Asbestiform antigorite – implications for the risk assessment of fibrous silicates

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Introduction

Investigation of historic asbestos workings in South Australia, during 2005, identified antigorite as the serpentine 'asbestos' mineral mined during the period 1940s to 1978 from a small quarry near Rowland Flat, 47 km northeast of Adelaide, South Australia (Keeling et al. 2006). The quarry supplied around 200 tpa of mixed asbestos and talc to Adelaide industrial minerals processor, SN Rodda & Co (SA) Pty Ltd, who produced a milled fibrous filler for various industrial uses, including vinyl floor tile manufacture. Past and present production of asbestos worldwide is dominated by chrysotile, while antigorite is widely regarded as the non-asbestiform variety of serpentine (e.g. Virta 2001). This situation continues despite fibrous antigorite, occurring with lateritic nickel ore, being identified in the 1980s as the likely cause of 25 cases of asbestosis in workers at the Szklary nickel plant in Poland (Wozniak et al. 1988) and abundant asbestiform antigorite veins in serpentinites in the Italian Western Alps (Groppo and Compagnoni 2007) regarded as a possible environmental hazard (Cardile et al. 2007, Pugnaloni et al. 2010). Confirmation of the identification and asbestiform character of Rowland Flat antigorite underscores the requirement for continuing mineralogical studies to refine our knowledge of fibrous minerals and improve the assessment of their potential health hazard. There remains a critical need to agree methods to determine the relative potency of various mineral fibres with regard to human health so that measures to minimise or avoid risk are appropriate and reflect the potential hazard.

Geology

Rowland Flat antigorite is present as cross-fibre veins and irregular patches within an altered calcsilicate marble bounded by mica-vermiculite-quartz schist. The marble formed from a silty dolomitic carbonate lens within marine Woolshed Flat Shale of Neoproterozoic age that recrystallised under lower amphibolite-grade metamorphic conditions during orogenic events in the Late Cambrian–Early Ordovician (Keeling et al. 2008). The deposit is close to the regional Williamstown Fault zone and the coarse-grained calcsilicate is fractured and brecciated and extensively altered, possibly by fluids channelled along the fault, resulting in a mixture of talc, serpentine and calcite with patches of chalcedonic quartz. The calcsilicate unit is 40-50 m wide, dips steeply to the east and has been traced along strike for ~750 m. Fibrous antigorite, in cross-fibre veins and replacing earlier-formed tremolite, is intimately associated with fine-grained calcite. The quarry site was chosen in an area where the rock is weathered and partly leached of calcite to give masses of fibrous antigorite in a talcose matrix.

Analyses

The white to pale green 'asbestos' from Rowland Flat was identified as antigorite from powder X-ray diffraction (XRD) patterns of selected fibre masses. For comparison, XRD traces were acquired for various serpentine asbestos samples held in the CSIRO Land and Water mineral collection. This revealed another sample of asbestiform antigorite labelled 'serpentine asbestos from Sierra Nevada, Granada, Spain' comprised of white asbestos fibres some 250 mm in length (Fig. 1). The overall XRD pattern, and reflections at d-spacing 2.52Å, 2.15Å and 1.56Å in particular, were used to positively identify antigorite, compared to chrysotile (Fig. 2). Fourier-transform Infrared (FTIR) analysis (acquired by R Frost, QUT) was diagnostic in identifying antigorite from chrysotile (Keeling et al. 2008) but Raman spectral analysis failed to give useful spectra for the antigorite samples, due to suspected high proportion of crystal structure defects (R Frost pers comm. 2006).

Fig. 1. Asbestiform antigorite from Granada, Spain (upper) and from Rowland Flat (lower)

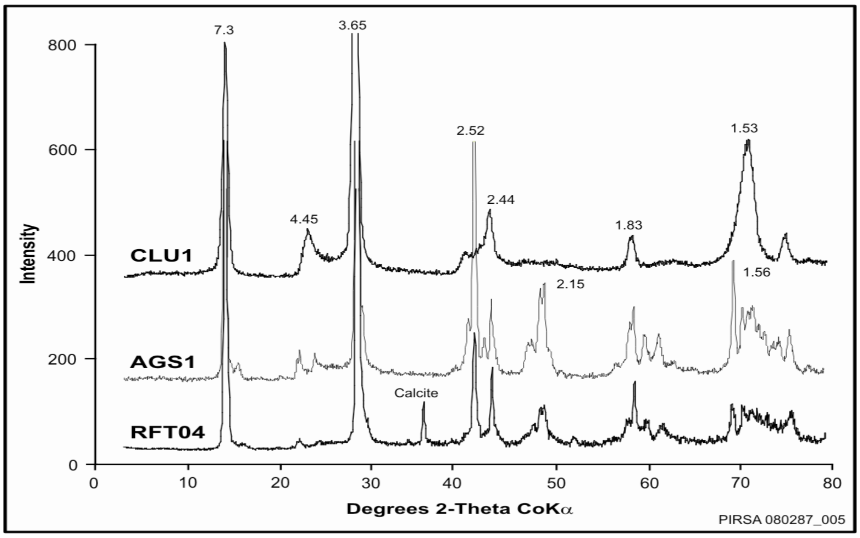

Fig. 2. XRD patterns of asbestiform antigorite from Rowland Flat (RFT04) and Granada (AGS1) and chrysotile from Lucknow, New South Wales (CLU1). Peak positions in angstroms.

Electron microscopy shows antigorite fibre bundles, tens of microns across, are composed of splintery, lath-shaped fibres 0.5-4 μm across, typically with a high aspect ratio exceeding 100:1 (Fig. 3). The fibres show parting down the long axis to give fibrils <0.2 μm width and <5 to >100 μm in length. Using transmission electron microscopy (TEM), the lath morphology of antigorite was obvious, as distinct from chrysotile tubes, and individual fibres were confirmed as antigorite by their characteristic electron diffraction pattern (Keeling et al. 2008). A high resolution TEM study of Rowland Flat antigorite by Fitz Gerald et al. (2010) show the laths result from poor cohesion at interrupted crystal domain boundaries and pores, while fibrils form from parting along crystal defects that are a consequence of compositional variation across individual crystals. From EDX analyses, an average composition of $(Mg_{2.647}Al_{0.10}Fe_{0.076})Si_2O_5(OH)_{3.62}$ for Rowland Flat antigorite was calculated based on the m = 17 polysome and assuming no Al in tetrahedral coordination (Keeling et al. 2008).

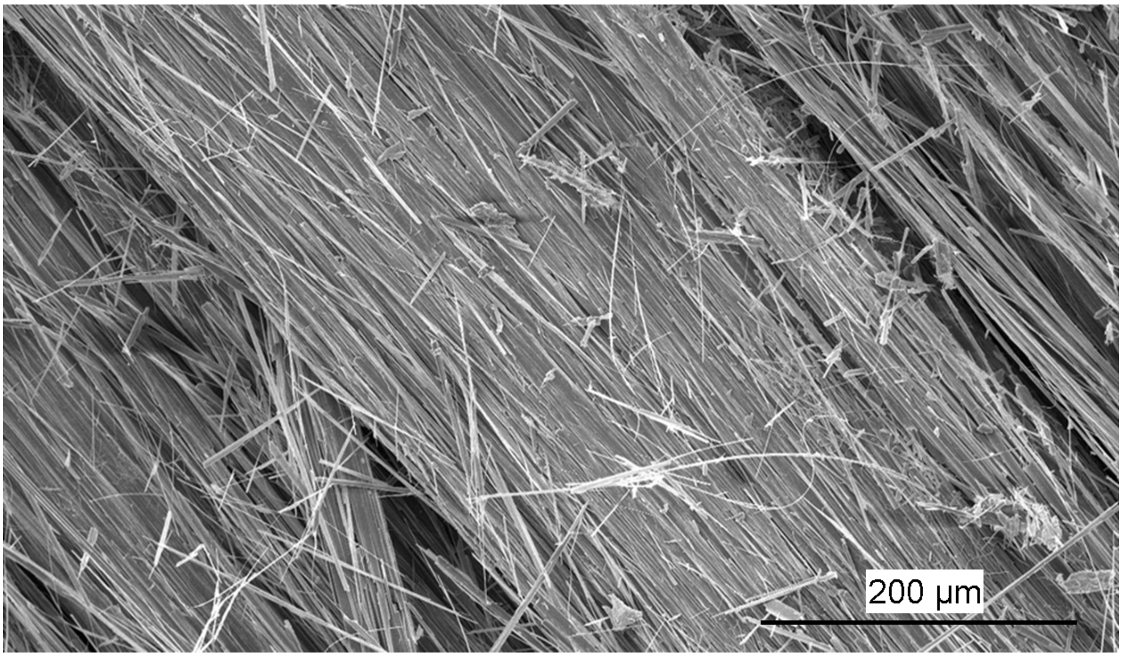

Fig. 3. Rowland Flat asbestiform antigorite, SEM secondary electron image of long thin fibres showing variable width and flexibility.

Health risk from mineral fibres

Asbestiform antigorite, such as that from Rowland Flat, Poland and Italy, appear to satisfy many of the determinant characteristics of an asbestos mineral and, on the basis of the Polish experience, pose a potential health risk. The mineralogical characteristics indicate that the risk is different to chrysotile, with which it is most likely to be confused, yet asbestiform antigorite is not recognized in most asbestos regulation. International epidemiological studies, largely around the asbestos industry, have resulted in a regulatory regime based on a definition of asbestos that includes six naturally occurring minerals: the serpentine mineral chrysotile and the amphibole minerals riebeckite asbestos (crocidolite), grunerite-cummingtonite asbestos (amosite), anthophyllite asbestos, tremolite asbestos, and actinolite asbestos. The focus on commercial asbestos has been useful and widely accepted but has distracted attention from work discriminating the relative hazard of particular mineral fibres and has not served to predict the hazard from other fibrous amphiboles including fluoro-edenite, winchite, richterite or magnesio-riebeckite or other fibrous silicates including erionite, balangeroite, carlosturanite and antigorite. Fibrous clays such as sepiolite, palygorskite (attapulgite) and halloysite have not been shown to have an adverse affect on health. This may reflect the fact that most commercial deposits produce fibres that are typically <5 μm long. As new uses and deposits are developed the physical and chemical characteristics may change and there is an argument for continual monitoring in order to predict or detect potential adverse health effects.

Current opinion is that fibres <3 μm diameter and >5 μm long are among the most dangerous as they can become lodged in the alveolar regions of the lung and are not easily cleared by macrophage-mediated phagocytosis. Their persistence in the lung may lead to asbestosis, lung cancer and mesothelioma. The degree of hazard is dependent on a variety of factors that are related to mineral variables still not fully understood but include fibre type, physical characteristics and chemistry. Testing *in vitro* to examine the effects of fibre interaction with cell cultures and *in vivo* involving fibre placement inside laboratory animals have been argued as generally too sensitive and not addressing fully the natural clearance mechanisms and biopersistence in humans. Epidemiological studies that relate to fibre exposures over 10 to 40 years previous are arguably most definitive but clearly are an unsatisfactory approach for assessing the risks with exposure to a new mineral form, or source with different characteristics. The need for further research into definitive tests for fibre characterisation and effects on human health is clear; the case for which is strongly advocated in the recent draft NOISH roadmap for research on asbestos fibres and other elongated mineral particles (NOISH, 2009).

References

Cardile V, Lombardo L, Belluso E, Panico A, Capella S, Balazy M (2007) Toxicity and carcinogenicity mechanisms of fibrous antigorite. *International Journal of Environmental Research and Public Health* **4**: 1-9.

Fitz Gerald JD, Eggleton RA, Keeling JL (2010) Antigorite from Rowland Flat, South Australia: asbestiform character. *European Journal of Mineralogy* **22** (4) (in press).

Groppo R, Compagnoni R (2007) Ubiquitous fibrous antigorite veins from the Lanzo Ultramafic Massif, Internal Western Alps (Italy): characterisation and genetic conditions. *Periodico di Mineralogia* **76**: 169-181.

Keeling JL, Raven MD, McClure SG (2006) Identification of fibrous mineral from Rowland Flat area, South Australia. Department Primary Industries and Resources, South Australia, report book 2006/02.

Keeling JL, Raven MD, Self PG, Eggleton RA (2008) Asbestiform antigorite occurrence in South Australia. *Proceedings 9th International Congress for Applied Mineralogy* (ICAM), Brisbane September 2008, AusIMM, Melbourne: 329-336.

NIOSH (2009) *Revised draft. NIOSH current intelligence bulletin. Asbestos fibers and other elongated mineral particles: State of the science and roadmap for research. January 2009.* Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health http://www.cdc.gov/niosh/review/public/099-C/pdfs/AsbestosRoadmapPublicCommentDraftV4.pdf <accessed 28 June 2010>.

Pugaloni A, Giantomassi F, Lucarini G, Capella S, Belmonte MM, Orciani M, Belluso E (2010) Effects of asbestiform antigorite on human alveolar epithelial A549 cells: A morphological and immunohistochemical study. *Acta histochemica* **122**: 133-146.

Virta RL (2001) Some facts about asbestos, United States Geological Survey fact sheet, FS-012-01, 4 p.

Wozniak H, Wiecek E, Stetkiewicz J (1988) Fibrogenic and carcinogenic effects of antigorite. *Polish Journal of Occupational Medicine and Environmental Health* **1**: 192-202.