High P-T phase relations and stability of a (21)-hydrous clinopyribole in the system K2O-Na2O-CaO-MgO-Al2O3-SiO2-H2O: An experimental study to 18 GPa

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ABSTRACT
Phase relations and stability of a mixed-chain (21)-hydrous clinopyribole [(21)-MHP] were investigated using a multi-anvil apparatus in the P-T range 5–18 GPa and 1100–1300 °C in a simplified KNCMASH-system. (21)-MHP is stable in the range 7–16 GPa and 1100–1400 °C, and coexists with clinopyroxene + sodic phase X ± potassic richterite ± aenigmatite-structured phase. Its breakdown products are sodic phase X + melt and Na-rich garnet + aenigmatite-structured phase toward high T (13 GPa/1600 °C) and P (18 GPa/1250 °C). In the KNCMASH-system investigated, the stability fields of potassic richterite and (21)-MHP only overlap between 7 and 10 GPa, and the P-stability of (21)-MHP exceeds that of potassic richterite by at least 3 GPa. The composition of (21)-MHP can be described as a combination of 1 potassic richterite + 2 omphacitic clinopyroxene K(Na2Ca2)(Mg6Al)Si12O34(OH)2 with variable degrees of Al2Mg–1Si–1-exchange and NaSiCa–1Al–1-exchange component dependent upon P and T. At P >10 GPa, both (21)-MHP and coexisting clinopyroxene contain excess Si compared with the ideal clinopyroxene, and (21)-MHP stoichiometries with up to 2.09 Si/6 O atoms and 12.4 Si/33 O atoms + stoichiometric (OH) respectively. This silica excess is attributed to the presence of VSi as Na(Mg0.5Si0.5)Si2O6 component in clinopyroxene and within the pyroxene-like slabs of (21)-MHP. A TEM analysis of (21)-MHP synthesized at 10 GPa/1250 °C shows a regular alternation of single- and double-tetrahedral chains without evidence for stacking disorder. Potential factors responsible for the unusually high P-T stability of (21)-MHP compared to all MHPs known so far are: (1) the fact that the unit-cell volume of (21)-MHP is 1.5% smaller than that of an equivalent mixture of potassic richterite + omphacite; (2) an Na-rich bulk composition that enables the presence of VSi-bearing clinopyroxene in solid-solution within the single-chain slabs of (21)-MHP; and (3) the availability of K to completely fill the large A-sites of the (21)-MHP structure. The results of this study demonstrate that mixed-chain hydrous pyriboles represent a new class of high-pressure silicate structures capable of storing water and alkali-elements under upper mantle P-T conditions. However, their stability is restricted to K-Na-rich bulk compositions.