

## High *P-T* phase relations and stability of a (21)-hydrous clinopyribole in the system $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ : An experimental study to 18 GPa

JÜRGEN KONZETT<sup>1,\*</sup> AND STEFANIE L. JAPEL<sup>2,†</sup>

<sup>1</sup>Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road N.W., Washington D.C., 20015-1305, U.S.A.

<sup>2</sup>Department of Earth and Planetary Sciences, Olin Hall, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218, U.S.A.

### 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 1100–1600 °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  $\text{K}(\text{Na}_2\text{Ca}_2)(\text{Mg}_6\text{Al})\text{Si}_{12}\text{O}_{34}(\text{OH})_2$  with variable degrees of  $\text{Al}_2\text{Mg}_{-1}\text{Si}_{-1}$ -exchange and  $\text{NaSiCa}_{-1}\text{Al}_{-1}$ -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 <sup>VI</sup>Si as  $\text{Na}(\text{Mg}_{0.5}\text{Si}_{0.5})\text{Si}_2\text{O}_6$  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 <sup>VI</sup>Si-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.