

## New structural and chemical data of woolly erionite from Oregon.

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Erionite is a naturally occurring fibrous mineral belonging to the ABC-6 family (Gottardi and Galli, 1985). It is well known that exposure to erionite fibers has severe effects on human health. In fact, it has been recognized as a Group-I carcinogen for humans (IARC, 1997) by both the International Agency for Research on Cancer (IARC) and the World Health Organization (WHO). Despite of being a nominally Fe-free phase, several chemical analyses on natural erionites report a Fe<sub>2</sub>O<sub>3</sub> content up to 3 wt.%. Similarly to amphibole asbestos, erionite toxicity has been partly ascribed to the presence of iron eventually participating to Fenton chemistry and inducing genotoxic damages. Ballirano *et al.* (2009) carried out a combined spectroscopic and crystal chemical investigation of erionite-K from Rome, Oregon. They demonstrated, from Mössbauer spectroscopy, that the small amount of iron oxide was occurring as nanoparticles located at the surface of the zeolite with dimensions ranging from 1 to 9 nm. Parallel investigations on samples from different localities are currently in progress and preliminary results are the object of the present work.

In particular, we report the crystal chemical characterization of an erionite sample from Durkee, Oregon (sample provided by the Smithsonian Institution, Washington) to be used as the starting point for a toxicity investigation. The sample, consisting of woolly bundles of fibres, has been analyzed by XRPD, SEM-EDS and FE-SEM. XRPD data, collected in parallel-beam, transmission geometry, were evaluated by the Rietveld method using the TOPAS (Bruker AXS, 2009) crystallographic software running in launch-mode. The strong anisotropic shape of the crystallites resulted in a diffraction-vector-dependent broadening of diffraction maxima that was modelled applying the ellipsoid-model approach of Katerinopoulou *et al.* (2012). A significant improvement of the fit was obtained as compared to the use of an isotropic shape of crystallites.

Refined cell parameters are  $a = 13.2360(5)$  Å and  $c = 15.0671(6)$  Å. Evaluation of the mean tetrahedral bond distances clearly indicates a preferential partition of Al on T2 site. Extraframework (EF) cations were allocated at the K1 site, located at the centre of the  $\epsilon$ -cage [4<sup>6</sup>6<sup>5</sup>], and in three Ca1, Ca2, and Ca3 located within the erionite cage [4<sup>12</sup>6<sup>5</sup>8<sup>6</sup>]. A further cationic site K2 was found at the centre of the boat-shaped 8-member rings (8MR) forming the walls of the erionite cage, as firstly reported by Schlenker *et al.* (1977) for a dehydrated erionite sample. The ellipsoid radii are of  $r_a = 153.1(15)$  nm and  $r_c = 864(53)$  nm with a  $r_c/r_a$  ratio of 5.7(9). Preliminary semi-quantitative chemical analysis of the bundles pointed out to a variable Fe<sub>2</sub>O<sub>3</sub> content of ca. 2-4 wt.% and the presence of Ca, Mg, Na and K as EF cations. However, detailed SEM analyses, carried out on dispersed fibres, clearly indicated the absence of both calcium and iron.

The reliability of the crystal chemistries of the new set of analyses has been evaluated using both the balance error formula (E%) and the Mg-content test (Dogan and Dogan, 2008). Up to 60% of analyses passed both the E% and Mg-content tests. The final mean crystal-chemical formula (Na<sub>5.42</sub>K<sub>2.0</sub>Mg<sub>0.25</sub>)[Al<sub>7.66</sub>Si<sub>28.34</sub>O<sub>72.16</sub>] • 29.86H<sub>2</sub>O has been computed hypothesizing a content of water of ca. 17%, and normalized on the basis of 36 (Si+Al). The calculated cationic site scattering from chemical formula (100.6 e<sup>-</sup>) is in good agreement with that obtained from the Rietveld refinement (105.2 e<sup>-</sup>).

Ballirano, P. Andreozzi, G.B., Dogan, M., and Dogan, A.U. (2009) *Am. Mineral.*, 94, 1262-1270.

Bruker AXS (2009) Topas V4.2: General profile and structure analysis software for powder diffraction data. Bruker AXS, Karlsruhe, Germany.

Dogan, A.U. and Dogan, M. (2008) *Environ. Geochem. Health*, 30, 355-366.

Gottardi, G. and Galli, E. (1985) *Natural zeolites*. Springer-Verlag, Heidelberg.

IARC (1997) Erionite. IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans. Silica and some silicates, 42, 225-239.

Katerinopoulou, A., Balic-Zunic, T., and Lundegaard, L.F. (2012) *J. Appl. Cryst.*, 45, 22-27.

Schlenker, J.L., Pluth, J.J., and Smith, J.V. (1977) *Acta Crystallogr.*, B33, 3265-3268.