Electron microprobe analyses are presented for astrophyllite-group minerals from hydrothermal veins and pegmatites of the Ilímaussaq complex, South Greenland. The analyses fall mainly into two groups: (1) niobophyllites with the highest Nb/(Nb+Ti) ratios yet recorded (~0.9), occurring only in the veins, and (2) an essentially continuous sequence from astrophyllite to niobophyllite with Nb/(Nb+Ti) up to 0.6, found in veins and pegmatites. It is highly likely that there is complete solid solution between astrophyllite and niobophyllite. More limited substitution of Mn for Fe has resulted in the formation of kupletskite in some rocks. Altered zones in certain astrophyllites and niobophyllites have compositional features similar to the type 'hydroastrophyllite'. The astrophyllite-group minerals in the hydrothermal veins crystallized at temperatures below 400°C at 1 kbar and under high pH and low oxygen fugacity, whereas those in the pegmatites were formed from water-rich melts which were hotter (≥450°C), less basic and more oxidized. © 2007 The Mineralogical Society.