Lawsonite Equilibria

comes more stable, but ΔS will tend to positive values. Typical trends in dehydration entropies per water molecule are indicated in figure 2 and are reasonably constant. From these data we may conclude that ΔS of reaction (1) will not change sign until temperatures near 175°C are reached. Further, when lawsonite breaks down at 250°C, laumontite will still be relatively stable in water at its saturated vapor pressure.

Scanty evidence (Coombs and others, 1959) indicates that laumontite would become unstable relative to anorthite, quartz, and water in the region of 300°C. For the reaction:

laumontite = anorthite + 2 quartz + 4 water

 $CaAl_2Si_4O_{12} \cdot 4H_2O = CaAl_2Si_2O_8 + 2SiO_2 + 4H_2O_{1iq}.$

We estimate:

 $\Delta G^{\circ} = +10.1 \text{ kcal } \text{; } \Delta S^{\circ} = +20.0 \text{ e.u. } \text{; } \Delta S \text{ at } 300^{\circ}\text{C}$ and liquid water = +40 e.u.

These figures also suggest laumontite breakdown to anorthite a little above 300°C which appears perfectly reasonable. It should be noted that at low pressures a field of stability of wairakite appears to be interposed between laumontite and anorthite (Coombs and others, 1959).

Returning to reaction (1) it is obvious that lawsonite is stable relative to laumontite at higher pressures and that the initial boundary slope will be positive. If we allow only for the compressibility of water, the transition pres-



Fig. 2. ΔS of the following dehydration reactions as a function of temperature (estimated by Fyfe).

A-B Muscovite = sanidine + corundum + water (liq).

C-D Brucite = periclase + water (liq).

E-F Boehmite = corundum + water (liq).

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(4)

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sure at 25°C is near 3700 atmospheres and the initial boundary slope 9.4 atmospheres/°C. As the temperature increases while ΔV and ΔS will retain negative signs over a considerable temperature range, the data of Sharp (1962) indicates that ΔS will become considerably smaller and the slope much flatter. We have made an estimate of the transition pressure at 300°C, and a value near 5000 atmospheres is indicated. The form of the curve is suggested in figure 1.

Little is known about the stability of thomsonite (a calcium zeolite) which may replace lawsonite in silica-poor environments. Synthesis experiments (Coombs and others, 1959) indicate stability up to temperatures of the order of 300°C at moderate pressures. The assemblage thomsonite-analcime, is known to replace plagioclase in zeolite facies alteration (Coombs and others, 1959, p. 63). For the reaction:

$\begin{aligned} \text{lawsonite} &+ 0.4\text{H}_2\text{O} = \text{thomsonite} \\ \text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O} + 0.4\text{H}_2\text{O} = \text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 2.4\text{H}_2\text{O} \\ & \Delta\text{V}^o = 27.04 \text{ cm}^3, \end{aligned}$

and it would be remarkable if ΔS° is not also positive. Hence as with laumontite, it appears that the lawsonite stability field will be replaced by thomsonite at low pressures and temperatures, and the boundary relations will be of the same form as with laumontite.

Zen (1961) has stressed the importance of consideration of relative partial pressures of water and carbon dioxide in low-grade metamorphism. Lawsonite may be replaced as indicated by the reaction:

1

(5)

 $Calcite + kaolinite = lawsonite + CO_2$

 $CaCO_3 + Al_2Si_2O_5(OH)_4 = CaAl_2Si_2O_7(OH)_2 \cdot 2H_2O + CO_2.$

For reaction (5) which is water independent:

 $\Delta G^{\circ} = +1.52 \text{ kcal} ; \Delta S^{\circ} = +37.1 \text{ e.u.} ; \Delta V_{\text{solid phases}} = -34.9 \text{ cm}^{3}.$

These figures imply that calcite-kaolin is stable at low temperatures, but lawsonite becomes relatively more stable with increasing temperature. In an environment where $P_{total} = P_{H_20} + P_{co_2}$ lawsonite will be favored by high ratios of P_{total}/P_{co_2} on account of the large ΔV solids term. For example, if P_{total} is 5000 bars, at 25°C; then the reaction (5) will be in equilibrium when P_{co_2} is approximately 100 bars (ideality assumed). Obviously, in any low-temperature environment where the fluid phase is rich in CO₂, lawsonite will not be favored.

CONCLUSIONS

As lawsonite frequently occurs in vein fillings with quartz or carbonate or is formed by the simple breakdown of plagioclase (McKee, 1962), the data presented have some bearing on the mineralogical processes. It should be stressed, however, that the stability field indicated is maximal for quartzbearing systems, and other phases such as prehnite, heulandite (more stable than laumontite at low temperature) will lead to some additional restriction on the field.

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