Francesco Turci (2002-2005)
Ph.D. in Chemical Sciences

Asbestos is an ubiquitous, naturally occurring fibre that has been linked to the development of malignant and fibrotic diseases of the lung and pleura. The risks of exposure to airborne asbestos are well understood and documented (Manning et al., 2002). Asbestosis (a

form of diffuse pulmonary fibrosis), lung cancers, and mesothelioma have all been linked to asbestos exposure in humans. Likewise, animal models have been successfully developed to study exposure–disease relationships. However, the molecular mechanisms by which asbestos fibres initiate disease remain unclear. An understanding of asbestos cytotoxic and genotoxic events may permit the prediction of disease potential for new fibrous materials of respirable dimensions that enter the workplace and the environment. There are several hypotheses that attempt to explain what the important variables are in relating fibres and disease; these include morphology, durability, surface chemistry, reactive oxygen species, and others. Most of these hypotheses have some support, and most are not mutually exclusive of one or more of the alternative hypotheses. To date, there is no single in vitro test that will predict disease for any given fibre, although we believe that a set of tests, both chemical and cellular, may correlate well with known toxicity of some fibres.
This doctorate thesis is divided into three main sections.
Part I: Comparative study of the potential pathogenicity of several asbestiform mineral sources
In this first part, Chapters 4-6, three asbestiform minerals were systematically analyzed and compared. Here we report a systematic investigation on asbestos hazard in the western Alps by means of a multidisciplinary approach whereby any sampled asbestiform mineral is characterized mineralogically, chemically, biochemically. Balangeroite is the first asbestiform mineral investigated (Cap. 4). It is present nearly ubiquitously in the Balangero mine area, where it is always associated with long fibre of chrysotile and with abundant magnetite. Balangeroite has also been found in two other localities of the western Alps, but it appears to be restricted to the Lanzo Massif. The chapter reports the physicochemical characteristics and the chemical reactivity (oxidant activity) of the balangeroite fibres. In order to predict whether balangeroite is pathogenic, the result of a series of physicochemical, biochemical and cellular tests were compared to crocidolite, a well known toxic asbestos. The Chapter 5 is devoted to chrysotile, the most abundant and widely used asbestos form. This study compares several natural and commercial sources of chrysotile minerals, sampled in the Italian Western Alps. One well characterized standard chrysotile from UICC (Chrysotile A, from Zimbabwe - Timbrell & Rendall, 1972) was used as a comparison. Two samples were collected in the Balangero former mine. One is a commercial chrysotile that was found in the disused storage area of the asbestos mine. The second mineral sample was collected from a natural outcrop close to the cultivated field. This latter sample is intergrown with significant amount of balangeroite fibres. The third chrysotile specimen was sampled in Val Malenco, in the Northern Central Alps.

Although the project does not strictly include such sampling location (the investigated area was restricted to the western Alps), the mineral was studied because of its unusual grade of mineralogical and chemical purity. In Chapter 6, a systematic study on three tremolite asbestos samples was performed. Some morphological and dimensional characteristics of the fibres as well as their structural and chemical reactivity is assessed. Morphological and structural data and chemical and biochemical reactivity of the three mineral asbestos samples are reported and compared. The first part of the study devoted to tremolite is intended to compare the morphologic and physicochemical characteristics of the three tremolite sample from the Western Alps. A subsequent part was committed to the study of the modifications in term of dimension, shape, crystallinity and chemical reactivity of the fibres induced by a mechanical comminution process.

Part II: Surface modifications induced by some microorganisms on asbestos fibres. The second part of this doctorate thesis is devoted to the understanding of the chemical effect of lichens, which are well-known physical and chemical weathering agents of mineral substrata, on chrysotile fibres. The study was projected in order to evaluate, following a multidisciplinary, biomimetic approach, the lichen-chrysotile interaction which may occur in nature. In order to analyze the chemical properties and the reactivity of lichen-modified chrysotile fibres, three lichen metabolites differing in their chemical nature are used, namely: i) oxalic acid, ii) norstictic acid, iii) pulvinic acid. Measures are performed to examine the extent of the modifications induced by the lichen metabolites and to asses whether such changes result in modifying the chemical-physical characteristics involved in the fibres toxicity. To understand the weathering effects of lichen metabolites, two natural occurring minerals, previously described in Part I are used: a relatively pure chrysotile specimen from the Central Internal Alps (Val Malenco, Lombardia, Italy) and a sample of chrysotile from the former asbestos mine of Balangero (Western Internal Alps, Val di Lanzo, Piemonte, Italy).

Part III: Characterization and chemical and biological reactivity of an iron-doped synthetic chrysotile The third and last part reports the study on some chemical factors regarded as responsible for chrysotile reactivity and toxicity. An iron-free and an iron-doped chrysotile, recently synthesized, were thoroughly tested and the UICC chrysotile, a well known toxic natural chrysotile, was employed as reference. Free radical generation and the effects of synthetic chrysotile fibres on human lung epithelial A549 cells are compared to that elicited by UICC chrysotile. Two different free radical release tests are performed on both fibres: the Fenton-like activity towards H2O2 which yields HO• production and the homolytic rupture of a C-H bond from the formate ion (HCO_2^- --> CO_2^{-}•). To evaluate the structural surrounding of the paramagnetic ions (involved in fibre reactivity), an EPR spectroscopical characterization of the iron-free and iron-doped (at 4 different extents) samples was also performed.

A general and comparative discussion can be found in Cap. 9. An appendix reports the papers pubblished during the doctorated.

The pdf file of the Thesis can be downloaded here (authenticated users only) or requested at francesco.turci@unito.it