7 APPENDIX

The electronic deposit includes five tables (A1 toA5) and the merged spectra, which are shown in Figure 2 as the heavy lines. All files are formatted as tab delimited text in two columns. The left column is wavenumbers (cm-1) whereas the right column is absorbance on a natural logarithm basis. The following is a list of the files, the specific mineral and the thickness:

Tremolite0.62.txt provides spectral data on a 0.62 micron thick

Canaan sample up to 4000 cm^{-1}

The rest of the files provide only the lattice modes (range of about 50 to 1200 cm-1).

Brucite1.0mic.txt provides brucite spectra for a thickness of 1.0 microns.

Talc0.41.text provides spectra of synthetic talc from a thickness of 0.41 microns.

Lizardite0.50.txt provides a combination of lizardite and chrysotile spectra for a thickness of 0.50 microns.

Saponite0.84.txt provides the Scottish sample with a thickness of 0.84 microns.

Montm0.75 txt shows the U.K. sample at a thickness of 0.75 microns.

Sapphire.txt and actinolite.txt spectra hve thickness very roughly of 1.0 microns.

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Table A1. Chemical analyses (in wt %) obtained using an electron microprobe. Water content is obtained from 100% less the measured total from electron microprobe analysis. b.l.d. = below the limit of detection.

	actinolite	talc, natural
SiO_2	54.74	63.15
TiO_2	0.02	0.007
Al_2O_3	0.65	0.005
Cr_2O_3	b.l.d.	b.l.d.
FeO	7.13	1.41
MnO	0.08	0.018
MgO	19.19	29.75
NiO	0.23	0.163
CaO	12.79	0.010
K_2O	0.03	b.l.d.
Na2O	0.23	b.l.d.
Total	94.90	94.53
H_2O	5.10	5.47

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Tables A2-A6 provide symmetry analyses of fundamental vibrational modes. R = Raman active. IR = IR active. T = translation. R = rotation/libration. Fately et al. (1979) provide tables relating crystallographic notation to the point symmetry used in spectrocopy. Farmer (1974) or Cotton (1971) provide character tables used to deduce the number and type of the vibrations. The top half of each table derives the number of vibrational modes whereas the bottom half provides the breakdown into types of atomic motions. Structural details needed to perform the analyses are provided by Wyckoff (1963), Smith and Bish (1999) and the cited references.

Table A2 provides a symmetry analysis of the modes involving H. Hydroxyl vibrations are treated separately from the lattice motions, because the small H^+ cation serves mainly to reduce the charge of the O^{2-} anion, and thus can be treated as an impurity ion. For most of the structures here, the position of the O-H bond is structurally controlled, e.g., perpendicular to the layers.

Tables A3-A6 describe the lattice and the external modes. A detailed analysis of the internal modes of the silicate chains and sheets is beyond the scope of this report, and is not warranted without single-crystal IR spectra.

Table A2. **Summary of IR activity derived from mineral structures**. Actinolite has the same structure as tremolite, and therefore the same numbers and types of IR modes. Symmetry analysis are given in the appendix (website) and by Buchanan, Caspers & Murphy (1963a). For brucite, we assume all O-H dipoles are parallel to the c-axis of the crystallographic stucture. *For these hexagonal structures, modes ⊥**c** should dominate the spectrum. †Analysis given for the triclinic polymorph. § Water molecules between the layers of the clay structures will have 2 O-H stretching modes and 1 H-O-H bending mode. X indicates any of the cations in the structure. Density in g/cm^3.

Mineral	Ideal formula	Lattice modes	OH modes
brucite	$Mg(OH)_2$	1 Mg-(OH) each ‖**c** + ⊥**c**∗	O-H ‖**c** +Mg-O-H ⊥**c**
tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	26 modes ‖**a** +31 modes ⊥**a**	O-H ‖**a** +2 X-O-H ⊥**a**
sapphirine	$(Mg_{3.5}Al_{4.5})(Al_{4.5}Si_{1.5})O_{20}$	102 modes total†	not expected
lizardite	$Mg_3Si_2O_5(OH)_4$	8 modes ‖**c** +13 modes ⊥**c**∗	2 O-H ‖**c** +4 X-O-H ⊥**c**
talc	$Mg_3Si_4O_{10}(OH)_2$	27 modes total	O-H +2 X-O-H
saponite	$Na_{0.3}Mg_3(Al_{0.3}Si_{3.7})O_{10}(OH)_2 \cdot 4H_2O$	talc + interlayer cations	O-H +2 X-O-H +water§
montmorillonite	$Na_{0.3}(Mg_{0.3}Al_{1.7})Si_4O_{10}(OH)_2 \cdot nH_2O$	talc + interlayer cations	O-H +2 X-O-H +water§

Table A3. **Tremolite.** Space group is $C2/m$=C^3_{2h} with 1 formula unit in the primitive unit cell. O3 is the hydroxyl site. The Mg_3O pyramid consists of the sites 2M1, M3, and O3 and will have stretching and bending motions as described. In addition to the modes enumerated below are hydroxyl motions: the O-H bond is parallel to the **a**-axis, and therefore the O-H stretch will be parallel to **a** with two H-O-M bends (parallel to **c** and roughly parallel to **b**).

site	symmetry	R A_g	R B_g	R,IR‖**c** A_u	R,IR⊥**c** B_u
M1	C_2	1	2	1	2
M2	C_2	1	2	1	2
M3	C_{2h}	0	0	1	2
Ca	C_2	1	2	1	2
2Si	C_1	2×3	2×3	2×3	2×3
5O	C_1	5×3	5×3	5×3	5×3
O	C_S	2	1	1	2
O3	C_S	2	1	1	2
total		28	29	27	33
acoustic		0	0	1	1
optic		28	29	26	32
T(Ca)		1	2	1	2
T(M2)		1	2	1	2
M_3O stretch		1	1	1	2
M_3O bend		1	1	1	2
T(M_3O)		1	0	0	1
R(M_3O)			1	1	1
chain		23	22	21	21

Table A4. **Lizardite**. Space group is $P31m$=C_{3v}^2 with 1 formula unit in the primitive unit cell. See Smith and Bish (1988) and Klein (2000) for structural details. O3 and O4 are hydroxyl sites. The motions of the edge-sharing Mg octahedra are difficult to deduce. In addition to the modes listed in the table are hydroxyl motions: The O-H bonds are parallel to the **c**-axis, and therefore two O-H stretches will be parallel to **c** with two (degenerate) H-O-M bends perpendicular to **c**. Chrysotile and the other serpentine minerals will differ in the polarizations of the modes and could have more IR modes. Serpentine minerals are complicated structurally because the various ways that the layers (Fig. 1e) can stack leads to polymorphism, and the mismatch between the tetrahedral and octahedral layers causes the layers to roll, forming the fibers of chrysotile. We present a factor group analysis of the triclinic lizardite structure because a complete crystallographic refinement is available (Mellini 1982).

site	symmetry	R, IR||**c** A_1	R,IR A_2	R,IR⊥**c** E
Mg	C_s	2	1	3
Si	C_3	1	1	2
O1	C_3	1	1	2
O2,O3	C_s	2×2	2×1	2×3
O4	C_{3v}	1	0	12
total		9	5	14
acoustic		1	0	1
optic		8	5	13
Mg-(OH)		5	2	7
Si sheet		3	3	6

Table A5. **Talc**. Space group is $C\overline{1}$=C_i^1 with 1 formula unit in the primitive unit cell. O2 is the hydroxyl site. The motions of the edge-sharing Mg octahedra are difficult to deduce. In addition to the modes listed in the table are hydroxyl motions: The O-H bond is perpendicular to the layers, and therefore the O-H stretches will be perpendicular to the layers with two H-O-M bends within the layers

site	symmetry	R A_g	IR A_u
M1	C_i	0	3
M2	C_1	3	3
2Si	C_1	2×3	2×3
6O	C_1	6×3	6×3
total		27	30
acoustic		0	3
optic		27	27
T(M1)		0	3
M-O motions		6	6
Si sheet		18	18

Table A6. **Sapphirine**. For the triclininc polymorph, space group is $P\overline{1}$=$C_i^1$with 2 formula units in the primitive unit cell (Merlino, 1980). The structure contains one Al atom in a octahedron linking the chains (the M8 site). For the cations in the sites M3, M5, M6 and M8, the coordinating oxygens are all linked to the Si tetrahedra. The remaining 5 octahedral sites are coordinated to O6 and O14. Due to the complexity of the structure, a breakdown of the optic modes into sub-categores was not attempted.

Sapphirine has varying degrees of ordering of Al/Mg or Al/Si in the octahedral and tetrahedral sites, respectively, and varying proportions of the three cations. Both monoclinic (Moore 1969) and triclinic (Merlino 1980) structures are known. The sample examined here is from the same locality studied by Moore (1969). From symmetry analysis, the monoclinic structure is expected to have 101 modes for IR light polarized ||**a** and 101 modes ⊥**a**. Christy et al. (1998) predicted 100 B_u modes by assuming that 2 acoustic modes occur in this symmetry, but only one acoustic mode is expected (see Farmer 1974 or Cotton 1971). Triclinic sapphirine should have 101 IR active modes and 1 acoustic mode (which varies with the orientation).

site	symmetry	R A_g	IR A_u
Al in M8 and M9	C_i	2x0	2x3
all other atoms	C_1	33x3	33x3
total		99	105
acoustic		0	1
optic		99	104