## Petedunnite (CaZnSi<sub>2</sub>O<sub>6</sub>): Stability and phase relations in the system CaO-ZnO-SiO<sub>2</sub>

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## ABSTRACT

The phase relations of petedunnite  $[CaZnSi_2O_6(pd)]$  were determined experimentally at P-T conditions up to 2.5 GPa and 1100 °C. Single-phase petedunnite is formed at high pressures (P > 0.8 GPa). Reversed experiments show that at lower pressures and temperatures >650 °C petedunnite decomposes to willemite  $[Zn_2SiO_4 (wil)]$ , hardystonite  $[Ca_2ZnSi_2O_7 (har)]$ , and quartz  $[SiO_2 (qtz)]$  according to the reaction 4 pd = wil + 2 har + 3 qtz. The boundary curve for this equilibrium reaction is given by P (GPa) = -0.093 (0.029) + 0.0014 (0.0003) T (°C), by disregarding the phase transition of quartz. The stability field of wil + har + qtz is restricted toward lower temperatures by zinc-feldspar [CaZn- $Si_{3}O_{8}$  (zfsp)] according to the known reaction: wil + 2 har + 7 qtz = 4 zfsp. These reactions intersect at 650(1) °C/0.78(0.01) GPa, generating an invariant point  $I_{pd}$ . Additionally, petedunnite-breakdown reaction is intersected by the low/high-quartz phase transition curve, generating an invariant point *I*<sup>ad</sup><sub>pdz</sub> at ~840 °C, 1.04 GPa. At temperatures <650 °C, further reactions occur in the system CaO-ZnO- $SiO_2$  including the doubly degenerate reaction zfsp = pd + qtz and 3 pd = har + wil + zfsp, which also intersect the invariant point  $I_{pd}$ . All reactions involving petedunnite display shallow positive slopes within the P/T-field, indicating that the crystallization of petedunnite is highly pressure sensitive over a wide temperature range. This means that an increasing petedunnite component in pyroxene shifts its stability field to higher pressures, similar to the effect of a jadeitic component.

The study of natural clinopyroxene and the correlation of its zinc content with published *P*-*T* conditions of these mineral assemblages confirmed a significant relationship between extraordinary high-zinc concentrations in pyroxene and high-metamorphic pressure conditions. In addition, the petedunnite component is obviously sensitive to the prevailing fluid conditions in terms of the fugacity ratio  $f_{s_2}/f_{o_2}$ . Furthermore, a distinct temperature dependency of the zinc component was observed in the range of trace element concentration. In consequence, Zn turns out to be a key element with regard to its implementation as a sophisticated petrogenetic indicator of metamorphic conditions. Therefore, routine measurement of zinc in element analyses of clinopyroxenes is strongly recommended.

**Keywords:** Zinc, clinopyroxene, petedunnite, stability, phase relations, skarn, petrogenetic indicator, geobarometry, experimental calibration