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LAWSONITE EQUILIBRIA

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ABSTRACT. The equilibrium conditions of the reaction lawsonite = anorthite + vapor have been determined betwen 370°C and 500°C at pressures in the range 4 to 8 kilobars. The boundary slope in this region is expressed by the relation $T_{eqm} = 259 + \frac{P}{41}$ where P is in bars. These data confirm the predictions of Newton and Kennedy.

Lawsonite is one of the critical minerals of rocks belonging to the glaucophane schist facies. The equilibrium decomposition of lawsonite thus sets some restrictions on physico-chemical variables operating in this metamorphic facies. Newton and Kennedy (1963) determined the conditions of the breakdown of lawsonite to silimanite-zoisite-quartz and vapor and the conditions of breakdown of the latter assemblage to anorthite and vapor. From these data and a knowledge of the entropies of the phases, the position of the boundary curve for the lawsonite = anorthite + vapor reaction was estimated. The data presented here confirm the accuracy of their prediction.

All experiments were conducted in cold seal rod bombs. Mixtures of natural materials were held at constant pressure and temperature in sealed silver tubes containing water. X-ray and optical methods were used to detect major changes in the proportions of phases present. Table 1 gives data on these materials. In some cases calcium chloride solution was added, but it had no pronounced catalytic action. All materials were ground to pass a 325 mesh screen. The experimental data are presented in table 2, and the phase relations deduced fr[illegible] data in figure 1. In four experiments very minor amounts of fine m[illegible] properties suggestive of zoisite were found, but the identification is uncertain. These four runs are all in the field of the zoisite assemblage found by Newton and Kennedy. Thus it appears that in much of the region studied, we may be dealing with the metastable lawsonite = anorthite + vapor equilibrium.

Newton and Kennedy extrapolated the existing entropy data for lawsonite and estimated a boundary slope of 45.7 bars degree^{-1}. Our experimental slope of 41 bars degree^{-1} agrees within the limits of both methods. King and Weller (1961b) provided data on the heat of this reaction at 25°C. From this and the entropy data the equilibrium conditions of the reaction can be estimated. The main uncertainty in these estimates involves extrapolation of the entropy of lawsonite above 25°C, an extrapolation that may involve very considerable error. Our estimates indicate that lawsonite would be in equilibrium with anorthite and liquid water near 250° ± 25°C at one atmosphere, in satisfactory agreement with the present data.

Whereas the data in figure 1 outlines the relative stability of anorthite and lawsonite, it gives only the most extensive possible field of stability for lawsonite. At low temperatures and pressures zeolites and other minerals, such as prehnite, may replace lawsonite. With present data it is possible to make some reasonable estimate of the magnitude of these effects.

TABLE 1

Chemical analyses and optical properties of lawsonite and anorthite used as starting materials

Oxide	A	B	C
SiO_2	38.11	43.13	44.49
TiO_2	0.29	nd	nd
Al_2O_3	30.91	35.87	36.00
Fe_2O_3	1.56	0.45	0.08
FeO	0.13	0.29	nd
MnO	0.01	nd	nd
MgO	0.03	0.08	0.04
CaO	17.54	19.27	19.49
Na_2O	0.06	0.65	0.59
K_2O	0.14	0.05	0.03
H_2O	10.72		
H_2O+		0.63	nd
H_2O-		0.35	nd
Total	99.53	100.77	100.72

Refractive Indices

	A	B	C	D
α	1.665 ± 0.002	1.5748	1.5748	1.57 ± 0.005
γ	1.686 ± 0.002	1.5880	1.5880	1.59 ± 0.005
An %		94.3	94.9	96 ± 2

A. Lawsonite. Analyst, D. Thaemlitz; optical properties, G. A. Davis; Blake Gardens, North Berkeley, California (Davis and Pabst, 1960).

B. Anorthite. Analyst, Y. Kawano; optical properties, I. Kato; crystal lapilli erupted in 1940, Miyake-jima volcano, Tokyo Prefecture, Japan (Kawano and Aoki, 1960).

C. Anorthite. Analyst, H. S. Washington; optical properties, I. Kato; crystal lapilli erupted in 1874, Miyake-jima volcano, Tokyo Prefecture, Japan (Kawano and Aoki, 1960).

D. Anorthite. Miyake Island, Tokyo Prefecture, Japan. Optical properties and universal stage An percent determination, Crawford.

The simplest reactions which field evidence suggests bear on this problem involve:

$$\begin{array}{llll} \text{laumontite} & = \text{lawsonite} & + \text{ 2 quartz} & + \text{ 2 water } (1) \\ CaAl_2Si_4O_{12}\cdot 4H_2O & = CaAl_2Si_2O_7(OH)_2\cdot H_2O + 2SiO_2 & & + 2H_2O; \\ \text{thomsonite} & = \text{lawsonite} & + \text{ 0.4 water} & (2) \\ CaAl_2Si_2O_8\cdot 2.4H_2O & = CaAl_2Si_2O_7(OH)_2\cdot H_2O + 0.4H_2O. & & \end{array}$$

Some data bearing on (1) are available, and we can make some reasonable guesses concerning (2).

Thermodynamic data (table 3) are available for leonhardite, a close relative of laumontite. Coombs (1952) described the conditions for the reversible conversion of laumontite to leonhardite. Laumontite in dry air loses water forming leonhardite, $Ca_2Al_4Si_{16}O_{24}\cdot 7H_2O$. Leonhardite, when soaked in liquid water at room temperature, is converted to laumontite. These observations

TABLE 2

Lawsonite–anorthite experiments

Starting material: Anorthite–lawsonite 1:1 molecular ratio				Starting material: Anorthite–lawsonite–quartz 1:1:4 molecular ratio				Starting material: Anorthite–lawsonite–CaCl₂ 1:1 molecular ratio, 0.2 M solution			
Temperature (°C)	Pressure (bars)	Time (days)	Product	Temperature (°C)	Pressure (bars)	Time (days)	Product	Temperature (°C)	Pressure (bars)	Time (days)	Product
515	8900	11	An (Law)	515	8900	11	An-Qtz (Law)	400	6950	63	No change
450	7800	70	An (Law, Zoisite)	450	7800	70	An-Qtz (Law)	450	6900	76	An (Law, Zoisite)
450	7800	35	Law (An)	450	7800	35	Law (An-Qtz)	450	6210	60	An (Law, Zoisite)
400	6950	68	Law (An)	400	6950	66	Law (An-Qtz)	350	6210	60	Law (An)
400	6950	66	Law (An)	400	6950	30	Law (An-Qtz)	425	6900	60	An (Law)
400	6950	30	Law (An)	350	6100	31	Law (An-Qtz)	400	6210	60	Law (An)
350	6100	31	Law (An)	400	5710	31	An-Qtz (Law)	400	5170	20	An (Law)
450	6900	76	An (Law, Zoisite)	353	5710	31	No change				
450	6210	60	An	450	4140	32	An-Qtz				
350	6210	60	Law (An)	300	4140	64	No change				
375	5530	58	Law (An)	300	4140	31	No change				
400	5170	31	An (Law)	444	2070	33	An-Qtz (Law)				
353	5170	31	No change								
450	4140	32	An								
300	4140	64	No change								
300	4140	31	No change								
444	2070	33	An (Law)								

NOTE: The mineral names appearing in parentheses in the Products columns were detected in minor amount in the product.
An = anorthite; Law = lawsonite; Qtz = quartz.

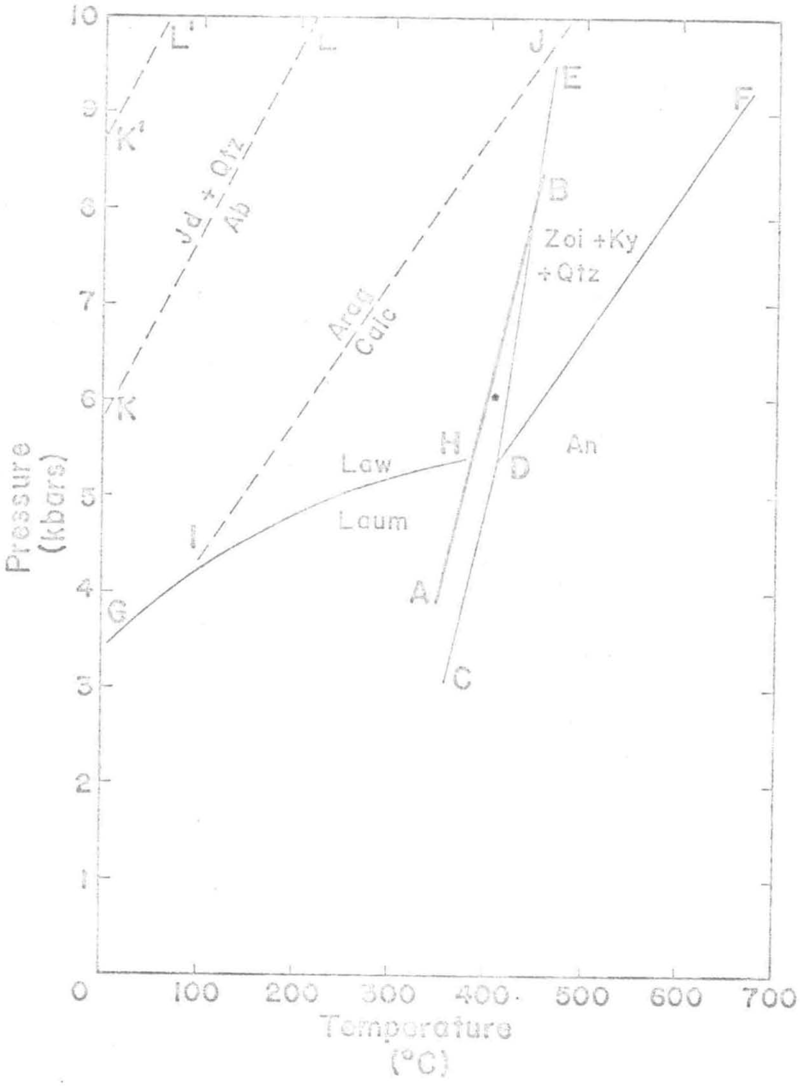

Fig. 1. Some experimentally determined [illegible] boundary relations concerned with lawsonite.

A–B Lawsonite = anothite + water (Crawford and Fyfe).
C–D Lawsonite = anorthite + water (estimated, Newtown and Kennedy, 1963).
D [illegible] zoisite + kyanite + quartz + water (Newton and Kennedy,

[illegible] kyanite + quartz = anorthite + water (Newton and [illegible], 1963).
G–H Lawsonite + quartz + water = laumontite (estimated by Fyfe).
I–J Aragonite = calcite (Clark, 1957; Crawford and Fyfe, 1964; [illegible] 1953; and MacDonald, 195[illegible]).
K–I and K'–I' Jadeite + quartz = albite (Fyfe and Valpy, 1959).

suggest that the free energy change of the reaction:

$$\text{leonhardite} + \text{water} = 2\ \text{laumontite} \qquad (3)$$

is extremely small, a few hundred calories at the most. As the uncertainty in the free energy of leonhardite is 1400 cals. we may equate the free energies of laumontite reactions to those known for leonhardite.

From table 3 we obtain the following data for the reaction:

$$\text{leonhardite} = 2\ \text{lawsonite} + 4\ \text{quartz} + 3\ \text{water}$$

$$\Delta G^0 = +4.4\ \text{Kcal}\ ;\ \Delta S^0 = -16.65\ \text{e.u.}\ ;\ \Delta V^0 = -68.85\ \text{cm}^3.$$

If we assume that ΔG^0 for reaction (3) is small, then for reaction (1) we obtain:

$$\Delta G^0 = +2.2\ \text{kcal}\ ;\ \Delta S^0 = -5\ \text{e.u.}\ ;\ \Delta V^0 = -22.55\ \text{cm}^3.$$

The entropy of laumontite has been estimated by considering average water contributions to leonhardite. Thus the high entropy assemblage laumontite is stable at low temperature. Therefore, as temperature increases laumontite be-

TABLE 3

Thermodynamic properties of minerals, water, and carbon dioxide at 25°C and 1 atmosphere

Mineral	$S_{298.15^\circ K}{}^0$ cal/deg mole	$\Delta G_{298.15^\circ K}{}^0$ kcal/mole		V cc/mole
		From elements	From oxides	
Anorthite $CaAl_2Si_2O_8$	48.4^g ±0.3	–	-23.8^a ±0.6	100.73^j ±0.15
Calcite $CaCO_3$	22.2^g ±0.2	-269.78^k		36.94^f ±0.02
Carbon Dioxide CO_2	51.06^k	-94.26^k		
Kaolinite $Al_2Si_2O_5(OH)_4$	48.53^h ±0.30	-888.1^h ±0.7		99.31^h ±0.30
Laumontite $CaAl_2Si_4O_{12} \cdot 4H_2O$	115.2^m (est)			205.4^m
Lawsonite $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$	56.8^i ±0.5	-1062.1^a ±0.8	-31.7^a ±0.6	101.33^d ±0.15
Leonhardite $Ca_2Al_4Si_8O_{24} \cdot 7H_2O$	220.4^i ±1.6		-67.8^a ±1.4	416.48^e
Quartz SiO_2	10.0^l			22.69^j ±0.005
Thompsonite $CaAl_2Si_2O_8 \cdot 2.4H_2O$				135.6^m
Water (liquid) H_2O	16.716^l			18.069^e ±0.003

[a] Barany (1962).
[b] Barany and Kelley (1961).
[c] Coombs (1952).
[d] Davis and Pabst (1960).
[e] Gray (1957).
[f] Graf (1961).
[g] Kelley and King (1961).
[h] King and Weller (1961a).
[i] King and Weller (1961b).
[j] Larsen and Berman [illegible]
[k] Latimer (1952).
[l] Rossini and others (1952).
[m] Calculated by W. S. Fyfe.

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:

$$\text{laumontite} = \text{anorthite} + 2\,\text{quartz} + 4\,\text{water} \tag{4}$$

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

We estimate:

ΔG° = +10.1 kcal [illegible] 20.0 e.u. ; ΔS at 300°C and liquid [illegible] 10 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-

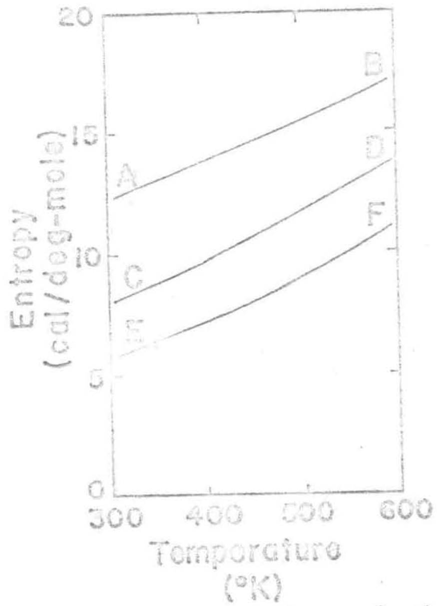

Fig. 2. ΔS of the following dehydration reactions as a function of temperature (estimated by [illegible]).
A–B [illegible] = [illegible]aridine + corundum + water (liq).
C–D [illegible] = periclase + water (liq).
E–F Boehmite = corundum + water (liq).

sure at 25°C is near 3700 atmospheres and the initial boundary slope 9.4 atmospheres/°C. As the temperat[illegible]es while ΔV and ΔS will retain negative signs over a considerab[illegible]e, the data of Sharp (1962) indicates that ΔS will become cons[illegible]ater and the slope much flatter. We have made an estimate of the transition pressure at 300°C, and a [illegible] 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:

$$\text{lawsonite} + 0.4H_2O = \text{thomsonite}$$

$$CaAl_2Si_2O_7(OH)_2 \cdot H_2O + 0.4H_2O = CaAl_2Si_2O_8 \cdot 2.4H_2O$$

$$\Delta V^\circ = 27.01 \text{ cm}^3.$$

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:

$$\text{Calcite} + \text{kaolinite} = \text{lawsonite} + CO_2$$

$$(5)$$

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

For reaction (5) which is water independent:

ΔG° [illegible] $\Delta S^\circ = +37.1$ 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 $P_{\text{total}} = P_{H_2O} + P_{CO_2}$ lawsonite will be favored by high ratios of $P_{\text{total}}/P_{CO_2}$ 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 CO_2, 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 quartz-bearing systems, and other phases such as prehnite, heulandite (more stable than laumontite at low temperature) will lead to some additional restriction on the field.

The plots on figure 1 show encouraging correlation with field observations. Three critical assemblages are commonly observed:

lawsonite–calcite–albite,
lawsonite–aragonite–albite,
lawsonite–aragonite–jadeite–quartz.

This sequence indicates increasing pressures of metamorphism. [illegible] ne that temperatures of glaucophane schist metamorphism are o[illegible] f 200-300°C (Brown, Fyfe, and Turner, 1962), the relative s[illegible] figure 1 are in the correct order. Coombs (1960) has o[illegible] a-calcite; Ghent (ms), the association lawsonite–aragonite–albite; and McKee (1962), the transition from lawsonite–albite to lawsonite–jadeite–quartz. It should be noted that much of the common jadeite of glaucophane schists contains significant amounts of diopside and acmite in solid solution which may significantly lower the pressure of formation. There is thus an excellent [illegible]lation between calorimetric data, direct experiment, and field observati[illegible]

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