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Lichen deterioration of asbestos and asbestiform minerals of serpentinite rocks in Western Alps

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ABSTRACT

Naturally Occurring Asbestos (NOA) on serpentinite outcrops are exposed to abiotic and biotic environmental forces which may affect their toxicity-relevant properties. Lichen colonization and deterioration were examined on monomineralic and polymineralic veins, containing asbestos (chrysotile, tremolite) and/or asbestiform minerals (antigorite, balangeroite, carlosturanite, diopside). The hyphal penetration of *Candelariella vitellina* within the different veins ranged from few hundreds of microns to several millimetres. The various NOA mineral species contacted by lichen hyphae were differently modified in their chemical composition. NOA were incubated in the laboratory with oxalic acid to mimic the dissolution process driven by lichen metabolites bearing acidic and chelating functions, typically pulvinic acid in the case of *C. vitellina*. The incubated fibres were chemically modified to the same extent of those colonized by *C. vitellina* in the field and were used to examine the effects of lichen deterioration on the toxicity-relevant release of Reactive Oxygen Species (ROS). Incongruent dissolution patterns observed in the cases of chrysotile-, chrysotile + balangeroite- and tremolite bearing veins were associated to a significant (even if not complete) inactivation of the surface. Conversely, the veins bearing minerals subjected to congruent dissolution (antigorite, diopside) maintained their reactivity. Lichen colonization may thus be associated to a bioattenuation process on some kinds of fibrous veins, but such effect cannot be generalized to all colonized NOA.

1. Introduction

The six commercially relevant asbestos minerals have been strictly regulated (USA, China) or banned (27 EU countries and 39 more) under worldwide workplace health and safety and public health regulations (International Ban Asbestos Secretariat, 2011). Nevertheless, some concern is growing about the widespread presence of Naturally Occurring Asbestos (NOA; US-EPA, 2011) – asbestos minerals found in place in their natural state, not commercially mined or used – which can be released into the air by natural processes (e.g., rock and soil weathering) or human activities (e.g., agriculture, construction), thus becoming a threat to human health (Culley et al., 2010). Shared scientific and procedural basis for assessing NOA occurrence in a given area and evaluating the associated risk has been invoked in order to develop effective public policies and minimize fibre hazard (Lee et al., 2008).

The natural occurrence of asbestos minerals is mostly associated to serpentinite rocks, where the fibres occur within different generations of metamorphic veins (O'Hanley, 1996; Virta, 2005). The largest deposits of asbestos were punctually mined in the serpentinite belt of several ophiolitic complexes around the world (eastern Canada, Russian Urals, California, north-eastern Greece, Cyprus and northwest Italy) (Ross and Nolan, 2003). Beside these wide, but rare commercial deposits, small occurrences of fibre-bearing surfaces are extremely common throughout all the serpentinite outcrops and may act as sources of fibre dispersion in natural environments (Lee et al., 2008).

The invoked characterization of the potential risk associated to NOA in the case of the widespread, but small sources of NOA, should take into account the following points:

(a) the six regulated asbestos minerals (namely, chrysotile, tremolite, actinolite, anthophyllite, riebeckite-crocidolite and

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grunerite-amosite) only partially account for the whole set of fibrous minerals comprised in NOA. In fact many studies have reported on asbestiform minerals not commercially exploited, but sharing a fibrous habit with asbestos, whose pathogenicity is mostly unknown (Baris et al., 1987; Comba et al., 2003; McDonald et al., 2004; Turci et al., 2009; Pugnaloni et al., 2010);

(b) NOA are more than likely to appear in polymineralic veins, including other fibrous minerals (Groppo and Compagnoni, 2007a);

(c) opposite to airborne fibres generated by human activities, naturally released fibres from serpentinite outcrops have been often affected by abiotic and biotic environmental forces for a long time, which may have modified their toxicity-related physico-chemical features (Favero-Longo et al., 2005a, 2009a; Daghino et al., 2008).

Serpentinites of the Italian Western Alps contain two asbestos minerals: (a) chrysotile, the serpentine asbestos most widely mined worldwide, always showing fibrous habit, and (b) tremolite, an amphibole which only occasionally occurs with fibrous habit (Groppo and Compagnoni, 2007a). Widespread asbestiform minerals are: (c) antigorite, having the same composition of chrysotile, but different crystalline structure, which in most cases displays a lamellar habit, but occasionally a pseudo-fibrous, columnar habit (Groppo and Compagnoni, 2007b); (d) carlosturanite, a serpentine-type phase (Compagnoni et al., 1985), mostly displaying a fibrous habit; (e) balangeroite, a Fe-rich mineral of the gageite group, mostly found with fibrous habit in association with chrysotile (Compagnoni et al., 1983); (f) diopside, a pyroxene which usually displays prismatic habit, but also occurs as a fibre in chrysotile + carlosturanite bearing veins (Ferraris, 1995; Groppo and Compagnoni, 2007a).

The toxicity of asbestos and asbestiform minerals is currently related to several physico-chemical features acting together such as fibrous habit, high biopersistence and redox-reactive iron ions at the surface, generating Reactive Oxygen Species (ROS) (Kane, 1996; Fubini and Fenoglio, 2007; Ballirano et al., 2008).

In mountain areas, physical environmental forces including temperature changes, freezing and thawing, and washing away by rain, were shown in laboratory experiments to induce a partial dissolution process of chrysotile, tremolite and balangeroite and, consequently, to affect their surface reactivity (Favero-Longo et al., 2009a). On the other hand, serpentinite rocks of mountain areas, including western Alps, are widely colonized by lichen-forming fungi (Favero-Longo et al., 2004), well known agents of physico-chemical deterioration on natural and artificial mineral substrata (Warscheid and Braams, 2000; St. Clair and Seaward, 2004; Gadd et al., 2012). Lichens physically support disaggregation processes through their expanding (wetting) and contracting (drying) thalli adhered to the rock surfaces and the penetration of their hyphae along mineral planes of weakness and intergranular voids (Adamo and Violante, 2000; de los Rìos and Ascaso, 2005). The release of molecules with acidic and chelating functions, leaching and/or complexing metal ions, mostly accounts for lichen-driven mineral dissolution and/or neoformation (Adamo and Violante, 2000). Primary metabolites, particularly the well-known chelator oxalic acid, and/or a wide range of slightly soluble secondary metabolites can be involved in these biogeochemical processes depending on species (Gadd, 1999; Chen et al., 2000).

Lichen communities were described on the asbestos-rich serpentinites of the chrysotile mine of Balangero (Torino, Italy) where the fibre rough texture improves bioreceptivity by increasing water retention and, possibly, propagule deposition (Favero-Longo et al., 2006). Chrysotile fibres contacted by the hyphal penetration component (*sensu* Favero-Longo et al., 2005b) of several lichen species, including *Candelariella vitellina* (L.) Müll. Arg., *Xanthoparmelia pulla* (Ach.) O. Blanco, A. Crespo, Elix, D. Hawksw. & Lumbsch, *Xanthoparmelia tinctina* (Maheu & A. Gillet) Hale, *Lecanora rupicola* (L.) Zahlbr. and *Acarospora cervina* A. Massal., were affected in their chemical composition (Favero-Longo et al., 2009a, b). The octahedral Mg-rich sheets, which compose the serpentine structure in association with tetrahedral silicate sheets, were selectively leached. The finding of oxalates at the interface between the mineral substrate and most of the investigated lichen species suggested oxalic acid as the most common, although not exclusive, leaching agent (Favero-Longo et al., 2007, 2009a, b). The removal of poorly coordinated iron ions, replacing some magnesium in chrysotile and related to its surface reactivity, upon the incubation with lichen chelants (including oxalic acid and lichen secondary metabolites, as pulvinic and norstictic acid), was shown in laboratory following a biomimetic approach (Turci et al., 2007). The induced chemical modification was associated to a partial decrease in the surface reactivity of the fibres, suggesting a bioattenuation role for lichens on asbestos-bearing rocks. The work also indicated that the specific chemical feature of each chrysotile source and, in general, of each fibrous mineral should be independently considered with regard to inactivation.

This paper aims to compare the lichen-driven modification of chemical composition and surface reactivity of chrysotile, occurring in monomineralic or polymineralic veins (chrysotile, chrysotile-balangeroite, chrysotile-diopside-carlosturanite), with that of other asbestos (tremolite) and asbestiform minerals (antigorite).

Four types of fibrous veins uncolonized or penetrated by lichen hyphae in the field were examined by means of light polarizing microscopy and scanning electron microscopy (SEM); elemental compositions of the fibres were obtained with energy dispersive X-ray spectroscopy (EDS). Observations and analyses were focused on veins covered by thalli of *C. vitellina*, a lichen species extremely common on serpentinites (Favero-Longo et al., 2004), which was ubiquitous on all the four selected vein types.

The asbestos and asbestiform fibres below the thalli, occurring in low amount and difficultly separable from other organic and inorganic materials, were not suitable to carry out the tests on the toxicity relevant surface reactivity. Fibres which were similarly modified in their chemical composition to those found below *C. vitellina* in the field were thus produced in the laboratory by incubating fresh fibres with oxalic acid. Although oxalic acid may not be secreted by *C. vitellina* (Favero-Longo et al., 2007, 2009b, this work), it is commercially available and displays a high solubility (14.3 g/100 ml at 25 °C) which makes it mostly suitable to generally mimic in vitro, in reasonable times, the deterioration driven by lichen metabolites with acidic and chelating functions (Turci et al., 2007).

The chemical modification of fibres was experimentally characterized in terms of: i) ion release in the supernatant by atomic emission spectroscopy (ICP-AES) and ii) mode of mineral dissolution (congruent *vs.* incongruent) by the SEM-EDS analysis of the cation to silicon ratio in solid residuals. The potency to release ROS in the presence of hydrogen peroxide (Fenton-like activity, Fubini et al., 1995) was finally evaluated for unaltered and leached fibres using the spin trapping technique coupled with electron paramagnetic resonance spectroscopy (EPR).

2. Material and methods

2.1. Analysis of lichen deterioration of fibrous minerals in the field

The physical interaction and the chemical deterioration effect of lichens on asbestos and asbestiform minerals were investigated on four types of fibrous veins (A-D) exposed at the surface of serpentinite rocks in Western Alps (Table 1):