STUDY OF THE COMPOSITION OF AMPHIBOLES IN THE TREMOLITE - FERRO-ACTINOLITE SERIES BY MICRO-RAMAN AND SEM-EDXS. D. Bersani[1], S. Andò[2], L. Scrocco[1], P. Gentile[2], E. Salvioli-Mariani[1] and P. P. Lottici[1]. [1]University of Parma, Physics and Earth Sciences Department, Parco Area delle Scienze 7/a, 43124 Parma, Italy, *danilo.bersani@unipr.it*, [2]University of Milano-Bicocca, Department of Earth and Environmental Sciences, Piazzale della Scienza 4, 20126 Milano, Italy.

Nephrite is the name attributed to a rock comprising mostly massive microcrystalline to cryptocrystalline felted amphiboles of the tremolite – ferro-actinolite series. Tremolite is the magnesic term $(Ca_2Mg_5Si_8O_{22}(OH)_2)$, while ferro-actinolite $(Ca_2Fe_5Si_8O_{22}(OH)_2)$ is the ferric one [1]. The members of the series can be distinguished by X = Mg/(Mg+Fe^{2+}) ratio: for $0.9 \leq X \leq 1$ we have tremolite, for $0.5 < X < 0.9$ actinolite, and for $X < 0.5$ ferro-actinolite (rare) [2].

The identification of the composition of nephrite is of great interest not only in mineralogy, but also in archaeology and art history, because nephrite is the main component of the so-called "true-jade". The other type of jade has pyroxene nature, being composed by the clinopyroxene jadeite $Na(Al,Fe^{3+})Si_2O_6$.

The attempt to obtain the composition of nephrite, and in particular the cation ratio x, in a completely non-destructive way by means of micro-Raman spectroscopy is not new. We start from the fundamental work on the cation distribution on amphiboles of Wang et al. [3] and from the application of Raman microspectroscopy on the study of jades proposed by Chen et al. [2] to develop a quick method for the identification of nephrite using both low-wavenumber and high wavenumber parts of the spectrum.
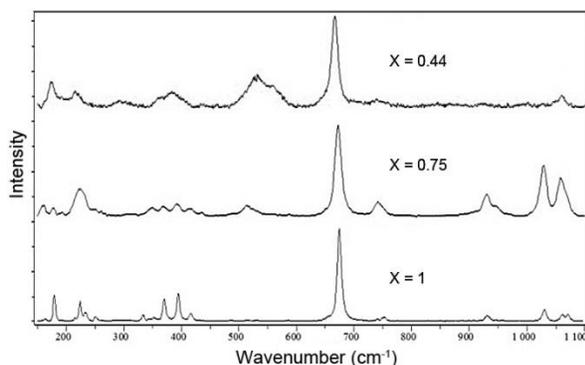

Fig. 1: Raman spectra at low wavenumbers of different minerals of tremolite – ferro-actinolite series with different X ratios.

In this work we analyzed by micro-Raman spectroscopy twenty samples of minerals in the tremolite – ferro-actinolite series, coming from different localities in the Alps, to study the relationship between the Raman spectra and the composition, obtained by SEM-EDXS, and the influence of different cations.

The main feature of the Raman spectra of tremolite - ferro-actinolite minerals in the low-wavenumber region (100-1100 cm^{-1}) is the A_g symmetry mode at nearly 675 cm^{-1}, related to Si-O symmetrical stretching (Fig.1). This mode, when substituting Mg^{2+} with the heavier Fe^{2+}, downshifts from 675 cm^{-1} in pure tremolite to 667 cm^{-1} in Fe-rich actinolite (X=0.5, at the border with ferro-actinolite). This trend is clearly evidenced in Fig.2. A linear interpolation process allows to obtain a simple formula relating the position of the main A_g band with the X = Mg / (Mg+Fe^{2+}) ratio.
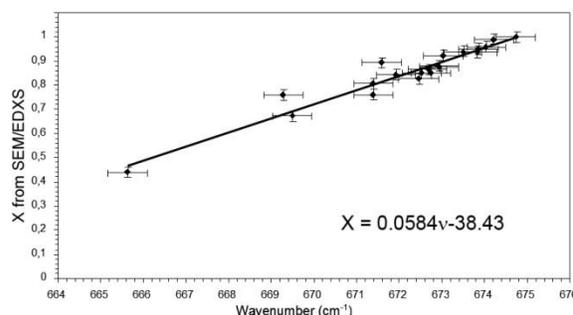

Fig. 2: Relation between the wavenumber v of the A_g main Raman peak at low wavenumber and the chemical composition X.

In the high-wavenumbers region (3600-3700 cm^{-1}) a number of OH stretching bands (from 1 to 4) is present. The number and relative intensity of these bands depend on the X value. This is due to the fact that in nephrites the OH group vibrations are influenced by the population of the 3 metal sites where Fe^{2+} or Mg^{2+} could be present [2]. When only Mg is present (as in pure tremolite), only one peak (at 3675 cm^{-1}) is observed. As the amount of iron increases, the other peaks, related to different combinations of Fe^{2+} and Mg^{2+} in the sites close to OH, arise at lower wavenumbers (Fig. 3). From a simple statistical model based on the population of the 3 sites, we obtain another relation useful to estimate the X value from the Raman spectrum: $X=(A_{12})/(1/3+A_{12})$, where A_{12} is the ratio between the areas of OH Raman bands at about 3675 and 3660 cm^{-1}, often the most visible ones.
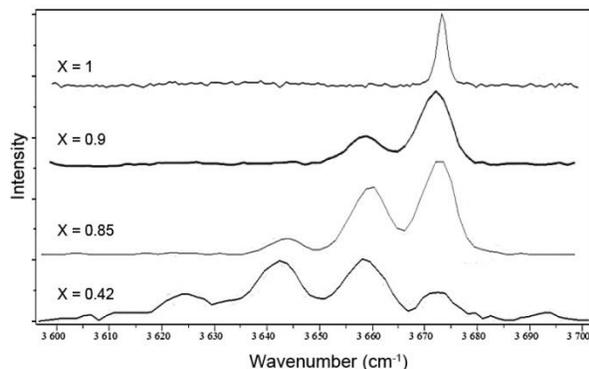
Fig. 3: Raman spectra at high wavenumbers of minerals of tremolite-actinolite series with different X ratios.

In Fig. 4 the composition (X value) estimated from the areas of the OH bands and that measured by SEM-EDXS is shown. Only for a couple of samples the obtained values are significantly different: they are two cases with compostion far from ideal nephrite, with many extra ions and with several microscopic compositional zonations.
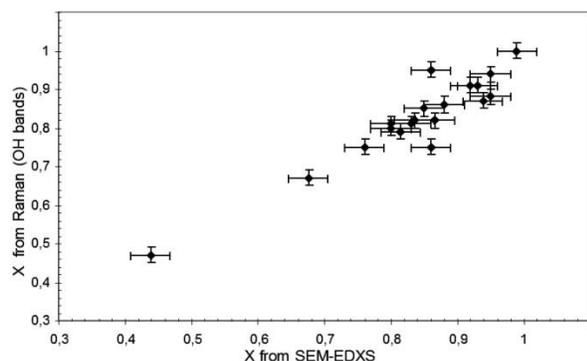

Fig. 4: Comparison between the compositions (X ratios) of the tremolite – ferro-actinolite samples estimated by the OH stretching bands and those obtained by SEM/EDXS.

We have therefore obtained two simple and independent methods to evaluate the composition of nephritic minerals from their Raman spectrum. The first one, based on the position of the main A_g band, shows a better sensitivity and linearity with the changes of the X value. On the other hand, the second method, based on the ratio of the OH stretching bands areas, is nearly insensitive to the spectrometer calibration.

We verified the shift to low frequencies of the main A_g peak with the increase of iron, by making a micrometric Raman map on a zoned, needle-shaped, tremolite crystal coming from Alpe Rosso (Vigezzo Valley, Italy). As visible in the microscope image (Fig.5 top)

the green colour, due to the presence of iron, increases from left to right (nearly along the maximum elongation of the crystal). The grey colour map (Fig. 5 bottom) represents the position of the A_g main band: lower lightness means lower wavenumber (higher Fe amount). As expected, the intensity of green color in the picture is well paralleled by the dark parts of the Raman map.
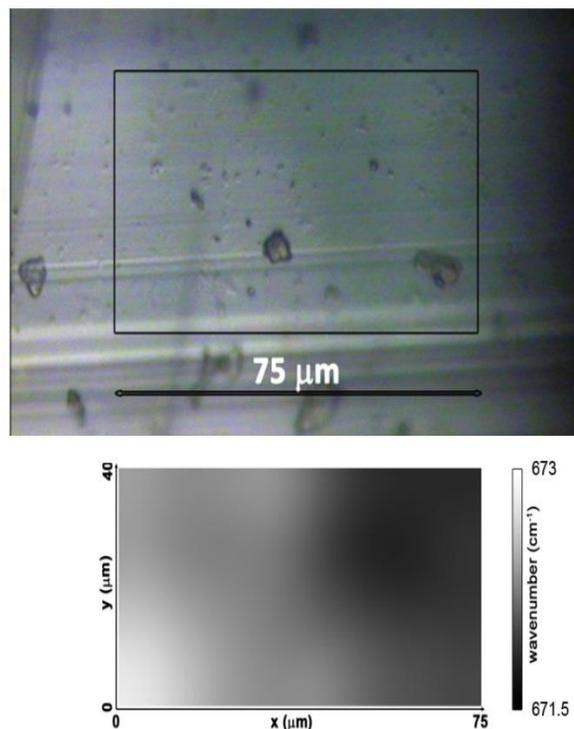

Fig. 5: Microscope image (top) and Raman map (bottom) representing the shift of the main A_g band obtained on a zoned actinolite crystal.

References. [1] Wang R. and Zhang W.-S. (2011) *J. Raman Spectrosc. 42*, 1324-1329. [2] Chen T.-H., Calligaro T., Pagès-Camagna S., Menu M. (2004) *Appl. Phys. A 79*, 177-180. [3] Wang A., Dhamelincourt P., Turrell G. (1988) *Appl. Spectrosc. 42*, 1441.