

Quantitative chemical analysis of erionite fibres using a micro-analytical SEM-EDX method

ALESSANDRO PACELLA^{1,*}, PAOLO BALLIRANO^{1,2} and GEORGIA CAMETTI^{1,3}

¹ Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185 Roma, Italy

*Corresponding author, e-mail: alessandro.pacella@uniroma1.it

² Laboratorio Rettoriale Fibre e Particolato Inorganico, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185 Roma, Italy

³ Institut für Geologie, Universität Bern, Freiestraße 3, 3012 Bern, Switzerland

Abstract: The quantitative chemical composition of a sample of erionite-Na from Rome, Oregon (USA) was retrieved by SEM-EDX standardless analysis. The analysed fibres have a diameter commonly smaller than 3 μm , *i.e.* those more easily inhalable, therefore representing a typical case encountered during environmental investigations. The claimed dependence of the toxicity and biological activity of the fibres to their crystal chemical features renders the reliable chemical characterization of paramount importance. To reduce the errors induced by particle size/morphology effects, an empirical procedure was adopted. In particular, correction factors were calculated for each oxide as a function of the particle diameter using shards of zeolites and feldspatoids of known bulk composition. Those correction factors have to be considered as sample specific. Experimental conditions were optimised in order to minimize the effect of alkali metal migration. Results indicate that particle effects cause on the oxide concentrations a relative underestimation of Al_2O_3 and K_2O by up to *ca.* 10 %, whereas Na_2O is overestimated by up to *ca.* 15 %. Moreover, the SiO_2 concentration is independent from dimension even in the case of very small particles. Finally, comparison between electron-microprobe and SEM-EDX bulk analyses of crystals pointed out a relative underestimation of Na, K, (of *ca.* 10–15 %) and Ca (of *ca.* 5 %) for the SEM data, in good agreement with reference structural investigations.

Key-words: SEM-EDX quantitative chemical analysis; erionite; fibres; particle effects; correction factors; alkali migration.

Introduction

Scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX) is a technique extensively used to characterize both morphology and chemical composition of mineral fibres, their size being generally too small for electron-microprobe (EMP) characterization (Gunter *et al.*, 2003; Meeker *et al.*, 2003; Bruni *et al.*, 2006; Gianfagna *et al.*, 2007; Mazziotti-Tagliani *et al.*, 2009). Nonetheless, SEM-EDX is commonly used to perform qualitative or semi-quantitative analysis of sub-micrometric particles and fibres, as a reliable quantification is not straightforward. In fact, the limited dimensions and irregular shape significantly modify the intensity of the characteristic X-rays generated by the sample, resulting in analyses affected by large errors whenever the ZAF or $\rho\phi z$ routine correction procedures are solely used. In particular, two problems affect the analysis of fibrous samples and sub-micrometric particles: the absent mass and the reduced absorption (Armstrong & Buseck, 1975; Small, 2002). The first effect causes a loss of X-rays intensity generated by the

sample as the particle size is smaller than the range of the primary electron beam and a significant fraction of the incident beam escapes from the particle before exciting the emission of X-rays. Therefore, the correction of the intensity of the characteristic X-ray lines by the Z factor in the ZAF correction procedure is not appropriate as in the case of a massive sample, which is assumed to be infinitely thick with respect to the penetration of the electron beam. The absent-mass effect is strongly influenced by the average atomic number of the particle. The second effect is due to the irregular shape and/or limited size of the fibre/particle affecting both the length of the X-ray absorption path within the particle and the X-ray take-off angle. In this case the X-ray take-off angle cannot be predicted from simple geometry, the absorption path length becoming unknown. The magnitude of the reduced X-ray absorption effect is largest in the case of the “soft” X-rays generated by light elements. Many efforts have been devoted to develop comprehensive correction algorithms and methods to minimize these effects in order to obtain reliable quantitative SEM-EDX analyses of micrometre-sized particles (Cliff &

Lorimer, 1975; Armstrong, 1991; Laskin & Cowin, 2001; Small, 2002; Ro *et al.*, 2003). Concerning the analysis of fibres, Paoletti *et al.* (2008, 2011) developed an empirical procedure for performing quantitative analysis by SEM-EDX of amphiboles fibres of environmental and health interest. Those authors determined the errors on the elemental concentration due to both the absent-mass and the reduced-absorption effects using shards of amphibole and pyroxene crystals whose composition was previously determined by EMP analysis. Correction factors as a function of fragments size were calculated for each elemental concentration and therefore applied to the analysis of the amphibole fibres. Notably, the error estimated on the element quantification was 3 % relative for light elements and below 2 % relative for heavy elements.

As in the case of amphibole fibres, the quantitative chemical composition of zeolites characterised by a fibrous morphology is of paramount relevance since their health relevance. In fact, the exposure of humans to erionite, a fibrous mineral belonging to the zeolite group (*e.g.* Gottardi & Galli, 1985; Armbruster & Gunter, 2001), has been linked to pulmonary diseases, mainly malignant mesothelioma (Baris *et al.*, 1978; Carbone *et al.*, 2011; Ryan *et al.*, 2011). As pointed out by Ballirano & Cametti (2015) and Ballirano *et al.* (2015), in spite of its environmental and health relevance, the mineralogy and crystal chemistry of erionite fibres have not been always properly addressed due to the micro-analytical difficulties above mentioned. In addition, most studies, focused on chemical reactivity and cell toxicity (*e.g.* Eborn & Aust, 1995; Long *et al.*, 1997), lack the detailed crystal-chemical characterization of the investigated samples. It is well known that interactions between fibrous material and biological environment are strongly dependent on both the geometry and the crystal chemistry of mineral fibres (Fubini, 1993). Therefore, the quantitative chemical analysis of erionite represents a fundamental step to understand the relationship among chemical features and biological activity of this mineral.

In the present work, the dependence of the SEM-EDX analysis on the dimension of the fragments of framework silicates was evaluated and quantified adopting the same empirical procedure reported by Paoletti *et al.* (2008, 2011). For this purpose, shards of zeolites and feldspathoids of different composition were used as a standard. In addition, we investigated the effect of the alkali metals migration during microanalysis of zeolite samples in order to minimize it during data collection. The resulting correction factors were employed to retrieve the quantitative composition of a sample of erionite from Rome (USA), which has been consistently used for chemical/biological activity experiments. An estimation of the accuracy of the chemical data from SEM is finally deduced by comparison with both EMPA and reference structure refinements. Analyses were carried out using a conventional SEM-EDX instrument and adopting the standard procedures commonly followed for environmental investigations.

Materials and methods

Samples description

In this work zeolite shards of two samples of prismatic zeolites (natrolite, ideally $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}] \cdot 16\text{H}_2\text{O}$, and scolecite, ideally $\text{Ca}_4[\text{Al}_8\text{Si}_{12}\text{O}_{40}] \cdot 12\text{H}_2\text{O}$) and two samples of feldspathoids (leucite, ideally $\text{K}_{16}[\text{Al}_{16}\text{Si}_{32}\text{O}_{96}]$, and nepheline, ideally $\text{Na}_6\text{K}_2[\text{Al}_8\text{Si}_8\text{O}_{32}]$) were analysed. The zeolite samples, natrolite MC11 and scolecite NK10, are both from the Lessini Mountains, Veneto (Italy). Leucite and nepheline, both picked from sample MMUR 7652/39, are from Mount Somma, Campania, (Italy) and were kindly provided by the Museo di Mineralogia of the University of Roma “La Sapienza”.

Each crystal was ground in an agate mortar under acetone to obtain fragments. For SEM-EDX analysis, the fragments were dispersed in double-distilled water and mounted on an aluminium stub with a standard double adhesive carbon tape (AGAR Leit), and then coated with carbon. The particle size was evaluated by measuring the mean diameter after SEM calibration by a standard device, and ranged from 0.5 to 8.0 μm , with the uncertainty determined as $\pm 0.02 \mu\text{m}$. For EMP analysis, a suitable fragment of each sample was embedded in epoxy, polished and carbon-coated.

The erionite-Na fibres from Rome analysed in the present work have been recently characterised by X-ray powder diffraction (XRPD) and SEM-EDX by Ballirano & Cametti (2015). This sample is chemically different with respect to that described by Ballirano *et al.* (2009). In fact, the latter has been classified as erionite-K on the basis of combined inductively coupled plasma-mass spectrometry (ICP-MS), thermogravimetric analysis (TGA) and subsequent subtraction from the chemical analysis of the TiO_2 and Fe_2O_3 content attributed to impurities. Structure refinements of erionite-Na and -K indicate a different extra-framework sites population consistent with a different chemical composition of the two samples.

SEM-EDX and EMP analytical conditions

The chemical composition of the prismatic samples (bulk composition) as well as of their fragments (so-called apparent composition) was obtained by SEM-EDX using a FEI Quanta 400 SEM equipped with EDX Genesis EDS system. Operating conditions were: 15 kV accelerating voltage, 11 mm working distance, 0° tilt angle, 1 μm beam diameter. At least 30 fragments were analysed for each sample. The analysis of fragments was carried out only on isolated particles in order to avoid possible contributions from the adjacent ones. For each oxide, the apparent concentration was obtained from the net peak intensity of the acquired spectra, by using the ordinary ZAF procedure. In detail, the protocol of data reduction was as follow: the contribution of the background (Bremsstrahlung X-rays) was subtracted from the counts of each characteristic peaks by the software. Therefore, the

concentration of each element was calculated using the following equation: $\text{wt.\%}_{\text{elem.}} = K \cdot [\text{ZAF}] \cdot 100$, where $K = I_{\text{elem.}}/I_{\text{std.}}$. The $I_{\text{std.}}$ values were calculated by the analytical software (EDAX Genesis 3.6: EDAX, 2003), as a standardless approach was adopted. Oxygen was calculated by stoichiometry.

The possible contribution arising from the tape was investigated and proved to mainly consist of C with traces of O, Na, and S (Supplementary Fig. S1, freely available online as Supplementary Material linked to this article on the GSW website of the journal: <http://eurjmin.geoscienceworld.org/>). In addition, no contribution from the Al stub was detected. It is worth noting that the area of the Na and S fluorescence lines are very similar.

In order to evaluate the quality of SEM-EDX data we performed a comparison with EMPA, using suitable fragments of the samples as a standard. The EMP chemical composition of each sample was determined using a Cameca SX-50 equipped with five wavelength-dispersive spectrometers. The samples were analysed under the following conditions: 15 kV accelerating voltage, 15 nA specimen current, 15 μm beam diameter (current density *ca.* 0.08 nA/ μm^2), 20 s peak counting time, and 10 s background counting time. The following standards were used: wollastonite (Si $K\alpha$, Ca $K\alpha$), corundum (Al $K\alpha$), orthoclase (K $K\alpha$), and jadeite (Na $K\alpha$). Those experimental conditions follow the suggestion of Morgan & London (2005) for the analysis of alkali aluminosilicate glasses, which are severely affected by Na loss. It is widely recognized that in certain minerals such as zeolites and in silicate glasses, alkali metals (particularly Na) can diffuse out or into the analysed volume during electron microanalysis (Sweatman & Long, 1969; Goldstein *et al.*, 1992; Reed, 1993). This effect depends on various factors, including SiO_2 and H_2O content of the analysed material and the dissipation of the beam energy around the excitation volume (Spray & Rae, 1995). As a consequence, collection of reliable analytical data for the micro-chemical characterization of zeolites is a difficult task. In order to minimize the effect of alkali metal migration, the use of a defocused beam or raster scan-mode and a short counting time are recommended (Spray & Rae, 1995). However, the reduced dimensions of fibres and sub-micrometric particles render unsuitable the use of a large beam. In contrast, a reduction of the counting-time may be attained thanks to the efficiency of modern Si(Li) detector in the EDX system (Spray & Rae, 1995). To define the best compromise between reduced counting time and adequate statistics of SEM-EDX data, the natrolite sample was analysed using three different counting times (10, 30, and 60 s).

Results

The SEM-EDX chemical analyses performed on the natrolite sample, using different counting times (Table 1), indicate a significant and almost linear decrease of the Na_2O content (up to 25 % relative) as the counting time is

Table 1. Dependence of the bulk composition and crystal-chemical formula of natrolite on the counting time as determined by SEM-EDX. Oxide data are normalized to 100 wt.% and compared to EMP analysis. The ideal $\text{Na}_2[\text{Al}_2\text{Si}_3\text{O}_{10}]$ composition is also reported. For each oxide, standard deviations are shown in brackets. Crystal chemical (anhydrous) formulae were calculated on the basis of 5 (Si + Al).

	SEM-EDX			EMPA	Ideal
	10 s	30 s	60 s		
SiO_2	54.9(4)	56.0(8)	57.4(6)	53.0(2)	52.37
Al_2O_3	29.3(4)	29.6(2)	30.3(2)	29.3(1)	29.62
Na_2O	15.8(4)	14.4(8)	12.3(7)	17.7(1)	18.01
Total	100.00	100.00	100.00	100.00	100.00
Si	3.07	3.08	3.09	3.03	3.00
Al	1.93	1.92	1.91	1.97	2.00
Na	1.71	1.54	1.28	1.97	2.00
O	9.89	9.81	9.68	10.00	10.00

increased (Fig. 1), at least within the investigated range. The comparison with EMPA highlighted that the reduction of the counting time to 10 s provides the most accurate SEM-EDX chemical characterization of the samples. Counting times shorter than 10 s, albeit desirable, were tested but discarded due to inadequate statistics. Therefore, all EDX spectra were collected using 10 s of counting time. Nevertheless, Na_2O content from SEM-EDX, under the best present experimental conditions, is underestimated of *ca.* 10 % with respect to EMPA. Figure 2 shows the apparent concentration/bulk concentration ratios for each oxide as a function of the fragment size (μm). It must be pointed out that, except for CaO , the investigated samples provided highly comparable results, showing a substantial independence of the error of the oxide concentration in the analysis of fragments (so-called matrix effect) on their chemical composition. Paoletti *et al.* (2011) ruled out the dependence of the correction factors on matrix effect in the

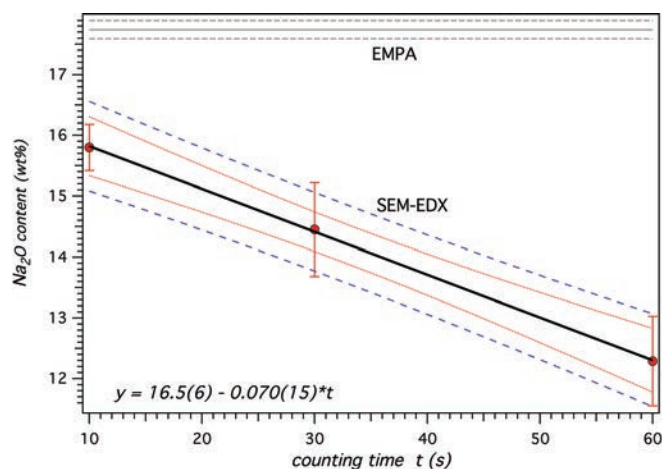


Fig. 1. Variation of the Na_2O content (wt.%) as a function of counting time (10, 30, and 60 s) in the natrolite sample. The Na_2O content determined from EMPA is also reported for reference. Red dotted and blue dashed lines represent the 95 % confidence and 95 % prediction bands, respectively. (online version in colour)

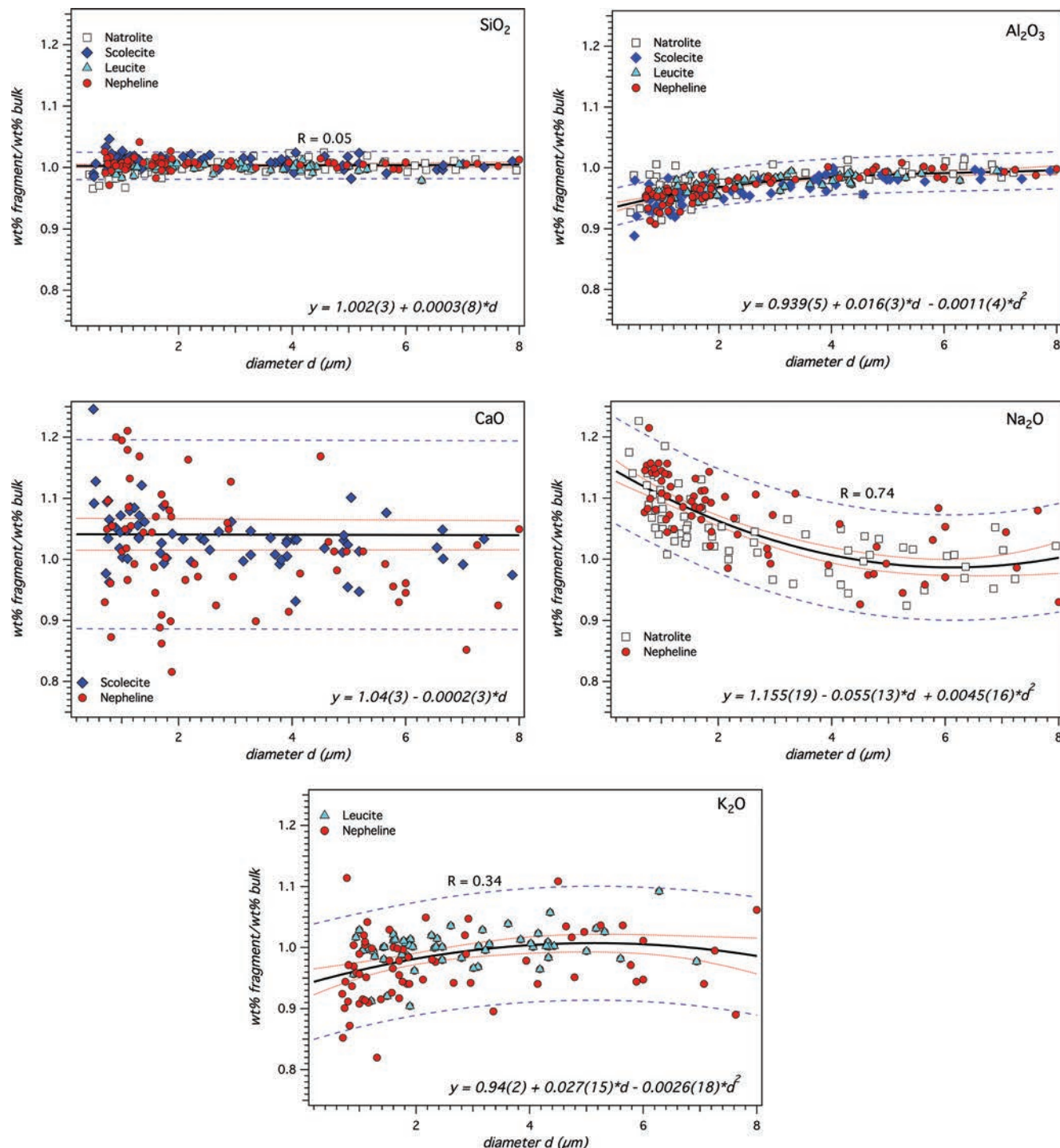


Fig. 2. Dependence of the apparent concentration/bulk concentration ratio on fragment size for each oxide of the investigated samples. Red dotted and blue dashed lines represent the 95 % confidence and 95 % prediction bands, respectively. (online version in colour)

analysis of amphibole and pyroxene fragments. The most striking behaviour observed is that the ratio values of Al_2O_3 , Na_2O and K_2O show fairly marked deviations from unity (*i.e.* apparent concentration corresponding to that of the bulk) for particles with diameter smaller than $3 \mu\text{m}$ (Fig. 2).

Based on such results, general trends between apparent oxide concentrations and particle size have been devised.

In detail, the apparent concentration of Al_2O_3 is underestimated with respect to that of bulk (ratios < 1) as the fragments size decreases. The relative deviation with respect to bulk compositions is of the order of 10 % for the smallest particles (below $1 \mu\text{m}$). Conversely, the Na_2O content has an opposite behaviour, being overestimated (ratios > 1) by *ca.* 15 % with respect to the bulk in the case of the smallest particles. Results concerning Na_2O are

in agreement with those previously obtained by Paoletti *et al.* (2008, 2011), who showed that Na is significantly overestimated in the analysis of particles of amphibole and pyroxene. On this basis, those authors suggested that the reduced-absorption effect prevails for Na. Nevertheless, in the analysis of particles with very limited size ($<0.5 \mu\text{m}$, therefore not considered in the present work) and reduced thickness, the contribution of C-tape to the apparent concentration of Na (and therefore Na_2O) could be significant, particularly for samples with low Na concentrations. Because of comparable X-ray ranges for both Na and S (*ca.* $2.4 \mu\text{m}$ and $2.0 \mu\text{m}$, respectively), calculated from the expression of Andersen & Hasler (1966)

$$R_X = \frac{0.064(E_0^{1.68} - E_c^{1.68})}{r} \quad (E_0 = \text{electron accelerating voltage; } E_c = \text{critical excitation voltage for the fluorescence line; } r = \text{density of the sample}),$$

it is expected that the area of the fluorescence line of Na arising from the C-tape is similar to that of S as in the case of the C-tape alone. Therefore, in this particular case, the contribution of Na arising from the C-tape may be as high as *ca.* 50 % of the total (Supplementary Fig. S2).

The K_2O content shows a behaviour similar to that reported for Al_2O_3 , partly masked by data scattering. Results obtained for K_2O using a standard sample with low K_2O content (nepheline), although significantly spread out, are in agreement with those of the sample with higher K_2O content (leucite). For SiO_2 , values are scattered around 1 and therefore its apparent concentration is comparable with that of the bulk even in the case of particles of small dimensions (Fig. 2). Results obtained on CaO showed values of the apparent concentration overestimated (up to *ca.* 25 %) with respect to that of the bulk of the scolecite sample for fragments smaller than $2 \mu\text{m}$. However, no trend was highlighted using the nepheline sample as a standard, the ratios being scattered around the value of 1 in the whole range of the analysed particle size. This discrepancy could be related to matrix effect, according to the significant differences in the chemical composition between the two samples used as a standard (Table 2). The dependence of the CaO content on fibres dimension has been investigated, despite the fact that erionite-Na from Rome does not contain Ca (Ballirano & Cametti, 2015). This approach is justified by the opportunity to derive useful data to be possibly exploited for the analysis of Ca-containing erionite fibres, such as those found in the neighbouring locality of Durkee, Oregon (Ballirano *et al.*, 2015). To render those observations quantitative, data reported in the various scatter-plots were fitted with lines (SiO_2) or second-degree polynomials (Al_2O_3 , K_2O and Na_2O). The linear fitting of CaO produced unreliable results due to the significant scattering of the data. Despite the moderate data scattering, SiO_2 content is within 1σ independent on fragment dimension as indicated by the regression line: $\text{wt.}\% \text{ fragment/wt.}\% \text{ bulk} = 1.002(3) + 0.0003(8) \times \text{diameter} (\mu\text{m})$. Differently, Al_2O_3 and K_2O were fitted with polynomials that are described by the same coefficients at the 1σ level. The physical meaning of the various polynomial fits is virtually

Table 2. Chemical composition (wt.%) obtained by SEM-EDX of the erionite fibres from Rome, compared to data from Ballirano & Cametti (2015). The crystal-chemical formula was calculated fixing the water content to 18.5 wt.%. The site scattering of the extra-framework cations is reported as $\sum_{\text{cat}} \text{s.s. (e}^-)$. Standard deviations are shown in brackets.

	B&C (2015)*	This work
SiO_2	72.9(16)	73.7(6)
Al_2O_3	16.0(9)	15.7(2)
Na_2O	5.7(10)	4.9(3)
K_2O	4.4(5)	4.9(5)
MgO	0.9(4)	0.7(3)
Total	100.00	100.00
Si	28.60(46)	28.76(11)
Al	7.40(46)	7.24(11)
Na	4.36(80)	3.75(27)
K	2.23(21)	2.45(27)
Mg	0.53(17)	0.42(17)
O	72.11(13)	72.10(14)
H_2O	29.69	29.60(17)
E%	-2.8	3.1
R	0.794(15)	0.799(3)
M/(M + D)	0.926(31)	0.936(27)
$\sum_{\text{cat}} \text{s.s. (e}^-)$	97(19)	93(6)

Note: *Data from Ballirano & Cametti (2015).

impossible to unravel, due to the constraint of a 100 wt.% sum of the oxides. Therefore, the increase of the apparent concentration of a particular oxide has to be counterbalanced by a decrease of the apparent concentration of one or more oxide. According to our data, the SiO_2 apparent concentration is substantially unaffected. The low values of the correlation coefficient R obtained for the regression curves of both SiO_2 and K_2O indicate a significant dispersion of data around the average trend. As reported in Paoletti *et al.* (2008, 2011), this dispersion may be due to: 1) the irregular geometry (shape and orientation) of the crystal shards, which causes a random take-off angle of X-rays from the particle, and therefore a random effect on the intensity of the peaks; 2) the uncertainty related to the measurement of the fragment size; 3) the compositional variability of the fragments.

Discussion

The EDX spectra of the erionite fibres revealed the occurrence of Na, K, and Mg as extra-framework (EF) cations (Fig. 3). In the case of small fibres ($0.5 < d < 0.7 \mu\text{m}$) the contribution of Na from C-tape may be estimated to be of $<2 \%$. Fibres were analysed using the same experimental conditions adopted for the analysis of bulk and fragmented samples. The SEM-EDX analyses were focused on fibres smaller than $3.0 \mu\text{m}$, *i.e.* those that are more easily inhalable. It should be pointed out that, in spite of the relatively short counting time used (10 s), several fibres were found to be unstable under the electron beam and, as a rule of thumb, it was impossible to analyse those with a diameter

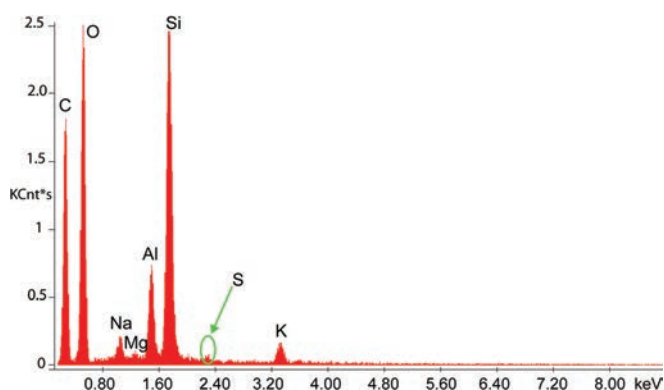


Fig. 3. SEM-EDX spectrum of an erionite fibre (0.6 μm) from Rome, Oregon (USA) showing the presence of Na, K, and Mg as extra-framework cations. Notably, the contribution to the spectrum by the C-tape is detectable from the presence of the *very* weak S fluorescence line (circled and arrowed peak). (online version in colour)

smaller than 0.5 μm . Besides, the increase of the counting time to 30 s caused a reduction of the apparent concentration of Na_2O and K_2O by up to 10 % and 30 %, respectively, confirming once more that alkali metals in zeolites are easily mobilized during electron micro-analysis. In order to retrieve the chemical composition of erionite fibres, the correction factors were calculated for each oxide as a function of the particle size using the regression equations obtained for the crystal fragments. Those correction factors have to be considered as sample specific.

Therefore, following Paoletti *et al.* (2008), the composition of the fibres, corrected for size-dependent effects, was determined by multiplying the apparent composition by the corresponding correction factor. Due to the relatively low content of MgO of the erionite fibres (<0.5 wt.%), no correction was applied to this oxide. The reliability of the chemical analyses was evaluated using both the balance error formula $E\%$ (Passaglia, 1970) and the K-content test

(Ballirano & Cametti, 2015). The mean composition of the fibres is reported in Table 2. According to its crystal-chemical formula, the sample was classified as Na-erionite. Present results are in very good agreement with those reported by Ballirano & Cametti (2015). The beneficial effect of introducing the size-dependent correction is represented by a marked reduction of data dispersion (Table 2). Nevertheless, the site scattering (s.s.) of the extra-framework cations of $93(6) e^-$ is in fairly good agreement with $115(2) e^-$ from structure analysis by the Rietveld method, as indicated by Ballirano & Cametti (2015). Such discrepancy is clearly due to the occurrence of alkali metals mobilization. In a recent work, aimed at the crystal chemical characterization of Fe-loaded erionite fibres (Ballirano *et al.*, 2015), a sample of the woolly variety of erionite from Durkee (Oregon, USA) permitted to obtain, due to its peculiar ribbon-like morphology, SEM-EDX data in excellent agreement with the sites scattering from the Rietveld refinement by employing a raster mode, which is inapplicable in the present case of loose fibres.

Finally, Table 3 shows the comparison between SEM-EDX bulk composition and EMP analyses of the investigated samples. As far as the chemical analyses are concerned, no significant differences were observed between the two oxide data sets, the only exception being Na_2O . The largest difference is smaller than 7 % if Na_2O is not taken into account. Natrolite and nepheline, characterized by similar contents, show an underestimation of Na_2O of *ca.* 11 %. In contrast, the small amount of Na_2O quantified for leucite is very similar using both analytical techniques. The crystal chemical formulae calculated from SEM-EDX data are affected by an underestimation of the content of Na, K and Ca in decreasing order. In the case of Na and K the underestimation is of *ca.* 10–15 %. It is worth noticing that, in the case of the analysed framework silicates, there is no marked dependence of the extent of alkali migration on the water content as both hydrous and anhydrous samples show comparable behaviour under the electron beam.

Table 3. Comparison of the bulk compositions and crystal-chemical formulae obtained by SEM-EDX and EMP analyses. For each oxide, standard deviations are reported in brackets. Formulae are calculated on the following bases: scolecite = 40 O; natrolite = 80 O; leucite = 96 O; nepheline = 32 O. The relative difference between SEM-EDX and EMP data is noted Δ .

	Scolecite			Natrolite			Leucite			Nepheline		
	SEM	EMPA	Δ (%)	SEM	EMPA	Δ (%)	SEM	EMPA	Δ (%)	SEM	EMPA	Δ (%)
SiO_2	55.0(2)	53.7(2)	2.4	54.9(4)	53.0(2)	3.4	57.3(2)	55.7(1)	2.7	44.4(1)	42.7(1)	3.9
Al_2O_3	29.4(1)	29.6(1)	−0.8	29.3(4)	29.3(1)	0.2	23.4(1)	23.1(1)	1.1	34.7(1)	34.4(2)	0.8
CaO	15.6(2)	16.7(2)	−6.5							1.9(1)	2.0(1)	−4.0
Na_2O				15.8(4)	17.7(1)	−10.9	0.39(6)	0.40(3)	−2.5	13.4(1)	15.1(2)	−11.3
K_2O							18.9(1)	20.7(1)	−8.7	5.5(1)	5.8(1)	−3.8
Total	100.00	100.00		100.00	100.00		100.00	100.00		100.00	100.00	
Si	12.32	12.09	1.9	24.81	24.24	2.3	32.67	32.24	1.3	8.42	8.19	2.7
Al	7.75	7.87	−1.5	15.63	15.77	−0.9	15.70	15.76	−0.4	7.75	7.79	−0.5
Ca	3.74	4.02	−6.9							0.39	0.41	−4.9
Na				13.85	15.73	−11.9	0.43	0.45	−4.4	4.94	5.64	−12.4
K							13.77	15.30	−10.0	1.34	1.41	−5.0
O	40.00	40.00	–	80.00	80.00	–	96.00	96.00	–	32.00	32.00	–

Conclusions

The effects of the exposure of humans to erionite fibres has started capturing in the recent past the interest of several researchers due to its carcinogenic potential higher than that of amphibole asbestos. The claimed dependence of the toxicity and biological activity of the fibres to their crystal-chemical features renders the reliable chemical characterization of paramount importance. However, the micro-chemical investigation of fibres suffers from systematic errors occurring due to the limited size and irregular shape (particle effects). In addition, framework-silicate samples are affected by severe alkali metal migration.

In this work, the quantitative chemical composition of erionite fibres from Rome, Oregon (USA) was retrieved by SEM-EDX analysis. Those fibres have a diameter smaller than 3 µm, *i.e.* those more easily inhalable, therefore representing a typical case encountered during environmental investigations. To reduce the errors induced by particle size/morphology effects, the same empirical procedure proposed by Paoletti *et al.* (2008) for the characterization of fibrous amphiboles was adopted. In particular, correction factors were defined for each oxide as a function of the particle diameter using fragments of zeolites and feldspathoids of known bulk composition. In addition, the experimental conditions were set in order to minimize the effect of alkali metal migration in both analyses of fragments and fibres. Comparison with EMP analysis of bulk standards, used to determine the correction factors, indicates that crystal chemical formulae calculated from SEM-EDX data are affected by a generalised underestimation of the content of Na, K and Ca in decreasing order. In the case of Na and K the underestimation has been estimated to be ca. 10–15 %, in good agreement with reference structural investigations.

Acknowledgements: The authors thank M. Serracino and M. Albano for technical assistance during EMP and SEM-EDX analyses. The authors also thank M. Mattioli who provided the natrolite and scolecite samples and J. Fournier for providing the sample of erionite from Rome. Critical comments and suggestions of Associate Editor Giuseppe Cruciani and three anonymous reviewers were greatly appreciated.

References

- Andersen, C.A. & Hasler, M.F. (1966): Extension of electron microprobe techniques to biochemistry by the use of long wave-length X-rays. in "X-Ray Optics and Microanalysis", R. Castaing, P. Deschamps, J. Philibert, eds. Hermann, Paris, 310–327.
- Armbruster, T. & Gunter, M. E. (2001): Crystal structures of natural zeolites. in "Natural Zeolites: Occurrence, Properties, Applications", D.L. Bish, D.W. Ming, eds. *Rev. Mineral. Geochem.*, **45**, Miner. Soc. America, Washington, D.C, 1–67.
- Armstrong, J. T. (1991): Quantitative elemental analysis of individual microparticles with electron beam instruments. in "Electron Probe Quantitation", K.F.J. Heinrich, D.E. Newbury eds. Plenum Press, New York, 261–315.
- Armstrong, J. T. & Buseck, P. R. (1975): Quantitative chemical analysis of individual microparticles using the electron microprobe: theoretical. *Anal. Chem.*, **47**, 2178–2192.
- Ballirano, P. & Cametti, G. (2015): Crystal chemical and structural modifications of erionite fibers leached with simulated lung fluids. *Am. Mineral.*, **100**, 1003–1012.
- Ballirano, P., Andreozzi, G.B., Dogan, M., Dogan, A.U. (2009): Crystal structure and iron topochemistry of erionite-K from Rome, Oregon, U.S.A. *Am. Mineral.*, **94**, 1262–1270.
- Ballirano, P., Pacella, A., Cremisini, C., Nardi, E., Fantauzzi, M., Atzei, D., Rossi, A., Cametti, G. (2015): Fe(II) segregation at a specific crystallographic site of fibrous erionite: a first step toward the understanding of the mechanisms inducing its carcinogenicity. *Micropor. Mesopor. Mat.*, **211**, 48–63.
- Bariş, Y.I., Sahin, A.A., Ozesmi, M., Kerse, I., Ozen, E., Kolacan, B., Altinörs, M., Göktepe, A. (1978): An outbreak of pleural mesothelioma and chronic fibrosing pleurisy in the village of Karain/Urgüp in Anatolia. *Thorax*, **33**, 181–192.
- Bruni, B.M., Pacella, A., Mazziotti Tagliani, S., Gianfagna, A., Paoletti, L. (2006): Nature and extent of the exposure to fibrous amphiboles in Biancavilla. *Sci. Total Environ.*, **370**, 9–16.
- 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., Zeyana, S.R., Steele, I., Tuncer, M., Way, S., Yang, H., Miller, A. (2011): Erionite exposure in North Dakota and Turkish villages with mesothelioma. *Proc. Natl. Acad. Sci. USA*, **108**, 13618–13623.
- Cliff, G. & Lorimer, G.W. (1975): The quantitative analysis of thin specimens. *J. Microscopy*, **103**, 203–207.
- Eborn, S.K. & Aust, A.E. (1995): Effect of iron acquisition on induction of DNA single-strand breaks by erionite, a carcinogenic mineral fiber. *Arch. Biochem. Biophys.*, **316**, 507–514.
- EDAX. (2003): Genesis v3.6 microanalysis software. EDAX Inc., Mahwah, NJ, USA.
- Fubini, B. (1993): The possible role of surface chemistry in the toxicity of inhaled fibers. in "Fiber Toxicology", D.B. Wahreit, ed. Academic Press, San Diego, 11, 229–257.
- Gianfagna, A., Andreozzi, G., Ballirano, P., Mazziotti-Tagliani, S., Bruni, B.M. (2007): Structural and chemical contrasts between prismatic and fibrous fluoro-edenite from Biancavilla, Sicily, Italy. *Can. Mineral.*, **45**, 249–262.
- Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C., Romig, A.D., Lyman, C.E., Fiori, C., Lifshin, E. (1992): Scanning Electron Microscopy and X-Ray Microanalysis (second edition). Plenum Press, New York, N.Y.
- Gottardi, G. & Galli, E. (1985): Natural zeolites. Springer-Verlag, Heidelberg.
- Gunter, M.E., Dyar, M.D., Twamley, B., Foit, F.F. Jr, Cornelius, S.B. (2003): Composition, Fe^{3+/ΣFe}, and crystal structure of non-asbestiform and asbestiform amphiboles from Libby, Montana, U.S.A. *Am. Mineral.*, **88**, 1970–1978.
- Laskin, A. & Cowin, J.P. (2001): Automated single-particle SEMEDX analysis of submicrometer particles down 0.1 µm. *Anal. Chem.*, **73**, 1023–1029.
- Long, J.F., Dutta, P.K., Hogg, B.D. (1997): Fluorescence imaging of reactive oxygen metabolites generated in single cell macrophage

- cells (NR8383) upon phagocytosis of natural zeolite (erionite) fibers. *Environ. Health Perspect.*, **105**, 706–711.
- Mazziotti-Tagliani, S., Andreozzi, G.B., Bruni, B.M., Gianfagna, A., Pacella, A., Paoletti, L. (2009): Quantitative chemistry and compositional variability of fluorine fibrous amphiboles from Biancavilla (Sicily, Italy). *Per. Mineral.*, **78**, 65–74.
- Meeker, G.P., Bern, A.M., Brownfield, I.K., Lowers, H.A., Sutley, S.J., Hoefen, T.M., Vance, J.S. (2003): The Composition and Morphology of Amphiboles from the Rainy Creek Complex, near Libby, Montana. *Am. Mineral.*, **88**, 1955–1969.
- Morgan, G.B. & London, D. (2005): Effect of current density on the electron microprobe analysis of alkali aluminosilicate glasses. *Am. Mineral.*, **90**, 1131–1138.
- Paoletti, L., Bruni, B.M., Arrizza, L., Mazziotti-Tagliani, S., Pacella, A. (2008): A micro-analytical SEM-EDS method applied to the quantitative chemical compositions of fibrous amphiboles. *Per. Mineral.*, **77**, 63–73.
- Paoletti, L., Bruni, B.M., Gianfagna, A., Mazziotti-Tagliani, S., Pacella, A. (2011): Quantitative Energy Dispersive X-ray (EDX) analysis of sub-micrometric particles using a Scanning Electron Microscope (SEM). *Micros. Microanal.*, **17**, 710–717.
- Passaglia, E. (1970): The crystal chemistry of chabazites. *Am. Mineral.*, **55**, 1278–1301.
- Reed, S.J.B. (1993): *Electron Microprobe Analysis* (second edition). Cambridge University Press, Cambridge, U.K.
- Ro, C., Osan, J., Szaloki, I., De Hoog, J., Worobiec, A., Van Grieken, R. (2003): A Monte Carlo program for quantitative electron-induced X-ray analysis of individual particles. *Anal. Chem.*, **75**, 851–859.
- Ryan, P.H., Dihle, M., Griffin, S., Partridge, C., Hilbert, T.J., Taylor, R., Adjei, S., Lockey, J.E. (2011): Erionite in road gravel associated with interstitial and pleural changes – An occupational hazard in Western United States. *J. Occup. Env. Med.*, **53**, 892–898.
- Small, J.A. (2002): The analysis of particles at low accelerating voltages (≤ 10 kV) with energy dispersive X-ray spectroscopy (EDS). *J. Res. Natl. Inst. Stand. Technol.*, **107**, 555–566.
- Spray, J.G. & Rae, D.A. (1995): Quantitative electron-microprobe analysis of alkali silicate glasses: a review and user guide. *Can. Mineral.*, **33**, 323–332.
- Sweatman, T.R. & Long, J.V.P. (1969): Quantitative electron-probe microanalysis of rock-forming minerals. *J. Petrol.*, **10**, 332–379.

Received 30 January 2015

Modified version received 10 May 2015

Accepted 25 August 2015