Direct evidence of Lowenstein's rule violation in swelling high-charge micas

E. Pavón, F. J. Osuna, M. D. Alba and L. Delevoye

Experimental Section

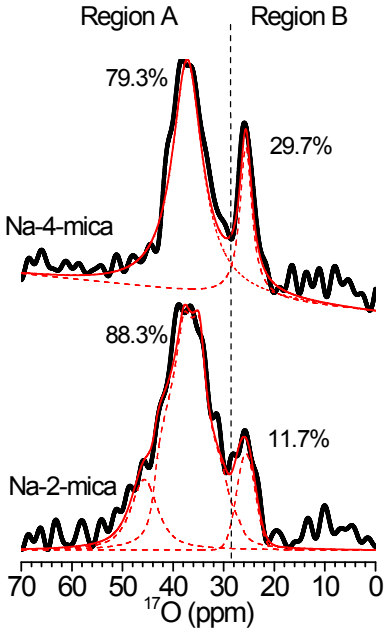
Synthesis

For Na-n-mica, $Na_n[Si_{8-n}Al_n]Mg_6O_{20}F_4$ (n= 2 or 4), synthesis, a procedure similar to that described by Alba et al.[1] was employed. Near-stoichiometric powder mixtures with the molar compositions (8 - n) SiO_2, (n/2) Al_2O_3, 6 MgF_2, and (2n) NaCl were used to synthesize Na-n-mica (n = 2 and 4). The starting materials were SiO_2 from Sigma (CAS no. 112945-52-5, 99.8% purity), $Al(OH)_3$ from Riedel-de Haën (CAS no. 21645-51-2, 99% purity), MgF_2 from Aldrich (CAS no. 20831-0, 98% purity), and NaCl from Panreac (CAS no. 131659, 99.5% purity). All reagents were mixed and ground vigorously before heating up to 900 °C in a Pt crucible for 15 h. After cooling, the solids were washed with deionized water and were dried at room temperature.

NMR Experiments

NMR spectra were acquired on a Bruker Avance III 18.8T spectrometer (^{1}H, 800.13 MHz; ^{17}O, 108.48 MHz) using a 4mm HX Thalahassee probehead. ^{17}O excitation was achieved by applying a central-transition selective π/2 pulse of 9 µs. The spinning frequency was 10 kHz, and the recycle delay was 1s. A total of 89216 and 56240 transients were added for Na-2-mica and Na-4-mica, respectively. Pulse sequences, such as double-frequency sweep (DFS) designed for signal enhancement of quadrupolar nuclei,[2] show large C_Q-dependent efficiency. Therefore, they were not used to preserve quantitative information. Chemical shifts were given in ppm with respect to water.

Suppl. Fig. 1. ^{29}Si MAS NMR spectra and integration of region A and B of the spectra



[1] M.D. Alba, M.A. Castro, M. Naranjo and E. Pavon, *Chemistry of Materials*, 2006, ***18***, 2867.
[2] L. A. O'Dell, K. J. Harris, R. W. Schurko, *Journal of Magnetic Resonance,* 2010, **203**, 156.