

Hydrous species in Al-bearing apophyllite: the verification of the substitution of $\text{Si}^{4+} + \text{H}_2\text{O}$ for $\text{Al}^{3+} + \text{H}_3\text{O}^+$

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The chemical compositions and hydrous species of seven different fluorapophyllites have been investigated using EMPA, TG-DTA, Micro-Raman spectroscopy and ^1H MAS NMR spectroscopy. Three fluorapophyllites contain aluminum of 0.4, 0.6, 0.9 wt%, respectively and substitute Si^{4+} for Al^{3+} . Al-bearing fluorapophyllites indicate more water contents than the other Al-free ones: the former contents of 16.9-17.3 wt% and the latter contents of 16.6 wt%. The Micro-Raman spectroscopic analysis indicates that Al-bearing fluorapophyllites have significantly higher peaks of 3100 and 3360 cm^{-1} than Al-free ones. ^1H MAS NMR measurements indicate the chemical shifts of 1.63 and 2.10 ppm in Al-bearing fluorapophyllites, but these shifts are not visible in Al-free ones. Thus, Al-bearing fluorapophyllites should contain a different hydrous species. Therefore, the following coupled substitution is suggested: $\text{Si}^{4+} + \text{H}_2\text{O}$ for $\text{Al}^{3+} + \text{H}_3\text{O}^+$. This substitution makes a hydrous fluid more alkaline, where fluorapophyllite crystallizes. Al-bearing fluorapophyllite plays an important role in crystallizing the zeolite minerals in alkaline fluids.