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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 $T_{eqm} = 250 + \frac{P}{41}$ 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 from these data in figure 1. In four experiments very minor amounts of fine needles with 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 $250^{\circ} \pm 25^{\circ}$ 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

A	в	С	
38.14	43.13	44.49	
0.29	nd	nd	
30.91	35.87	36.00	
1.56	0.45	0.08	
0.13	0.29	nd	
0.01	nd	nd	
0.03	0.08	0.04	
17.54	19.27	19.49	
0.06	0.65	0.59	
0.14	0.05	0.03	
10.72			
	0.63	nd	
	0.35	nd	
99.53	100.77	100.72	
A	В	С	D
65 ± 0.002	1.5748	1.5748	1.57 ± 0.005
86 ± 0.002	1.5880	1.5880	1.59 ± 0.005
	94.3	94.9	96 ± 2
	$\begin{array}{c} A\\ 38.14\\ 0.29\\ 30.91\\ 1.56\\ 0.13\\ 0.01\\ 0.03\\ 17.54\\ 0.06\\ 0.14\\ 10.72\\ \hline \\ 99.53\\ A\\ 65 \pm 0.002\\ 36 \pm 0.002\\ \end{array}$	$ \begin{array}{cccc} A & B \\ 38.14 & 43.13 \\ 0.29 & nd \\ 30.91 & 35.87 \\ 1.56 & 0.45 \\ 0.13 & 0.29 \\ 0.01 & nd \\ 0.03 & 0.08 \\ 17.54 & 19.27 \\ 0.06 & 0.65 \\ 0.14 & 0.05 \\ 10.72 & & & \\ \end{array} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

- 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:

laumontite	= lawsonite	+ 2 quartz	+2 water (1)
$CaAl_2Si_4O_{12}\cdot 4H_2O$	$= CaAl_2Si_2O_7(OH)_2\cdot H_2O$	$+ 2SiO_2$	$+ 2H_2O;$
thomsonite	= lawsonite	+ 0.4 water	(2)
CaAl_Si_Os · 2.4H_O	= CaAl ₂ Si ₂ O ₇ (OH) ₂ · H ₂ O	$+ 0.4 H_{2}O.$	

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, $Ca_2Al_4Si_{18}O_{24} \cdot 7H_2O$. 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-CaCl ₂ 1:1 molecular ratio, 0.2 M solution							
Tem- perature (°C)	Pressure (bars)	Time (days)		Product	Tem- perature (°C)	Pressure (bars)	Time (days)	Pro	oduct	Tem- perature (°C)	Pressure (bars)	Time (days)		Product
515	8900	14	An	(Law)	515	8900	14	An-Qtz	(Law)	400	6950	68		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. William A. Crawford and W. S. Fyfe

Lawsonite Equilibria





- A-B Lawsonite = anothite + water (Crawford and Fyfe).
- C-D Lawsonite = anorthite + water (estimated, Newtown and Kennedy, 1963).
- D-E Lawsonite = zoisite + kyanite + quartz + water (Newton and Kennedy, 1963).
- Zoisite + kyanite + quartz = anorthite + water (Newton and Kennedy, D-F 1963).
- G-H Lawsonite + quartz + water = laumontite (estimated by Fyfe). I-J Aragonite = calcite (Clark, 1957; Crawford and Fyfe, 1964; Jamieson, 1953; I-J and MacDonald, 1956).
- K-I and K'-I' Jadeite + quartz = albite (Fyfe and Valpy, 1959).

suggest that the free energy change of the reaction:

leonhardite + water = 2 laumontite(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:

leonhardite = 2 lawsonite + 4 quartz + 3 water

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

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

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

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 _{298.15K} °° cal/deg mole	ΔG _{298.1} kcal/r	v			
		From elements	From oxides	cc/mole		
Anorthite CaAl ₂ Si ₂ O ₈	$48.4^{ m g} \pm 0.3$	-	-23.8^{a} ± 0.6	100.73^{J} ± 0.15		
Calcite CaCO ₃	$22.2^{g} \pm 0.2$	-269.78 ^k		36.94 ^f ±0.02		
Carbon Dioxide CO ₂	51.06 ^k	-94.26 ^k				
Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄	48.53 ^h ±0.30	-888.1 ^ь ±0.7		99.31 ^h ±0.30		
Laumontite CaAl ₂ Si ₄ O ₁₂ · 4H ₂ O	115.2 ^m (est)			205.4 ^m		
Lawsonite CaAl ₂ Si ₂ O ₇ (OH) ₂ · H ₂ O	$56.8^{1} \pm 0.5$	-1062.1^{a} ± 0.8	$-31.7^{a} \pm 0.6$	101.33^{d} ± 0.15		
Leonhardite Ca ₂ Al ₄ Si ₈ O ₂₄ · 7H ₂ O	220.4^{i} ± 1.6		$-67.8^{a} \pm 1.4$	416.48°		
Quartz SiO ₂	10.0 ¹			22.69 ¹ ±0.005		
Thompsonite CaAl ₂ Si ₂ O ₈ · 2.4H ₂ O	-			135.6 ^m		
Water (liquid) H ₂ O	16.716 ¹			18.069° ±0.003		
^a Barany (1962).		h King and	l Weller (196	la).		
^b Barany and Kelley (1961)	¹ King and Weller (1961b).					
^e Coombs (1952).	¹ Larsen and Berman (1934).					
^d Davis and Pabst (1960).	^k Latimer (1959).					
^e Gray (1957).		¹ Rossini and others (1952).				
^r Graf (1961).		^m Calculate	ed by W. S. F	Tyfe.		
^g Kelley and King (1961).						

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).

267

(4)

William A. Crawford and W. S. Fyfe

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.

Lawsonite Equilibria

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.

8

12

This sequence indicates increasing pressures of metamorphism. If we assume that temperatures of glaucophane schist metamorphism are of the order of 200-300°C (Brown, Fyfe, and Turner, 1962), the relative stability fields in figure 1 are in the correct order. Coombs (1960) has observed lawsonitecalcite; 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 correlation between calorimetric data, direct experiment, and field observation.

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