

# Quantifying the A-site occupancy in amphiboles: a Raman study in the OH-stretching region

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Amphiboles are members of a large group of fibrous silicates of extreme interest in geology [1] and environmental science [2]. Amphiboles are probably the most complex among the rock-forming minerals. Their very flexible structure, consisting of several different cationic/anionic sites, and the manyfold chemical substitution occurring at these sites give rise to a large number of permutations resulting in a large number of species; in this scenario, each amphibole name refers to a range of compositions instead of a specific mineral chemistry. In trying to put some order into this matter, several Commissions of the IMA (International Mineralogical Association) have been convened. The last IMA report, which dates back to 2012 [3], divides the Amphibole Supergroup into subgroups based on the dominant atomic species in a specific site and the resulting charge arrangements. Even though such a division assigns specific names to specific root compositions ("end-members"), there are more than 110 end-member names, each being commonly associated to extensive chemical variability. Thus several ambiguities have not been removed. Consequently, each amphibole sample needs a proper characterization in terms of both composition and crystal-structure; this issue is particularly important in asbestos studies, where international regulations are indeed based on names.

To fully unravel the stoichiometry of a sample, the use of different analytical techniques in a combined-fashion is required, adopting in particular those micro-analytical techniques offering local atomic arrangement sensitivity. In this respect, vibrational spectroscopy has proven to be a valid tool for addressing the issue of site-occupancies in amphiboles: among such techniques, Fourier-Transform Infra-Red spectroscopy is the most widely applied [4], while Raman spectroscopy has been used to characterize amphiboles only in few papers [5 and refs therein]. On the other hand, Raman spectroscopy presents two great advantages over the other vibrational techniques, namely a very high spatial resolution and no need for sample preparation.

Aim of this work is to correlate Raman information with the site-occupancy of selected, well characterized, synthetic amphiboles, in order to provide a calibration curve to determine the composition of unknown natural amphiboles. In fact, we observed that the OH stretching region strongly depends both on the nature of the cations and on the degree of occupancy, because of a different local atomic arrangement, and can thus be used as an internal probe to access the local chemical structure. In this work, in particular, we focused our attention on two synthetic systems, prepared at different experimental (T,P) conditions (the potassium-richerite  $K(NaCa)Mg_5Si_8O_{22}(OH)_2$  – tremolite  $\square(Ca_2)Mg_5Si_8O_{22}(OH)_2$  join [6] and the  $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$  [7]), showing that Raman spectroscopy can be successfully used in amphiboles investigations to provide direct information on the nature of cations and degree of site occupancy.

## References

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