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## High-Pressure Transformations in $\text{CaSiO}_3$ \*

Eric Essene

Department of Geology and Mineralogy, The University of Michigan,  
Ann Arbor, Michigan 48104

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*Abstract.* Wollastonite transforms to a triclinic high-pressure polymorph, wollastonite II, at pressures  $> 25$  kb. The equilibrium boundary [ $P(\text{bars}) = -4.7 \times T(^{\circ}\text{C}) + 32.810$ ] has a rather flat negative  $P-T$  slope. The rapid reactivity of the transition over at least a  $1000^{\circ}\text{C}$  range, its insensitivity to  $T$  and its location around 30 kb are indicative of its potential for a pressure calibration curve at high  $T$ .

Wollastonite reacts to form pseudowollastonite at  $1125^{\circ}\text{C}$  and 1 atm, and pseudowollastonite congruently melts at  $1544^{\circ}\text{C}$  (Osborn and Schairer, 1941). Kushiro (1964) followed these reactions to 25 kb finding steep positive slopes on a  $P-T$  diagram.

Wollastonite itself has several closely related monoclinic and triclinic polytypes (Peacock, 1935; Trojer, 1968; Wenk, 1969; Ito *et al.*, 1969; Jefferson and Brown, 1973) which have very small differences in volumes. These polytypes are sensitive to shear (Wenk, 1969; Coe, 1970) and are insensitive to  $P-T$  of formation (Wenk, 1969), as is characteristic of non-reconstructive and polytypic reactions where  $\Delta G_r$  is small. The identification of a specific polytype requires single-crystal X-ray data impossible to obtain on the fine-grained run products of this study, and it is fortunate indeed that the specific polytype is unlikely to petrologically and experimentally significant.

Ringwood and Major (1967) converted wollastonite at high pressures to a new polymorph which was about 5% denser than wollastonite at room  $P-T$ . They placed the equilibrium at about 30 kb for  $T = 900^{\circ}\text{C}$ , an excellent estimate in light of these experiments. Trojer (1969) refined the structure of this phase finding "...irregular layers of Ca atoms...interconnected by pairs of Ca atoms and  $\text{Si}_3\text{O}_9^{-6}$  rings...located in between the layers". Trojer's data yield a cell volume of 37.59 cc, 6.2% denser than wollastonite. The dense polymorph is here designated wollastonite II. Wollastonite II was synthesized at 27 kb and  $1600^{\circ}\text{C}$  by the writer and W. Hibberson while preparing a probe standard of  $\text{CaSiO}_3$ . Reversals were then sought on the reactions wollastonite I = wollastonite II and wollastonite I = pseudowollastonite.

The experiments were conducted on the 5/8" Australian National University piston-cylinder apparatus modified from the design by Boyd. Talc/BN cells were used except at  $600^{\circ}\text{C}$  where the pressure medium was entirely talc. Pressures were measured on an advancing ram and were corrected uniformly by  $-10\%$  (Green *et al.*, 1966). Temperatures were measured with a Pt/Pt-10% Rh thermocouple and are nominal values. Because of the exceptionally

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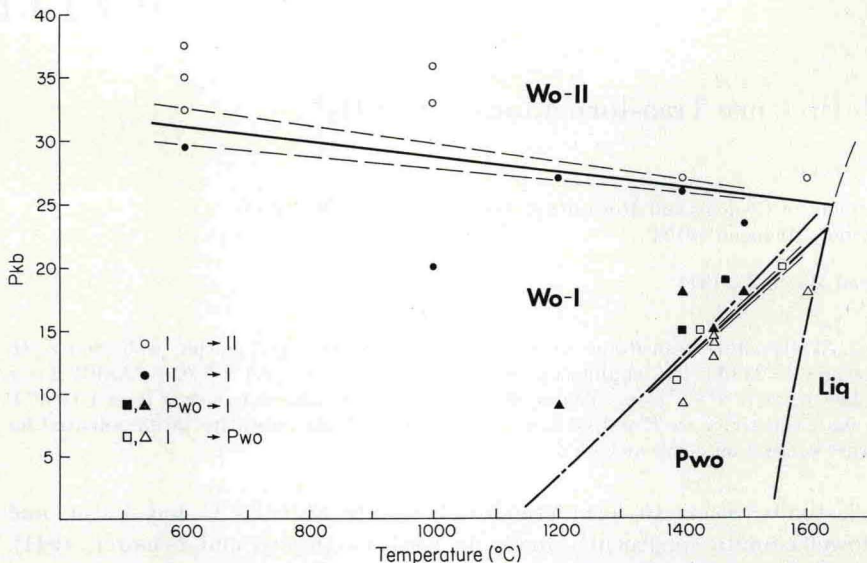


Fig. 1.  $P$ - $T$  phase diagram for  $\text{CaSiO}_3$ . Inferred equilibria are shown by solid lines and error limits are dashed. These experiments are represented by open and closed circles and triangles. Kushiro's inferred equilibria are shown by dash-dot lines and his reversals by open and closed squares. *Wo-I* wollastonite I; *Wo-II* wollastonite II; *Pwo* pseudowollastonite; *Liq* liquid

flat slope of the wollastonite I—wollastonite II reaction, systematic errors of even  $50^\circ\text{C}$  yield only 0.24 kb error in the location of this curve. Run times varied from two days at  $600^\circ\text{C}$ , to 8 hrs at  $1200^\circ\text{C}$ , to hrs at  $1600^\circ\text{C}$ . Starting materials for the runs plotted on the figure were 50/50 mixtures of wollastonite I—wollastonite II and wollastonite I—pseudowollastonite for each transformation. The wollastonite and pseudowollastonite used were purchased from Tem-Pres and had about a 10–30 micron grain size. The wollastonite II strating material was synthesized from Tem-Pres wollastonite and had about the same grain size. 5% excess water was added for the  $600^\circ\text{C}$  runs, the  $900^\circ\text{C}$  runs were slightly dampened and higher  $T$  runs were dry. The runs proceeded to at least 90% of completion as determined by both optical and X-ray examination of run products.

The wollastonite-pseudowollastonite equilibrium obtained in this study agrees well with reversals given by Kushiro (1964) (see Fig. 1). The experimental slope of this transition may be combined with  $S_T$  data (Robie and Waldbaum, 1968) to calculate  $\Delta V_T$  from the relation  $\Delta S/\Delta V = dP/dT$ . Since expansion data are available for pseudowollastonite (Skinner, 1966), one may calculate the volume ( $40.73 \pm 0.25$  cc) of wollastonite at  $1125^\circ\text{C}$ , and its average thermal expansion between  $25^\circ$  and  $1125^\circ\text{C}$  ( $+2.0 \pm 0.7\%$ ). This agrees well with extrapolations of thermal expansion data on wollastonite—ferrosilite solid solutions (Skinner, 1966), which give a 2.3% expansion at  $1125^\circ\text{C}$  for pure wollastonite.

Wollastonite I reacts to form wollastonite II above 25 kb (see Fig. 1). The equation of the boundary is  $P = -4.7 \text{ bars}/^\circ\text{C} \times T^\circ\text{C} + 32,810 \text{ bars}$ . The slope,  $-4.7 \text{ bars}/^\circ\text{C}$ , is rather flat and negative. Combination of the experimental data with  $\Delta V_{298}^\circ$  allows estimation of  $\Delta S_r$  if the effect of  $P$  and  $T$  on  $\Delta V$  is neglected. By this calculation, wollastonite II has an entropy of 0.3 e.u. greater than wol-

lastonite I at the transformation  $P$ - $T$ . This is perhaps surprising as the substantially lower volume of wollastonite II might have been expected to generate a lower entropy than that of wollastonite I (Fyfe and Verhoogen, 1958; Strens, 1967). Considering the small  $\Delta S_r$ , it is still possible that  $\Delta S_r^\circ$  at 298° K has a different sign than  $\Delta S_r$  at  $P$ - $T$ . The effect of  $P$  on  $S$  is easily calculated from thermal expansion by the relation  $-\delta S/\delta P = \delta V/\delta T = V\alpha_p$ . If wollastonite I has 2% expansion over 1000° C then its change of  $S$  from 1 atm to 33 kb is approximately  $-0.6$  cal/mol° C. Then the  $\Delta S^\circ_{298}$  (I = II) will approach zero if the thermal expansion of wollastonite II is 1% for a 1000°  $T$  change. The  $\Delta S^\circ_{298}$  (I = II) could be negative if wollastonite II has a smaller or negative  $\alpha$ . High-temperature X-ray data are needed on wollastonite I and II in order to resolve this speculation.

At temperatures somewhere below 600° C,  $\text{CaSiO}_3$  is expected to transform to a  $\text{CaSiO}_3$ -hydrate in the presence of excess water. The reaction  $\text{xonotlite} = 6$  wollastonite +  $\text{H}_2\text{O}$  backbends to lower  $T$  at high  $P_{\text{H}_2\text{O}}$ , but xonotlite will eventually be replaced by rosenhahnite at high  $P_{\text{H}_2\text{O}}$  (Essene, 1966). The wollastonite I—wollastonite II reaction cannot be investigated at low  $T$  and high  $P_{\text{H}_2\text{O}}$  because of the formation of hydrated calc-silicates.

Wollastonite II is unstable in the earth's crust, forming only at depths greater than about 100 km. High-pressure rocks which might carry a  $\text{CaSiO}_3$  phase are the grospsydites (eclogitic rocks with grossular-rich garnet and tschermakitic omphacite,  $\pm$  kyanite,  $\pm$  corundum described by Sobolev *et al.*, 1968). Sobolev kindly sent the writer one of his most calcic grospsydites, but no  $\text{CaSiO}_3$  was found. However  $\text{CaSiO}_3$  is unstable with corundum and kyanite, and wollastonite II should be sought for in grospsydites lacking these phases.

The wollastonite I—wollastonite II equilibrium may be useful for pressure calibration at high  $P$ - $T$ . It has several advantages over presently used transformations (melting of alkali halides, quartz = coesite, kyanite = sillimanite, albite = quartz + jadeite, calcite = aragonite). Pure wollastonite I is easy to obtain, and wollastonite II is simply synthesized<sup>1</sup>. Unlike the melting curves of the alkali halides, the transformation is largely independent of temperature so that the troublesome effect of pressure on thermocouple readings is minimized. The reaction is rapidly reversed over a thousand degree interval from 600–1600° C, and no difficulty has yet been encountered with reaction rates near the equilibrium boundary, unlike kyanite = sillimanite. Furthermore no problems of back-reaction during quenching have been encountered as is the case for calcite-aragonite. This reaction is also conveniently located at high enough pressures to provide calibration for many experiments, while melting of alkali halides has not been pursued above 20 kb. Once this reaction is carefully reversed with a hydrostatic gas apparatus, it may ultimately prove useful as a secondary pressure calibration curve.

1 It should be noted that even small amounts of impurities may shift the I = II equilibrium significantly if an impurity concentrates largely in one polymorph. This is due to the relatively small  $\Delta V_r$ . For instance if wollastonite I has 1 mol-%  $\text{FeSiO}_3$  in solid solution and none will enter II near the phase boundary, the equilibrium boundary will shift in pressure by  $\Delta P = R \cdot T^\circ\text{K} \cdot 41.84 \cdot \ln. 99/\Delta V$ . At 1000° K  $\Delta P = 320$  bars, a significant shift of pressure if the curve is to be used for purposes of calibration. Similar difficulties are encountered for calcite-aragonite, and impure natural starting materials should be avoided in careful equilibrium determinations for solid-solid reactions with small  $\Delta V_r$ .

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Dr. E. Essene  
Department of Geology  
The University of Michigan  
Ann Arbor, Michigan 48104, USA