Supplementary Material (ESI) for JEM
This journal is © 2005 Royal Society of Chemistry

SUPPORTING INFORMATIONS

1) Sample preparation for light and Scanning Electron Microscopy. a) Observations under reflected light microscopy (Leitz mod. Orthoplan) were carried out on polished cross-sections (20 x 20 x 5mm) obtained after including field-samples in a polyester resin and stained using the periodic acid Shiff (PAS) method [a] to highlight lichen development within the lithic substrate. b) SEM observations were conducted on fracture samples, gold or platinum coated, using a Stereoscan S360 Cambridge Electron Microscopy and LEO 1550 (Gemini Series) field emission SEM.

[a] R.B. Whitlach, R.G. Johnson, *Journal of Sedimentary Petrology* **1974**, *44*, 1310-1312]

2) SEM-EDS analysis. Analysis were performed on carbon coated samples with Stereoscan S360 equipped with a QX 2000 Lynk Analytical EDS and Leo 1550 equipped with an IXRF EDS system.

Analytical data on chrysotile fibres from serpentinite outcrops (A, B, C) and one asbestos cement roof, uncolonized or contacted by lichen hyphae, are reported in Table 1 and 2, respectively.

	Outcrop A						**Outcrop B**				**Outcrop C**			
	uncolonized by lichens		below *C. vitellina*		below *N. pulla*		uncolonized by lichens		below *L. rupicola*		uncolonized by lichens		below *X. tinctina*	
	Av. [a]	*S.E.*	*Av.* [b]	*S.E.*	*Av.* [b]	*S.E.*	*Av.* [c]	*S.E.*	*Av.* [a]	*S.E.*	*Av.* [b]	*S.E.*	*Av.* [c]	*S.E.*
SiO_2	40.8	0.5	43.4	0.3	43.1	0.7	42.0	0.2	43.6	1.9	41.5	0.5	42.3	0.9
Al_2O_3	3.3	0.5	6.8	0.4	7.6	2.2	3.6	0.2	3.1	0.2	2.5	0.2	4.7	0.6
$FeO_{(tot)}$	3.7	0.4	5.2	0.4	3.1	0.3	6.3	0.3	7.4	0.8	4.3	0.4	6.7	1.7
MgO	39.4	0.2	31.9	0.8	33.2	2.1	35.5	0.3	29.9	1.1	38.9	0.5	33.8	1.3
H_2O	12.8	0.0	12.4	0.1	12.5	0.1	12.5	0.0	12.2	0.1	12.7	0.0	12.4	0.1

Table 1: Chemical average composition (as oxides wt %) of chrysotile in serpentinites. For every outcrop, columns report chemical composition of chrysotile not interested by lichen colonization (first column), followed by chrysotile colonized by *C. vitellina*, *N. pulla*, *L. rupicola* and *X. tinctina*. Data are presented as means ± S.E. of 7 [a], 5 [b] or 3 [c] independent EDS analyses. The results on MgO wt. % were statistically analyzed by a one-way Analysis of Variance (ANOVA) and Tukey's test ($p < 0.05$ was considered significant): outcrop A: uncolonized vs. *C. vitellina* $p<0.031$ and *N. pulla* $p<0.012$; outcrop B: uncolonized vs. *L. rupicola* $p < 0.028$; outcrop C: uncolonized vs. *X. tinctina* $p<0.006$.

	Asbestos-cement roof			
	uncolonized by lichens		below *C. vitellina*	
	Av. [c]	*S.E.*	*Av.* [a]	*S.E.*
SiO_2	40.4	2.3	45.3	3.2
Al_2O_3	6.5	2.1	7.6	4.8
$FeO_{(tot)}$	1.7	1.3	3.3	1.2
MgO	38.3	1.7	27.3	4.9
H_2O	12.8	0.1	12.3	0.2

Table 2: Chemical average composition (as oxides wt %) of chrysotile in an asbestos-cement roof. Columns report chemical composition of chrysotile not interested by lichen colonization (first column), followed by chrysotile colonized by *C. vitellina*. Data are presented as means ± S.E. of 8 independent EDS analyses. The results on MgO wt. % were statistically analyzed by a one-way Analysis of Variance (ANOVA) and Tukey's test ($p < 0.05$ was considered significant): uncolonized vs. *C. vitellina* $p<0.010$.

3) X-Ray Diffraction on chrysotile samples uncolonized/colonized by lichens in field condition.

XRPD analyses of colonized/ no colonized by lichens chrysotile fibres were performed with Siemens D5000, with 0–20 geometry and Cu Kα radiation). Spectra are shown in the following figure.

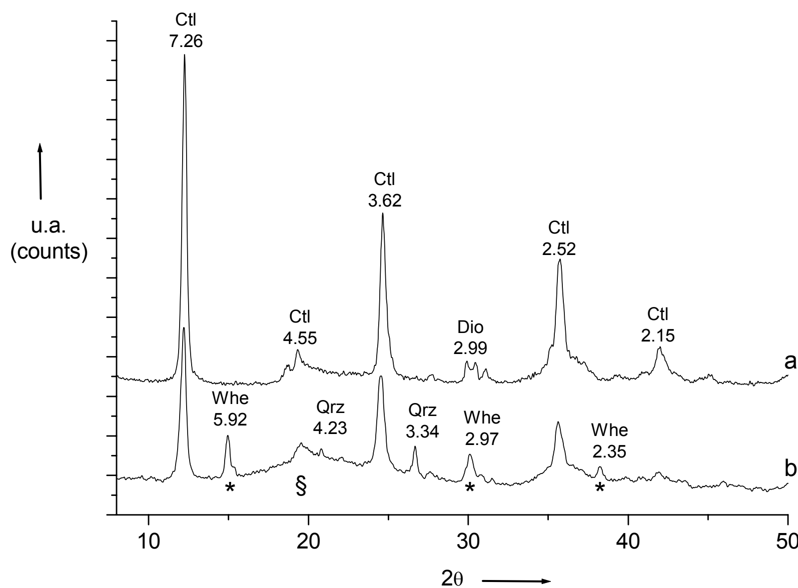
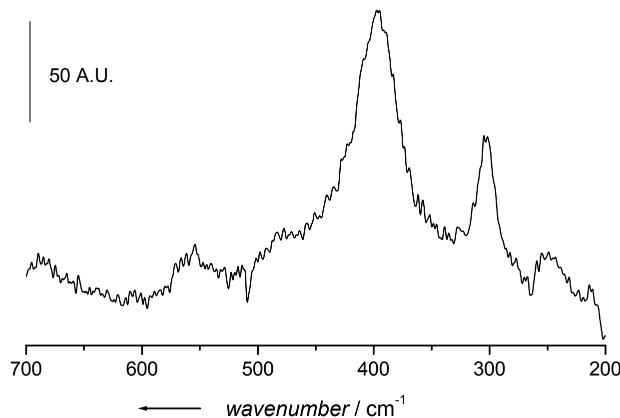


Figure: X-ray diffraction pattern of asbestos-rich serpentinite (a) uncolonized by lichens and (b) at *C. vitellina* interface. On pattern b, marked peaks (*) indicate the neoformation of Ca-oxalate. Broadening of the spectral region around 2θ = 20° (§) is consistent with neoformation of amorphous silica. Quartz occurrence may be due to the retention by lichen thalli of air-bearing particulate. Ctl, chrysotile; Dio, diopside; Qtz, quartz; Whe, whewellite (peaks were compared with the standard JCPD).

4) Micro-Raman Spectroscopy

Minerals at lichen-rock interface were analyzed using a LabRam HR800 (Jobin Yvon), equipped with a laser HeNe, with excitation at 632.8 nm, a CCD detector and a microscope Olympus BX41. The spectra were registered in a backscattering geometry with a resolution of 2 cm^{-1}.

Raman spectrum of goethite (α-FeOOH), detected at *C. vitellina* – asbestos interface, is reported (see ref. [a] for spectrum assignment).



[a] D. Bersani, P.P. Lottici, A. Montenero **1999**, *J. Raman. Spectrosc., 30*, 355-360.

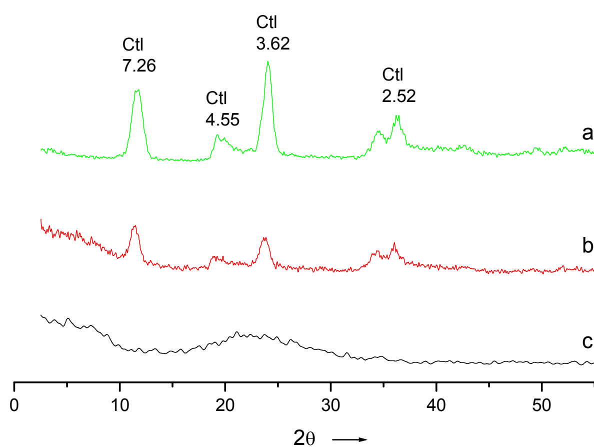
5) Laboratory biomimetic leaching tests. Chrysotile fibres from the Balangero asbestos mine were placed in lots of 200 mg into 200 ml of oxalic acid aqueous solutions 0.005 mM, 0.5 mM and 50 mM. All the experiments were carried out at 25° without stirring for 35 days. At the end of the experiments, the samples were filtered and drained. SEM-EDS analysis were performed with Stereoscan S360 equipped with a QX 2000 Lynk Analytical EDS on the dried filtered material.

Analytical data are reported in Table 3.

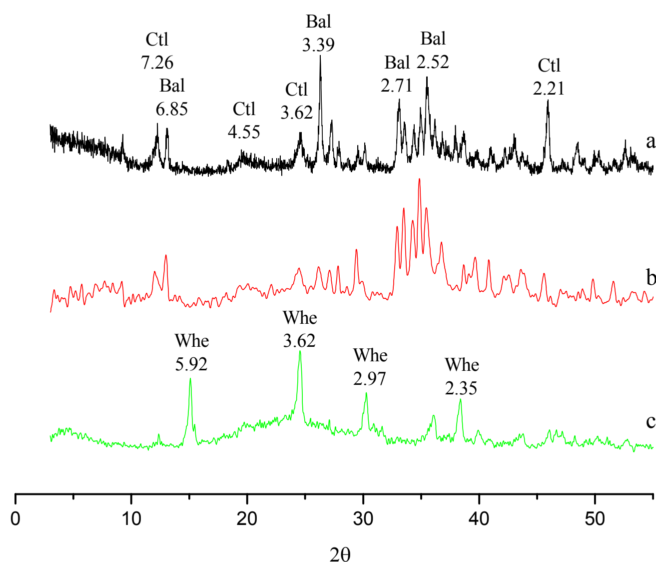
	Untreated		Oxalic acid					
	0 mM		0.005mM		0.5 mM		50mM	
	Av.	*S.E.*	*Av.*	*S.E.*	*Av.*	*S.E.*	*Av.*	*S.E.*
SiO_2	43.4	0.9	49.0	1.6	50.0	4.8	87.2	0.3
Al_2O_3	1.3	0.7	0.0	0.0	0.6	0.6	0.0	0.0
$FeO_{(tot)}$	5.9	0.1	7.5	1.6	5.6	2.5	0.0	0.0
MgO	37.0	0.4	31.0	0.9	30.9	1.3	0.4	0.2
H_2O	12.5	0.0	12.5	0.0	12.9	0.0	12.4	0.0

Table 3: Chemical average composition (as oxides wt %) of chrysotile after biomimetic leaching tests. Columns report chemical composition of chrysotile incubated with oxalic acid from 0 to 50 mM. Data are presented as means ± S.E. of 3 independent EDS analyses.

6) X-Ray Diffraction on chrysotile samples treated with oxalic acid in the laboratory for 35 days.



Chrysotile untreated (a), treated with oxalic acid 0.5 mM (b) and 50 mM (c).



Chrysotile mixed to balangeroite, a fibrous mineral characteristic of the Balangero asbestos mine, untreated (a), treated with oxalic acid 0.5 mM (b) and 50 mM (c).

7) Free radical release measurement

In order to detect the Fenton activity of the fibres in aqueous suspension, hydrogen peroxide and the spin trapping agent DMPO (5,5'-dimethyl-pyrroline-N-oxide), which in aqueous medium gives the stable $[DMPO\text{-}OH]^\bullet$ adduct, have been employed following a well established technique.[a] The intensity of the typical four lines 1-2-2-1 EPR (Electron Paramagnetic Resonance spectroscopy) spectrum of $[DMPO\text{-}OH]^\bullet$ is a direct measure of the amount of $OH^\bullet$ radicals generated. 0.250 ml of H_2O_2 (0.5 M in H_2O), 0.250 ml of DMPO (0.05 M) and 0.500 ml of phosphate buffer (1M) were added to 22.5 mg of the solid sample. The radical formation was evaluated by recording at 10', 30', 60' the EPR spectrum of the $[DMPO\text{-}OH]^\bullet$ adduct. EPR experimental conditions were: microwave power 10 mW; modulation 1000 mG; scan range 120 G; field set 3345.

[a] B. Fubini, L. Mollo, E. Giamello, *Free Rad. Res.* **1995**, *23*, 593-614