

Exploring the potential of Raman spectroscopy for crystallochemical analyses of complex hydrous silicates: I. Amphiboles

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ABSTRACT

Detailed Raman spectroscopic and electron microprobe studies of 33 amphibole ($AB_2C_5T_8O_{22}W_2$, $C_5 = M1_2M2_2M3$) crystals from 6 amphibole subgroups were performed to check whether the Raman scattering arising from OH bond stretching vibrations can be used for the identification and site-occupancy analysis of amphiboles. Several results can be gained from this study. (1) C-site Mg and Fe^{2+} on the M1M1M3 triplet linked to the W-site OH⁻ lead to two-mode behavior of the OH bond stretching mode: up to four Raman peaks separated by $\sim 16\text{ cm}^{-1}$ from each other can be observed and their fractional intensities can be used to quantify the concentration of M1M1M3 chemical species as well as to estimate the overall C-site occupancy by Mg and Fe^{2+} . (2) The coexistence of Mg and Fe^{2+} on the B site also leads to two-mode behavior but the peak splitting is only $\sim 3\text{ cm}^{-1}$. The fractional intensities of these split components can be used to refine the B-site occupation factors of Mg and Fe^{2+} . (3) The presence of B-site Li, Na, and Ca results in one-mode behavior of the OH Raman peaks, i.e., slight shift of the peak positions depending on the concentration of distinct chemical species. The total replacement of B-site Ca by Na should reduce the peak positions by 6.5 cm^{-1} , whereas that of Li by $\sim 13\text{ cm}^{-1}$. (4) A-site occupancy leads to strong broadening as well as to a strong shift of the OH peaks toward higher wavenumbers. The full-width at half maximum (FWHM) of OH-stretching peaks associated with filled A sites is ~ 22 vs. $\sim 8\text{ cm}^{-1}$ for OH peaks associated with vacant A sites. For ^TAl-poor amphiboles the M1M1M3-OH peaks shift toward higher wavenumbers by $\sim 37\text{ cm}^{-1}$ in the case of ^WOH–A-cation–^WF species and by 60 cm^{-1} in the case of ^WOH–A-cation–^WOH species with respect to the peak position for ^WOH–A-vacancy–^WOH species. (5) High content of ^CAl, i.e., ^{M2}Al > 1 atom per formula unit (apfu) seems to lead to one-mode behavior and an additional shift toward lower wavenumbers by $\sim 4\text{ cm}^{-1}$. (6) OH peaks with FWHM $\sim 30\text{--}40\text{ cm}^{-1}$ may indicate high content of ^TAl (1 or 2 apfu), which can be verified by analyzing the FWHM of the Raman peak near 670 cm^{-1} , generated by vibrations of bridging oxygen atoms in TO₄ rings. (7) The W site occupancy factor of the OH groups can be estimated using the intensity ratio η between the total Raman scattering generated by OH bond stretching and the Raman peak near 670 cm^{-1} generated by TO₄-ring vibrations. A small value of η (< 0.09) combined with the presence of strong Raman scattering near $750\text{--}780\text{ cm}^{-1}$ is indicative of oxo-amphiboles. Guidelines for non-specialists how to use the Raman scattering of OH bond stretching modes for “rough” but preparation-free, non-destructive, and easy-to-handle crystallochemical quantitative analyses of amphiboles are suggested.

Keywords: Amphibole, Raman spectroscopy, electron microprobe analysis