Accurate and precise thermal expansivities of kyanite, andalusite and sillimanite, from 10 – 1573 K measured using time-of-flight neutron powder diffraction.

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Powder and single-crystal diffraction data measured from the three geologically important Al_2SiO_5 polymorphs, kyanite, andalusite and sillimanite, over the last five decades have given varying accounts of each polymorph's thermal expansion; the scatter between and even within experimental datasets is often quite large, particularly for parameters that vary little with temperature – such as the inter-axial angles in the triclinic form, kyanite. Furthermore, there are no lattice parameter determinations below 273 K, where the thermodynamic functions vary substantially, or above 1200 K.

Lattice parameters of natural specimens of kyanite, andalusite and sillimanite have been measured in the range 10 – 1573 K using the High-Resolution Powder Diffractometer (HRPD) at the ISIS neutron spallation source. The time-of-flight method, combined with the long 95 m primary flight path on HRPD produces neutron powder diffraction data with one of the highest resolutions in the world, which is essentially independent of Q. Hence it is possible to obtain lattice parameters to very high precision. Moreover, since neutrons are a highly penetrating bulk probe, there is no need for corrections due to surface effects or substrate thermal expansion and it is trivial to acquire data in complex low- and high-T sample environments. High accuracy of the measured lattice parameters is ensured by admixture of a NIST silicon powder standard with the specimens.

For kyanite, the improved precision reveals the true behaviour of α, β and γ for the first time, permitting derivation of accurate thermal expansion tensor coefficients. For both andalusite and sillimanite, the measurements reveal hitherto unknown regions of substantial negative linear expansivity below room temperature, along the *c*-axis in andalusite and along the *a*-axis in sillimanite. Above 1200 K, sillimanite exhibits an anomalous increase in thermal expansion that may be due to the onset of Al/Si tetrahedral site disorder.