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Exploiting XPS for clarifying toxicity of mineral fibers

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The chemistry of surface layers of nanometer thickness can dramatically change the reactivity of a material. X-ray photoelectron spectroscopy (XPS) combines a high surface sensitivity in the nm range with far greater spatial resolution and accuracy than ever before, allowing the understanding of the mechanisms of the chemical reactions occurring at the samples surface. These features together with the possibility of quantitative analysis of the outermost layers of the materials make XPS technique extremely versatile for the characterization of mineral fibers, which are responsible for serious health problems and respiratory diseases. In the present work the results obtained investigating by XPS fluoro-edenite (Fantauzzi et al., 2012), crocidolite (Pacella et al., 2014), tremolite (Pacella et al., 2015) and, recently, erionite (Ballirano et al., 2015) from different countries and after different surface treatments are summarized and discussed.

Iron in fibrous minerals is reputed to be important for its biological effects, since it may catalyze the Haber – Weiss reaction, generating the reactive oxygen species •OH. An analytical strategy was developed in order to be able to differentiate between Fe(II) and Fe(III), being the toxicity of the two cations different. In fluoro-edenite the iron chemical state was related to radical production and proposed to account for the toxicity of such fibers (Fantauzzi et al., 2012). Notably, fluoro-edenite has been declared highly dangerous for human health by the International Agency for Research on Cancer in 2014. The same XPS approach was also useful for the identification of iron chemical state following fiber incubation in solution. The surface composition of crocidolite (Pacella et al., 2014) and tremolite (Pacella et al., 2015) samples immersed in a buffered H_2O_2 solution (pH = 7.4) up to 168 h was monitored to shed a light on the dissolution dynamics that may occur in vivo.

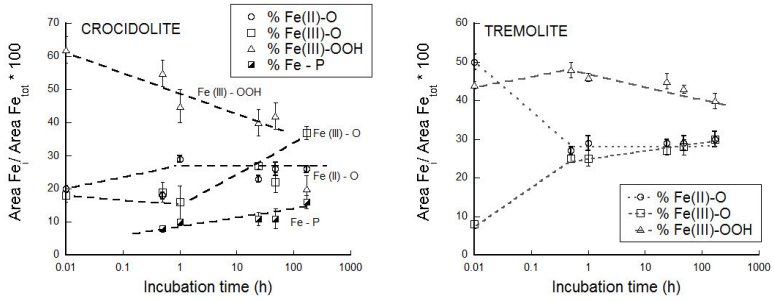

Figure 1: relative intensities of $Fe2p_{3/2}$ signal components for crocidolite and for tremolite in the range 0–168 h. Dashed lines are given as guides to the eye.

XPS provided evidence of iron enrichment at the crocidolite surfaces and, after one hour of exposure to the solution, an increase of Fe(II) content at the surface was found, indicating that the dissolution reaction was faster than the oxidation. Longer incubation time revealed that the Fe(II) content on the surface remained unchanged while Fe(III) bonded to the silicate structure increased (Fig. 1). Also an increase of Fe oxide-hydroxide content and the precipitation of Fe-phosphate were reported suggesting the formation of a coating upon time. In the case of tremolite it was found that Fe(III) content rapidly increases both in the silicate framework and in oxy-hydroxides, while Fe(II) content decreases upon incubation (Fig. 1). It can be thus concluded that for tremolite the oxidation reaction is faster than the dissolution one. Finally, XPS allowed the characterization of erionite surface in an investigation involving chemical, structural and surface modifications of samples of fibrous erionite after incubation in $FeCl_2$ solutions at different salt concentrations (Ballirano et al., 2015). XPS results demonstrated that the iron content increases with ferrous loading and that iron is present as Fe(II). Simultaneously, sodium depletion was observed, thus elucidating that Fe(II) is fixed by the fibers within the erionite structure through an ion-exchange process mainly involving Na.

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