

New morphological, chemical, and structural data of woolly erionite-Na from Durkee, Oregon, U.S.A.

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ABSTRACT

A detailed morphological, crystal-chemical, and structural characterization of erionite from the type locality of Durkee, Oregon, has been carried out by combining field emission scanning electron microscopy (FESEM) and laboratory parallel-beam transmission X-ray powder diffraction (XRPD). According to the crystal-chemical formula $(\text{Na}_{5.38}\text{K}_{1.99}\text{Mg}_{0.24})[\text{Al}_{7.66}\text{Si}_{28.34}\text{O}_{72.09}]\cdot 29.83\text{H}_2\text{O}$, the sample has been classified as erionite-Na. The Rietveld refinement has indicated that the extraframework cations are located at three Ca1, Ca2, and Ca3 sites, the first one containing all available Mg. Moreover, the absence of the additional K2 site found in both dehydrated erionite and erionite-K has been demonstrated for this erionite sample. Furthermore, our results revealed the absence of Fe and Ca although previous investigations have reported the presence of a variable content of both these elements in erionite samples from Durkee. This is relevant information because it is well known from amphibole asbestos that Fe^{2+} has been claimed to be one of the causes of carcinogenesis by participating in Fenton chemistry and producing free radicals.

Keywords: Erionite-Na, Durkee Oregon, woolly morphology, crystal-chemistry, crystal structure, Rietveld method, scanning electron microscopy, laboratory parallel-beam transmission X-ray powder diffraction

INTRODUCTION

Erionite is a fibrous zeolite belonging to the so-called ABC-6 family (Gottardi and Galli 1985). It usually occurs in volcanic ash altered by weathering processes. From the structural point of view, it is hexagonal, space group $P6_3/mmc$. The erionite framework, topological code [ERI] (Meier and Olson 1992), consists of $(\text{Si},\text{Al})\text{O}_4$ tetrahedra linked together to form single-six rings (S6R) and double six-rings (D6R). S6R originate erionite cages by bridging adjacent columns at the level of the cancrinite (ϵ) cages. D6R connect columns of ϵ cages along the z direction. An average chemical formula $\text{K}_2(\text{Na},\text{Ca}_{0.5})_8[\text{Al}_{10}\text{Si}_{26}\text{O}_{72}]\cdot 30\text{H}_2\text{O}$ has been proposed for erionite by Coombs et al. (1997). However, due to a significant chemical variability, three different species, erionite-K, erionite-Ca, and erionite-Na have been identified, depending on the most abundant extraframework (EF) cation.

In the past few years fibrous erionite has been thoroughly investigated because of its link to malignant mesothelioma (MM). In fact, in vivo studies unambiguously proved that erionite is several times more tumorigenic than chrysotile and crocidolite asbestos (Bertino et al. 2007). As a consequence of this, the International Agency for Research on Cancer (IARC) listed erionite as a Group 1 Human-Carcinogen (IARC 1987, 2011). The toxicity of erionite has been partly ascribed to the presence of ion-exchanged or surface-deposited iron participating in Fenton

chemistry and generating reactive oxygen species that induce DNA damage (Eborn and Aust 1995). In fact, although erionite being a nominally Fe-free phase, Fe_2O_3 contents up to 3 wt% have been reported (Eberly 1964; Dogan et al. 2006). Dogan et al. (2006) reported that erionite from Rome (Oregon, U.S.A.) has a Fe_2O_3 content even higher than the Cappadocia erionite, the latter being responsible for the malignant mesothelioma epidemic (Baris et al. 1978, 1987). Ballirano et al. (2009) carried out a combined spectroscopic and crystal-chemical investigation of erionite-K from Rome hypothesizing that iron resides on the zeolite surface in the form of oxide-like nanoparticles with dimensions spanning from 1 to 9 nm. Notably, it was proposed that even upon inhalation of Fe-free fibers, they could imbibe Fe via ion exchange because protein injury can lead to metal ion release (Carr and Frei 1999). In any case, whether Fe is introduced with erionite or is captured in the lungs, it was highlighted that the Fenton chemistry occurs on the surface of the fibers and that the coordination state of Fe^{2+} and Fe^{3+} is critical for inducing cytotoxicity and genotoxic damage (Fach et al. 2003; Ruda and Dutta 2005).

Several recent studies aimed at the investigation of fiber toxicity have been dedicated to the study of their surface reactivity, mainly by XPS analysis (Fantauzzi et al. 2010, 2012). The success of those investigations is strongly dependent on a detailed crystal-chemical and structural characterization of the fibers. At the same time, a significant effort has been devoted to improve the reliability of chemical data extracted from micro-analytical

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investigations carried out through transmission electron microscopy (TEM) (Dogan 2011), scanning electron microscopy (SEM) (Dogan and Dogan 2008), and electron microprobe analysis (EMPA) (Lowers et al. 2010) to properly constraint XPS experiments. This task is inherently very difficult for fibers and especially for zeolites because of the well-known problems related to the small crystal dimensions and their instability under the electron beam that leads to fairly unreliable analytical results. As far as the structural characterization of fibers is concerned, a significant number of papers fully exploiting the capabilities of laboratory parallel-beam transmission X-ray powder diffraction have been recently published (Ballirano et al. 2008, 2009; Pacella et al. 2008; Andreozzi et al. 2009; Ballirano and Cametti 2012). This instrumental set up coupled with the preparation of the sample as a capillary mount allows an almost complete removal of preferred orientation and therefore significantly improving the reliability of the structural data even at non-ambient conditions (Ballirano 2011a, 2011b, 2011c).

The present study is dedicated to the detailed crystal-chemical characterization of a sample of woolly erionite from the type locality near Durkee, Oregon (U.S.A.), by combining data from X-ray powder diffraction (XRPD) and SEM analysis. The reported results are expected to provide a sound background for future experiments aimed at understanding the relationships among morphology, crystal chemical and structural features, and biological activity of erionite.

EXPERIMENTAL METHODS

Scanning electron microscopy (SEM)

The analyzed erionite sample was provided by the Smithsonian Institution, Washington, D.C. (NMNH R4066-1). At Durkee, Oregon, erionite occurs in thin seams in gray, rhyolitic welded ash-flow tuffs (Sheppard 1996). The hand specimen consists of ribbons and bundles aggregating to form a hank with white color and pearly luster as reported by Eakle (1898). SEM images were collected at the Centro di ricerca per le Nanotecnologie applicate all'Ingegneria della Sapienza (CNIS) using a field emission SEM (FESEM) Zeiss Auriga 405 with an accelerating voltage in the range 1.3–6 kV at a working distance in the range 2.8–3.5 mm. A preliminary set of chemical analyses was collected on bundles of erionite fibers. Moreover, two samples were prepared for a micro-chemical characterization by dispersing a small aliquot of fibers in distilled water in a beaker and subsequently pipetting and depositing a few droplets of the dispersion onto two aluminum stubs with double adhesive carbon tape. One of the stubs was coated with carbon, the other with gold, to check the possible occurrence of analytical differences arising from the coating. Analyses were collected for each stub positively verifying that the analytical results are independent from the coating type. The micro-chemical characterization was performed at the Dipartimento di Scienze della Terra, Sapienza Università di Roma using a FEI Quanta 400 SEM equipped with an EDX Genesis EDS system. Operating conditions were: 15 kV accelerating voltage, 11 mm working distance, 0° tilt angle. Chemical data were collected at 30 analytical points. The final crystal chemical formula was calculated, after renormalization of the chemical analyses hypothesizing a water content of 18.5 wt% [corresponding to ca. 30 atoms per formula unit, (apfu)], on the basis of 36 (Si+Al+Fe³⁺) apfu.

To evaluate the quality of SEM-EDX microchemical data we performed a preliminary, thorough comparison with EMPA, using a fairly large prismatic erionite-Ca crystal as a standard. The sample, from Faedo, Colli Euganei, Italy, is a crystal of the same batch investigated by EMPA by Passaglia and Tagliavini (1995). Compositions were determined using a Cameca SX50 electron microprobe with the following conditions: 10 s counting time (peak), 5 s counting time (background), beam diameter 20 µm, excitation voltage 15 kV, specimen current 20 nA, wavelength-dispersive spectrometry (WDS). The following standards were used: wollastonite (Si and Ca), rutile (Ti), corundum (Al), magnetite (Fe), metallic Mn (Mn), barite (Ba), celestine (Sr), periclase (Mg), orthoclase (K), and jadeite (Na). The raw data were corrected on-line for drift, dead time, and background; matrix correction has been performed with a standard ZAF program. Results of the

chemical analyses are compared in Table 1. As can be seen, no relevant differences among the three data sets were observed, the SEM-EDX being characterized by a very marginal increase of the data dispersion indicating the full reliability of the technique. At any case, we unsuccessfully attempted to prepare a sample of erionite from Durkee for EMPA analysis by embedding small hanks of fibers in epoxy. Unfortunately, the polishing procedure unavoidably produced the separation of the fibrils resulting in irregular, unpolished, surfaces. As a consequence, the resulting EMPA cannot be considered as reliable.

X-ray powder diffraction (XRPD)

Bundles of fibers were selected under a binocular microscope on the basis of the absence of any recognizable impurity phase. They were subsequently disaggregated using a knife and carefully hand-ground in an agate mortar under ethanol. The powder was loaded in a 0.7 mm diameter borosilicate capillary that was aligned onto a standard goniometer head. XRPD data were collected, up to a $(\sin \theta/\lambda)_{\max}$ of 0.619 Å⁻¹, using a parallel-beam Bruker AXS D8 Advance Diffractometer, operating in θ - θ geometry, equipped with Göbel mirrors on the incident beam, Soller slits on both incident and (radial) diffracted beams, and a PSD VANTEC-1 detector. Experimental details of the XRPD data collection are reported in Table 2. A careful scrutiny of the diffraction pattern confirmed the absence of any detectable crystalline impurity, within the limits of the diffractometer sensitivity, which is estimated to be of ca. 0.1 wt%. The structural refinement was carried out by the Rietveld method using TOPAS v.4.2 (Bruker AXS 2009) running in launch mode. Peak shape was modeled through fundamental parameters approach (FPA), imposing the following full axial parameters: divergence slit: 0.3°, source length 12 mm, sample length and receiving slit length 15.3(2) mm. The starting structural model, taken from Alberti et al. (1997), consists of a part of the framework atoms, four EF cationic sites, K1, Ca1, Ca2, and Ca3; and six water molecules sites (OW7, OW8, OW9, OW10, OW11, and OW12). Both the occupancy of all EF cationic and water molecules sites and the displacement parameters of all sites were refined. However, because of the occurrence of correlations, displacement parameters of the sites were constrained, according to the structural data of Ballirano et al. (2009):

TABLE 1. Chemical data of erionite-Ca from Faedo, Colli Euganei, Italy, as obtained from SEM-EDX and EMPA

	P&T1995	Present work*	
	EMPA	EPMA	SEM-EDX
Morphology			prismatic
SiO ₂	54.87	54.38 (53.58–54.95)	55.46 (54.25–56.01)
Al ₂ O ₃	16.77	16.45 (16.17–16.68)	16.22 (16.17–16.43)
TiO ₂	–	0.07 (0.00–0.09)	–
SrO	0.12	0.02 (0.00–0.27)	–
BaO	0.02	0.08 (0.00–0.24)	–
CaO	6.72	6.95 (6.62–7.47)	6.38 (5.90–7.24)
MnO	–	0.06 (0.00–0.26)	–
MgO	0.05	0.11 (0.05–0.19)	0.12 (0.00–0.22)
Na ₂ O	0.32	0.12 (0.04–0.30)	0.12 (0.00–0.30)
K ₂ O	2.62	3.22 (2.89–3.51)	3.17 (2.60–3.90)
H ₂ O	18.50	18.50	18.50
Total	100	100	100
Unit-cell atomic content			
Si	26.45	26.53 (26.43–26.58)	26.76 (26.71–26.77)
Al	9.54	9.47 (9.34–9.62)	9.24 (9.15–9.32)
Ti	–	0.02 (0.00–0.09)	–
Sr	0.01	0.01 (0.00–0.08)	–
Ba	–	0.02 (0.00–0.04)	–
Ca	3.47	3.64 (3.45–3.96)	3.30 (3.05–3.83)
Mn	–	0.03 (0.00–0.11)	–
Mg	0.04	0.08 (0.04–0.14)	0.09 (0.00–0.16)
Na	0.30	0.11 (0.04–0.29)	0.11 (0.00–0.28)
K	1.62	2.00 (1.80–2.21)	1.95 (1.59–2.53)
O	71.73	72.14	71.80 (71.53–72.44)
H ₂ O	29.81	30.17	29.84
R	0.735	0.737	0.743 (0.741–0.746)
M/(M+D)	0.539	0.562	0.609
Na/M	0.155	0.053	0.054
E%	5.8	–1.4	4.4

Notes: Crystal chemical formula calculated on the basis of 36(Si+Al+Fe³⁺) apfu. EMPA results of Passaglia and Tagliavini (1995), labeled as P&T1995, are reported for comparison. Minimum and maximum values are reported in parentheses.

R = Si/(Si + Al); M = Na + K; D = Ca + Mg + Sr + Ba;

E% = 100 * [(Al+Fe)_{ab} - Al_{th}]/Al_{th} where Al_{th} = Na + K + 2 * (Ca + Mg + Sr + Ba)

* Mean values renormalized hypothesizing a water content of 18.5 wt%.

TABLE 2. Experimental details of XRPD data collection

Instrument	Bruker AXS D8 Advance
Radiation	CuK α
Primary and secondary radius (mm)	250
Detector	PSD VANTEC-1
Sample mount	Rotating capillary (60 r/min)
Incident beam optics	60 mm multilayer (Göbel) X-ray mirror
Detector window (°)	6
Divergence slits (°)	0.3
Soller slits	Primary beam (2.3°); diffracted beam (radial)
Angular range (°2 θ)	4–145
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.619
Step size (°2 θ)	0.022
Counting time (s)	10

$B_{11} = B_{12}$; $B_{01} = B_{02} = B_{03} = B_{04} = B_{05} = B_{06}$; $B_{Ca1} = B_{Ca2} = B_{Ca3}$; $B_{Ow8} = B_{Ow9} = B_{Ow10} = B_{Ow11} = B_{Ow12} = 2B_{Ow7}$. Absorption was modeled following the Sabine model for cylindrical samples (Sabine et al. 1998) and the background was fitted by a Chebyshev polynomial of the first kind. The occurrence of preferred orientation was tested by means of spherical harmonics (four refinable parameters up to the sixth order). The choice of the number of terms to be used followed the procedure described by Ballirano (2003). As expected for a capillary mount, only a marginal improvement of the fit was observed as a result of the nearly complete absence of texture. A first refinement was carried out considering an isotropic shape of the crystallites. The refinement smoothly converged to the following agreement indices: $R_{wp} = 4.92\%$, $R_p = 3.44\%$, $R_B = 0.89\%$ (Young 1993). However, a careful scrutiny of the Rietveld plots (Fig. 1a) indicated an imperfect fitting of the shape of a few peaks due to the strongly anisotropic shape of the crystallites. Therefore, a second refinement was performed using the recently proposed ellipsoid-model of Katerinopoulou et al. (2012) describing the diffraction-vector dependent broadening of diffraction maxima. In the hexagonal symmetry, the shape ellipsoid parameters b_s are constrained as $b_{11} = b_{22} = 2b_{12}$; $b_{13} = b_{23} = 0$. The orientation of the ellipsoid is such that the principal radii $r_a \perp c$ and $r_c \parallel c$. A significant improvement of the fit was obtained as compared to the use of an isotropic shape of crystallites as indicated by the final agreement indices: $R_{wp} = 3.36\%$, $R_p = 2.45\%$, $R_B = 0.47\%$. Final Rietveld plots are shown in Figure 1b.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

From a morphological point of view, the sample consists of sub-parallel or bent bundles of fibers with a woolly aspect. The diameter of the bundles ranges from 10 to 20 μm (Fig. 2a). Each fiber is composed of very thin and curled fibrils as outlined in Figure 2b. The diameter of the fibers ranges from 0.3 to 2 μm , whereas that of a single fibril may be as small as 15 nm (Fig. 2c). The longer fibers are tensile, elastic, and flexible, but they are potentially extremely pathogenic upon inhalation because they cannot be phagocytized. The woolly aspect of the fibers is typical of the locality of Durkee, Baker County, as first reported by Eakle (1898). In addition, Gude, and Sheppard (1981) described a woolly erionite sample from the Reese River deposit, Nevada, identical in appearance to that from Durkee. Notably, the morphology of both of these erionite is peculiar as it differs from that of erionite samples from other localities, which have been described as prismatic or acicular in habit.

The EDX spectra acquired on the bundles of fibers revealed in accordance with reference data the occurrence of Ca, Mg, Na, and K as EF cations. In addition, a small amount of Fe content was detected (Fig. 3). Moreover, preliminary semi-quantitative analyses pointed out that both, the CaO and Fe₂O₃ content widely differs depending on the analytical point, indicating a significant inhomogeneity of the sample. In particular, the Fe₂O₃ and CaO content ranged from zero up to 4 wt%, and from zero up to 6 wt%, respectively. It must be noted that, as highlighted by FESEM images (Fig. 2), it was very hard to discriminate and analyze a single fiber. For this reason a new set of analyses was

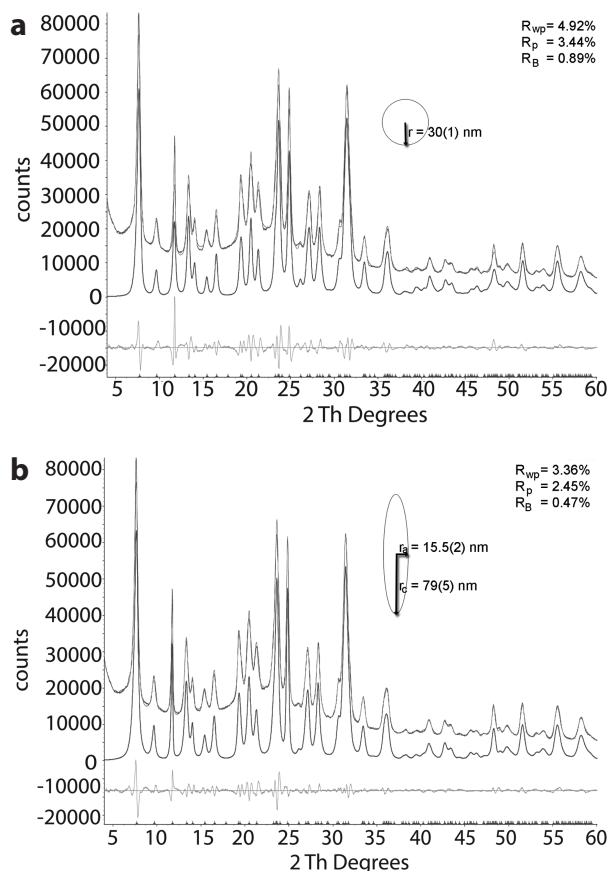


FIGURE 1. Top: experimental (dots) and total calculated (continuous); middle: calculated erionite; bottom: difference plot of the refinement of erionite-Na from Durkee, Oregon. (a) Refinement with an isotropic crystallites shape; (b) refinement with an anisotropic crystallites shape. Vertical bars refer to the position of the Bragg reflections. Inset: shape of the ellipsoid and corresponding r_a and r_c principal radii.

carried out on isolated bundles obtained by dispersion in distilled water. In this case, the collected spectra clearly indicated the absence of both CaO and Fe₂O₃ (Fig. 4). On this basis, the presence of these elements in the erionite fibers was ruled out and attributed to impurity phases. As confirmation of this, FESEM images revealed the presence of small particles of variable size (from 1 to 10 μm) and irregular shape resting at the fiber surface (Fig. 5). Their chemical composition was qualitatively evaluated and the corresponding spectra showed that both Ca and Fe are associated to these particles (Fig. 6).

The reliability of the chemical analyses of the fibers was evaluated using both the balance error formula E% (Passaglia 1970) and the Mg-content test (Dogan and Dogan 2008). Using the above-mentioned experimental cautions, approximately 70% of the analyses passed both tests. The average chemical composition is reported in Table 3. The MgO content did not exceed 0.54 wt%, whereas Na resulted the most abundant EF cation with a Na₂O content ranging from 4.78 to 6.44 wt%. The final average crystal-chemical formula, calculated from 16 analytical point passing both the E% and the Mg-content tests, of (Na_{5.38}K_{1.99}Mg_{0.24})[Al_{7.66}Si_{28.34}O_{72.09}] $\cdot$ 29.83H₂O allows

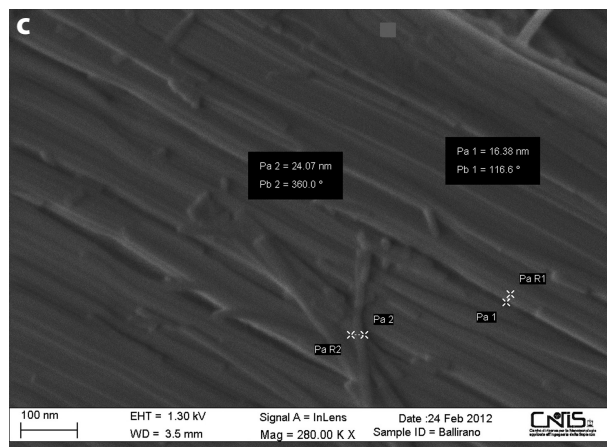
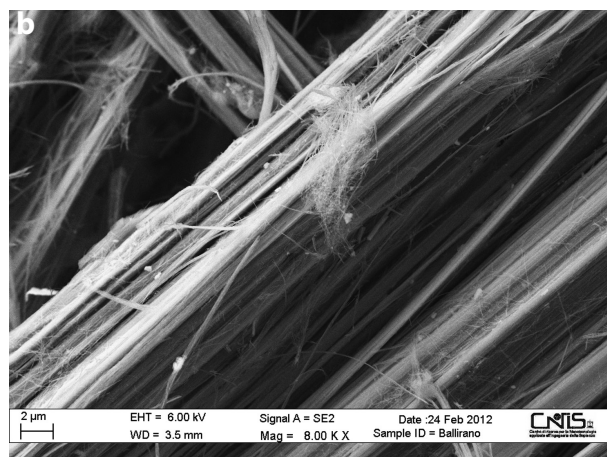
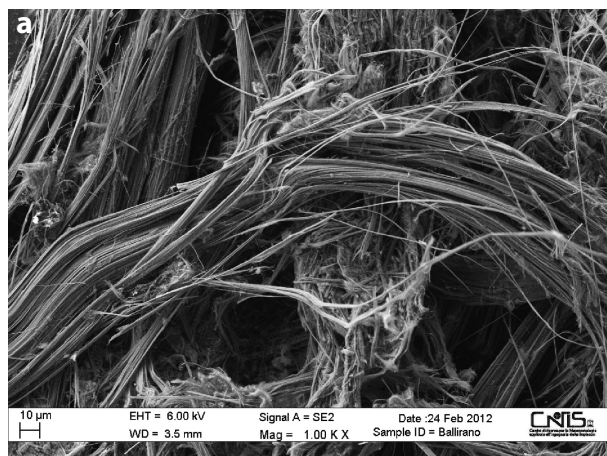


FIGURE 2. FESEM images of woolly erionite- Na . Bundles of fibers (a) and fibrils (b,c).

a sample classification as erionite- Na . The calculated $R = \text{Si}/(\text{Al}+\text{Si})$ ratio of 0.787 is identical to that found by Passaglia et al. (1998) for the erionite sample no. 25 from Durkee. The abundance of Na and the absence of Ca result in a very high $M/(M+D)$ ratio of 0.97 ($M = \text{Na}+\text{K}$; $D = \text{Ca}+\text{Mg}+\text{Mn}$). A similar value of $M/(M+D) = 0.95$, was previously found in only one of

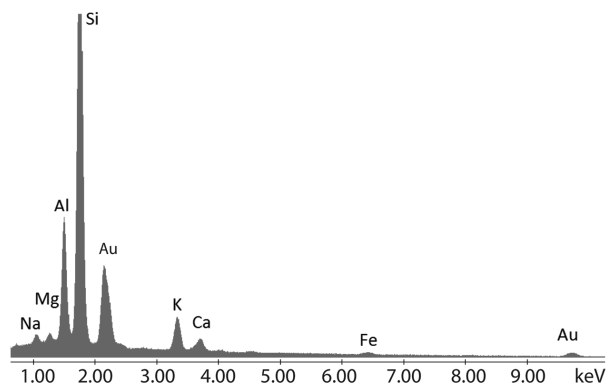


FIGURE 3. Preliminary SEM-EDX spectrum of bundles of erionite- Na . The S and Au peaks arise from the stub adhesive and the coating, respectively.

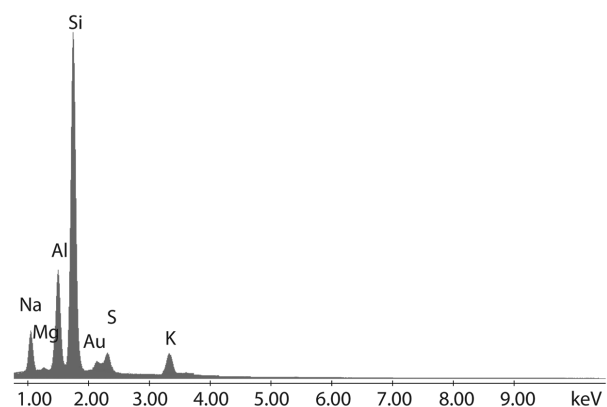


FIGURE 4. SEM-EDX spectrum of dispersed fibers of erionite- Na .

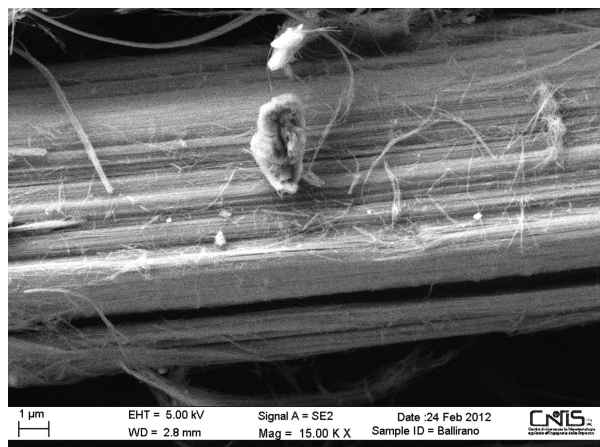


FIGURE 5. FESEM images of small particles associated with erionite- Na fibers.

the large set of 25 erionite samples analyzed by Passaglia et al. (1998) (sample no. 8 from Phillip Island, Australia). In fact, its chemical composition, in term of EF cations, is very close to that of the erionite investigated in this work, the exception being a higher K_2O content. Besides, sample no. 25 from Durkee has a chemical composition significantly different from that of the

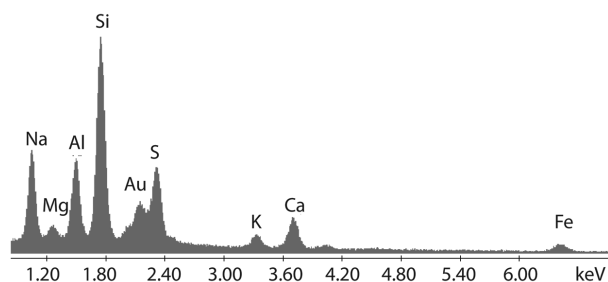


FIGURE 6. SEM-EDX spectrum of small particles occurring with erionite-Na fibers.

present sample, and as a result, it can be classified as erionite-Ca. Moreover, chemical data obtained in the present work differ from those previously obtained on woolly erionite samples by various authors (Eakle 1898; Staples and Gard 1959; Gude and Sheppard 1981). In particular, in the case of erionite-Na from Durkee the $\text{Si}/(\text{Al}+\text{Fe}^{3+})$ ratio is significantly larger (reference samples do not exceed 3.50 instead of 3.69 of the present sample) as well as the $\text{M}/(\text{M}+\text{D})$ ratio (less than 0.80 in reference samples: Sheppard and Gude 1969).

Structural refinement

Micro-structural parameters and framework. Cell parameters $a = 13.2356(5)$, $c = 15.0652(6)$ Å, and $V = 2285.6(2)$ Å³ are similar to those reported in Ballirano et al. (2009) for erionite-K from Rome, Oregon, as expected from the similar R value. A comparison with reference data of cell parameters of erionite samples from Durkee is reported in Table 4. A good agreement is observed with the data of Passaglia et al. (1998) for a sample characterized by an identical R value but a different EF cationic content. The cell parameters of Sheppard and Gude (1969) are systematically larger than those of both the present work and Passaglia et al. (1998). However, the c/a ratios are identical within 1σ.

From the refined anisotropic crystal shape parameters b_{11} and b_{33} , the principal ellipsoid radii $r_a = 15.5(2)$ nm and $r_c = 79(5)$ nm were computed using the relations $r_a = 1/(a \cos 30^\circ b_{11}^{0.5})$ and $r_c = 1/(c b_{33}^{0.5})$, leading to a r_c/r_a ratio of 5.1(9). Moreover a ϵ_0 micro-strain (lattice strain) of 0.200(7) was obtained (Ballirano and Sadun 2009). For comparison purposes, the refinement with unique average crystallite size gave spherical crystallites with radius $r = 30(1)$ nm and a ϵ_0 micro-strain of 0.207(12).

The r_a value is comparable with the diameter of a single fibril observed by FESEM. On the contrary, the coherency along the fiber axis is significantly shorter than the full length of the fibril. This is clearly an effect of the bending of the fibrils that reduces the coherence along the c -axis.

Fractional coordinates, isotropic displacement parameters, and site scattering (s.s.) are reported in Table 5, relevant bond distances and angles in Table 6, and bond valence analysis in Table 7. CIF data deposited on the MSA website.¹

¹ Deposit item AM-13-1105, CIF. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

The mean bond distances $\langle \text{T1-O} \rangle = 1.631$ Å and $\langle \text{T2-O} \rangle = 1.646$ Å clearly indicate a disordered Si/Al distribution ($\langle \text{T1-O} \rangle - \langle \text{T2-O} \rangle = -0.015$ Å) and the preferential partition of Al at the T2 site. The R ratio has been calculated by using both the Jones' determinative curves (Jones 1968) and the regression equation of Passaglia et al. (1998). The population of the two T1 ($\text{Al}_{4.21}\text{Si}_{19.79}$) and T2 ($\text{Al}_{3.26}\text{Si}_{8.74}$) sites, determined using the Jones' determinative curve, provides an R value of 0.793. On the other hand, an R value of 0.783 has been obtained using the regression equation of Passaglia et al. (1998). Both values are reasonably close with that of 0.787 obtained from chemical data. On the contrary, the corresponding mean bond distances $\langle \text{T1-O} \rangle = 1.630$ Å and $\langle \text{T2-O} \rangle = 1.705$ Å obtained from the isotropic crystallite shape refinement seem to indicate a very strong preference of Al for T2 ($\text{Al}_{7.80}\text{Si}_{4.20}$). However, the mean $\langle \text{T-O} \rangle$ bond distances result in an R value of 0.671, which is

TABLE 3. Results of quantitative SEM-EDX microanalyses of erionite from Durkee, Oregon

	1	2	3	Present work*
Morphology	woolly	woolly	acicular/prismatic	woolly
SiO ₂	57.16	57.40	58.35	58.74 (58.17–59.36)
Al ₂ O ₃	16.08	15.60	13.32	13.46 (13.19–13.83)
Fe ₂ O ₃	–	–	0.16	–
BaO	–	–	0.68	–
CaO	3.50	2.92	4.11	–
MgO	0.66	1.11	0.83	0.33 (0.14–0.54)
Na ₂ O	2.47	1.45	0.36	5.75 (4.78–6.44)
K ₂ O	3.51	3.40	2.72	3.22 (2.69–3.67)
TiO ₂	–	–	–	–
P ₂ O ₅	–	–	–	–
MnO	–	–	–	–
H ₂ O	17.30	17.58	19.47	18.50
Total	100.68	99.46	100.30	100.00
Unit-cell atomic content				
Si	27.04	27.27	28.31	28.34 (28.24–28.44)
Al	8.96	8.73	7.61	7.66 (7.56–7.76)
Fe ³⁺	–	–	0.06	–
Fe ²⁺	–	–	–	–
Ba	–	–	0.13	–
Ca	1.77	1.49	2.14	–
Mg	0.47	0.79	0.60	0.24 (0.10–0.38)
Na	2.27	1.34	0.34	5.38 (4.43–6.05)
K	2.12	2.06	1.68	1.98 (1.66–2.29)
O	71.95	71.60	72.16	72.09 (71.69–72.39)
H ₂ O	27.29	27.85	31.57	29.77
R	0.751	0.757	0.787	0.787 (0.784–0.790)
M/(M+D)	0.662	0.599	0.425	0.969
Na/M	0.517	0.333	0.168	0.731
E%	1.2	10.0	–0.9	–2.3
Species	–Na	–K	–Ca	–Na

Note: Chemical analyses of reference samples are reported for comparison.

* Mean values, from 16 analytical points renormalized hypothesizing a water content of 18.5 wt%.

1. Chemical analysis by Eakle (1898).

2. Chemical analysis by Staples and Gard (1959).

3. Chemical analysis of sample no. 25, by Passaglia et al. (1998).

TABLE 4. Comparison of cell parameters of erionite samples from Durkee

	1	2	present work
Morphology	woolly	acicular/prismatic	woolly
a (Å)	13.254(6)	13.233(1)	13.2357(5)
c (Å)	15.100(10)	15.055(4)	15.0652(6)
V (Å ³)	2297(3)	2283.1(6)	2285.6(2)
c/a	1.1393(12)	1.1377(4)	1.1382(1)
Species	–Na	–Ca	–Na

Notes: 1. Sheppard and Gude (1969) recalculated from the original d -spacings of Staples and Gard (1959).

2. Passaglia et al. (1998): sample no. 25.

TABLE 5. Fractional coordinates, isotropic displacement parameters, site multiplicity and occupancy, and site scattering (s.s.) of erionite-Na (Si, Al site partition from Jones' 1968 determinative curves)

Site	Site mult.	x	y	z	B_{iso} (Å ²)	Site occ.	s.s. (e ⁻)	Proposed site partition	s.s. (e ⁻) from site partition
Framework									
T1	24	0.2331(3)	0.0001(4)	0.10454(16)	0.88(5)	1		Si _{19.75} Al _{4.21}	
T2	12	0.0958(4)	0.4246(5)	¼	0.88(5)	1		Si _{8.74} Al _{3.26}	
O1	24	0.3483(5)	0.0239(5)	0.6604(5)	1.34(13)	1			
O2	12	0.1005(4)	2x	0.1269(7)	1.34(13)	1			
O3	12	0.1270(3)	2x	0.6402(8)	1.39(19)	1			
O4	12	0.2634(6)	0	0	1.34(13)	1			
O5	6	0.2307(6)	2x	¼	1.39(19)	1			
O6	6	0.4616(7)	2x	¼	1.39(19)	1			
EF cations									
Ca1	4	½	2/3	0.924(16)	12.3(13)	0.112(29)	5.4(14)	Mg _{0.24}	2.9
Ca2	4	½	2/3	0.0893(15)	12.3(13)	0.806(23)	35.5(10)	Na _{3.48}	38.3
Ca3	4	½	2/3	0.7068(28)	12.3(13)	0.44(3)	19.4(14)	Na _{1.90}	20.9
K1	2	0	0	¼	2.63(24)	1	38	K _{1.99}	37.8
						$\Sigma_{cat.}$	98(4)		99.9
Water molecules									
OW7	6	0.2375(14)	2x	¾	5.0(3)	0.641(22)	30.8(11)		
OW8	12	0.2565(18)	2x	0.9674(28)	9.9(6)	0.404(17)	38.8(16)		
OW9	12	0.498(5)	2x	0.950(4)	9.9(6)	0.239(18)	22.9(17)		
OW10	12	0.4365(13)	2x	0.6601(16)	9.9(6)	0.565(15)	54.2(14)		
OW11	12	0.2707(26)	2x	0.647(4)	9.9(6)	0.363(24)	34.8(23)		
OW12	12	0.4365(13)	2x	0.050(17)	9.9(6)	0.704(23)	67.6(22)		
						Σ_{water}	249(10)		

TABLE 6. Relevant bond distances (Å) and angles (°) of erionite-Na from Durkee, Oregon

T1-O2	1.622(5)	O1-T1-O2	109.7(5)
T1-O4	1.625(3)	O1-T1-O3	105.5(4)
T1-O1	1.629(9)	O1-T1-O4	107.0(5)
T1-O3	1.649(7)	O2-T1-O3	109.2(5)
<T1-O>	1.631	O2-T1-O4	111.5(4)
		O3-T1-O4	113.6(5)
T2-O5	1.598(7)	O1-T2-O1	107.9(5)
T2-O6	1.647(8)	O1-T2-O5 x2	113.4(5)
T2-O1 x2	1.670(7)	O1-T2-O6 x2	104.6(5)
<T2-O>	1.646	O5-T2-O6	112.3(7)
T1-O1-T2	140.3(6)	T1-O4-T1	151.4(6)
T2-O2-T1	144.2(7)	T2-O5-T2	149.4(11)
T1-O3-T1	138.2(8)	T2-O6-T2	164.8(11)
K1-O2 x6	2.957(10)		
K1-O3 x6	3.348(9)		
Ca1-OW11x3	1.79(16)	Ca1-Ca3	1.97(24)
Ca1-OW8 x3	1.88(9)	Ca1-Ca2	2.49(24)
Ca1-OW12 x3	2.66(12)	OW8-OW11	1.75(7)
Ca1-OW10 x3	2.68(12)		
Ca2-OW8 x3	2.54(4)		
Ca2-OW12	2.68(3)		
Ca2-O5 x3	3.376(19)		
Ca3-OW11x3	1.70(6)	Ca3-Ca3	1.30(8)
Ca3-OW7 x3	2.29(3)	OW7-OW11	1.73(6)
Ca3-OW10 x3	2.47(3)		
Ca3-OW11 x3	2.64(7)		
Ca3-OW10 x3	3.10(4)		
Ca3-OW8 x3	3.16(5)		
		OW9-OW9	1.51(13)
		OW9-OW12	1.63(10)
		OW9-OW12	1.66(10)

Note: In italic never occurring short distances.

unsupported by both chemical and unit-cell volume data. This result can be rationalized considering the detrimental effects of an imperfect peak-shape modeling on the accuracy of the structural parameters determination. Therefore, an effort has to be made to adequately model the anisotropic broadening of diffraction maxima to extract reliable structural information from fibrous samples.

TABLE 7. Bond valence analysis (v.u.) following Breese and O'Keeffe (1991)

	K	Na	Mg
K1-O2 x6	0.107 x6		
K1-O3 x6	0.037 x6		
Σ	0.864		
Ca1-OW8 x3			0.607 x3
Ca1-OW10 x3			0.069 x3
Σ			2.028
Ca2-OW8 x3		0.134 x3	
Ca2-OW12 x3		0.092 x3	
Ca2-O5 x3		0.014 x3	
Σ		0.720	
Ca3-OW10 x3		0.164 x3	
Ca3-OW11 x3		0.105 x3	
Ca3-OW10 x3		0.030 x3	
Σ		0.897	

Extraframework cations. Chemical data indicate a total site scattering (s.s.) of 99.9 e⁻ for the EF cations. This value is in reasonable agreement with the s.s. of 98(4) e⁻ obtained from the Rietveld refinement (Table 5). Similarly, a total of 31.2(13) water molecules pfu has been obtained from the refinement, in good agreement with reference data (Coombs et al. 1997; Ballirano et al. 2009). Notably, the s.s. value of 100(5) e⁻ and 42(5) water molecules pfu, obtained with the isotropic crystallite shape model, confirms the fundamental role played by an accurate fitting of the peak shape for extracting reliable structural parameters.

The K atom lies at the K1 site located at the center of the cancrinite cage. The fully occupied site is 12-fold coordinated by six O2 atoms and six O3 atoms at 2.957(10) Å and 3.348(9) Å, respectively (Table 6). For this site, bond valence analysis, performed using the parameters of Breese and O'Keeffe (1991), results in 0.86 valence units (v.u.) (Table 7). This site does not provide a favorable coordination for Na as indicated by bond valence analysis (0.36 v.u.). Therefore, reported values of less than 2 K apfu indicate a partly vacant K1 site or, more plausibly, an inaccurate chemical analysis. Attempts to detect the occurrence of electron density at the K2 site, located at the center of the boat-shaped 8-member rings (8MR) forming the walls of the erionite cage, failed. As reported in Ballirano et al. (2009),

this site corresponds to that found by Schlenker et al. (1977) in dehydrated erionite and to the site labeled as Ca4 by Gualtieri et al. (1998) in two erionite samples. It has been shown that the K2 site provides a very favorable coordination for K atoms at room temperature. However, in our case the available K is entirely located within the cancrinite cages and, as a consequence of this, the K2 site is empty. The remaining EF cationic sites (Ca1, Ca2, and Ca3) are located at $(1/3, 2/3, z)$, along the threefold axis (see Figs. 7–9). These sites were refined using the Mg scattering factor for the Ca1 site and the Na scattering factor for the Ca2 and Ca3 sites, following the same approach adopted by Ballirano et al. (2009) for erionite-K from Rome. Atomic fractional coordinates and displacement parameters are reported in Table 4. Values are in good agreement with those reported for erionite-K from Rome in Ballirano et al. (2009), and those reported for erionite-Ca from Tunguska (Russia) by Alberti et al. (1997). Differences in both s.s. and population of the EF cationic sites are clearly related to the different chemical composition. The Ca1 site has a very low s.s. of $5.4(14) \text{ e}^-$ and the associated high standard deviation of bond and contact distances render a meaningful discussion about its coordination and site assignment difficult. However, a fairly regular sixfold coordination [$\text{Ca1-OW8} \times 3$ at $1.88(9) \text{ \AA}$ and $\text{Ca1-OW10} \times 3$ at $2.68(12) \text{ \AA}$] well fitting the occurrence of Mg (Table 6) has been identified. This assignment is confirmed by a bond-valence sum of 2.03 v.u. The value of 0.24 apfu obtained from chemical analysis for Mg corresponds to a s.s. value of 2.9 e^- . It is worth noting that, this value is in reasonable agreement with the results obtained from the structural refinement, under the hypothesis that all Mg content is located at Ca1, as in the case of erionite-K (Ballirano et al. 2009). However, the coordination of Mg is different in erionite-Na and -K as both Ca1 and Ca2 sites in erionite-K are slightly displaced off-axis, and the OW9 water molecule site is significantly displaced in erionite-Na as compared to both erionite-K and -Ca (Alberti et al. 1997). Therefore, Na is located at both Ca2 and Ca3 sites. The Ca2 site has the largest s.s. value [$35.5(10) \text{ e}^-$] among the three EF cationic sites located within the erionite cage. It is characterized by a ninefold coordination [$\text{Ca2-OW8} \times 3$ at $2.54(4) \text{ \AA}$, $\text{Ca2-OW12} \times 3$ at $2.68(3) \text{ \AA}$, and $\text{Ca2-O5} \times 3$ at $3.376(19) \text{ \AA}$] leading to a bond-valence sum of 0.72 v.u. The Ca3 site, not occurring in erionite-K, is at bonding distance with OW7, OW10, and OW11 sites. However, according to the bond-valence analysis and taking into account the short non occurring contact OW7-OW11 [$1.73(6) \text{ \AA}$], a ninefold coordination may be proposed, consisting of $\text{Ca3-OW10} \times 3$ at $2.47(3) \text{ \AA}$, $\text{Ca3-OW11} \times 3$ at $2.64(7) \text{ \AA}$, and $\text{Ca3-OW10} \times 3$ at $3.10(4) \text{ \AA}$, leading to a bond valence sum of 0.90 v.u.

Concerning the water molecule positions, the most relevant difference with respect to Rome and Tunguska erionite samples is related to the displacement of OW9 (from $x \sim 0.44$, $y = 2x$; $z = \sim 0.92$ to $x \sim 0.50$, $y = 2x$; $z = \sim 0.95$).

Water molecules site scattering of erionite-K and -Na are similar, a part for an inversion between neighboring OW8 and OW9 sites.

On the contrary, differences are very significant with respect to erionite-Ca (Alberti et al. 1997). Besides, in the case of the present erionite-Na sample, OW9 is linked exclusively to framework oxygen atoms and other H_2O molecules different from OW8, OW11, and OW12 of erionite-K (Ballirano et al. 2009).

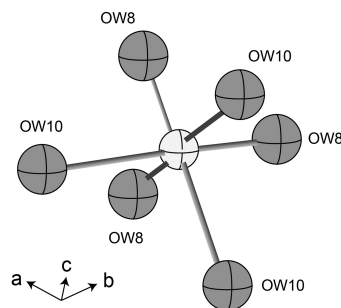


FIGURE 7. Ca1 site coordination (CrystalMaker 8.7; CrystalMaker Software 2012).

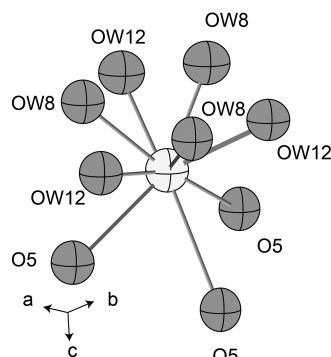


FIGURE 8. Ca2 site coordination (CrystalMaker 8.7; CrystalMaker Software 2012).

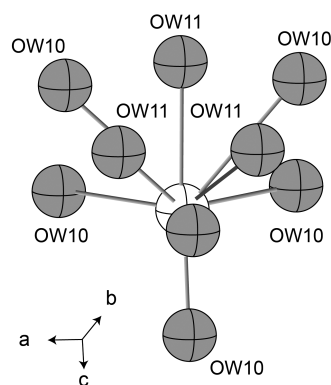


FIGURE 9. Ca3 site coordination (CrystalMaker 8.7; CrystalMaker Software 2012).

ENVIRONMENTAL AND HEALTH RELEVANCE

Although previous investigations have reported the presence of a variable Fe and Ca content in erionite samples from Durkee, our results revealed the absence of both these elements. In particular, the absence of Fe, confirming the findings of Ballirano et al. (2009) for erionite-K from Rome, is of significant interest because it is well known from amphibole asbestos that Fe has been claimed to be one of the causes of carcinogenesis by participating in Fenton chemistry and producing free radicals

(e.g., Kane et al. 1996; Fubini and Otero Aréan 1999; Kamp and Weitzman 1999; Robledo and Mossman 1999). Notably, it was proposed that, in addition to the presence of Fe, the ion exchange properties of erionite could play a primary role in its toxicity (Eborn and Aust 1995). In fact, cations may be readily exchanged whenever a zeolite is in contact with human body fluids. It is worth noting that Ballirano and Cametti (2012) have shown that Mg in Ca1 is the most mobile cation during heating of erionite-K, despite its large ionic potential. Notably, results of in vitro experiments on amphibole asbestos revealed that the release of Mg^{2+} can have different effects on lipid packing, membrane permeability, and can counteract Ca^{2+} uptake by blocking the calcium uniporter (Bergamini et al. 2007; Pacella et al. 2012). Further studies are in progress on the erionite sample studied here, concerning the exchange properties of erionite in contact with a physiological solution and the reactivity (detection of oxy-radicals and monitoring of lipid peroxidation). The combined approach consisting of the full characterization of the fibrous erionite coupled with the cation exchange properties and reactivity studies is very promising to shed new light on the role of the ion exchange in the interaction between fibers and organic environment. The possible role of erionite as a carrier within the human body for nanoscale iron-bearing materials also needs to be carefully investigated.

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