretite refractive index field on the diagram, and XRD analysis was not performed for structural identification.

CSDS WITH 1.48 HIGH DISPERSION LIQUID FOR ZEOLITE DIFFERENTIATION

CSDS is a powerful technique for determining an accurate refractive index, which can be particularly

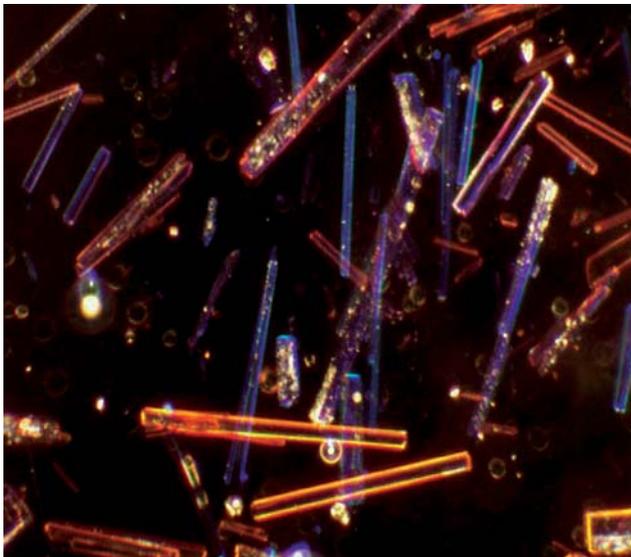


Figure 4. Natrolite in 1.48 HD CSDS at 100X magnification.

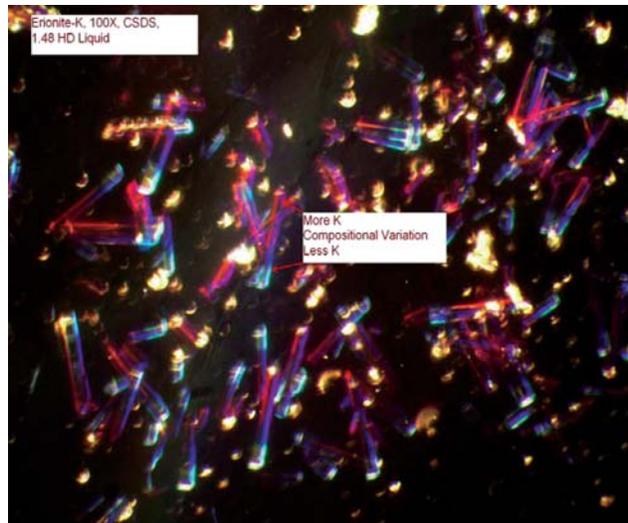


Figure 5. Chase Creek "erionite" (offretite) in 1.48 HD CSDS at 100X magnification.



Figure 6. Rome, Oregon, erionite in 1.48 HD CSDS at 200X magnification.

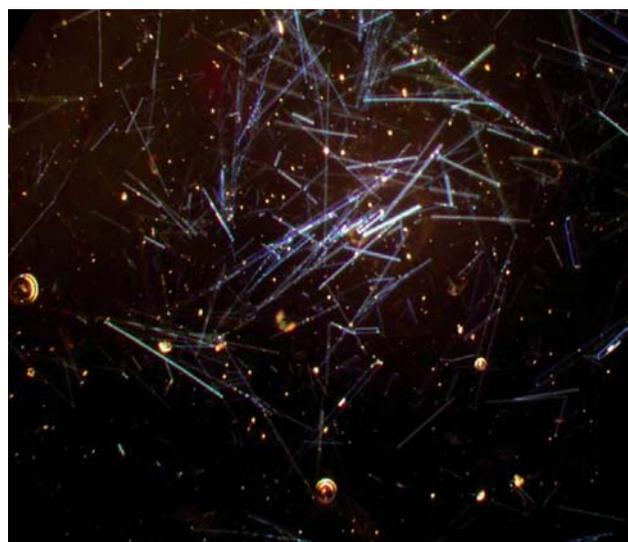


Figure 7. Mordenite in 1.48 HD CSDS at 100X magnification.

valuable for discerning subtle differences in refractive index. It has been used successfully used for more than 25 years for the identification of asbestos species and can be applied to refractive index determination for other crystalline substances. Zeolite species can be difficult to differentiate using the Becke line technique due to their similar refractive indexes. Series A liquids present challenges for CSDS, because they do not have high dispersion and, therefore, do not always produce good CSDS colors. Unfortunately, high dispersion liquids in the refractive index range of most zeolites (1.46-1.52) are not available.

For this study, a 1.48 high dispersion refractive index liquid was formulated from appropriate proportions of Cargille 1.550 Series E HD liquid and triacetin. The 1.550 Series E liquid is composed mostly of ethyl cinnamate (1.5590 refractive index at 20 °C) and some triacetin (refractive index of 1.4306 at 20 °C). A calibrated Cargille refractive index glass was used to check for the dispersion staining colors that were produced. Figure 3 is a CSDS photomicrograph obtained of glass beads that shows magenta-blue CSDS colors indicating a match between the glass and liquid.

Figures 4-7 are CSDS images obtained from analy-

sis of some of the zeolites procured for the study using the formulated 1.48 high dispersion refractive index liquid. The natrolite specimen in Figure 4 is presented to show good CSDS for refractive indexes above and below 1.48. Natrolite refractive indexes (Table 1) range from 1.473-1.483 for alpha (perpendicular to fiber length) and 1.485-1.496 for gamma (parallel to fiber length). The blue color for perpendicular and gold color for parallel fiber orientations are consistent. Figure 5 is an offretite (Chase Creek erionite) specimen; the image shows the sensitivity of the 1.48 refractive index liquid for discerning compositional changes along fiber length, which is represented by changes in CSDS colors. The changes in CSDS colors may reflect epitaxial overgrowth or intergrowths of offretite-erionite as suggested by the XRD/TEM data obtained on the specimen.

The validated Rome, Oregon, erionite specimen is in Figure 6. The image was obtained using a 20X CSDS objective made by placing a round piece of black electrical tape on the back focal plane objective lens. This image indicates that good CSDS colors can be obtained on small erionite fibers at total magnifications greater than 100X using the 1.48 liquid. The blue CSDS color is consistent for the lower refractive index (<1.48, Table 2) obtained for the erionite fibers compared to the liquid by the Becke-line technique. Mordenite examined by CSDS using the 1.48 liquid is provided in Figure 7. This image illustrates the fact that mordenite has a slightly lower refractive index than erionite, which could not be determined by refractive index measurements obtained by the Becke line technique (Table 2).

CONCLUSIONS

Fibrous zeolite identification is not typically a less-than-straightforward process but frequently requires correlation of data from different analytical techniques. Perhaps the best lesson learned from this exercise is that integrated analysis is essential for accurate zeolite identification. Identifications by visual examination, microscopy and elemental analyses alone, without struc-

tural validation by XRD, may lead to misidentifications. Type locality and/or documented locality specimens should be validated by XRD prior to characterization for use as reference material of a given species. Preliminary study of a 1.48 high dispersion liquid formulated from appropriate amounts of Cargille Series E 1.550 liquid and triacetin shows promise for differentiating erionite from other fibrous zeolites. The findings from the intended study comparing scolecite ($\text{Ca}[\text{A}_{12}\text{Si}_3\text{O}_{10}] \cdot 3\text{H}_2\text{O}$), mazzite ($(\text{K}_2\text{Na}_2\text{Mg,Ca})_5[\text{Al}_{10}\text{Si}_{26}\text{O}_{72}] \cdot 28\text{H}_2\text{O}$), perliolite ($\text{K}_9\text{Na}(\text{Ca,Sr})[\text{Al}_{12}\text{Si}_{24}\text{O}_{72}] \cdot 15\text{H}_2\text{O}$) and erionite from the Cappadocian region of Turkey for refinement of the 1.48 liquid and dispersion curves will be made available in the future.

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