Geophysical Research Abstracts,
Vol. 10, EGU2008-A-07713, 2008
SRef-ID: 1607-7962/gra/EGU2008-A-07713
EGU General Assembly 2008

Chemical and biochemical reactivity of a bioweathered polymineralic fibrous vein (chrysotile-carlosturanite-diopside)

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Insights on asbestos-related diseases led to ban in Europe (99/77/EC) the use of the six commercial fibrous minerals, i.e. chrysotile, crocidolite, amosite, tremolite, antophyllite, actinolite. Asbestos-bearing rocks in mountain areas (e.g. serpentinites), however, may still be source of airborne fibres. In Western Alps, the regulated asbestos chrysotile and tremolite often intergrow with several other asbestiform minerals, such as fibrous antigorite, balangeroite, diopside and carlosturanite. Any study on the natural sources of airborne fibres, which residents and workers in mountain areas may be exposed to, should thus consider both (a) the co-occurrence of different fibrous minerals, and (b) the weathering, atmospheric or due to lichenized and not lichenized fungi, likely affecting the minerals at the exposed surface or even in depth.

In this study, a polymineralic vein from Western Alps (Sampeyre, Varaita Valley, Italy) was shown (XRPD) to consist of three intergrown fibrous phases (chrysotile-carlosturanite-diopside, Ctl:Cst:Dio = 4:3:1). The chemical composition (ICP-AES), the extent of surface area (BET) and the presence of paramagnetic ions (EPR) were studied. The morphology and chemical composition of each of the fibrous components were characterized by SEM-EDS. Cell-free (free-radical production: spin-trapping technique) and cellular in vitro tests (LDH leakage as a marker of cytotoxicity, PPP activity as a marker of oxidative stress) were performed in order to assess the chemical and biochemical reactivity of the whole sample.

Bioweathering driven by lichenized and not-lichenized fungi was evaluated considering the compositional changes of the fibres colonized in the field by the lichen *Candelariella vitellina* (L.) Muell. Arg. and incubated in the laboratory with the soil fungi *Cladosporium cladosporioides* (Fresen.) G.A. de Vries (autochthon of Sampeyre) and *Verticillium leptobactrum* W. Gams.

In order to mimic bioweathering under controlled conditions, the fibres were incubated in solutions of oxalic acid (0.5 and 50 mM), an acidic and chelating molecule involved in fungal-driven weathering. In order to assess the potential hazard of the fibres, the physico-chemical characteristics and chemical/biochemical reactivity of the treated fibres, were compared to the untreated ones. We observed that the polymineralic vein of chrysotile-carlosturanite-diopside exhibits both chemical and biochemical reactivity, behaving similarly to a previously studied commercial chrysotile sample. Fibres colonized by lichens were slightly (carlosturanite, chrysotile) or not (diopside) chemically modified by respect to the uncolonized ones while soil fungi influenced dissolution equilibria of the fibres in the incubation medium.

Following the mimicking approach, only the incubation with oxalic acid 50 mM significantly affected the chemical composition of the three minerals: carlosturanite and chrysotile were completely converted into silica debris. A significant reduction of chemical and biochemical reactivity was parallely observed. Similarly to what observed in fibres colonized by lichens and fungi, incubation with 0.5 mM oxalic acid slightly modified the chemistry of chrysotile, while did not significantly affect carlosturanite and diopside, thus inducing poorly or not significant reduction of reactivity in cell-free and cellular tests.

We here confirm that a highly concentrated solution of oxalic acid (50 mM) deeply affects the chemical composition of polymineralic veins and inactivates chemical and biochemical reactivity. As previously observed in studies on relatively pure fibrous minerals, the solubilization and consequently the change in reactivity induced by a less concentrated solution of oxalic acid (0.5 mM) are strictly related to the dissolution pathway of each mineral and to the paragenesis of the vein.

Potential bioattenuation driven by fungi and lichens should be thus evaluated case by case not only with regard to microorganism diversity (species, strains) but also taking in account the composition of veins, inclusive of not regulated asbestiform minerals.

[List of Acronyms: BET, Brunauer–Emmett–Teller surface area measurement; EPR, electron paramagnetic resonance spectroscopy; ICP-AES, inductively coupled plasma, atomic emission spectroscopy; LDH, lactate dehydrogenase; PPP, pentose phosphate pathway; SEM-EDS, scanning electron microscopy coupled with energy dispersive spectroscopy; XRPD, X-ray powder diffraction spectroscopy]