



Surface alteration mechanism and topochemistry of iron in tremolite asbestos: A step toward understanding the potential hazard of amphibole asbestos



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ABSTRACT

Non-occupational, environmental and unintentional exposure to fibrous tremolite, one of the most widespread naturally occurring asbestos, represents a potentially significant geological risk in several parts of the world. The toxicity of amphibole asbestos is commonly related to iron content and oxidation state, but information available on surface iron topochemistry and amphibole alteration mechanism is still rather poor. With the aim to shed a light on this mechanism, two tremolite samples, one from Italy (Castelluccio) and one from USA (Maryland), immersed in a buffer solution (pH 7.4) with H₂O₂ were characterized by a multi-technique approach. X-ray photoelectron spectroscopy (XPS) and high resolution–transmission electron microscopy (HR-TEM) were used to investigate the surface chemistry of the incubated samples and to detect structural modifications of the fibres, while inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the concentration of dissolved elements.

An original four-step model for amphibole alteration pathway is proposed. The alteration process starts with an incongruent dissolution of the amphiboles that produces an amorphous, altered surface layer and that is followed by iron oxidation and formation of FeOOH species. Then the congruent dissolution of the altered layer starts and, subsequently, the residual Fe oxi-hydroxides aggregates and insoluble, Fe-rich, amorphous nanoparticles on top of the fibres are formed. The results are compared to those obtained on crocidolite, a highly toxic amphibole asbestos with a 10 to 20 times higher iron content than tremolite. The high chemical reactivity observed in the literature for tremolite appears to be related not only to its iron content and oxidation state, but also to the low nuclearity of iron on the altered surfaces, in contrast to pronounced Fe clusterization at crocidolite surfaces. This is a significant step toward a conceivable explanation of why asbestos tremolite is potentially as toxic as crocidolite.

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1. Introduction

The fibrous form of the amphibole tremolite is one of the six recognised types of asbestos (together with amosite, crocidolite, fibrous anthophyllite, fibrous actinolite, and chrysotile). Tremolite asbestos is

one of the most dangerous and widespread “naturally occurring asbestos” (NOA), a term referring to asbestos fibres as a natural constituent of soils or rocks and as opposed to asbestos in commercial products, mining or processing operations. Any activity which causes NOA-bearing soils and rocks to be disturbed can potentially result in the release of asbestos fibres into the air. Unintentional, environmental and non-occupational exposure to asbestos dust is recognized as a significant geological hazard in Italy, Corsica, Greece, Cyprus, Turkey, USA, Australia, and a number of other places. Due to the extremely high bio-persistence, strong scarring, and inflammatory action when inhaled, tremolite asbestos is considered to be co-responsible for mesothelioma and lung cancer even when it is present as a contaminant phase embedded within other asbestos fibres, particularly chrysotile,

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but also within non-asbestos materials, as for example vermiculite and talc (International Agency for Research on Cancer, 1977; Churg et al., 1984; World Health Organization, 1986; McDonald and McDonald, 1997; Bernstein et al., 2003).

The molecular mechanisms underlying the fibrogenic and tumorigenic effects of all types of asbestos are not yet fully established. Different physicochemical factors have been involved, mainly related to their fibrous habit, high bio-persistence, and surface reactivity (Fubini and Otero-Aréan, 1999; Kamp and Weitzman, 1999; Manning et al., 2002). The most robust mechanism proposed is based on a structure-activity relationship for asbestos and includes generation of iron-mediated reactive oxygen species (ROS) and free radicals (Gazzano et al., 2007; Turci et al., 2011). Notably, free radical release may be induced by iron-catalysed reactions in the presence of H_2O_2 (Fenton reaction) as well as in the absence of H_2O_2 (Haber–Weiss Cycle), which may take place in various biological compartments. A large amount of experimental evidence suggest that the generation of ROS and other radicals catalysed by iron ions at the fibre surface plays an important role in asbestos-induced cytotoxicity and genotoxicity (Xu et al., 2002; Huang et al., 2011).

Iron is absent in the ideal stoichiometric formula of tremolite [$Ca_2Mg_5Si_8O_{22}(OH)_2$], nevertheless iron contamination of asbestos commonly takes place and in natural tremolite Fe^{2+} might easily replace Mg producing the isomorphous tremolite-ferro-actinolite solid solution [$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$]. In amphiboles, such a substitution commonly occurs in the strip of edge-sharing octahedra of the structure denoted as $M(1)$, $M(2)$ and $M(3)$ and also in the larger $M(4)$ site (Fig. 1).

In tremolite asbestos containing up to 5 wt.% FeO_{tot} , in particular, Fe^{2+} was found to be equally distributed over $M(1)$, $M(2)$ and $M(3)$ sites, whereas Fe^{3+} was ordered only at $M(2)$ site (Ballirano et al., 2008; Pacella et al., 2008, 2010). Notably, for amphibole asbestos both iron site distribution and oxidation state, especially at the fibre surface, were demonstrated to influence chemical reactivity as well as cell toxicity (Pacella et al., 2010, 2012; Fantauzzi et al., 2012). Moreover, a set of iron-doped synthetic chrysotile asbestos fibres was used to show that free radical yield is related to the occurrence of isolated iron sites at the fibre surface (active surface sites) that share a specific oxidation and coordination state (Gazzano et al., 2007; Turci et al., 2011).

The central role of surfaces (composition, surface area, properties) in asbestos fibre toxicity has long been recognized (e.g., Light and Wei, 1977; Zalma et al., 1987). The definition of surface alteration mechanism(s) is an important step toward deep understanding of the

various amphibole asbestos hazard potentials and the background for further studies on their toxicity. This knowledge might also open insights into the discovery of possible inactivation strategies. In particular, iron-bearing species with different oxidation states, chemical composition and “nuclearity” (that is clustering or aggregation state) might precipitate on fibre surfaces after fibre partial dissolution (Shen et al., 2000; Turci et al., 2007; Pacella et al., 2014). The process of fibres coating with Fe oxo-hydroxides and/or Fe-rich phases is a candidate to moderate asbestos toxicity and may eventually represent one of the mechanisms of formation of “ferruginous bodies” (pulmonary-coated mineral fibres), which are known to be formed by coating an asbestos fibre with an iron protein mucopolysaccharide complex (Churg and Warnock, 1981; Pascolo et al., 2011, 2013; Gualtieri et al., 2013). In spite of such a strong relevance, a mechanism describing the alteration of asbestos surfaces, as well as iron oxidation and clustering, is not available so far. Given the highly different Fe content between tremolite and some of the other amphibole asbestos (e.g., crocidolite, amosite), it is not even clear if the same mechanism applies and the topochemistry of iron at fibre surface is comparable or not. Detailed investigation of the various asbestos alteration pathways is therefore needed to fill the existing gaps, the subject being characterized by both a broad geochemical interest and a specific environmental and medical relevance.

This study aims at shedding light on this complex mechanism by investigating the dissolution process, the surface modifications and the iron topochemistry of tremolite asbestos. Building on obtained results, an original model for amphibole alteration pathway is proposed and the possible role of surface iron nuclearity on asbestos toxicity is elucidated.

2. Experimental

Two samples of fibrous tremolite with highly different Fe content were suspended in a buffered leaching hydrogen peroxide solution (pH = 7.4, 37 °C) from 0.5 h to 168 h (one week) and then investigated by a multi-analytical approach. The extreme incubation conditions used are based on the approach previously adopted for measuring the surface reactivity of the same tremolite samples (Pacella et al., 2010). Although far from mimicking a real cellular environment, such conditions were chosen to promote the dissolution reactions that may occur in vivo in a reasonable experimental time. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to measure the ion release into the leaching solution. After each incubation experiment X-ray

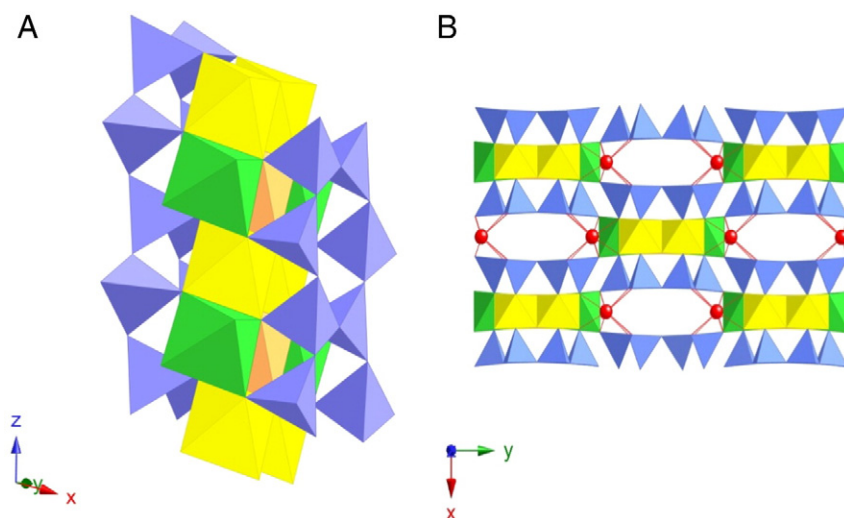


Fig. 1. C2/m tremolite structure. A): double chain of tetrahedra and strip of octahedra elongated in the c-direction (“I-beam” blocks); B): projection onto (001) showing the “I-beam” blocks linked by M(4) sites (in red). The various octahedra are distinguished by colours: Yellow = M(1), green = M(2), orange = M(3).

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