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Correlation between Si-Al disorder and hydrogen-bonding distance variation in ussingite ($Na_2AlSi_3O_8OH$) revealed by one- and two-dimensional multi-nuclear NMR and first-principles calculation

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Abstract

Ussingite ($Na_2AlSi_3O_8OH$) is a mineral with a unique interrupted framework structure and strong hydrogen bonding. It contains 4-, 6-, and 8-membered tetrahedral rings resembling feldspars, but, unlike the latter, is partially depolymerized. There are four crystallographically distinct tetrahedral (T) sites, two of which (T1, T2) are Q^4 [i.e., having 4 next nearest neighbor (NNN) T sites], and the other two (T3, T4) are Q^3 (i.e., having 3 NNN T sites), each with NNN (in brackets) of T1(1T2, 1T3, 2T4), T2(1T1, 2T3, 1T4), T3(1T1, 2T2), and T4(2T1, 1T2). There is one unique OH site in the T4-O8-H···O2-T3 configuration, where O8 and O2 are nonbridging O atoms (NBO). In the ordered structure, T1 is fully occupied by Al, and the other three T sites by Si. Previous X-ray and neutron diffraction and ^{1}H and ^{29}Si NMR studies gave contradictory conclusions regarding Si-Al disorder. In this study, we were able to unambiguously clarify the issue via comprehensive one- and two-dimensional ^{1}H, ^{29}Si, ^{27}Al, and ^{23}Na NMR and first-principles calculation. It was revealed that there is ~3% Si-Al disorder that occurs between neighboring T1-(O)-T2 sites, such that the formation of Al-O-Al linkage and Al(Q^3) are avoided. The disorder was found to result in the development of Si(Q^3) sites with various NNN, including 3Al and 3Si, and neighboring OH sites having significantly shorter and longer hydrogen-bonding distances than in the ordered structure, with ^{1}H chemical shifts near 15~16 ppm and 11 ppm, in addition to a main peak near 13.9 ppm. Good correlation was found between ^{1}H chemical shift, hydrogen-bonding (O-H, H···O, and O···O) distances, and Si-O distances in the Si-O-H···O-Si linkage. This suggests that Si-Al disorder is correlated with variation in hydrogen-bonding distances via through-bond transmission of bond valence variations. This could be a universal phenomenon also applicable to other hydrous minerals. The revelation of preferential partition of Al in Q^4 over Q^3 sites to avoid the formation of Al-OH and Al-NBO provides insight into their behavior in other partially depolymerized hydrous aluminosilicate systems, such as glasses and melts.

Keywords: Si-Al disorder, hydrogen bonding, NMR, first-principles calculation, ussingite, depolymerized, hydrous