Report of the EMP and Raman spectroscopic analysis of adachiite – $Ca(Fe^{2+}))_3Al_6(Si_5Al)O_{18}(BO_3)_3(OH)_3(OH)$

A single crystal (~6mm x 3mm) was analyzed by electron microprobe and Raman spectroscopy.

For electron microprobe analysis the specimen was embedded in a gypsum mount and polished. The measurements were carried out using a Cameca SX-100 SEM system with a wavelength-dispersive detector. The energy of the electron beam was 15 keV and the beam current was 20 nA. The following standards were used: LiF for F, albite for Na, MgO for Mg, Al_2O_3 for Al, andradite for Si, Ca, and Fe, vanadinite for Cl and V, orthoclase for K, $MnTiO_3$ for Ti and Mn, Cr_3O_3 for Cr, olivinite for Cu, $SrTiO_3$ for Sr, and Ba-glass for Ba. The acquisition times were 20 s for Na, K, Mg, Ca, Mn, Fe, Al, Ti, and Si, 60 s for Ba, Sr, Cu, Cr, and Cl, and 120 s for F. Background measurements on both sides of the peak were carried out with half of the counting time of the respective element.
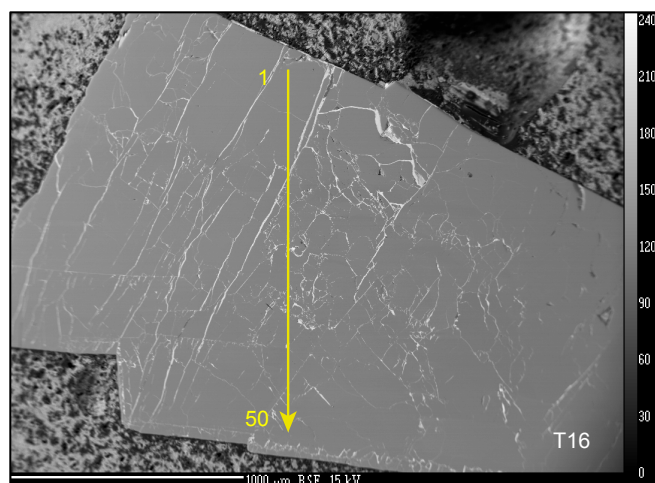

50 points were measured along the line in the BSE image. The bright veins contain very high contents of iron. Therefore, 8 data points were excluded from the calculation of the chemical formula. We used the program WinTcac (Yavuz et al. 2014) for the calculations with the following normalizations: (T+Y+Z)=15, (OH+F+Cl)=4, boron was estimated stochiometrically, the contents of water calculated. The oxidation state of iron was assumed to be divalent. The averaged oxide sum amount to 100.32 ± 0.56 wt%, the calculated formula is $(Ca_{0.56\pm0.04}Na_{0.3\pm0.02}\square_{0.13\pm0.02})(Fe^{2+}_{1.76\pm0.08}Mg_{0.59\pm0.03}Al_{0.55\pm0.11}Ti_{0.10\pm0.02})Al_6(Si_{5.12\pm0.07}Al_{0.88\pm0.07})O_{18}(BO_3)_3(OH)_3(OH_{0.86\pm0.02}O_{0.13\pm0.02})$, which is close to the chemistry reported by Dr. Nishio-Hamane and co-workers in their 2014 paper in the Journal of Mineralogical and Petrological Sciences.

Raman scattering experiments were conducted in backscattering geometry with a Horiba Jobin-Yvon T64000 triple-monochromator spectrometer (holographic gratings of 1800 grooves/mm) equipped with an Olympus BX41 confocal microscope (Olympus LM Plan FLN 50x objective with a numerical aperture of 0.5) and a Symphony liquid-N_2-cooled charge-coupled device detector. Raman spectra were excited by a Coherent 90C Fred Ar^+ plasma laser using a wavelength of 514.5 nm and an output laser power of 600 mW. The achieved spectral resolution was ~2 cm^{-1} and the accuracy in determining the peak positions was ~0.35

cm^{-1}. Polarized Raman spectra were collected in the spectral range 15 – 4000 cm^{-1} in $\overline{y}(zz)y$, $\overline{y}(zx)y$, and $\overline{y}(xx)y$ scattering geometry (Porto's notation); x, y, and z are the Cartesean coordinate axes with z parallel to the crystallographic c axis in the hexagonal setting, while the crystallographic a axis is either along x or along y. The acquisition time was chosen to yield a satisfactory signal-to-noise ratio, i.e., the spectra were collected for 20 s at 10 accumulations. The OriginPro® 9.1 software package was used for data evolution. The collected spectra were baseline corrected with a spline function, normalized for the Bose-Einstein occupation factor and the acquisition time. Peak positions, full widths at half maximum, and integrated intensities were determined from fits with pseudo-Voigt functions. The criterion for the maximum number of analyzed peaks is for all peaks $\Delta I < I/2$, where I and ΔI are the calculated magnitude and uncertainty of the peak intensities.
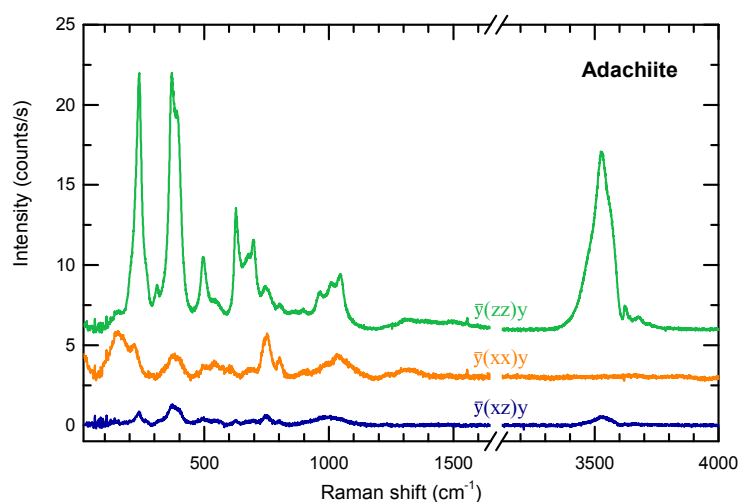
The graphic above shows the Raman spectra in the spectral region of the lattice vibrations and the O–H bond stretching measured in the 3 scattering geometries, which are vertically offset for clarity.
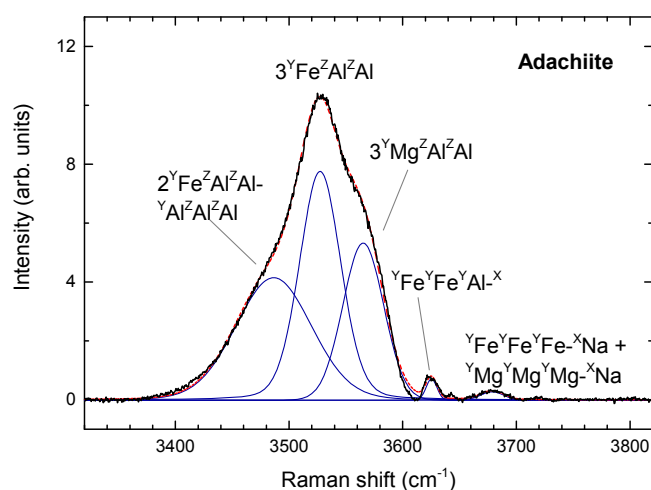
In the first part of our study, we focused on the OH stretching modes and further analyzed the spectrum taken in $\overline{y}(zz)y$ directions. Taking the local chemical environment of the anionic sites into account, we considered for the V site the three coordinating triplets of YZZ octahedra individually and for the W site the YYY octahedral triplet plus the X site in the

vicinity. Peaks below 3600 cm^{-1} are related to OH in the V site, peaks above to OH in the W site. We assigned the dominant ^{V}OH mode at 3537±1 cm^{-1} to 3^{Y}Fe^{Z}Al^{Z}Al, which is the most probable YZZ configuration. The mode at 3485±2 cm^{-1} is related to 2 ^{Y}Fe^{Z}Al^{Z}Al-^{Y}Al^{Z}Al^{Z}Al. The ^{Y}Al substitution in one of the 3 triplets increases strength of the octahedral cation–oxygen bond and thus weakens the O–H bonding so that the mode shifts to lower wavenumbers. The third ^{V}OH mode at 3565±1 cm^{-1} is related to the significant ^{Y}Mg substitution and assigned to 3^{Y}Mg^{Z}Al^{Z}Al. The ^{W}OH mode at 3625±1 cm^{-1} is related to a vacant X site in the vicinity to the W site and the YYY triplet. It is assigned to ^{Y}Fe^{Y}Fe^{Y}Al-^{X}□. The second ^{W}OH mode at 3679±1 cm^{-1} is related to a sodium-occupied X site and assigned to a combination of ^{Y}Fe^{Y}Fe^{Y}Fe-^{X}Na and ^{Y}Mg^{Y}Mg^{Y}Mg-^{X}Na.

The position of the dominant ^{V}OH mode is shifted to lower wavenumbers by about 30cm^{-1} compared to schorl, where the tetrahedral ring is fully occupied by ^{T}Si. This frequency shift is in agreement with similar downward shifts in amphiboles and micas, in which ^{T}Si is replaced by ^{T}Al (Hawthorne et al. 1996, Am. Min. 81, 782-784).

The results from the adachiite sample will be included in the first part of our study on the identification of tourmaline species and crystallchemical analysis using the OH stretching vibrations. The manuscript will soon be submitted to American Mineralogist. The second part will focus on the lattice vibrations.