Correlation between Si-Al disorder and hydrogen-bonding distance variation in ussingite (Na$_2$AlSi$_3$O$_8$OH) revealed by one- and two-dimensional multi-nuclear NMR and first-principles calculation

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ABSTRACT

Ussingite (Na$_2$AlSi$_3$O$_8$OH) 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 $^{29}$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

INTRODUCTION

Ussingite (Na$_2$AlSi$_3$O$_8$OH) is a mineral characterized by a unique interrupted framework structure and strong hydrogen bonding (Fig. 1). It has been found in limited localities in the world, as a secondary mineral in pegmatite in the Lovozero and Khibina massifs of the Kola Peninsula, Russia, in the Ilmaaussaq intrusion, Greenland, and in sodalite xenoliths in an alkalic gabbro-syenite complex in Mont Saint-Hilaire, Canada. Its chemical composition has been reported to be close to the ideal chemical formula (cf. Anthony et al. https://handbookofmineralogy.org/).

The crystal structure of ussingite has been determined by single-crystal X-ray diffraction (XRD) (Rossi et al. 1974) and powder neutron diffraction (Williams and Weller 2012). It has a space group $P_1T$, $Z = 2$ with lattice parameters: $a = 7.2474(1)$ Å, $b = 7.6813(1)$ Å, $c = 8.6432(1)$ Å, $a = 90.835(1)^\circ$, $\beta = 99.771(1)^\circ$, $\gamma = 122.581(1)^\circ$ at 4 K (Williams and Weller 2012). The structure contains 4-, 6-, and 8-membered tetrahedral rings resembling feldspars, but, unlike the latter, is partially depolymerized. There are nine crystallographically distinct oxygen sites, seven of which are bridging O atoms that each link two tetrahedral (T) cations, and the remaining two (O2, O8) are nonbridging O atoms (NBO) that each bond to one T cation and one H via O-H or H···O bond. The bulk NBO/T (NBO per tetrahedral cation), a parameter describing the degree of depolymerization of the system, is 0.5. There are four T sites, two of which (T1, T2) are Q$^4$ [i.e., having four next nearest neighbor (NNN) T sites], and the other two (T3, T4) are Q$^3$ [i.e., having three NNN T sites]. Their NNN environments (in brackets) are T1(1T2,1T3,2T4), T2(1T1,2T3,1T4), T3(1T1,2T2), T4(2T1,1T2), so that the T3/T4 sites are not NBO to one another, but are each surrounded by three T1/T2 sites. There is only one unique H site located in the T4-O8-H···O2-T3 linkage, with O8-H, H···O2, and O···O distances of 1.070(8), 1.412(7), and 2.481(5) Å at 4 K (Williams and Weller 2012).

The crystal structure of ussingite from X-ray diffraction (Rossi et al. 1974) did not show any Si-Al disorder. In the ordered structure, T1 is occupied by Al, and the other T sites by Si. The possibility of Si-Al disorder was suggested by Ribbe (1974), who noted that the exchange of 5% of Al in the T1 site with Si in the T3 site resulted in a better fit to an empirical equation for T-O bond distances. Oglesby and Stebbins (2000) reported $^{29}$Si