

The system Al_2O_3 - P_2O_5 - H_2O at temperatures below 200 °C: Experimental data on the stability of variscite and metavariscite $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$

KIRSTEN DRÜPPEL,^{1,*} ANDREAS HÖSCH,² AND GERHARD FRANZ¹

¹Technical University Berlin, Institute for Applied Geosciences, Department of Mineralogy, Sekr. ACK9, Ackerstrasse 71-76, D-13355 Berlin, Germany

²Röntgenstrasse 7a, D-10587 Berlin, Germany

ABSTRACT

The system Al_2O_3 - P_2O_5 - H_2O contains many phosphate minerals that occur in various geologic environments. The natural occurrence of variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, orthorhombic), including its monoclinic polymorph metavariscite, is largely restricted to soils and aluminous rocks like Al-rich igneous rocks and shales, which interacted with P-rich hydrothermal solutions or groundwater. Variscite dehydrates to berlinite (AlPO_4) and a hydrous P-Al-rich fluid. This dehydration reaction $\text{AlPO}_4 \cdot 2\text{H}_2\text{O} = \text{AlPO}_4 + 2\text{H}_2\text{O}$ is, however, metastable, at low concentrations of P in the fluid, because berlinite breaks down at lower temperature to augelite [$\text{Al}_2\text{PO}_4(\text{OH})_3$] + $\text{H}_3\text{PO}_4 + \text{H}_2\text{O}$ and trolleite [$\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$] + $\text{H}_3\text{PO}_4 + \text{H}_2\text{O}$. The variscite/metavariscite = berlinite equilibrium has been investigated by synthesis experiments from mixtures of γ - Al_2O_3 and excess phosphoric acid at pressures between 1 and 5 kbar and temperatures of 100–200 °C using standard cold-seal vessels. The hydration-dehydration equilibrium is mainly controlled by temperature and only weakly by pressure. At 4 and 5 kbar, variscite/metavariscite were found at temperatures of ~150 °C, at lower pressure at 115–125 °C in accordance with their natural mode of occurrence. In this T range, however, variscite/metavariscite is not the sole phase but is always accompanied by variable but generally minor amounts of wavellite and trolleite $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$. Secondary wavellite $\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$, hydrated Al-phosphate $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ ($1.1 \leq x \leq 1.3$) and Al-metaphosphate hexahydrate $\text{Al}(\text{H}_2\text{PO}_4)_3$ formed during quenching and/or drying of the runs. Berlinite is the reaction product at temperatures 200 °C/4–5 kbar and 150 °C/1–3 kbar and may be associated with augelite and trolleite.

Keywords: Al-orthophosphates, berlinite, hydrothermal experiments, metavariscite, stability, variscite