Investigation of Structure Composition Relationships in the Serpentine Minerals by Combined *X*-ray K-emission Spectrometry and High-resolution Electron Microscopy

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Summary High-resolution electron microscopy along with simultaneous energy dispersive analysis of the emitted *X*-rays unequivocally establishes that chrysotile and antigorite are polymorphs with each being free of aluminium, and that lizardite has aluminium in both octahedral and tetrahedral sites.

Serpentine minerals [idealized formula $Mg_3Si_2O_5(OH)_4$] occur in three well known forms: lizardite, which has a platy morphology; antigorite, which is also essentially platy but is thought to be corrugated; and chrysotile, which is tubular. All three are known,[1,2] from *X*-ray and other studies, to be made up of layers, separated by *ca.* 0·7 nm, the components of which are a two-dimensional network of $Mg(O,OH)_6$, edge-sharing, octahedra intimately attached to sheets of linked, corner-sharing SiO_4 tetrahedra, see Figure 1. On the basis of known bond distances and simple geometry it is clear that, in structures corresponding to the idealized formula, the Mg-containing component is too large to enmesh perfectly with the contiguous

SiO_4 tetrahedral component, some oxygens being common to both the octahedral and tetrahedral sheets. The tubular morphology of chrysotile, as well as the corrugated structure of antigorite are thought, on the basis of circumstantial evidence, to arise from this very cause. Moreover the flatness of the two-component sheets in lizardite is thought to arise from an equalizing of the octahedral and tetrahedral meshes which, in turn, is supposed to occur as a result of substitution by Al^{3+} ions of either Mg^{2+} (in octahedral sites) and/or Si^{4+} (in tetrahedral sites).

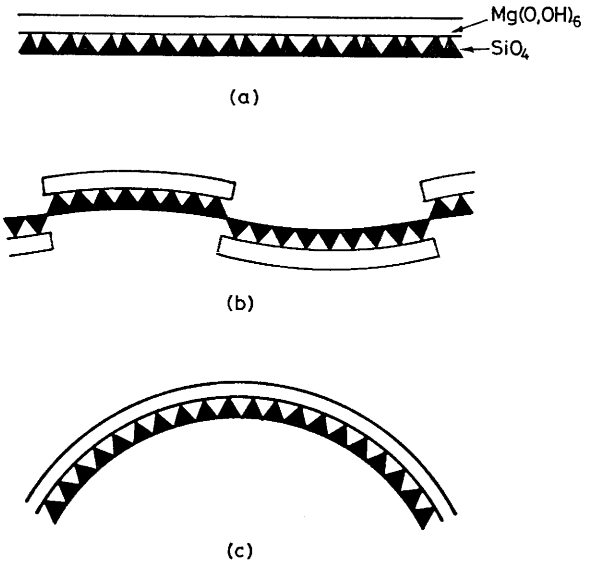

Figure 1. Schematic illustration of the supposed structure of, (a), lizardite; (b), antigorite; and (c), chrysotile. (See text).

Hitherto it has been difficult to test the validity of this picture owing *inter alia* to the co-existence of minute quantities of at least two, often of all three, members of the serpentine minerals in, ostensibly, a 'pure' sample. Clear cut answers, free from the ambiguities of chemical and structural averaging have, therefore, been hard to obtain. Here we show that high-resolution electron microscopy and energy dispersive analysis (EDA) resolve the problem.

Full details of the experimental work and of the three geologically distinct sources of serpentine will be given elsewhere.[3] Suffice it to note that: (a) a double-tilt, high resolution electron microscope, specially modified so as to permit an Si(Li) *X*-ray detector to be positioned *ca.* 2·0 cm from the specimen and lattice imaging down essentially any desired zone-axis, was used. (b) Colloidal graphite was painted on to all exposed inner parts of the microscope (to minimize spurious *X*-ray signals). (c) Absorption and *X*-ray fluorescence corrections (particularly serious when there are trace impurities of iron) were taken into account. (d) Calibration, for quantitative EDA, was achieved using special silicate standards (previously prepared for electron probe microanalysis). (e) Specimen diameter ranging from 30 to 150 nm could be routinely focussed upon and the EDA could be used to detect the presence of any spurious micaceous and talc-like impurities. (f) Specimen thickness (generally <50 nm) could be estimated from known theoretically computed image variation with thickness.[4] (g) High resolution images (taken at screen magnifications up to 300,000) identified the particular mineral unambiguously.

It transpired that antigorite and chrysotile are, to all intents and purposes, compositionally identical; neither contains any significant amounts of aluminium (Figure 2), but they may possibly differ in (OH) content. The flat lizardite does, however, contain Al^{3+} ions, it being estimated from the observed composition that 16% of the Mg^{2+} in octahedral sites and 12% of the Si^{4+} (tetrahedral) were replaced by the aluminium. It was also noted that large tubular specimens of chrysotile did contain traces of Al, there being a rough correlation between the radius of curvature and the inverse of the Al content.

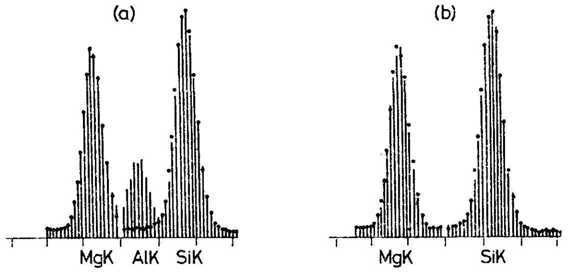

Figure 2. Typical K-emission spectra recorded from microscale regions of the three serpentines. The spectra are superimposed in pairs to assist comparison. (a) Lizardite/chrysotile, (b) antigorite/chrysotile. Note the Al-K_α peak in lizardite.

More significant than the results themselves and the light they throw on geochemical aspects of the serpentines is the implication of what may shortly be accomplished with electron microscopes that function with smaller spot sizes and still higher resolutions.[5]

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