

## Medium-range order in disordered K-feldspars by multinuclear NMR

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### ABSTRACT

The structures of K-rich feldspar,  $(K>Na)AlSi_3O_8$ , are currently described as “ideal” crystals with periodic average structures from Bragg diffraction maxima obtained by reciprocal-space techniques. Polymorphism is explained by variable substitutional disorder of framework Si and Al cations in tetrahedral T sites, and positional disorder of cavity alkali cations in a single M site. Here, high-resolution magic angle spinning multinuclear magnetic resonance spectroscopy, leading to <sup>29</sup>Si, <sup>27</sup>Al, and <sup>23</sup>Na spectra at 9.4 as well as <sup>27</sup>Al, <sup>39</sup>K, and <sup>23</sup>Na spectra at 19.6 T, has been used to investigate the “real” structures along the order-disorder series of K-feldspar crystals. The “ideal” and “real” structure coincides only in the perfectly long-range ordered triclinic end-member of the low-microcline structure. Long-range disordered structures (either with monoclinic or triclinic symmetry by X-ray diffraction) show non-random disorder at the medium-range scale, triclinic-like distortions with four sets of T sites for framework atoms, two sets of M sites for alkali atoms, and Al-O-(K,Na) multi-site correlations by NMR spectroscopy. The K-feldspar structures can be described by a medium-range structure using the number of Al atoms per four-membered rings of tetrahedra, with “...-2-0-2-0-...” chains for microcline and orthoclase where the Al-occupancies  $t_1O > t_2m > t_2O \approx t_1m$ , and with “...-1-1-1-1-...” chains for valencianite and sanidine, in which  $t_1O > t_2m \approx t_2O \approx t_1m$ . Framework cations respect Loewenstein’s rule (Al-O-Al avoidance), as well as some additional constraints of charge dispersion involving deficiency of Si atoms in Q<sup>4</sup> (4Si,0Al), (1Si,3Al), and (0Si,4Al) environments, constraints which are particularly strong in valencianite. These “real” structure features cannot be described by “ideal” structures owing to the lack of resolving power of the reciprocal-space techniques.

**Keywords:** K-feldspars, NMR, medium-range order, valencianite, order-disorder series