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Laboratoire PPME

Raman Spectroscopy of Asbestos - Polymorphs of Serpentine

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Asbestos

Group of silicate minerals, characterized by crystals with thin fibrous habit.

Highly resistant to fire, heat and chemical attack. Good tensile strength. Largely used in buildings in recent past.

Group	Species	Formula
Serpentine	chrysotile	$Mg_3\ [Si_2O_5]\ (OH)_4$
	Amosite	$(MgFe^{2+})_7\ [Si_8O_{22}]\ (OH)_2$
	Actinolite	$Ca_2\ (MgFe^{2+})_5\ [Si_8O_{22}]\ (OH,F)_2$
Anfibole	Antofillite	$(MgFe^{2+})_7\ [Si_8O_{22}]\ (OH,F)_2$
	Crocidolite	$Na_2Fe^{2+}{}_3Fe^{3+}{}_2\ [Si_8O_{22}]\ (OH)_2$
	Tremolite	$Ca_2Mg_5\ [Si_8O_{22}]\ (OH)_2$

Danger

The release of thin fibers on the air during the working and the use of asbestos, cause high illness risks.

Very dangerous are the *inhalable fibers* (length > 5µm ; diameter < 3µm).

Asbestosis	Mesothelioma	Lung Cancer

Important risk parameters:

Fibrous habit	Chemical Composition	Biopersistence

SERPENTINES

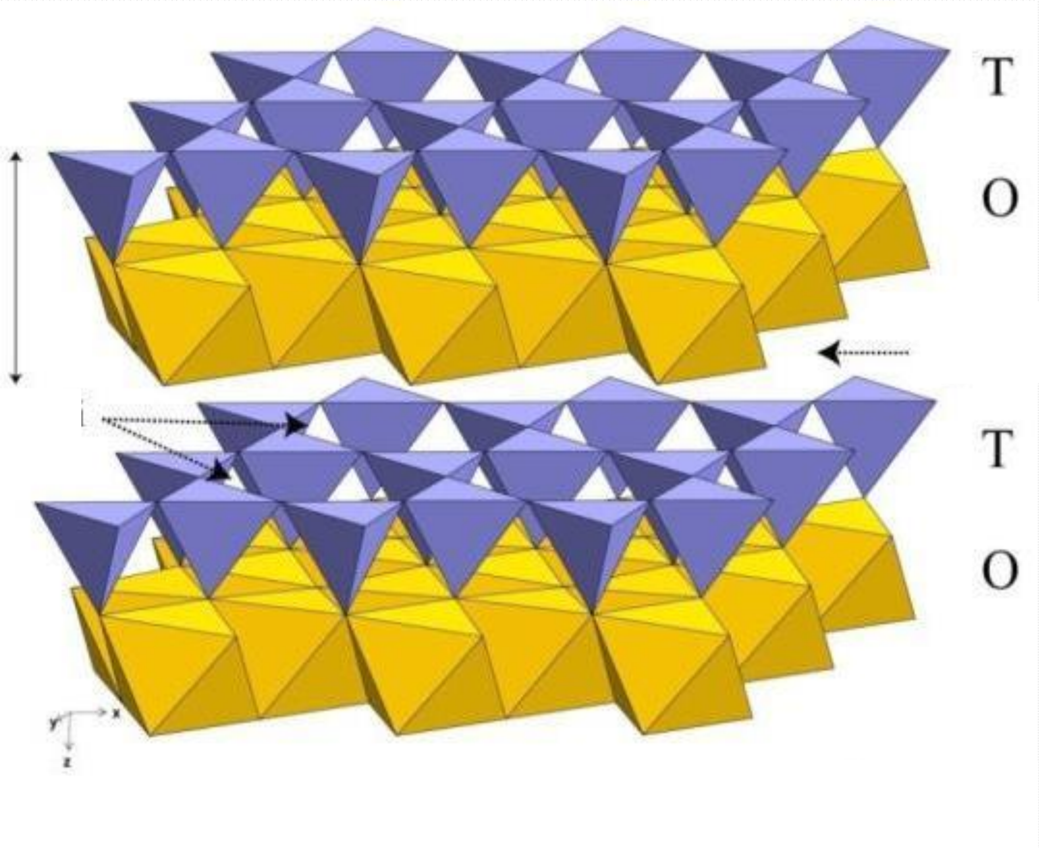
Group of phyllosilicates, originating from the hydration of mafic minerals (olivine, pyroxene).

Retrograde metamorphism of ultrabasic rocks.

Prograde metamorphism of older serpentinites.

Trioctahedral Phyllosilicates 1:1 (TO)

$Mg_3Si_2O_5(OH)_4$



T layer: SiO_4 tetrahedra

O layer: MgO_6 octahedra

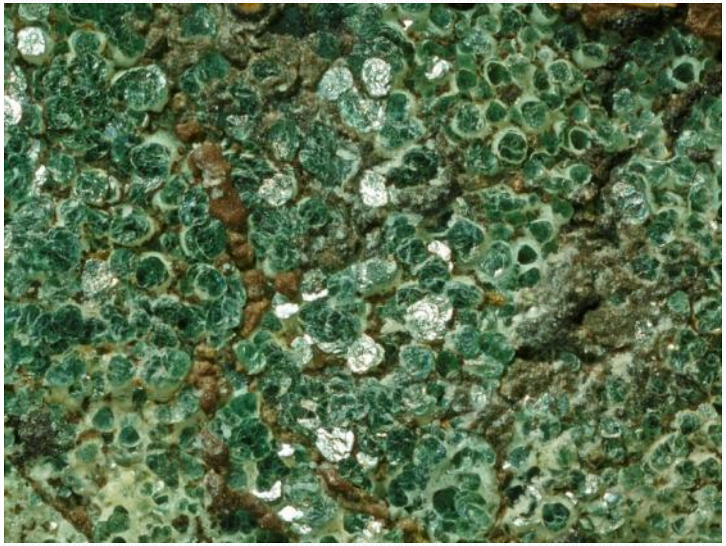
Main minerals:
- Lizardite
- Antigorite
- Chrysotile
- Polygonal Serpentine

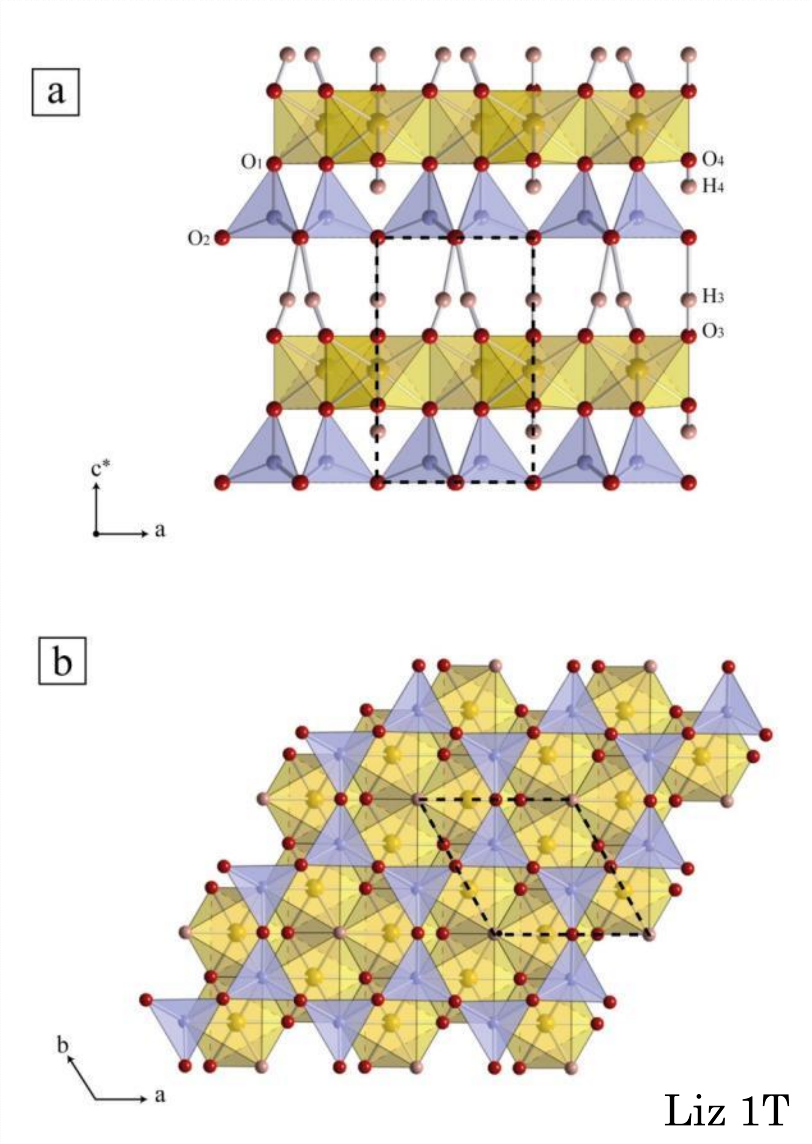
13% wt in H_2O

Structural «problem»: **mismatch** between T and O layers

Lizardite

Tiny plates habit





Liz 1T

Most abundant in outcrops.

Simplest configuration.

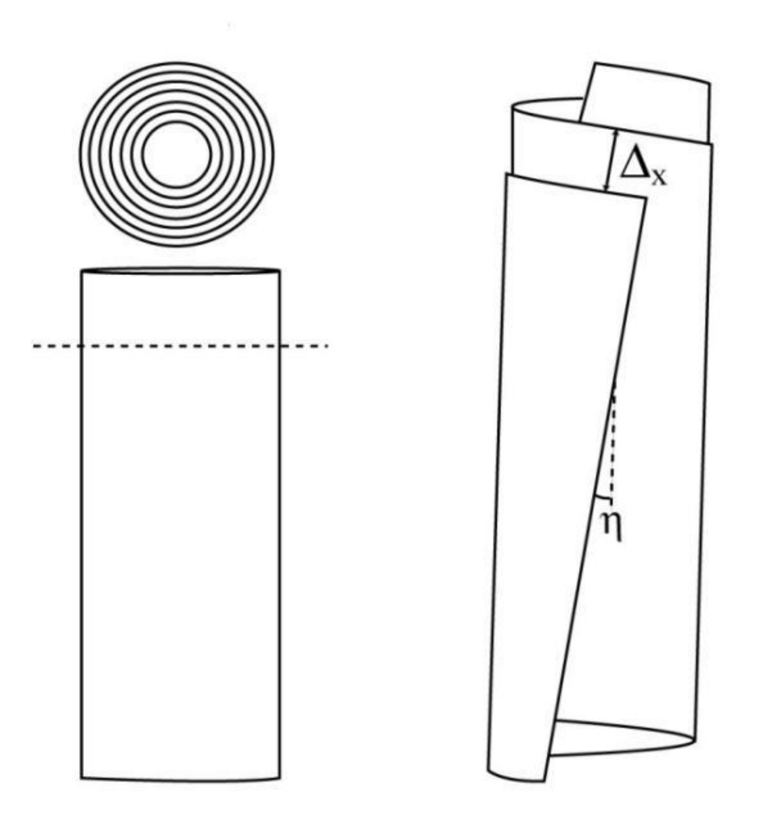
Planar geometry of the layers
→ Si, Mg partly substituted by Al

Politypes -1T -2H1

Not dangerous

Fibrous habit

Chrysotile



Asbestiform variety

Less abundant than lizardite and antigorite

Cylinder or *spiral structure*

the lattice mismatch causes a roll-up along a crystallographic axis:
X (orto- and clino-) or Y (para-)

d < 100 nm

Usually found in silky veins

Highly dangerous

Antigorite

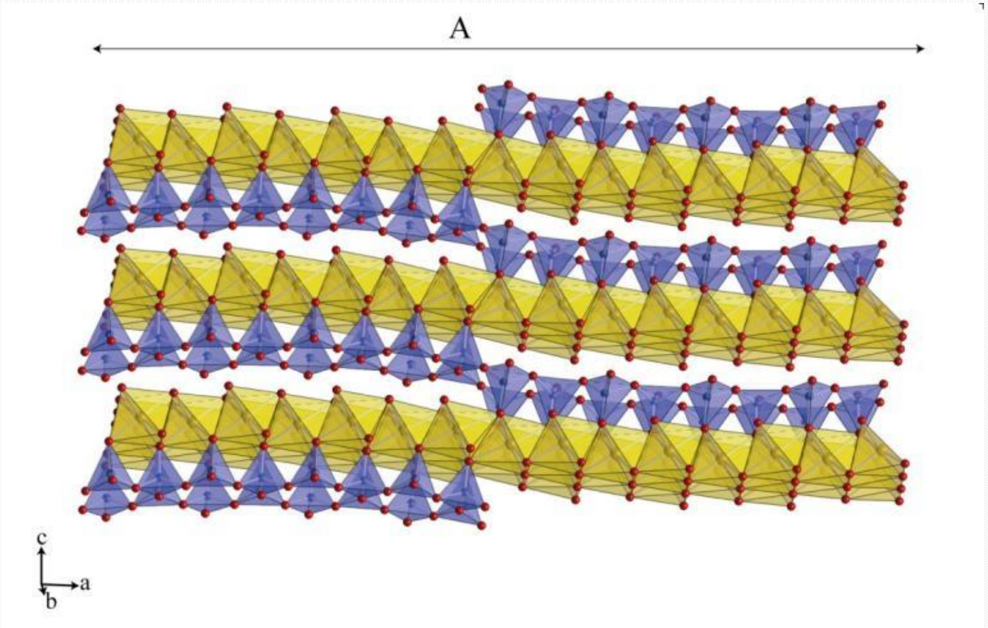
Tiny Plates Habit

Polymorph stable at high T

Wave structure

Regular waves along *a*
period A = 31-55 Å

deficit in Mg and OH groups



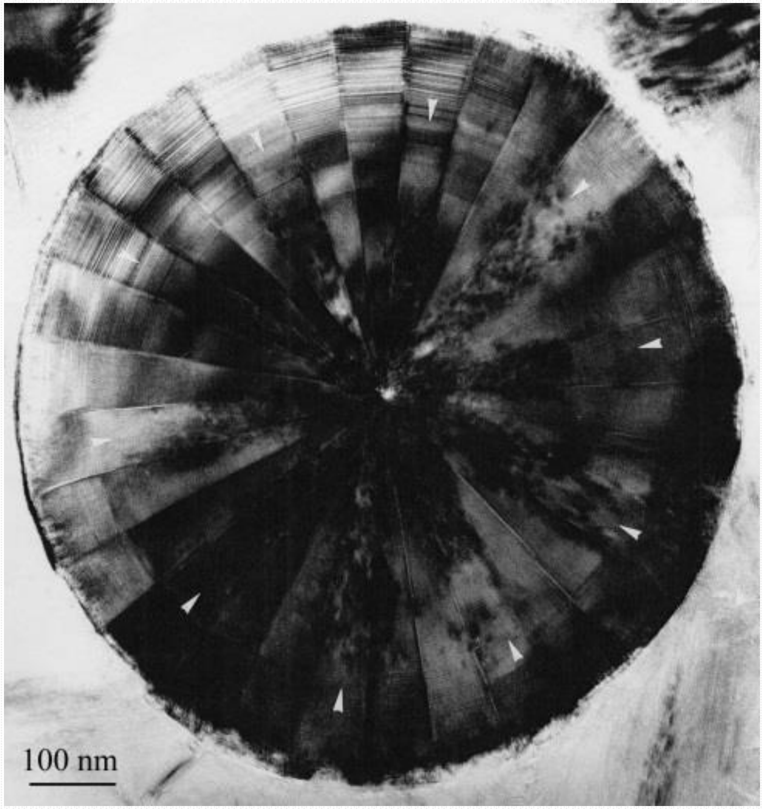
- Variable A value
- disorder
- diffuse defects

Dangerous?

Monoclinic

Polytipism

Polygonal Serpentine

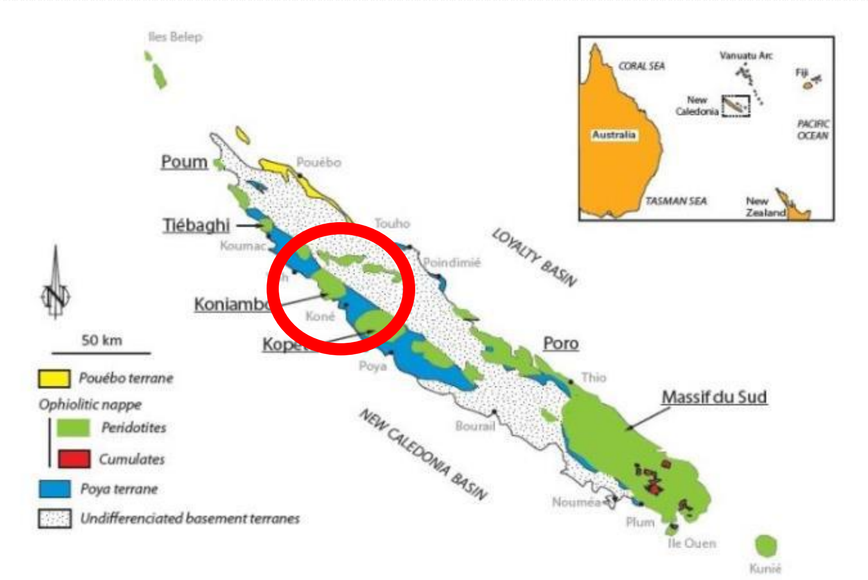


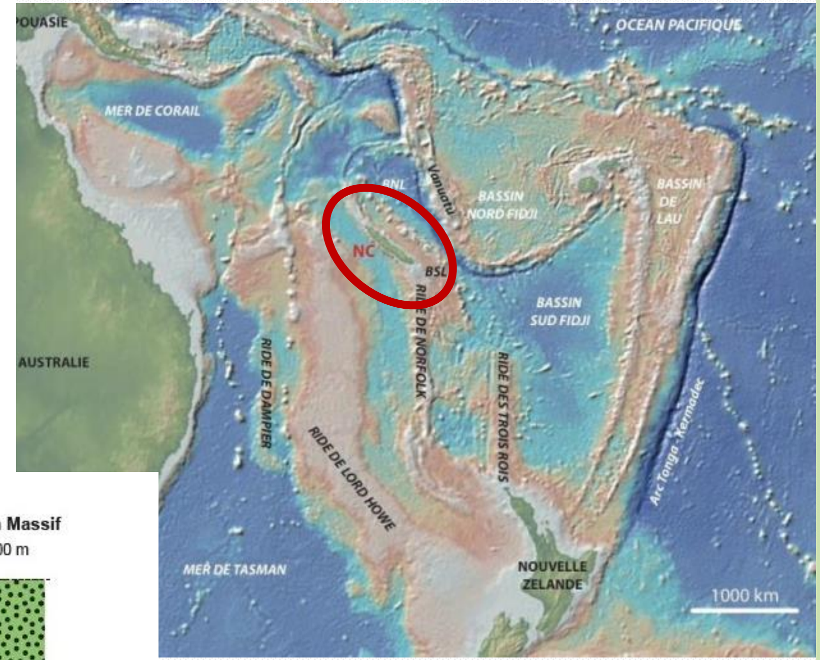
Intermediate between chrysotile and lizardite

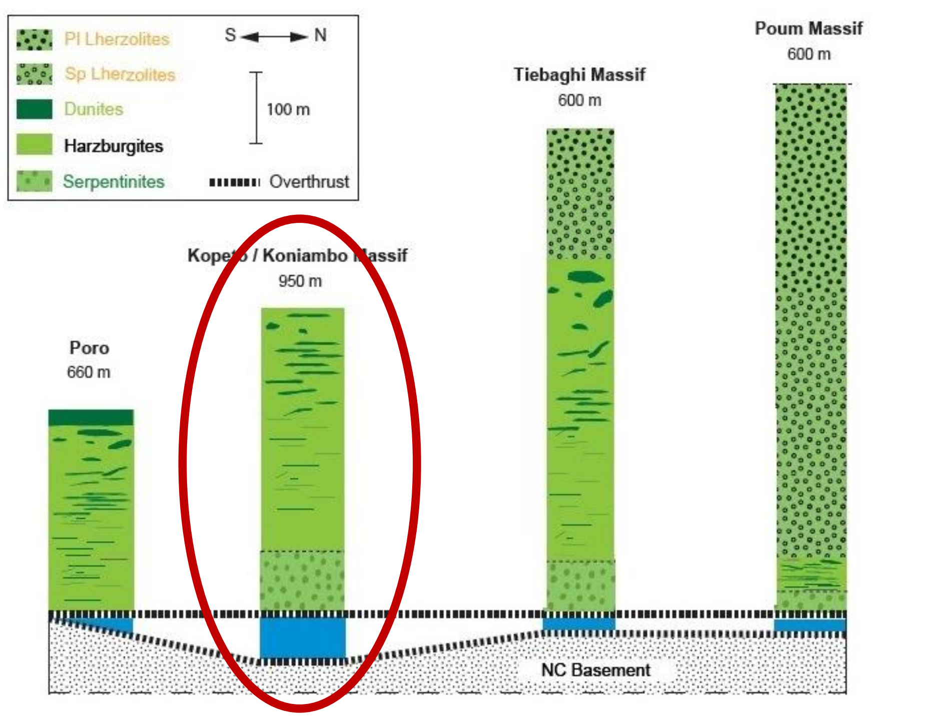
Polygonal Fibers
- Rull-up of the sheets along X axis
- Series of plane layers (lizardite type) and curve junctions
- 15-30 sectors
- d > 100 nm

Dangerous

Nouvelle Caledonie







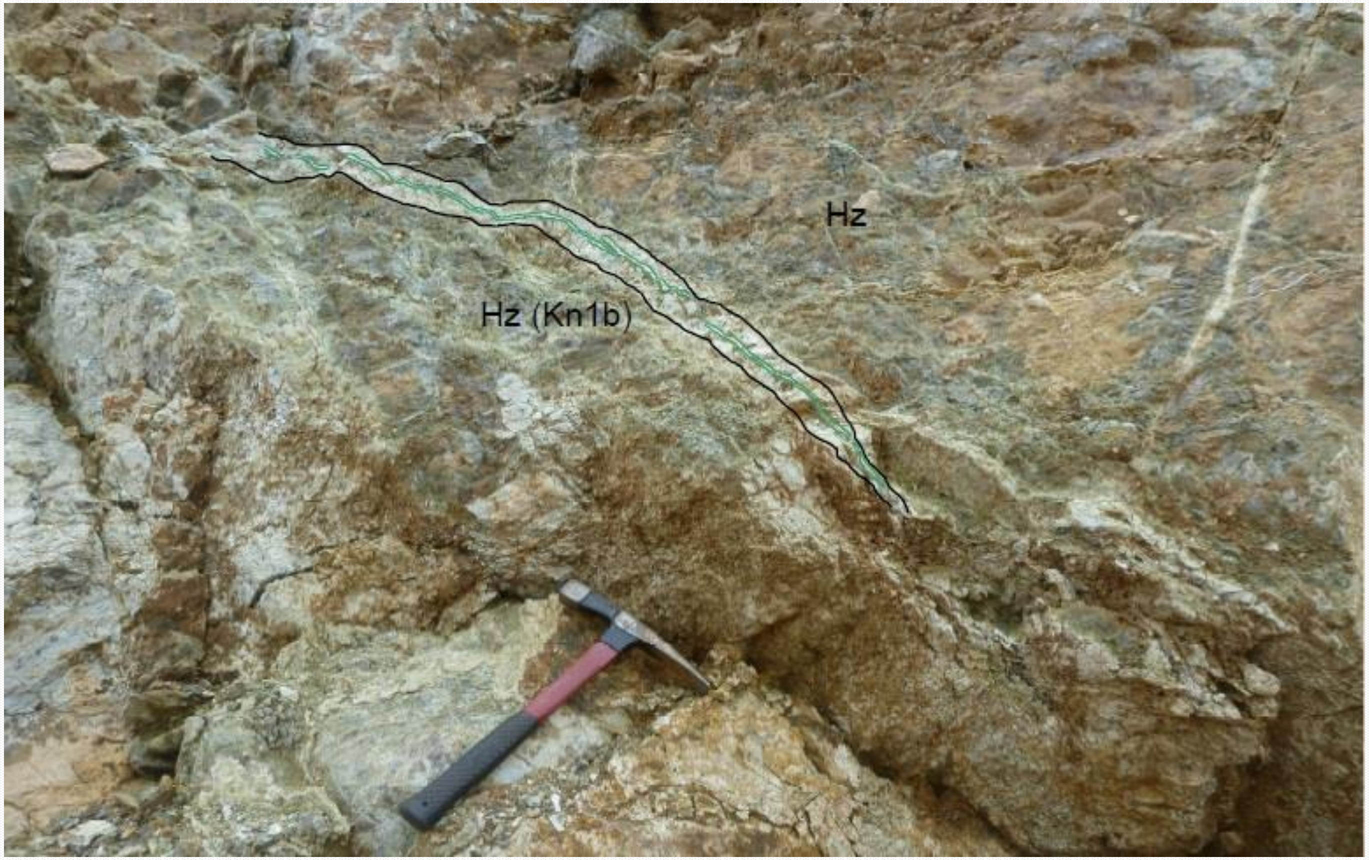
KONIAMBO MASSIF

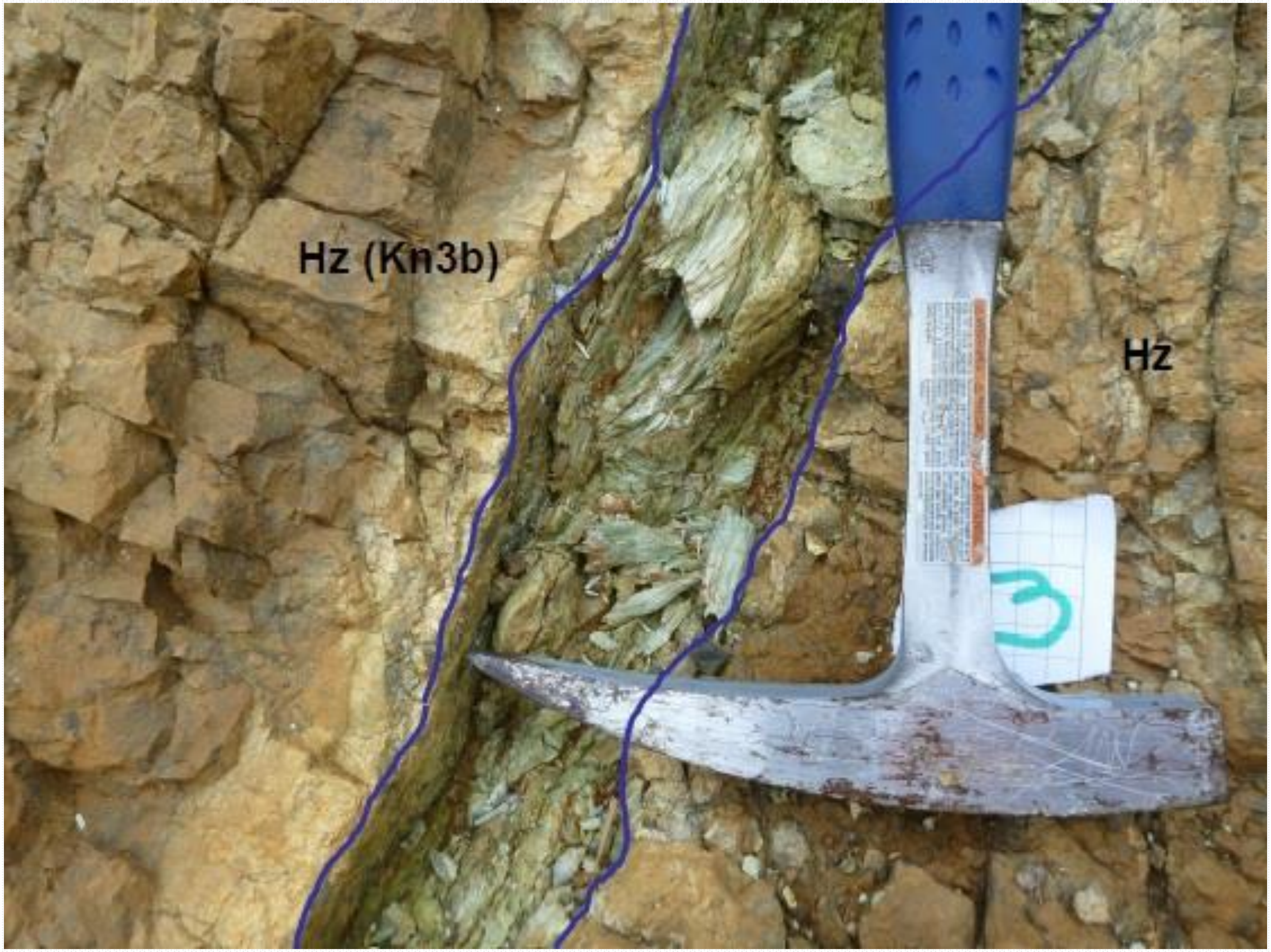
Series of harzburgites and minor dunites

Serpentinized harzburgites e dunites

Poya Unit (basalts, gabbros, dolerites)

Identification on the field





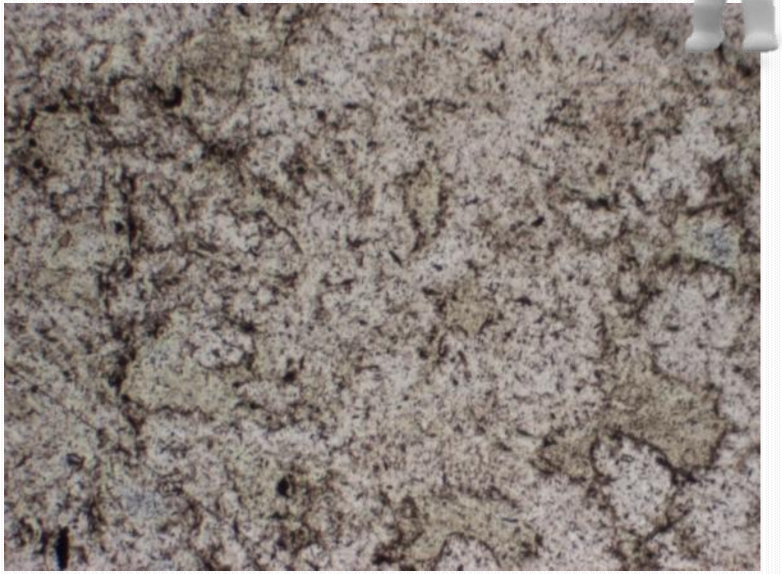
Hz (Kn3b)
Hz

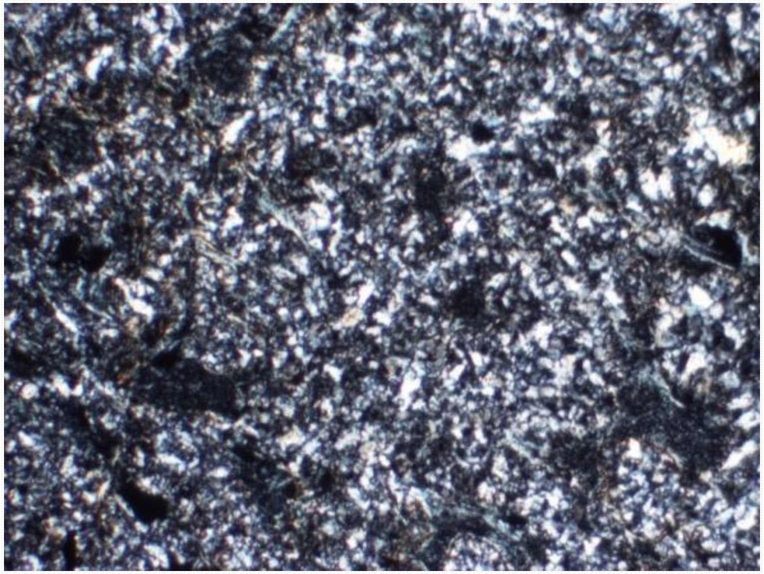

4

Optical microscopy

Optical properties

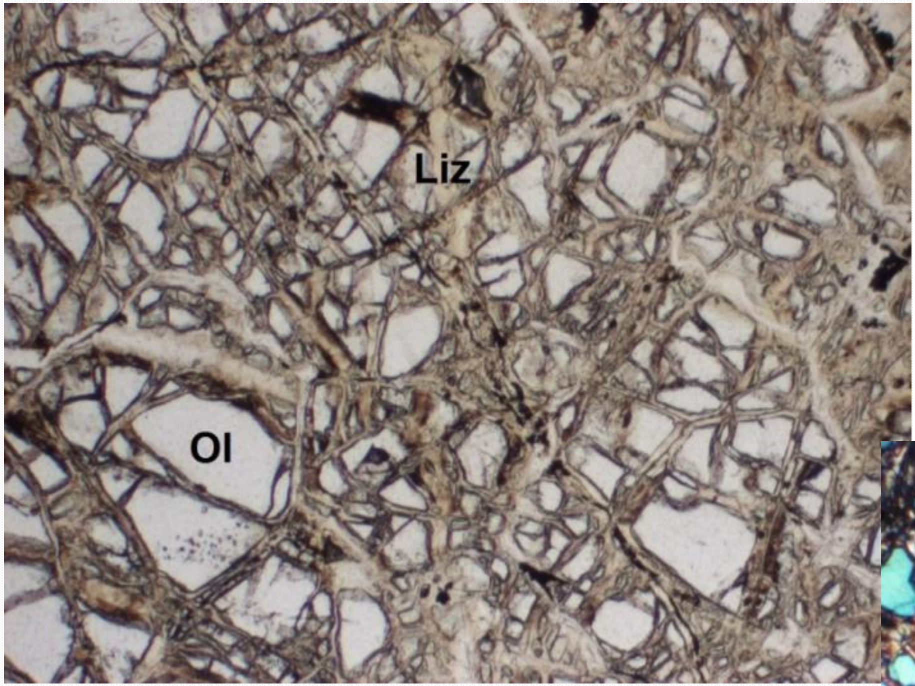
- Light colour, from colourless to pale green
- Plate/fiber habit
- Interference colours (I order) from ligth gray to blue-gray, (fibrous serpentine II order)
- Low refractive index *n*



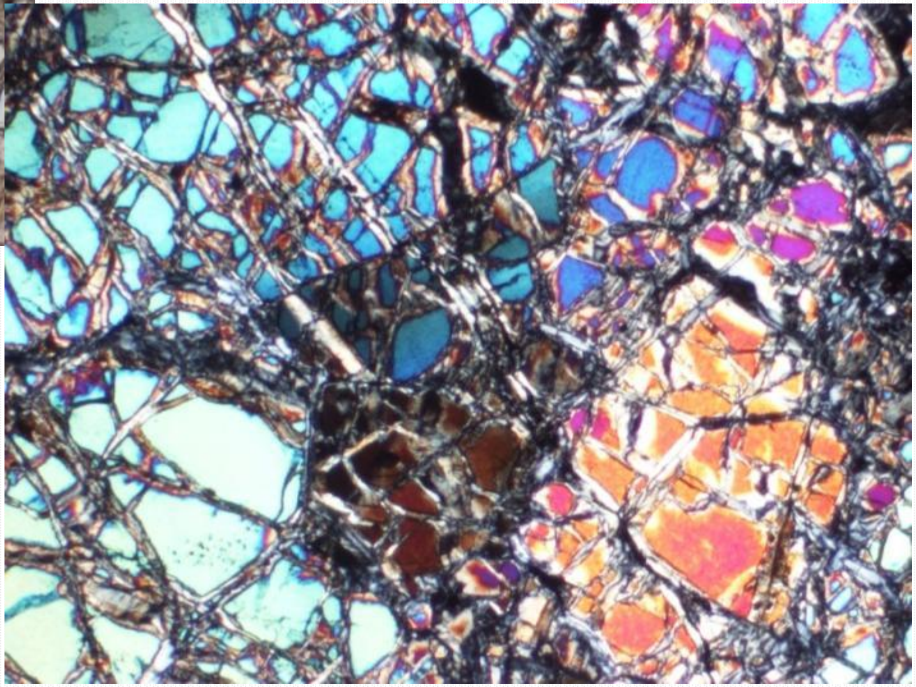


TEXTURE

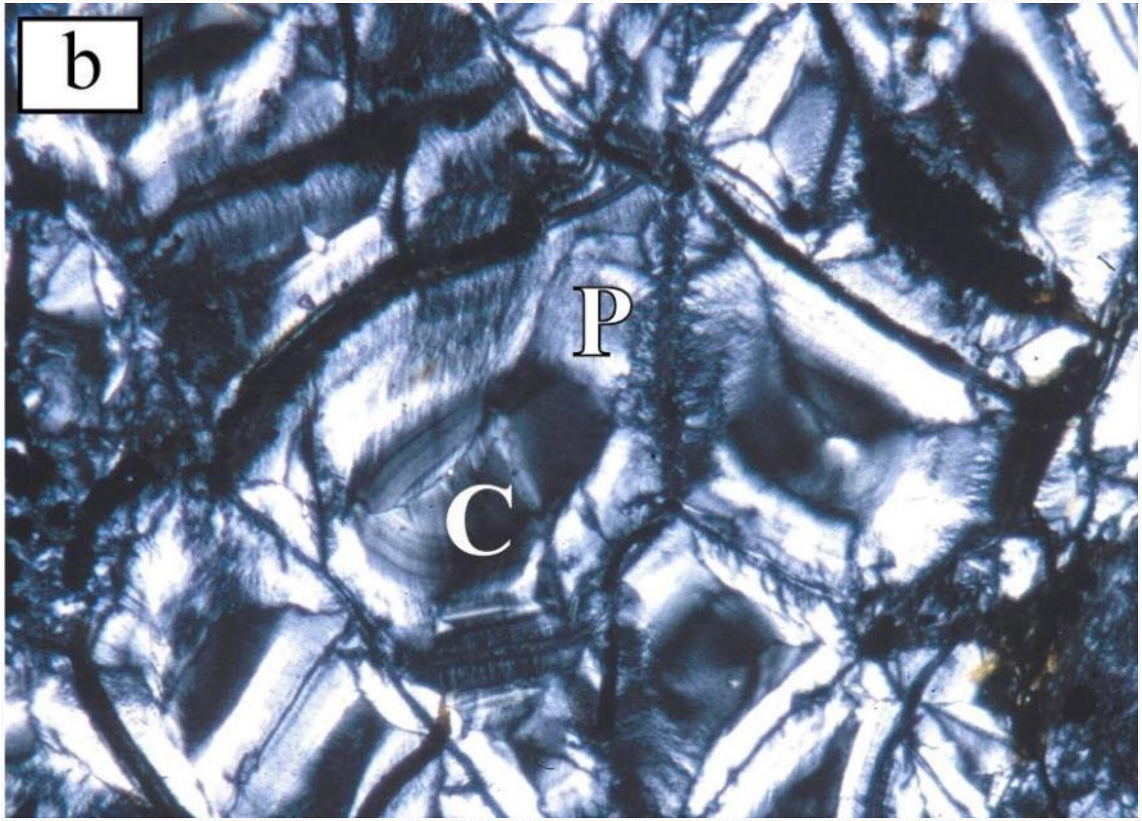
Serpentinized rocks present different textures, depending on the amount of untransformed minerals of the protolith.



Pseudomorph Weaving texture

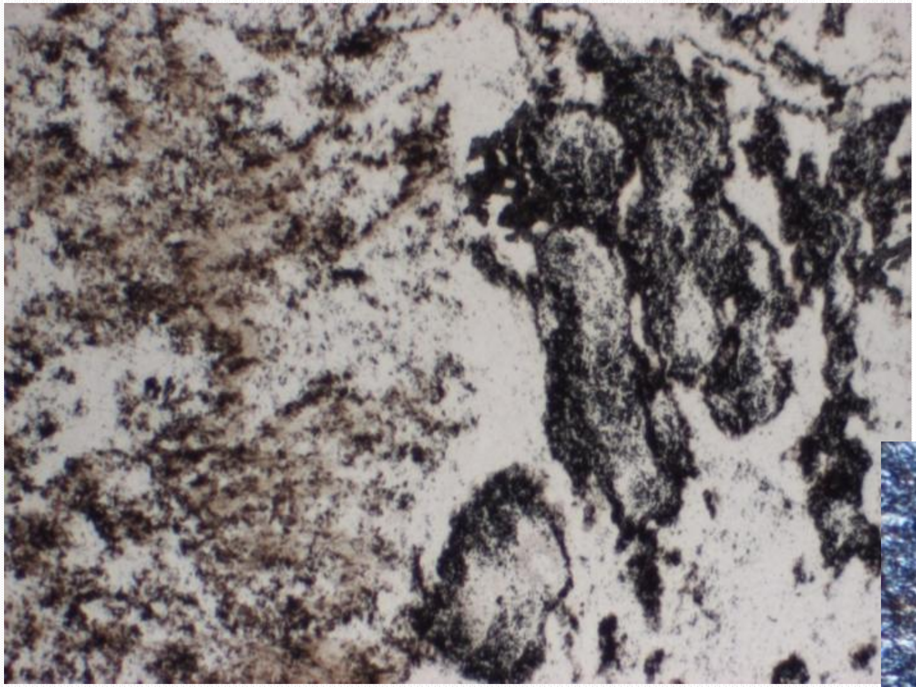


Texture

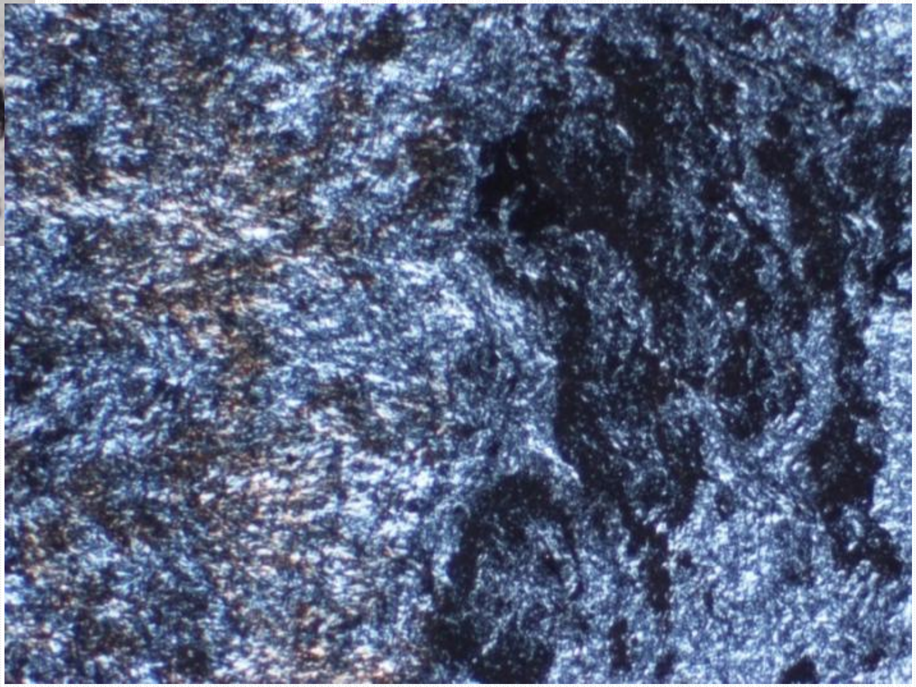


Pseudomorph «hourglass» texture

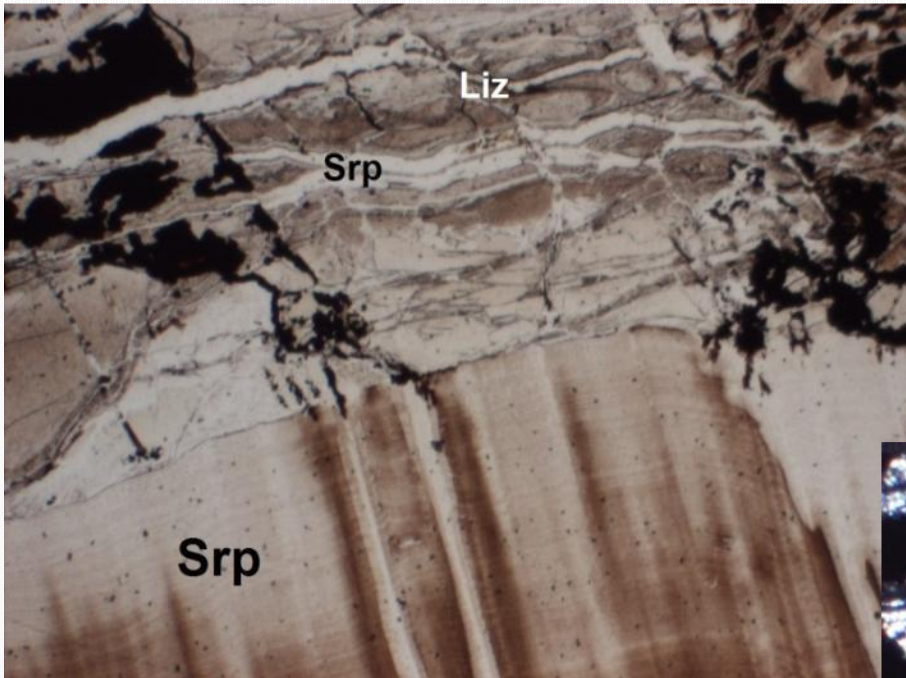
Texture



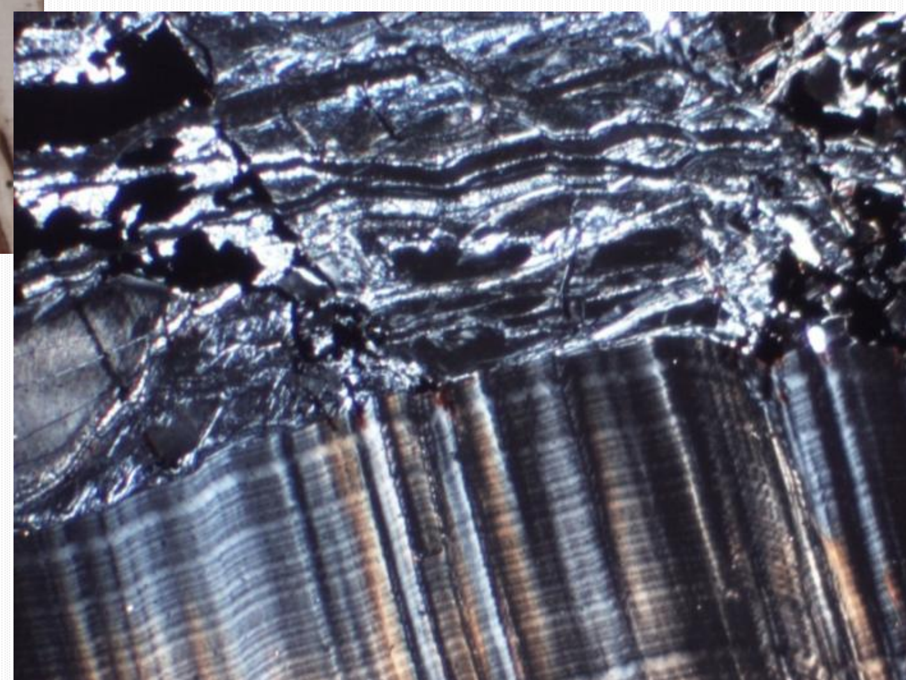
Non pseudomorph texture



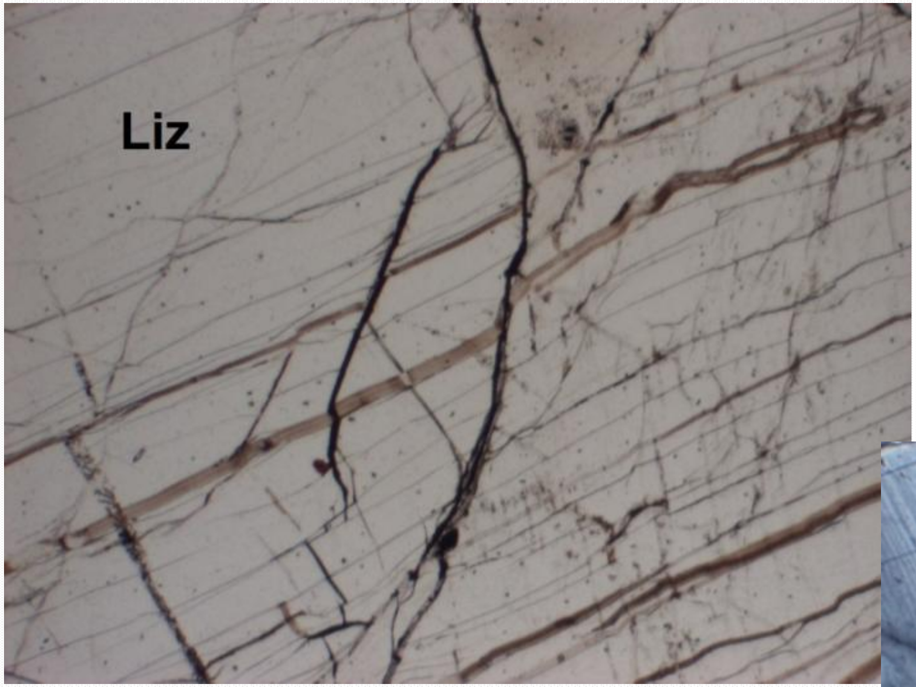
Texture



Fibrous late veins

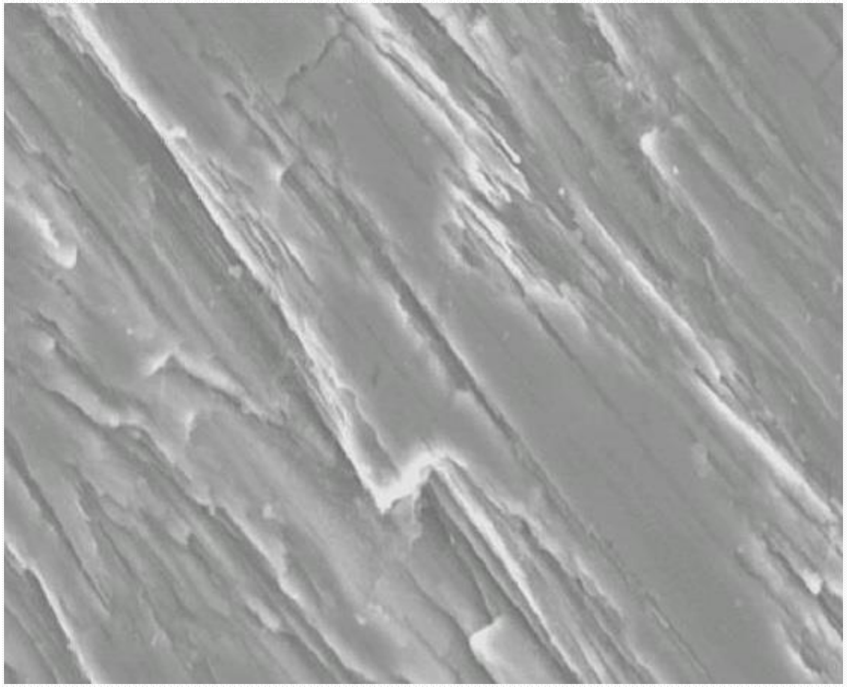


Texture

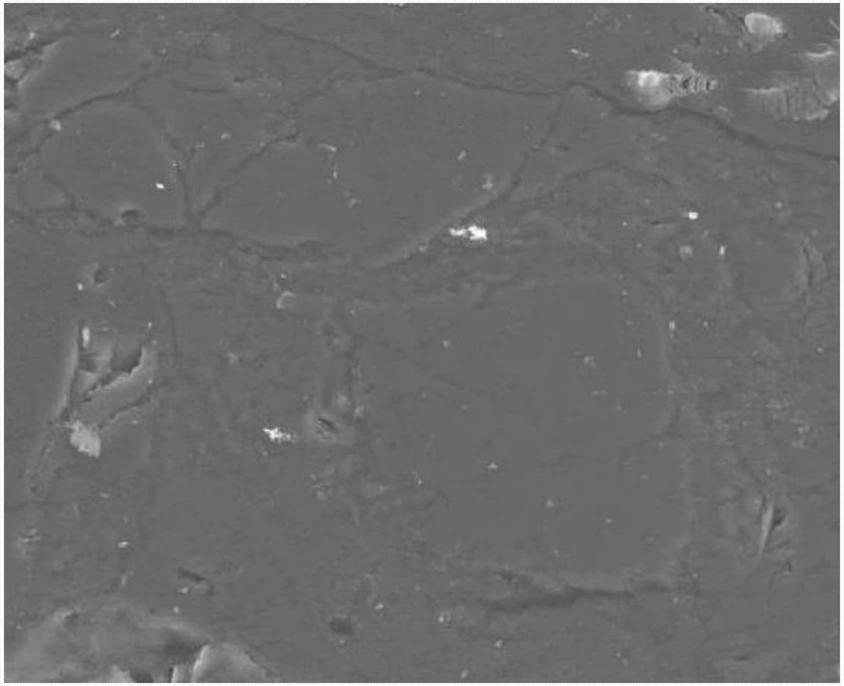


Isotropic late veins

Electron microscopy
SEM



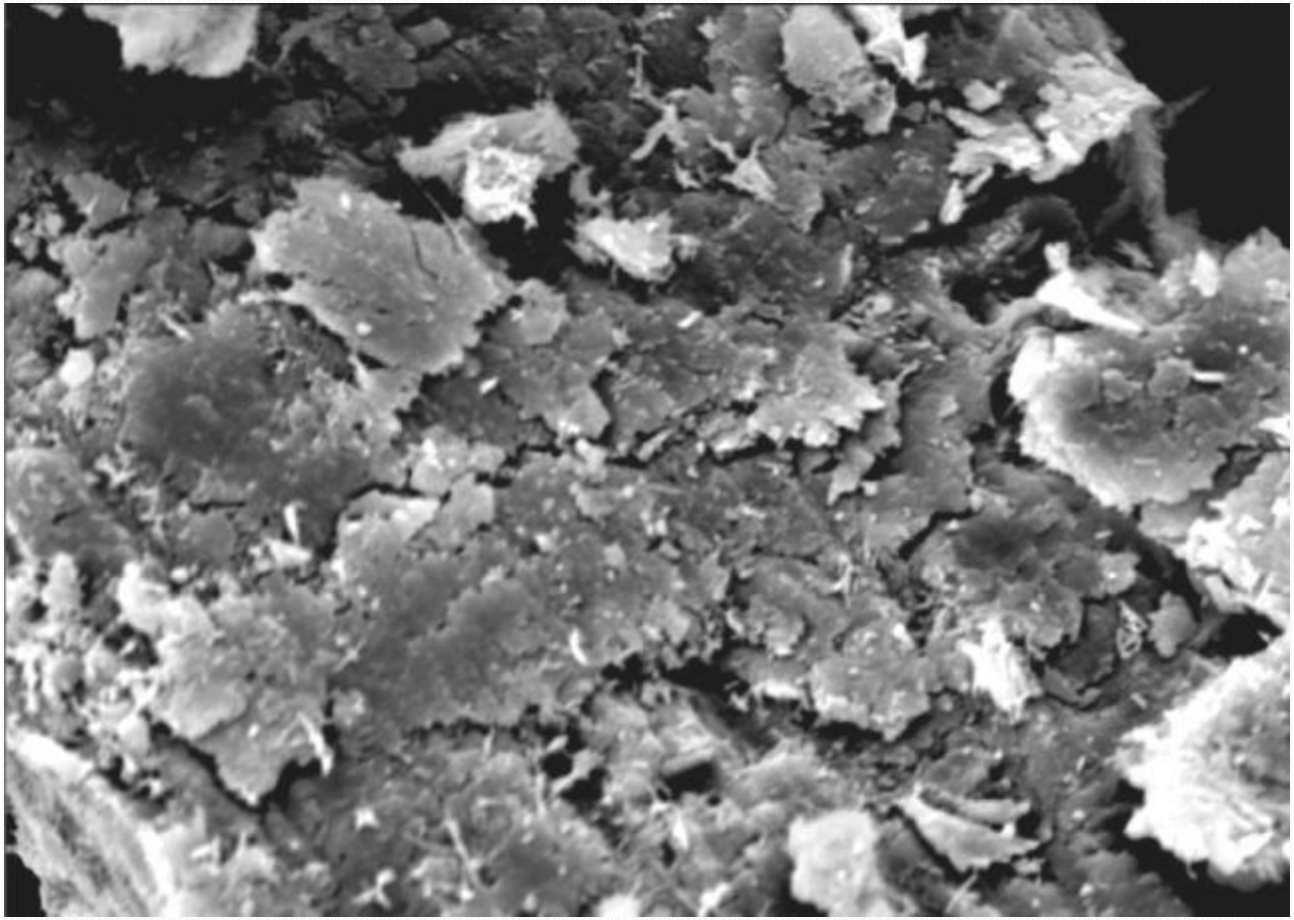
Antigorite



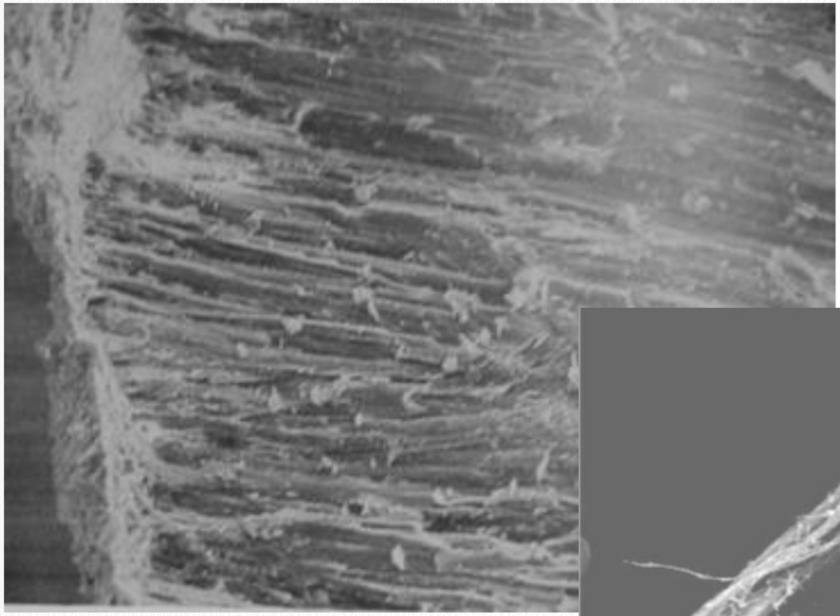
Only morphology and textural information

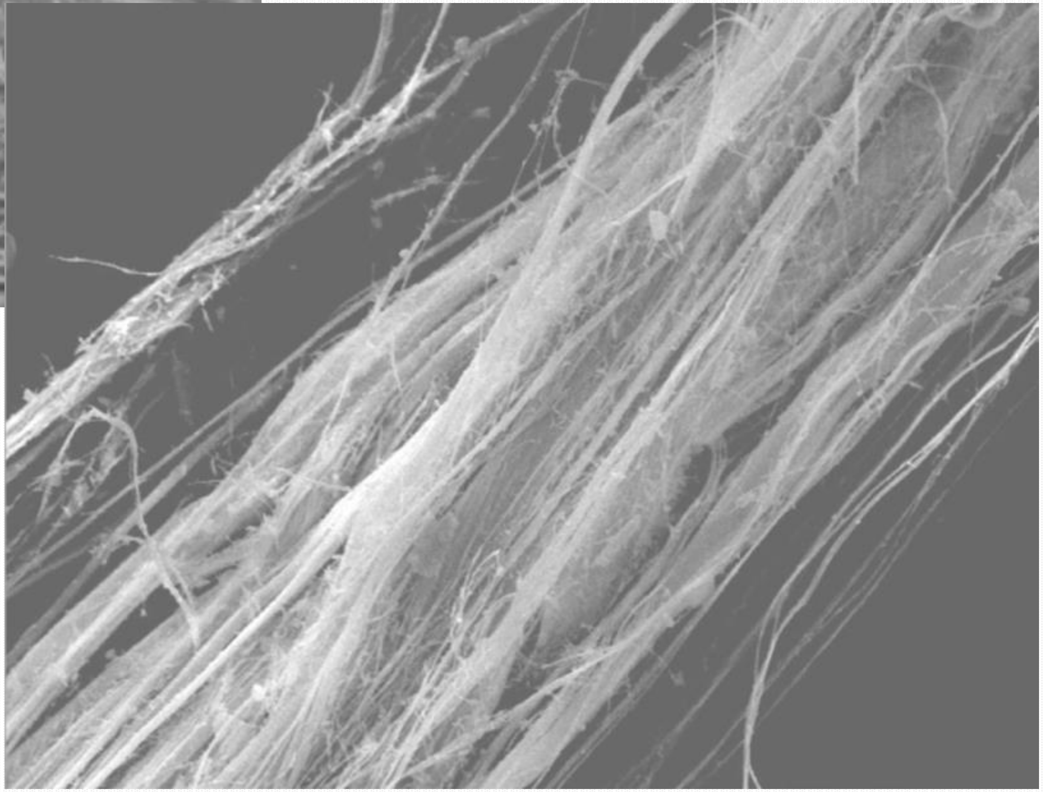
No help from EDXS

Lizardite

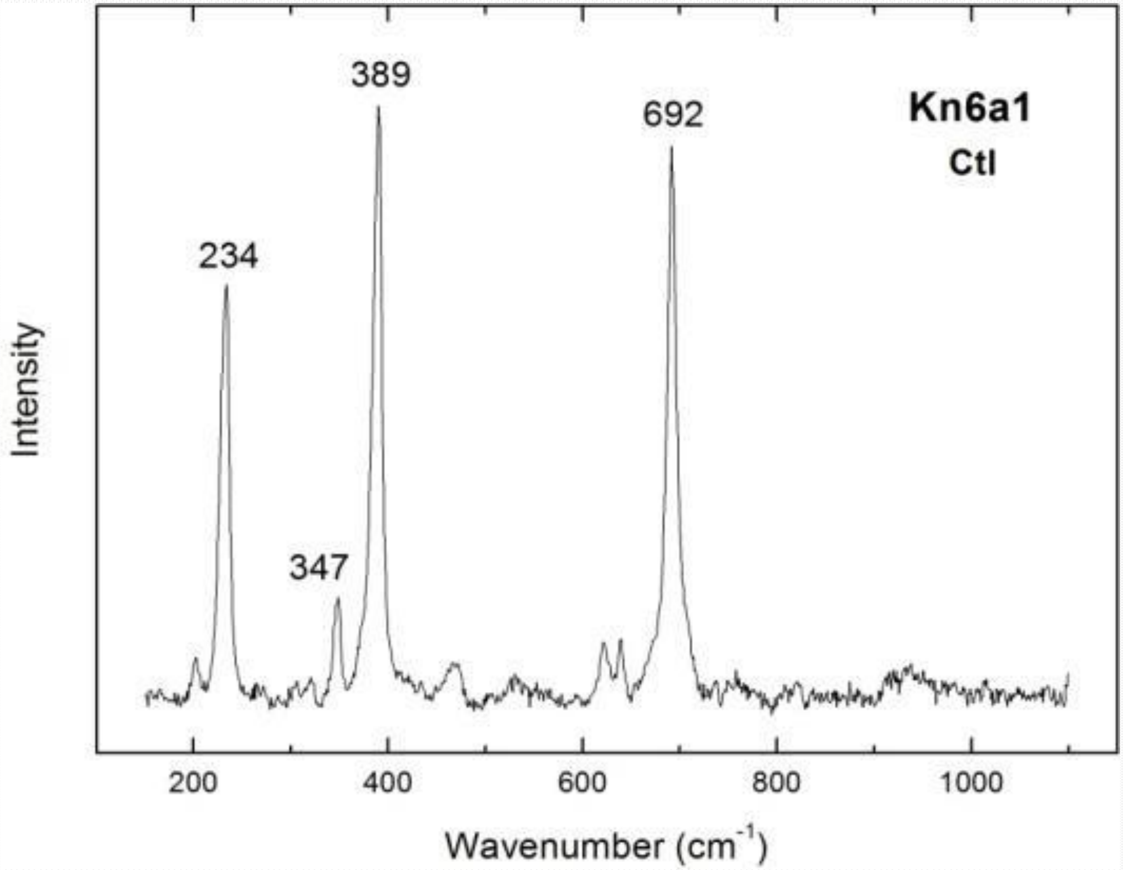


Chrysotile





Raman on serpentine polymorphs



Micro-Raman

Low-wavenumbers region (150-1100 cm^{-1})

Different literature works

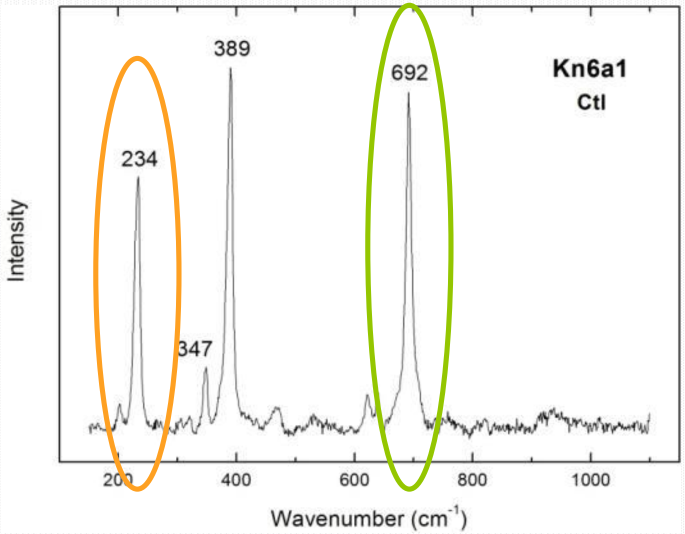
(Groppo *et al.*, 2006; Rinaudo *et al.*; 2003).

	Crisotilo	Antigorite	Lizardite
ν_{as} Si-O_{nb}	1105	-	1096
ν_{as} Si-O_b-Si (E1)	-	1044	-
ν_s Si-O_b-Si.	692	683	690
Translation OH-Mg-OH	620	635	630
Deformation SiO_4-AlO_4	-	520	510
ν_5(e) SiO_4	389	375	388
Bending SiO_4	345	-	350
Vibrations O-H-O	231	230	233

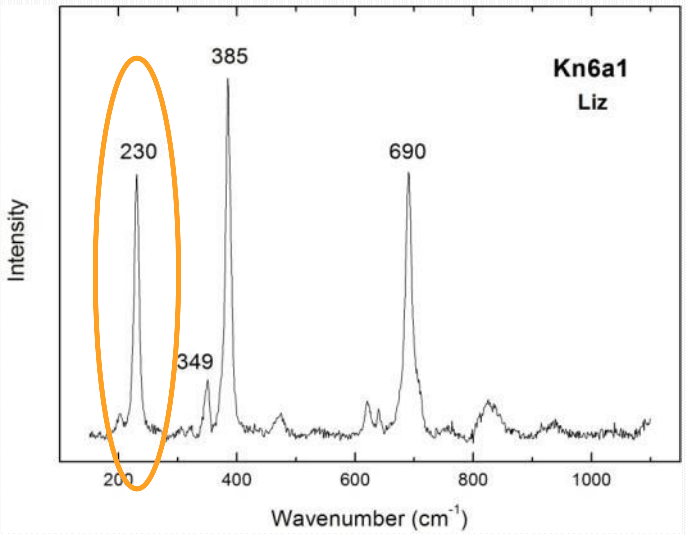
- We found partial agreement with literature
- Many «intermediate» cases (even involving antigorite)
- Hard to distinguish chrysotile and lizardite
- Polygonal serpentine?

Low wavenumbers (150-1100 cm^{-1})

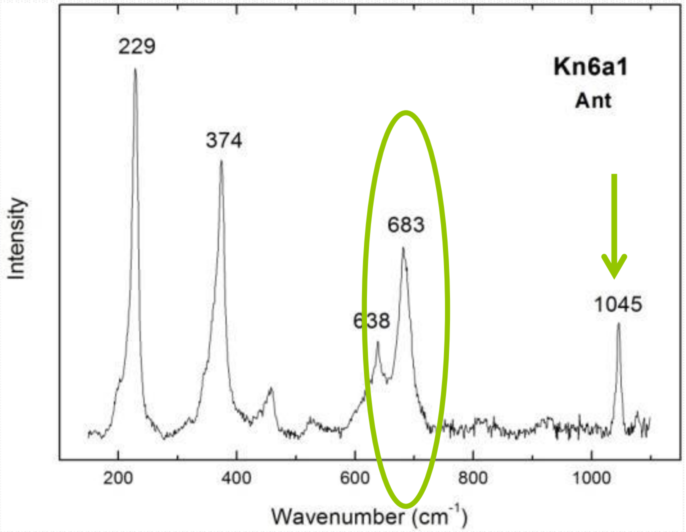
Chrysotile



Lizardite



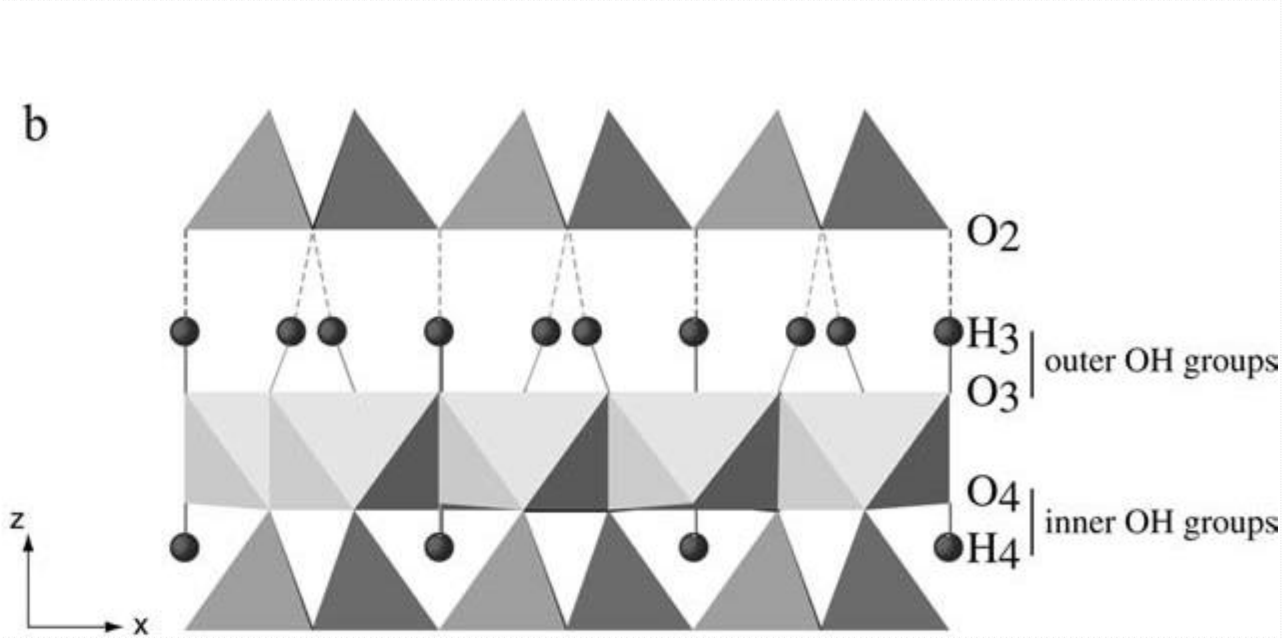
Antigorite



OH-stretching region

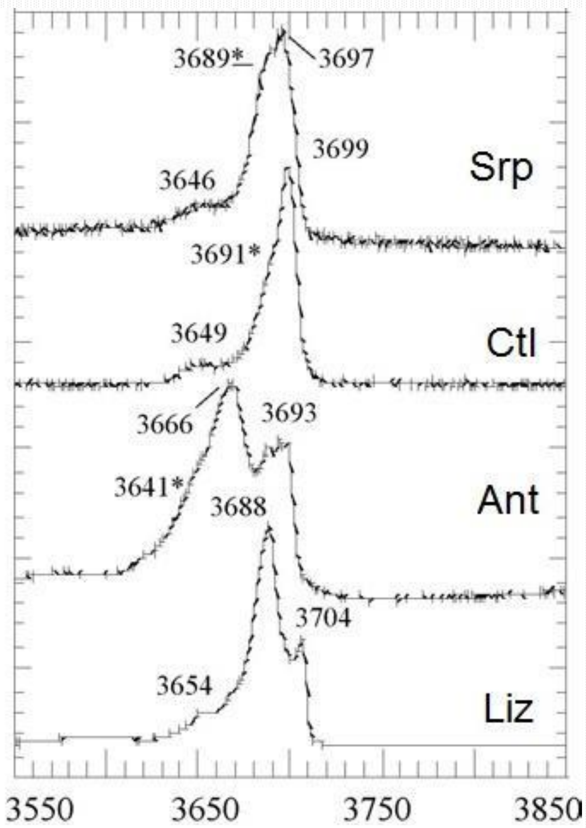
OH is a very sensitive local probe for the micro-structure.

6 non-equivalent OH: 3 inner and 3 outer groups

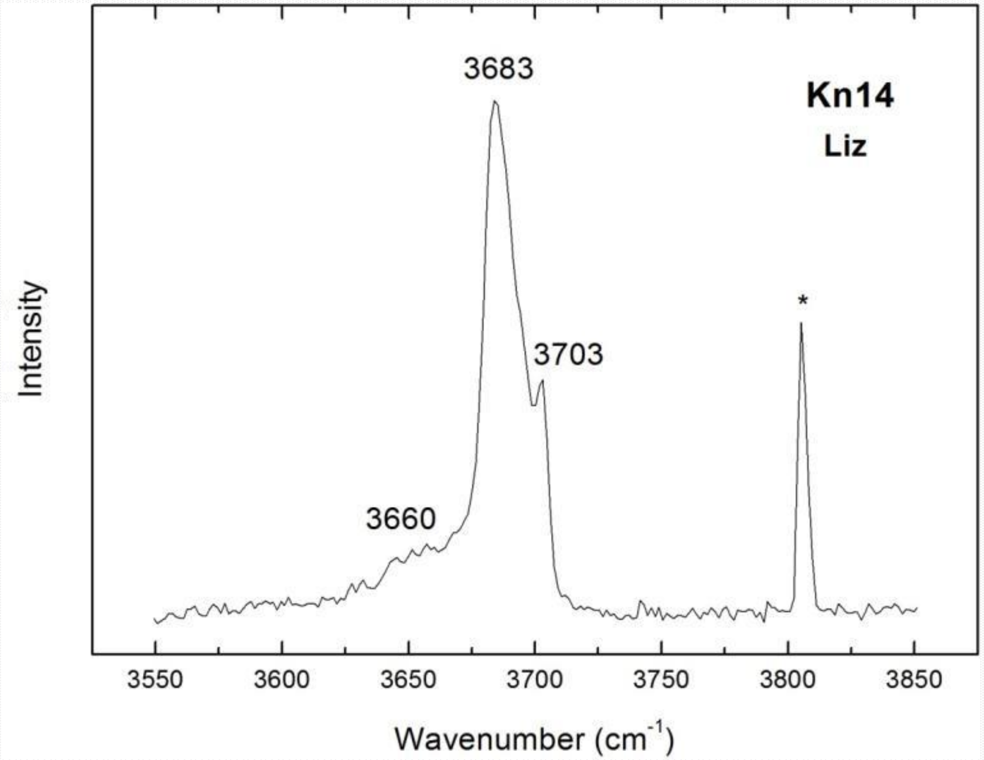


From: Auzende, Daniel, Reynard, Lemaire, Guyot, Phys. Chem. Minerals (2004) 31: 269

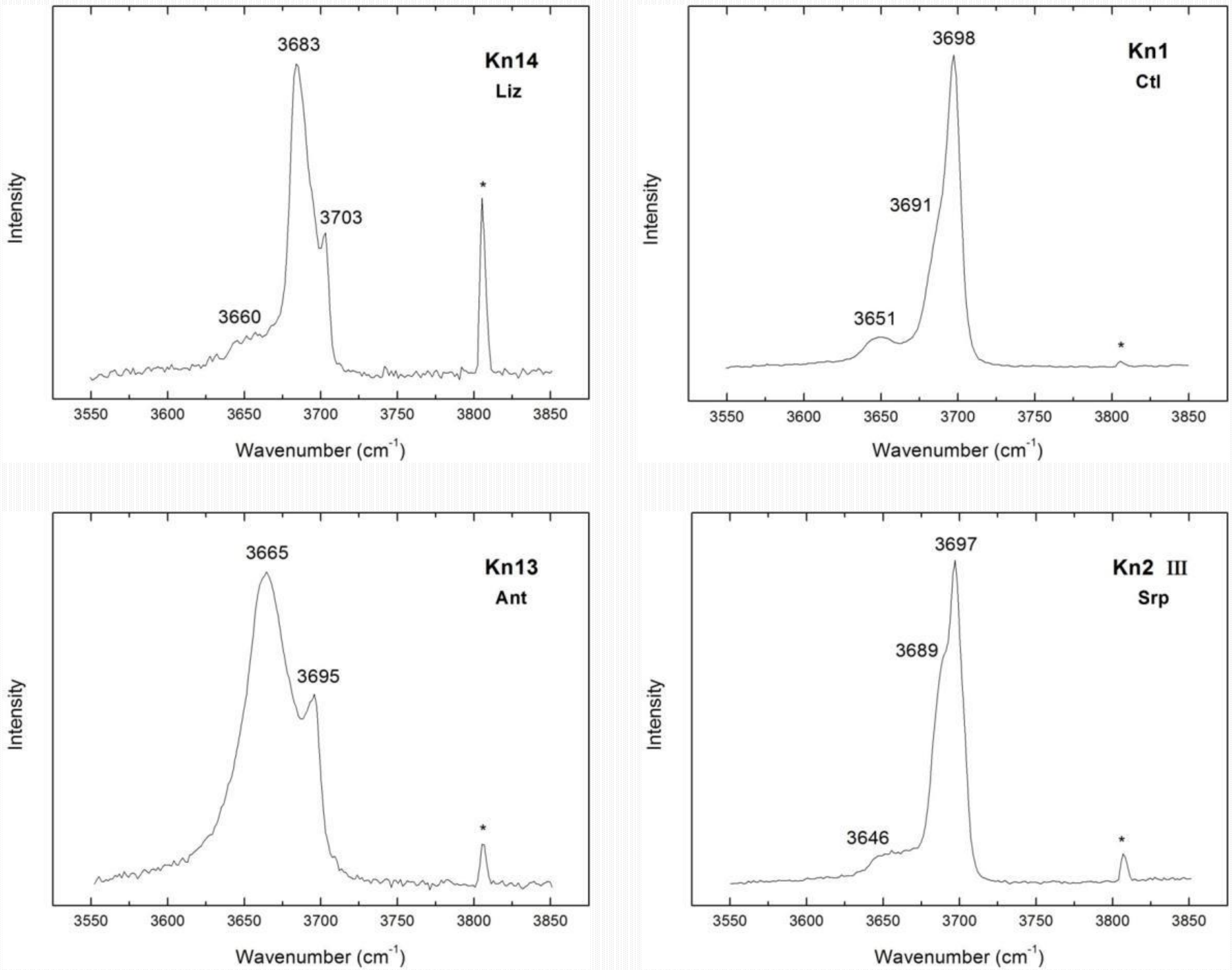
OH-stretching region (3550-3850 cm^{-1})



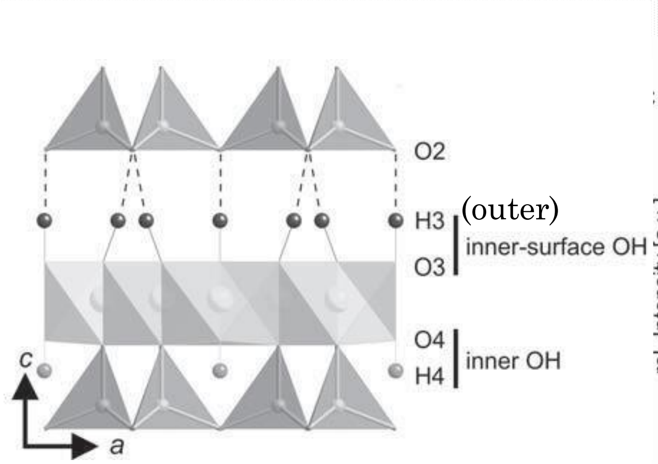
Tratto da Auzende et al. 2004; Lamaire, 2009.

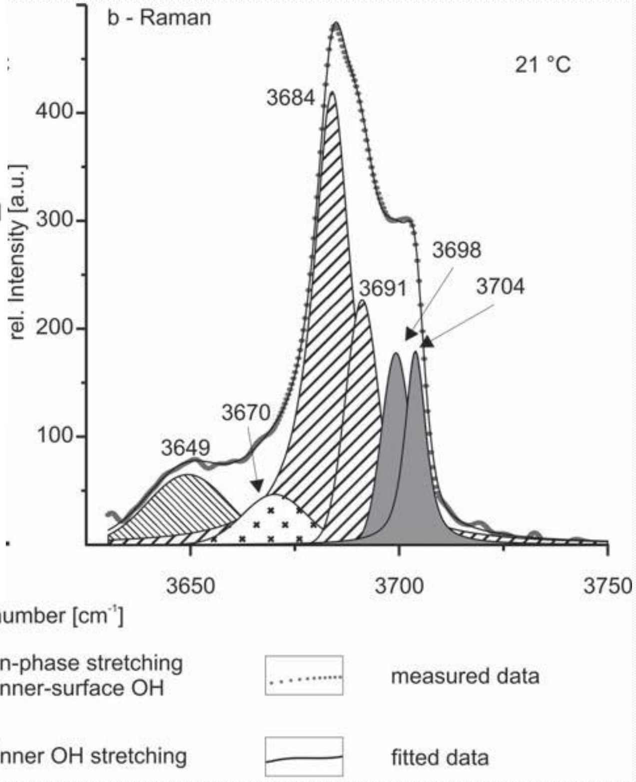


OH-stretching region (3550-3850 cm^{-1})



Example: Lizardite



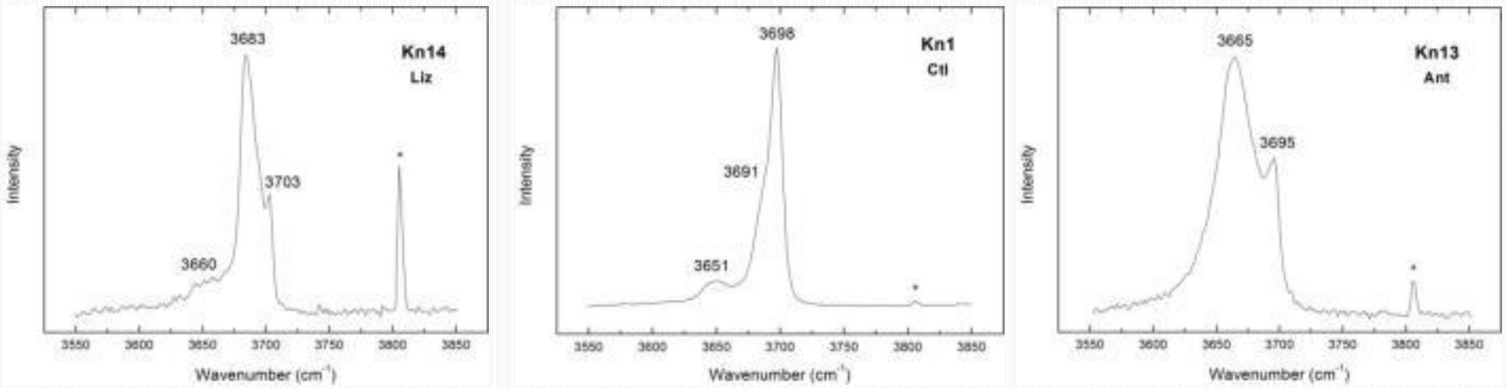


From Roy Trittschack, Bernard Grobéty, Monika Koch-Müller
American Mineralogist Nov 2012, 97 (11-12) 1965-1976; DOI: 10.2138/am.2012.4162

In the OH stretching region we found better agreement between our Raman spectra and

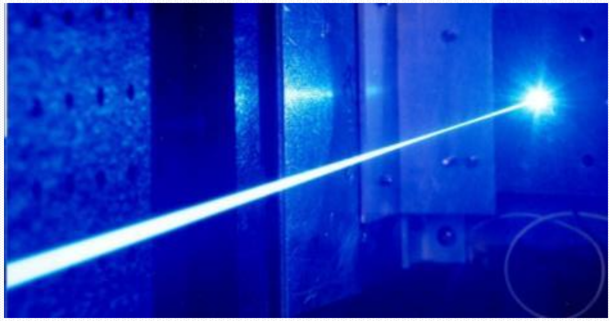
- bibliography
- microscopy observations
- texture-shape
- well known standard samples

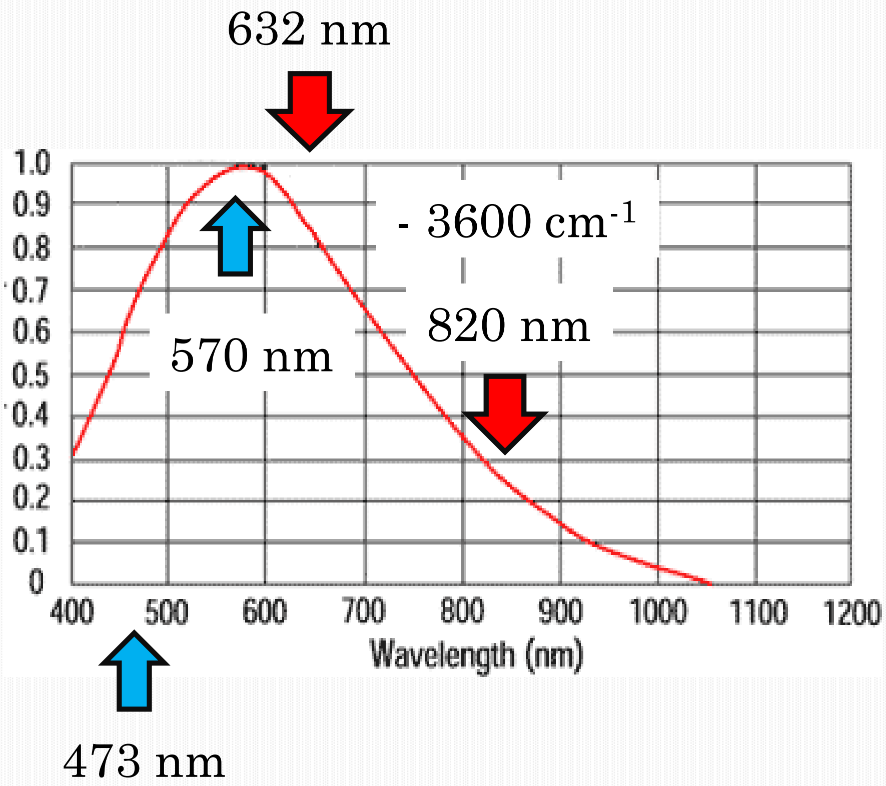
Very few doubtfut cases
Easy to distinguish the polymorphs (even polygonal serpentine)



Very good Raman signal in the OH region using a blue laser (473.1 nm doubled Nd:YAG)

WHY?



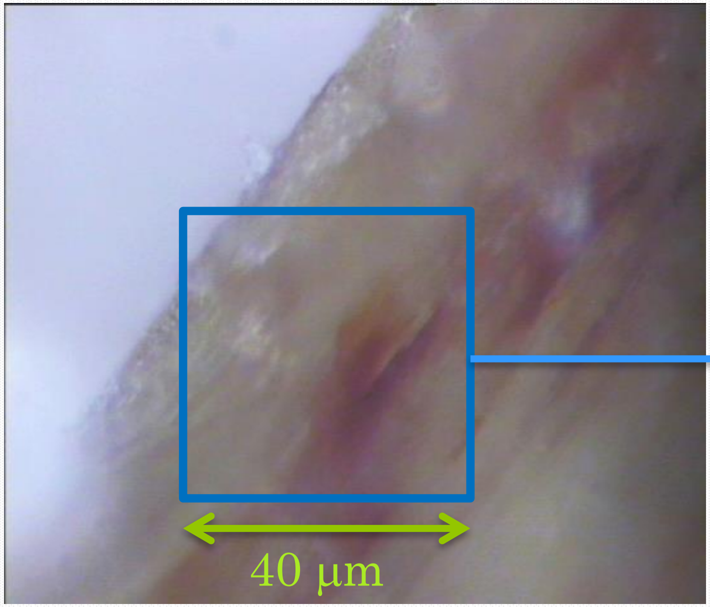


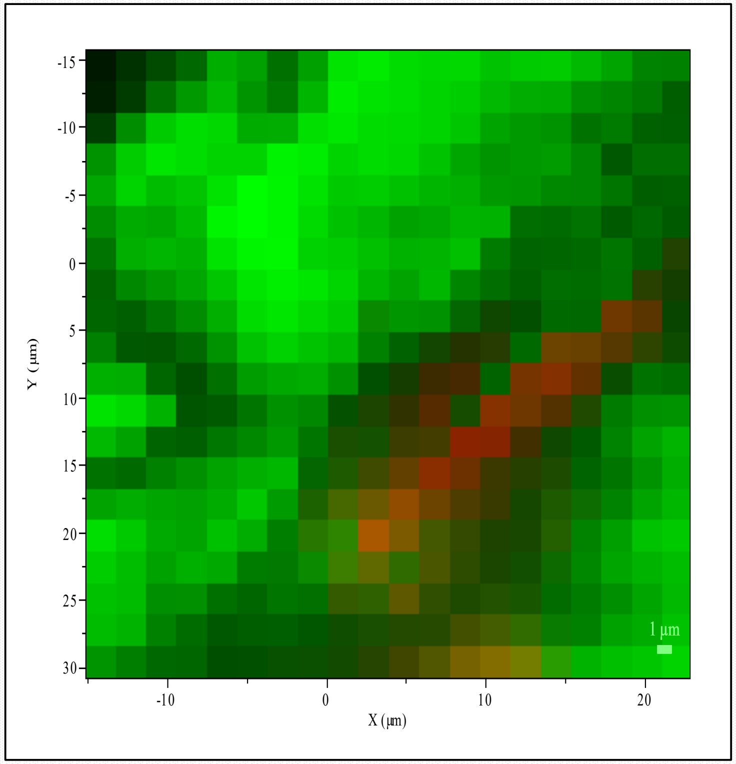
Typical CCD are made of Si
Eg = 1,12 eV = 1100 nm
Max sensitivity at 600 nm

In addition, take into account the 4th power of wavenumber in the scattering efficiency.

We performed Raman micro-mapping

Example: columbite in fersmite

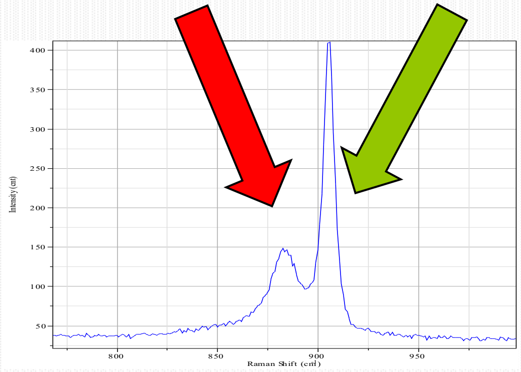




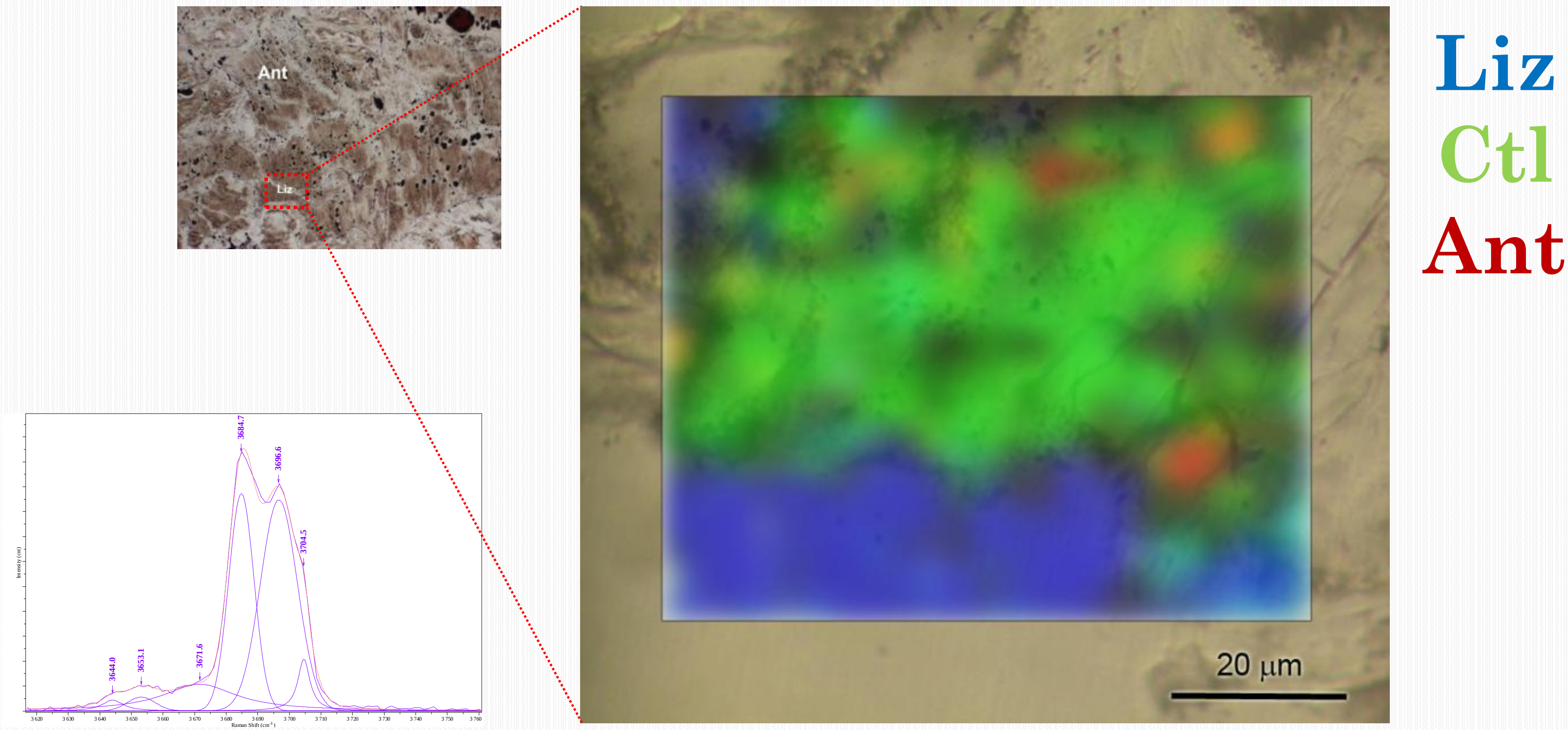
Rectangular grid of Raman spectra
(in this case 20x20 = 400 spectra)

The false colours image is obtained by parameters extracted from spectra

i.e. Red = area of columbite peak
Green = area of fersmite peak

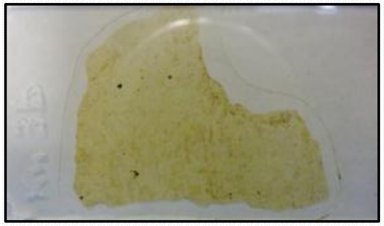


Micro-Raman Maps

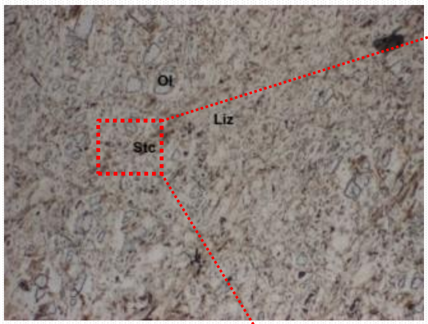


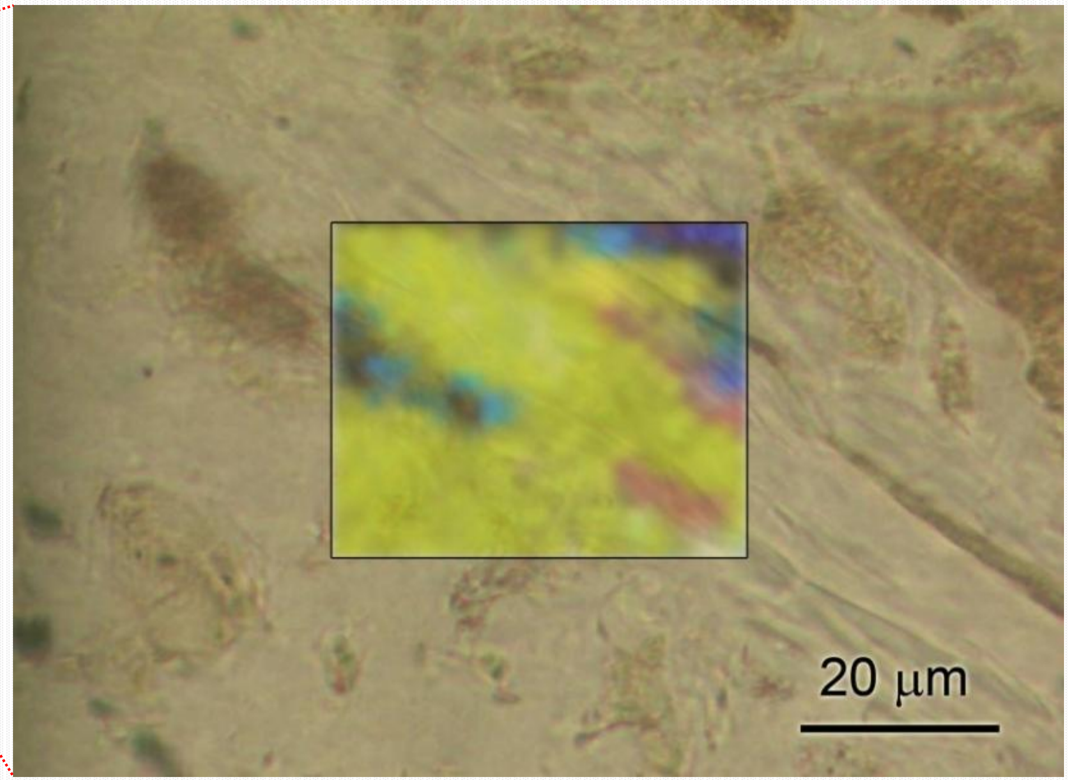
Spectra obtained in the OH-stretching region were deconvoluted to separate the contributions of the different polymorphs.
Acquisition times, from few hours to overnight.

Es. sample
Kn3b



Serpentinized peridotitic protolith with mesh texture. Isotropic veins, supposed to be polygonal serpentine.





Liz
Srp
Ant

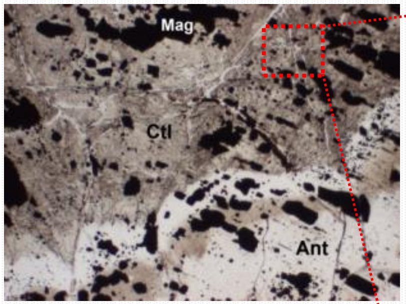
Polygonal serpentine veins between lizardite veins and stitchite (Cr and Mg carbonate). Minor antigorite in the small cracks.

Es. Sample **Kn2**

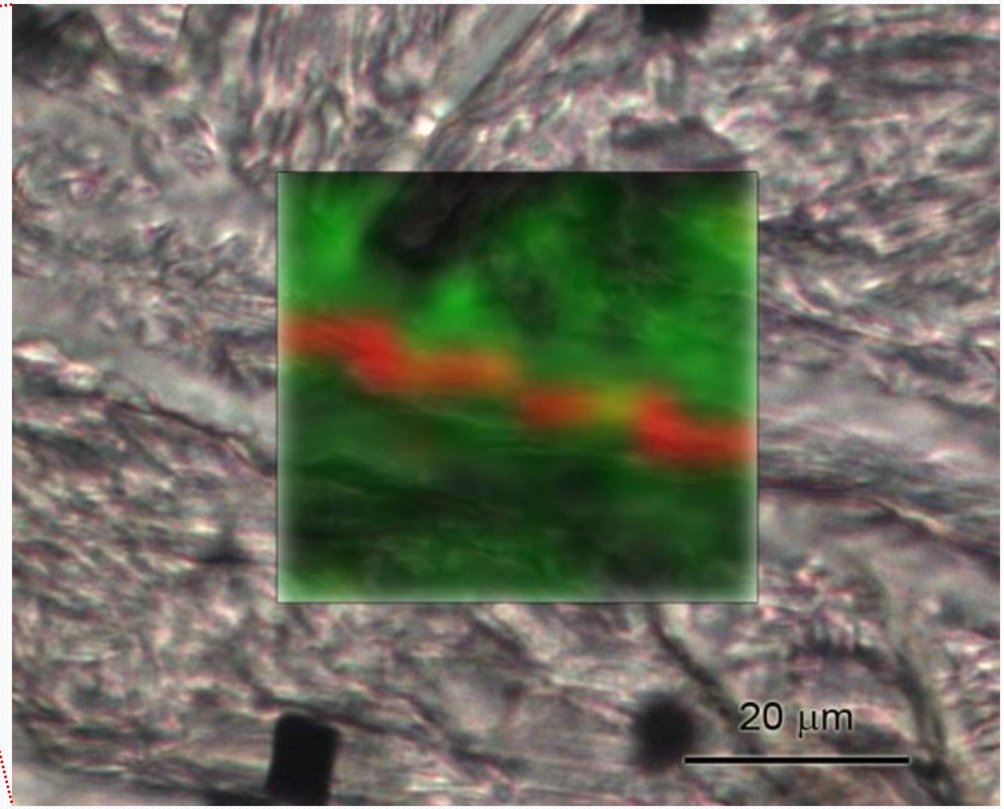
8 levels

Series of micrometric veins, both fibrous and isotropic.

Sample Kn2 – Level V



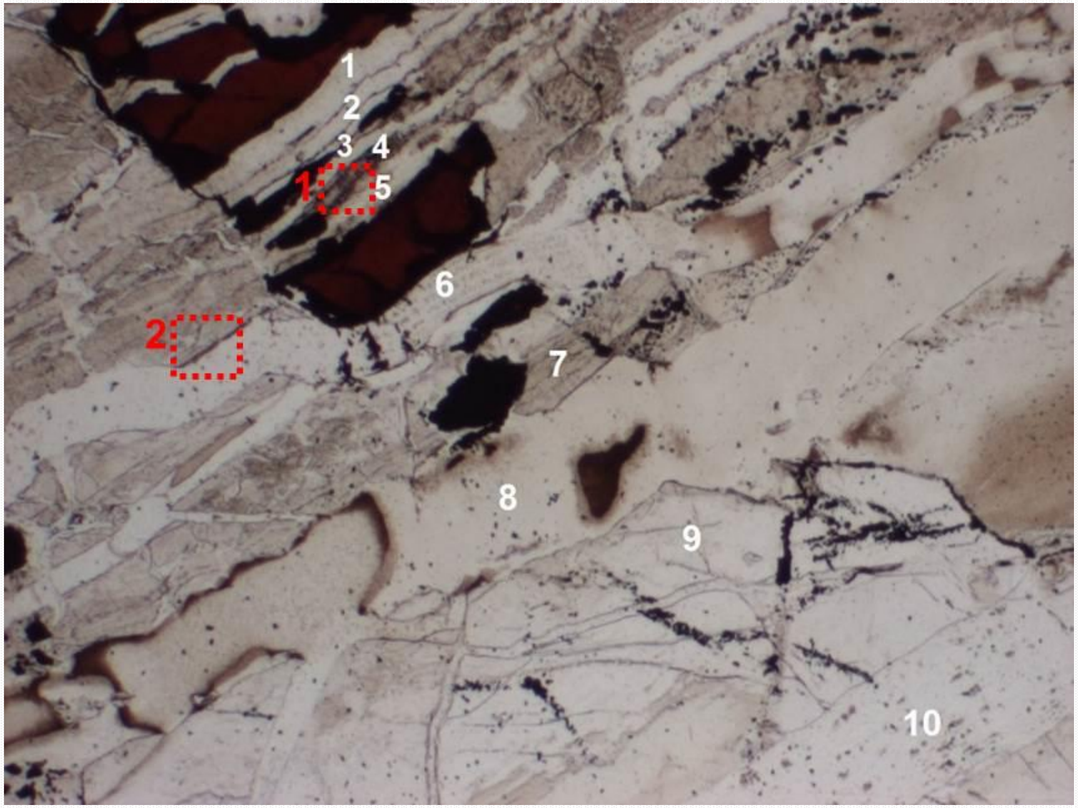
Ctl
Ant



Micrometric antigorite vein inside a chrysotile vein.

The usual situation is the opposite. Probably an increase in the fluid temperature caused the partial transformation of chrysotile into antigorite.

Sample Kn2- Livello VI



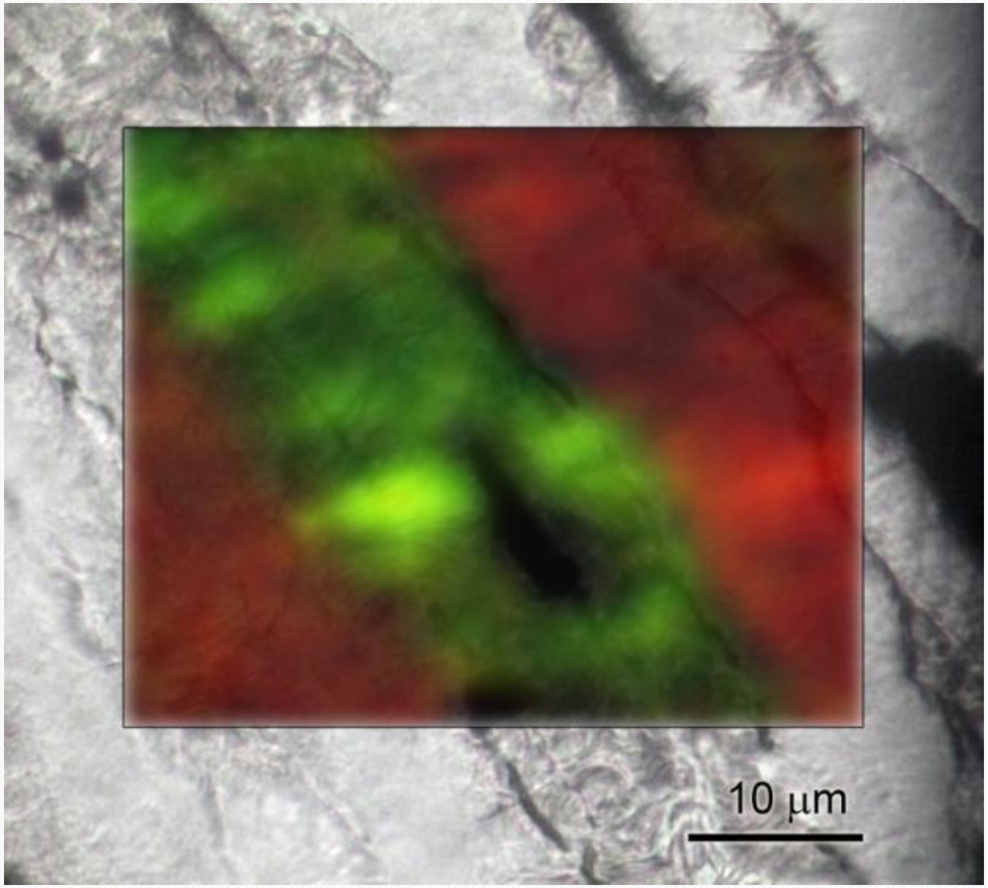
Point spectra:
1) Ant; 2) Ant; 3) Ant; 4) Ctl; 5) Ant; 6) Liz; 7) Ctl; 8) Liz; 9) Ctl; 10) Liz

Mapped areas:
1) chrysotile vein between two antigorite veins;
2) Contact between antigorite and lizardite

Map1.

micrometric chrysotile vein between two antigorite veins

Liz
Ctl
Ant



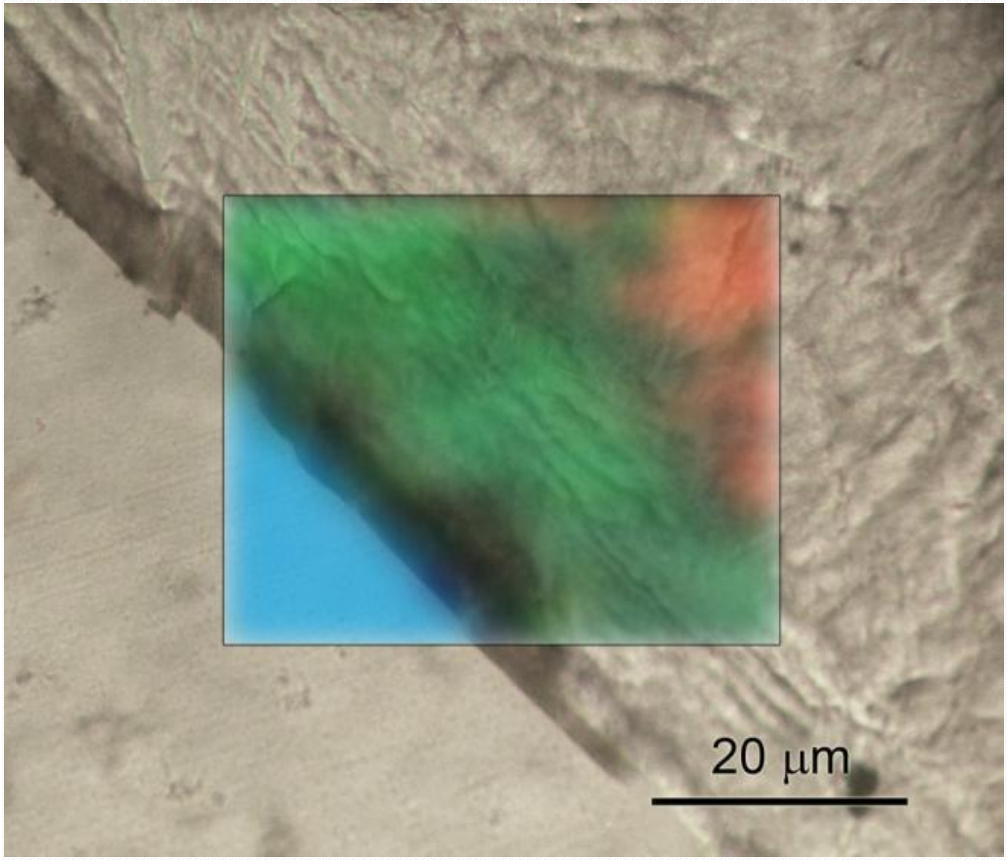
This is a more standard case, where the decrease in pressure and in the fluid temperature lead to a gradual traformation of the originary antigorite into chrysotile.

Map 2.
Contact between antigorite and lizardite veins. A fibrous chrysotile layer is detected.

Complex case.

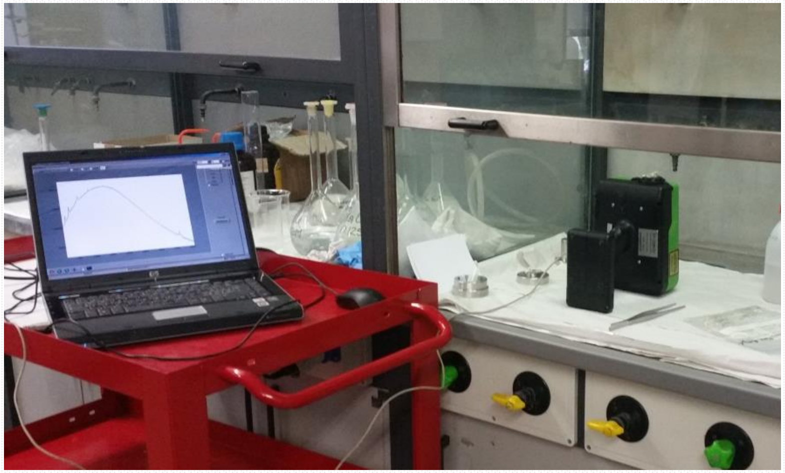
It is possible that antigorite and lizardite were already present, formed from fluids with different Al content (or in different P-T conditions).

Chrysotile is originated by the polymorph transformation of lizardite and antigorite.

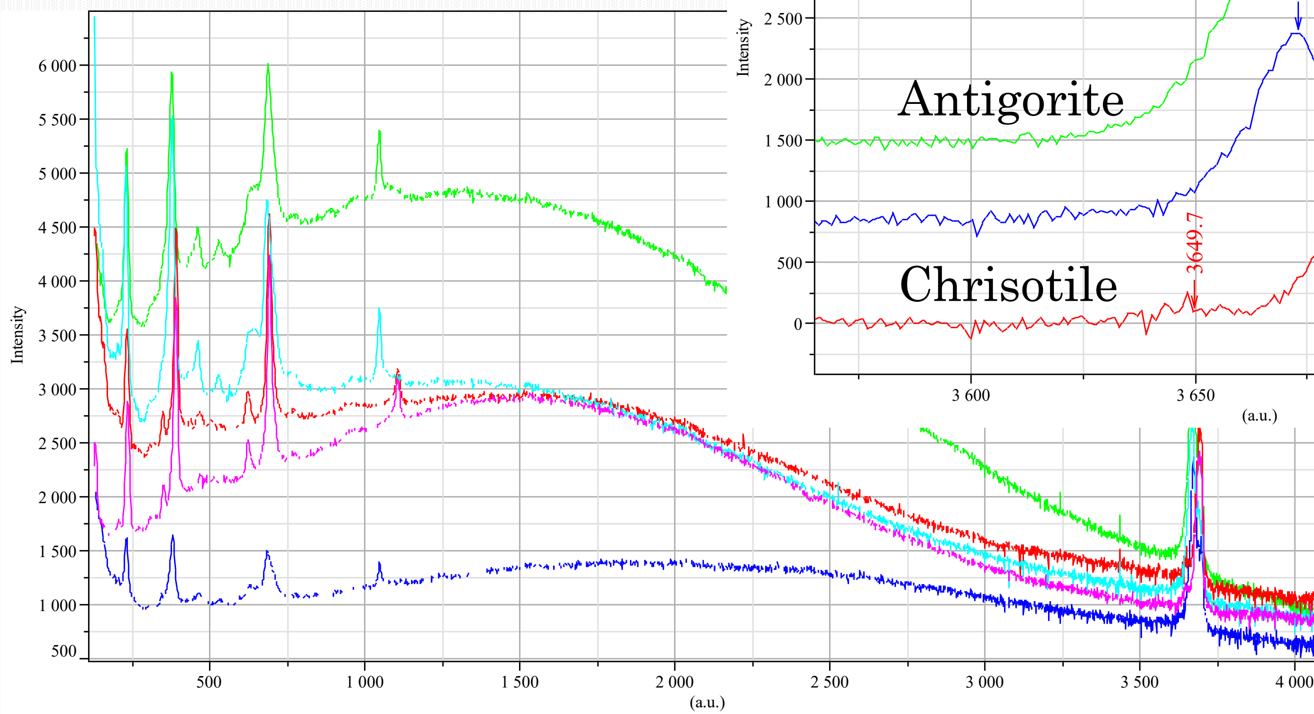


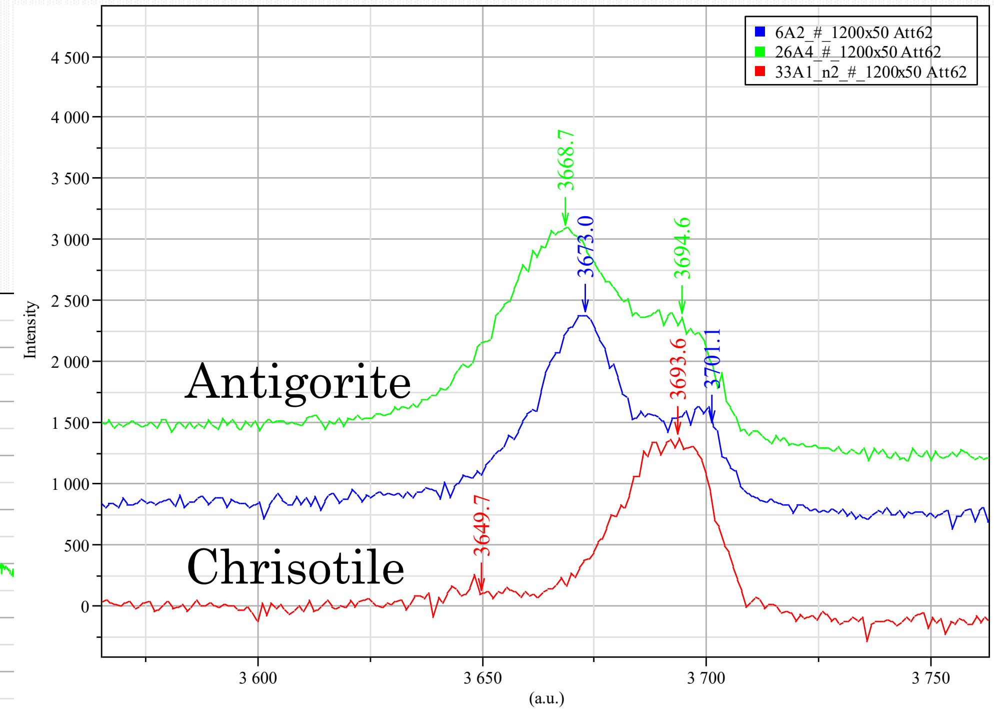
Liz Ctl Ant

Serpentine study by portable Raman



Enwave Raport
632 nm
Resolution 6 cm^{-1}
Range up to 4000 cm^{-1}


Intensity
(a.u.)


6A2_#_1200x50 Att62
26A4_#_1200x50 Att62
33A1_n2_#_1200x50 Att62
3668.7
3673.0
3694.6
3693.6
3701.1
3649.7
Antigorite
Chrisotile
Intensity
(a.u.)

CONCLUSIONS 1

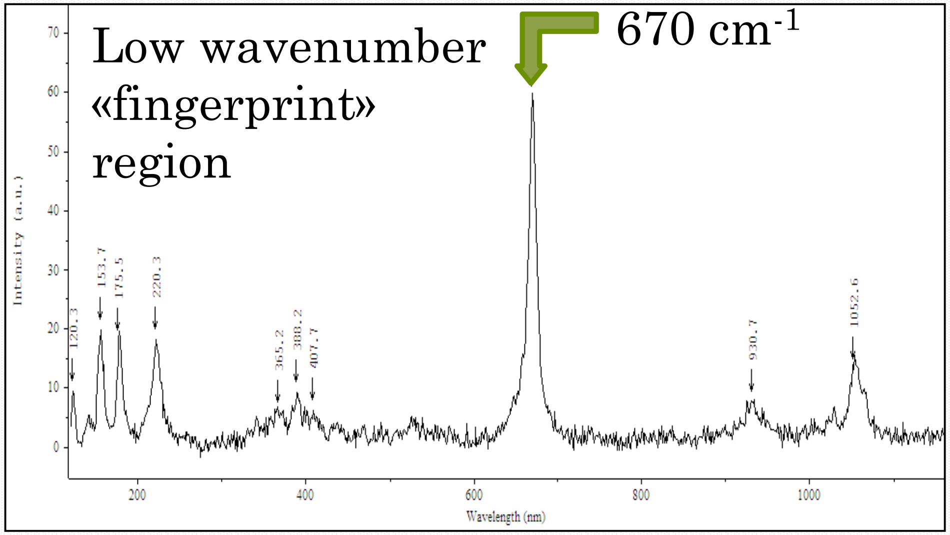
- ✓ Optical and electronic microscopy are very useful for a first identification of the minerals and for the observation of the textural relationship between the different phases.
- ✓ In many cases the correct identification only by microscopy is not certain.
- ✓ Raman spectroscopy, especially in the OH stretching region, allowed the discrimination of all the serpentine polymorphs.
- ✓ Raman micro-mapping allowed to study the presence of the different polymorphs and their structural and textural relationship, with an unparalleled detail level. This will be very helpful for a deeper understandig of the serpentinization process.

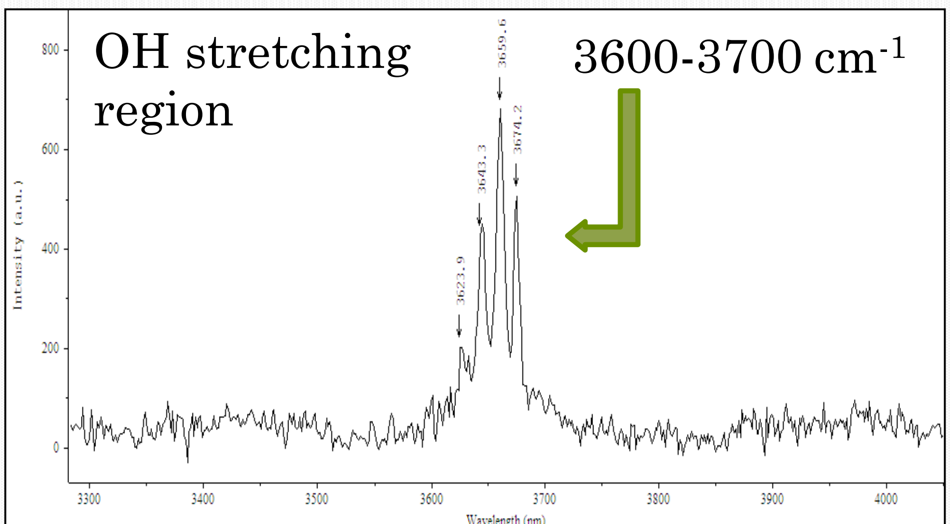
PERSPECTIVES 1

- Identification of dangerous asbestos in building materials, in soils and in the environment.
- Study of serpentinization processes in different environmental conditions.
- Identification of asbestos fibers in tissues and hystological samples.

Not only serpentines: different asbestos

The case of Nephrite





$(Ca_2(Mg^{2+},Fe^{2+})_5Si_8O_{22}(OH)_2)$

Series *tremolite (Mg-rich term)*

- ferroactinolite (Fe-rich term).

$X=Mg/(Mg^{+}+Fe^{2+})$.

$X \geq 0.9$ tremolite

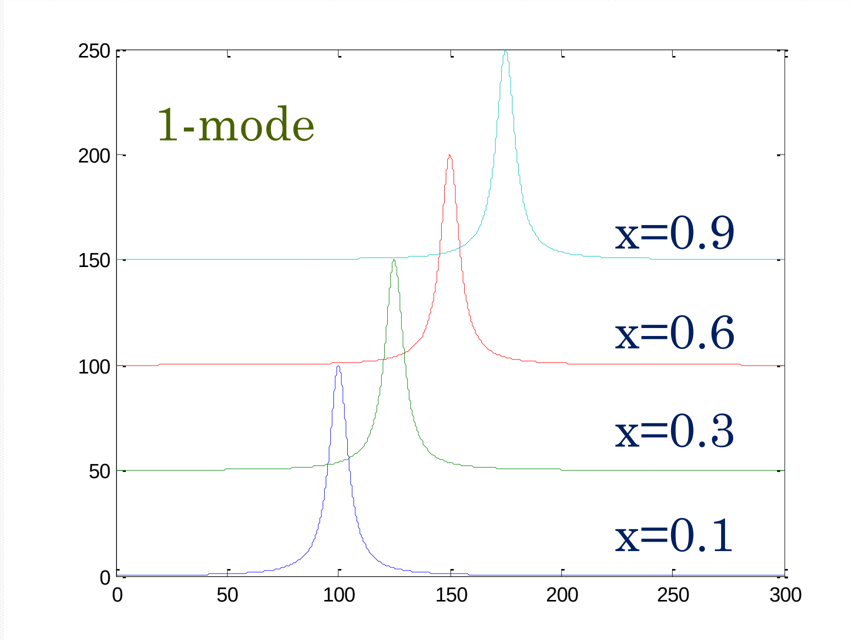
$0.5<X<0.9$ actinolite

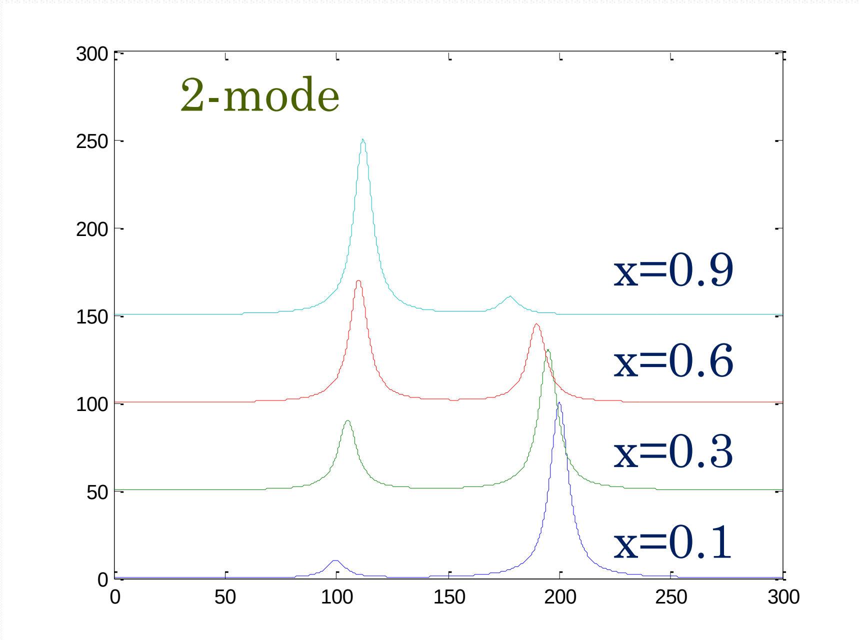
$X<0.5$ ferro-actinolite

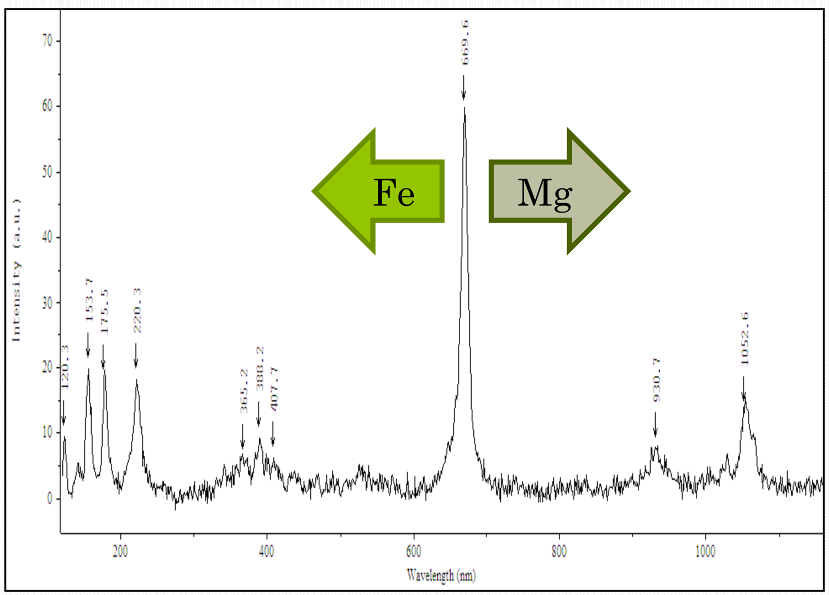
1-mode Vs. 2-mode behavior

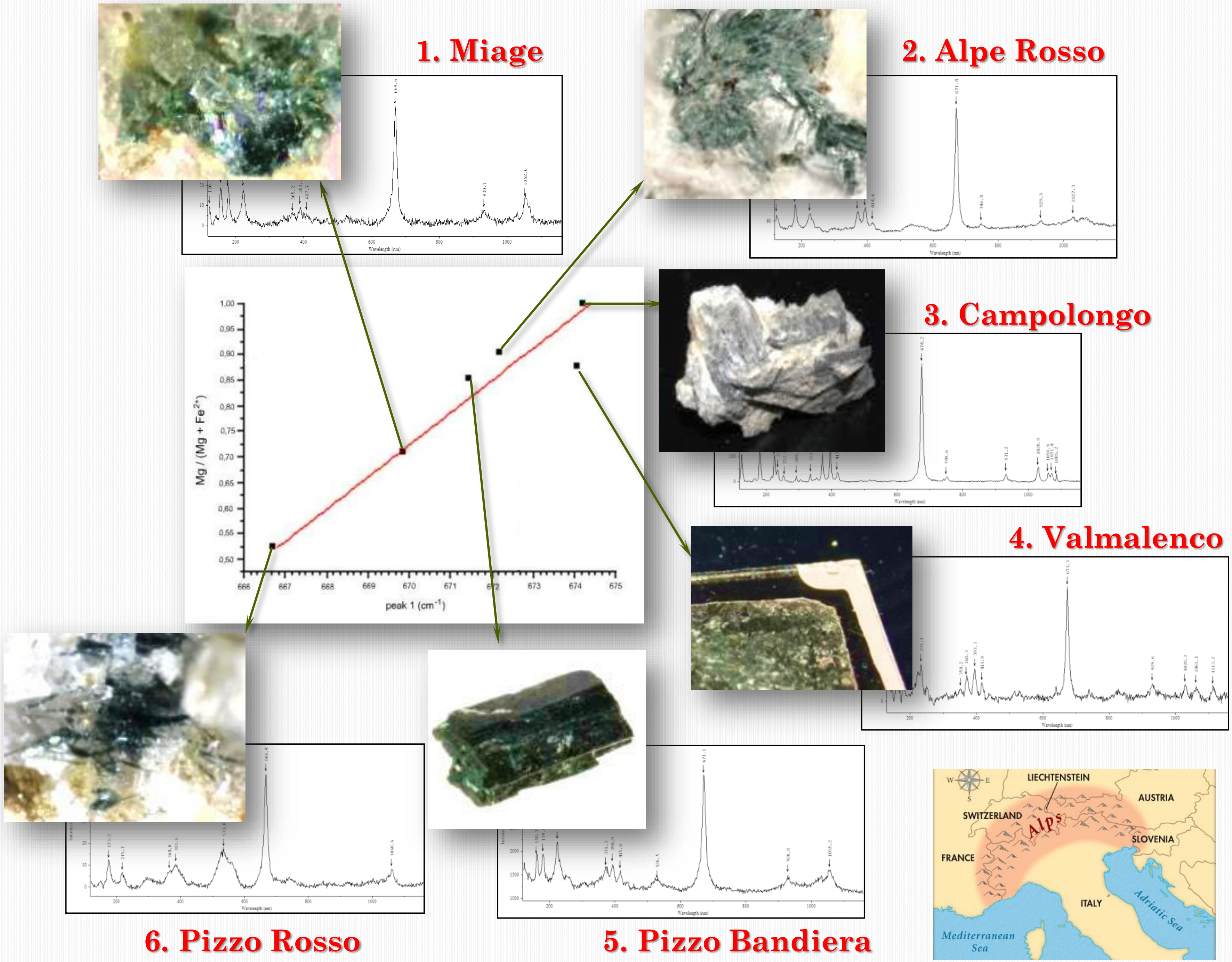
Solid Solution ABZ - ACZ

$AB_xC_{1-x}Z$



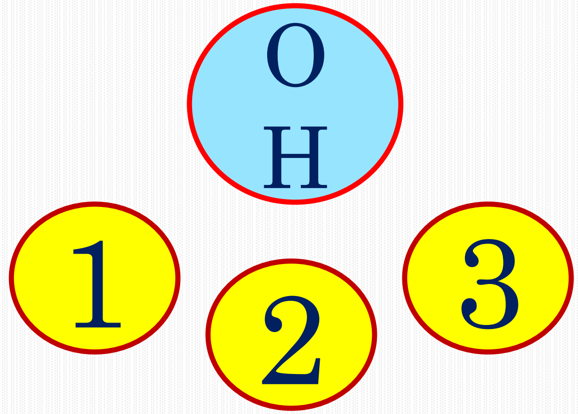


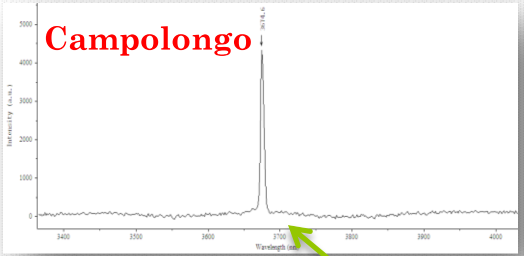


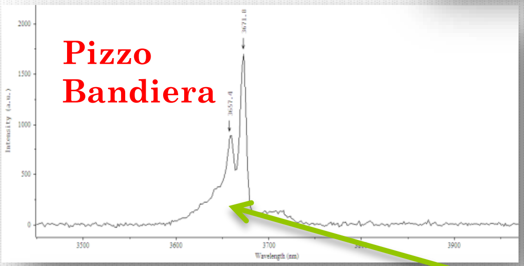

1. Miage
2. Alpe Rosso
3. Campolongo
4. Valmalenco
5. Pizzo Bandiera
6. Pizzo Rosso
Mg / (Mg + Fe2+)
peak 1 (cm-1)
1,00
0,95
0,90
0,85
0,80
0,75
0,70
0,65
0,60
0,55
0,50
666
667
668
669
670
671
672
673
674
675
LIECHTENSTEIN
AUSTRIA
SWITZERLAND
Alps
SLOVENIA
FRANCE
ITALY
Adriatic Sea
Mediterranean Sea

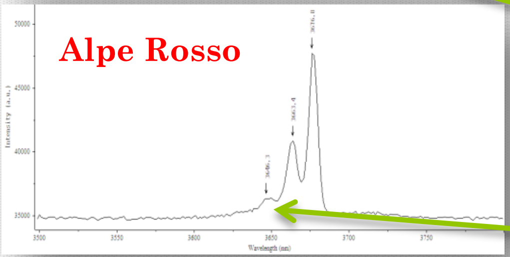
OH stretching in tremolite-actinolite

2 possible metals (Mg-Fe) in 3 sites near OH









4 possible configurations:

1,2,3 = Mg (Mg, Mg, Mg) in tremolite

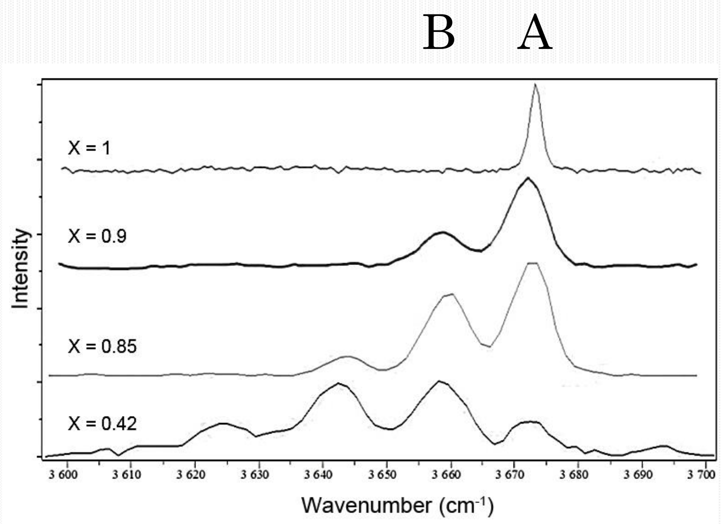
Mg, Mg, Fe

Mg, Fe, Fe

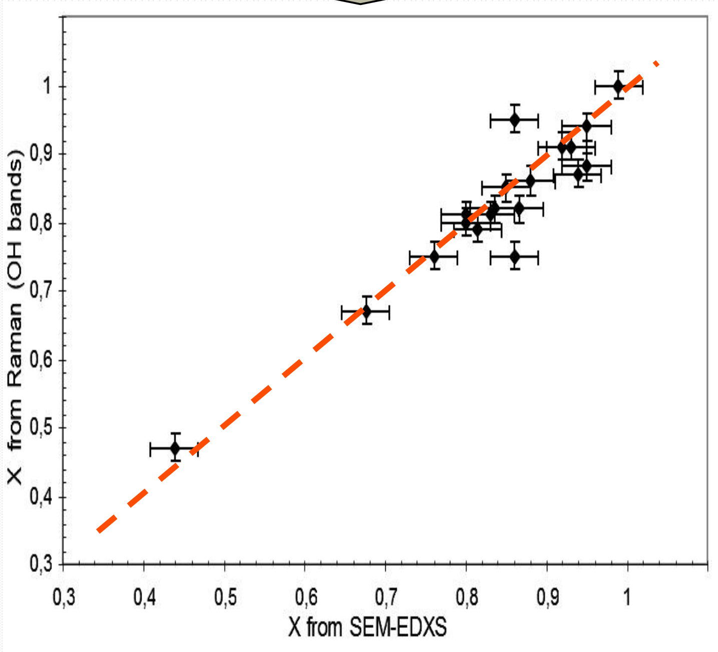
Fe, Fe, Fe

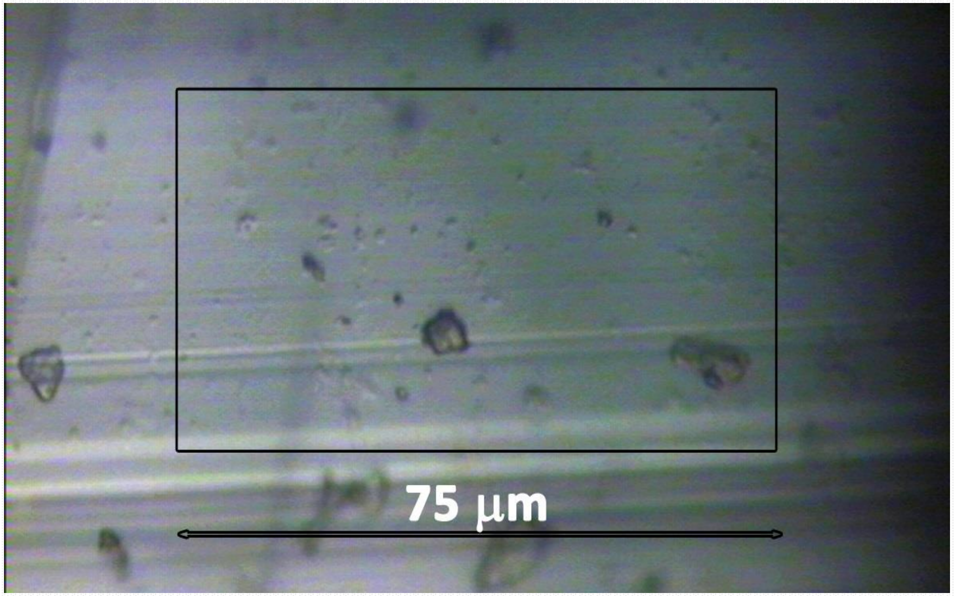
Increasing Iron

Simple statistical model:
X=(A12)/(1/3+A12),
(A12 = area A / area B)



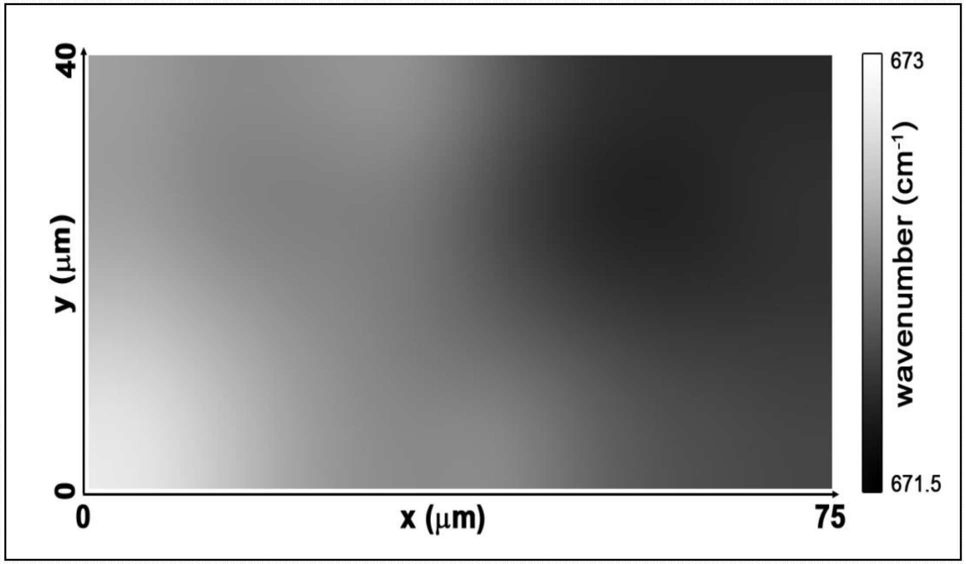
Comparison between the values of
X= Mg^{2+} /(Mg^{2+} +Fe^{2+})
measured by SEM-EDXS and estimated by the OH Raman stretching bands.





Micro-photo of a zoned actinolite crystal.

Green colour, increasing from left to right, is due to Fe^{2+} ions.



Raman Map of the position (wavenumber) of the main peak (671-673 cm^{-1})

Darker = lower position = more Fe^{2+}

Thank you!