

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 groszpydites (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 groszpydites, 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 groszpydites 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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