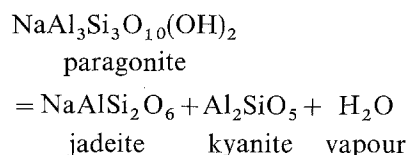# Experimental Determination of the Reaction
Paragonite = Jadeite + Kyanite + H₂O, and Internally Consistent Thermodynamic Data for Part of the System Na₂O – Al₂O₃ – SiO₂ – H₂O, With Applications to Eclogites and Blueschists

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Abstract. Hydrothermal reversal experiments have been performed on the upper pressure stability of paragonite in the temperature range 550–740° C. The reaction

$$NaAl_3Si_3O_{10}(OH)_2$$
$$\text{paragonite}$$

$$= NaAlSi_2O_6 + Al_2SiO_5 + H_2O$$
$$\text{jadeite} \quad \text{kyanite} \quad \text{vapour}$$

has been bracketed at 550° C, 600° C, 650° C, and 700° C, at pressures 24–26 kb, 24–25.5 kb, 24–25 kb, and 23–24.5 kb respectively. The reaction has a shallow negative slope (-10 bar °C^{-1}) and is of geobarometric significance to the stability of the eclogite assemblage, omphacite + kyanite.

The experimental brackets are thermodynamically consistent with the lower pressure reversals of Chatterjee (1970, 1972), and a set of thermodynamic data is presented which satisfies all the reversal brackets for six reactions in the system Na₂O–Al₂O₃ –SiO₂–H₂O. The Modified Redlich Kwong equation for H₂O (Holloway, 1977) predicts fugacities which are too high to satisfy the reversals of this study. The $P-T$ stabilities of important eclogite and blueschist assemblages involving omphacite, kyanite, lawsonite, jadeite, albite, chloritoid, and almandine with paragonite have been calculated using thermodynamic data derived from this study.
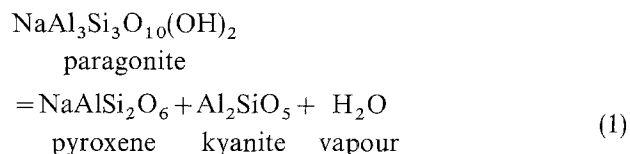
Introduction

The stability relations of paragonite and of paragonite with quartz have been studied recently by Chatterjee (1970, 1972) and by Ivanov and Gusynin (1970) at pressures up to 7 kb.

Recent descriptions of high-pressure assemblages from blueschist and eclogite facies metabasities (Bearth, 1973; Abraham et al., 1974; Miller, 1974, 1977; Holland, 1977, 1979; Raith et al., 1977) have identified paragonite as an important constituent. Holland (1977, 1979) has described the textural relationships among the phases paragonite, omphacite (Jd₅₀) and kyanite and concluded that the pyroxene composition was buffered at P and T according to the reaction:

$$NaAl_3Si_3O_{10}(OH)_2$$
$$\text{paragonite}$$

$$= NaAlSi_2O_6 + Al_2SiO_5 + H_2O \quad (1)$$
$$\text{pyroxene} \quad \text{kyanite} \quad \text{vapour}$$

The experiments of Chatterjee (1970, 1972) provide excellent thermochemical data for the calculation of the $P-T$ coordinates of this equilibrium, but the slope is highly dependent on the estimated entropy of paragonite which in turn is linked to the imperfectly known state of Al–Si order in the synthetic albite. Pressures for reaction (1) have been calculated by several authors; at 600° C the estimates vary from 24.5 kb (Holland, 1977), 22.5 kb (Delany and Helgeson, 1978) to 21 kb (Wall and Essene, 1972, reported in Vernon 1975, p. 59).

Starting Materials

Paragonite was synthesized from NaAlSi₂O₆ glass prepared by P.A.M. Anderson, and natural kyanite from a quartz vein in the

Austrian Alps, in a 1:1 molar ratio. The glass and kyanite were ground together repeatedly under acetone to thoroughly homogenize them and about 200 mg of the mix was sealed with excess H_2O in a gold tube. The sample was crystallized at 18 kb, 650° C for 24 h. Only X-ray peaks belonging to the paragonite powder pattern (Chatterjee, 1974) were observed. The sample was scanned at $1/8°\ 2\theta$/min using $Cu-K\alpha$ radiation and a synthetic $MgAlO_2$ spinel internal standard, and a least squares cell refinement was performed, which gave the following values, nearly identical to data reported by Chatterjee (1974) in spite of the much higher H_2O pressures involved.

	a Å	b Å	c Å	$\beta°$	VJ bar⁻¹
This study	5.130 (1)	8.893 (2)	19.268 (2)	94.17 (1)	13.199 (3)
Chatterjee, 1974	5.130 (1)	8.893 (2)	19.270 (3)	94.22 (2)	13.200 (3)

Natural crystalline white *jadeite* from a vein in serpentinite collected and described by Coleman (1961) was used in the reversal mix in this study. It contains insignificant impurities and has an X-ray pattern almost identical to that of a synthetic jadeite made from albite. The analysis (Coleman, 1961, p. 215) shows CaO (0.13 wt %), MgO (0.12 wt %), Fe_2O_3 (0.45 wt %) as principal impurities.

A natural pale blue *kyanite* crystal from a quartz-kyanite vein cutting through eclogite from the Dorfertal Valley, Hohe Tauern, Austria was separated, crushed, and clean clear cleavage flakes were removed for use. The major impurity is 0.4 wt % Fe_2O_3 (from microprobe analyses).

Experimental Procedure

An end-loaded piston cylinder apparatus with a 3/4″ diameter pressure chamber and NaCl pressure medium was used for all experimental runs of this study. The pressure cell and the experimental method used has been described in detail by Newton in Johannes et al. (1971). In this study however, pistons with a bevelled shoulder were used in order to prolong the piston life. Two different sizes of bevelled pistons were used in conjunction with pyrophyllite gasket rings. The effects on pressure calibration of using the bevelled as opposed to the flat-topped pistons are discussed below.

The reversal mixture was made up of the crystalline starting materials paragonite, jadeite and kyanite in reacting proportions. Major peaks on the X-ray diffractogram were approximately the same heights for all reacting phases. The mixture was repeatedly ground in acetone to homogenize the reactants and then baked at 350° C for a few hours to remove organic sludge contaminant from the acetone.

About 7 mg of sample, together with excess deionized water was loaded in a small platinum capsule and welded shut. The capsule was folded and compressed between pliers to check for water leaks before being inserted in the pressure cell.

Once mounted in the press the run was brought to the final $P-T$ conditions following the method of Danckwerth and Newton (1978). This method initiates the run under conditions of retreating piston and has been shown (see below) to provide a practically friction-free situation. Pressures were monitored continuously and were controlled to ± 0.1 kb nominal. Chromel-alumel thermocouples, uncorrected for pressure, were used and temperatures were controlled automatically; they are believed accurate to $\pm 5°$ C. At the end of a run, the power was turned off, and the run quenched within a few seconds. On disassembly the geometry of the salt and graphite heater were checked; these almost always came out so cleanly that the inside salt parts could be pushed out of the graphite cylinder undeformed (except for a certain uniaxial

shortening of the assembly as a whole). The capsule was slit open with a razor and the run rejected if there was no visible liquid water. Direction of reaction was detected by unambiguous changes in peak heights on the diffractometer trace. Kinetics of this reaction are such that the mixtures reacted strongly in times of less than 3 days at temperatures above 500° C.

Pressure Calibration

The problem of pressure calibration in piston cylinder studies has long been a controversial one, but the more recent use of the salt pressure cell (Johannes et al., 1971; Mirwald et al., 1975; and Johannes, 1978) has led to great improvements in pressure determination. To perform thermodynamic evaluation of experimental results, the conditions of temperature and pressure must be known very closely, and therefore the techniques used in this study were carefully checked against the reliable gas-apparatus determination of the equilibrium jadeite + quartz ⇌ albite by Hays and Bell (1973). It was particularly important to see whether the bevelled piston and its pyrophyllite ring contributed any friction to the cell and to see whether such friction, if any, was related to the size of the ring.

Natural jadeite (described above) and quartz were mixed in a 1:1 molar ratio and added to synthetic albite to provide a starting mix similar to that of Johannes et al. (1971) and Hays and Bell (1973). The run procedure described earlier was employed at the calibration temperature of 600° C to determine the pressure of the equilibrium. Runs with a conventional flat-topped piston in this laboratory have bracketed the equilibrium between 16.0 and 16.5 kb at 600° C (D. Jenkins, personal communication), in perfect agreement with the gas apparatus determination. Results for the two bevelled pistons are given in Table 1: both pistons gave results identical to those from the flat-topped piston (16.0–16.5 kb) indicating that no friction correction need be applied to the bevelled piston, salt-assembly experimental runs. In addition, the two piston types gave the same results in the paragonite – jadeite – kyanite experiments at somewhat higher pressures (Table 1) where frictional differences, if present, should be greater. The talc pressure medium has been much used in piston cylinder work, and so a piston-in talc assembly bracket at 700° C on the paragonite – jadeite – kyanite equilibrium was determined for comparison, which lies 2 kb higher in pressure than the salt determination (Table 1). Newton and Smith (1967) also determined a 2 kb correction for talc assemblies at about 20 kb. Therefore there can be little doubt about the low-friction nature of the salt cell determinations used in this study.

Table 1. Experimental results for reactions (1) and (5)

No.	T°C	Pkb	Time (hours)	Comments[a]	Piston[b]
Limiting runs on reaction (1)					
P32	550	24	69	P	a
P23	550	25	69	NR	b
P24	550	26	67	JK	b
P17	600	24	46	P	b
P15	600	25	27	NR	b
P31	600	25.5	72	JK	a
P22	600	26	71	JK	b
P18	650	24	70	P	a
P19	650	25	61	JK	a
P10	700	23	25	P	b
P29	700	24	25	NR	b
P30	700	24.5	24	JK	a
P3[c]	700	25	17	P	b
P9[c]	700	26	21	JK	b
P20	740	23	24	P+glass	b
P21	740	24	23	K+glass	b
Calibration runs on reaction (5)					
JAQ4	600	16.0	24	A	a
JAQ6	600	16.5	8	JQ	a
JAQ2	600	16.0	24	A	b
JAQ5	600	16.5	30	JQ	b

[a] P: paragonite growth; JK: jadeite+kyanite growth; NR: no reaction; A: albite growth; JQ: jadeite+quartz growth
[b] a: piston with 1/16″ bevel; b: piston with 1/8″ bevel
[c] Performed with the talc pressure cell

Paragonite — Jadeite — Kyanite Equilibrium Results

Table 1 and Figure 1 summarize the experimental results on the reversal of the equilibrium. Brackets were determined at 550° C, 600° C, 650° C, and 700° C. Runs at 500° C were also made, but peak height changes in diffractograms from runs of 3 days duration were ambiguous. At 740° C partial melting phenomena were encountered, limiting the range where reaction was kinetically practicable to 550–700° C. The determined brackets are 550° C, 24–26 kb; 600° C, 24–25.5 kb; 650° C, 24–25 kb; 700° C, 23–24.5 kb. As predicted thermodynamically (Holland, 1977; Delany and Helgeson, 1978) the equilibrium has a shallow negative slope and provides a useful geobarometer. The brackets presented here are reversals in that both products and reactants were present in the starting mix, and direction of reaction determined the brackets.

Thermodynamic Data for Paragonite Reactions

Using H_2O fugacities calculated through the polynomial recently published by Delany and Helgeson (1978), reaction (1) can be fit by the expression

$$\ln f_{H_2O} = 13.093 - \frac{8,532}{T} + 0.3306 \frac{P\,(\text{kb})}{T}.$$

Several reactions involving paragonite breakdown at lower pressures have been studied by Chatterjee (1970, 1972) and by Ivanov and Gusynin (1970). It is of importance to this study to demonstrate thermodynamic consistency of these experiments with reaction (1). The cell dimensions of paragonite synthesized at high pressure suggest that paragonite has well behaved physical properties throughout its stability range.

(a) Entropy Quantities

Low temperature calorimetry has not been performed on paragonite and consequently its standard third law molar entropy must be estimated from phase equilibrium studies. This has been attempted by Zen (1972); Chatterjee (1970, 1972); and by Ivanov and Gusynin (1970). These estimates suffered from the lack of published high temperature heat capacity data for paragonite. Recently the heat capacity of synthetic paragonite has been measured in the range 350–750 K (Holland and D. Perkins III, unpublished data) by differential scanning calorimetry. The sample used was prepared as described earlier at 18 kb, 650° C. The heat capacity as a function of temperature is almost identical to that of muscovite, but heat capacities at any temperature are marginally lower. The paragonite data have been extrapolated to 1,000 K by graphical comparison with the muscovite heat capacities (from Robie et al., 1978) and fit by the following polynomial equation:

$$C^0_{P(\text{paragonite})} = 852.30 - 6.1512 \times 10^{-2}\,T$$
$$+ 1.9066 \times 10^5\,T^{-2} - 8.8661 \times 10^3\,T^{-1/2}\,\text{J mol}^{-1}\,\text{K}^{-1}.$$

With this information it is possible to derive the 298 K, 1 bar entropy and enthalpy of reaction (1) through use of the relation

$$\Delta H^0_{298} - T\Delta S^0_{298} = -\left[\int_{298}^{T} \Delta C^0_p\,dT - T \cdot \int_{298}^{T} \frac{\Delta C^0_p}{T}\,dT \right.$$
$$\left. + \int_{1}^{P} \Delta V_s\,dP + RT \cdot \ln f_{H_2O,P,T} \right].$$

It was found that neglecting compressibilities and thermal expansions of the solid phases introduced considerable errors at the high pressures pertaining to reaction (1). Compressibility data for muscovite (Birch, 1966) and thermal expansion data for fluorphlogopite (Takeda and Morosin, 1975) were assumed representative for paragonite. Plotting the right hand
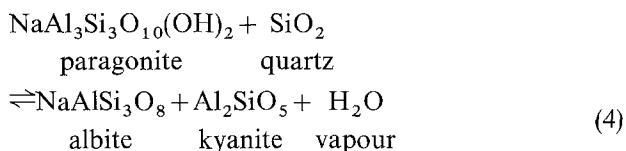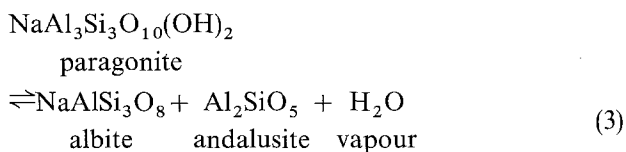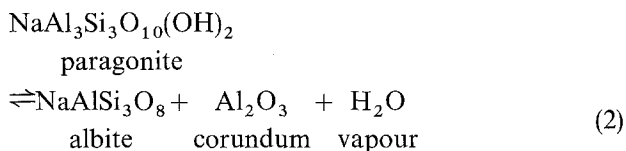
Table 2. Thermodynamic data for phases involved in reactions (1–6)

Phase	$V\,cm^3$	$S^0\,J/K$	$\Delta H_f^0\,J$	$\alpha V^0 \times 10^5$ $J\,bar^{-1}K^{-1}$	$\beta V^0 \times 10^6$ $J\,bar^{-2}$
quartz	$22.688^{a}{}^* \pm 0.001^{**}$	$41.46^{a}+0.20$	$-910,700^{a}\pm1,000$	12.15^{d}	5.18^{c}
kyanite	$44.09^{a}\pm0.07$	$83.76^{a}\pm0.34$	$-2,594,080^{g}\pm1,650$	11.95^{d}	1.90^{e}
andalusite	$51.53^{a}\pm0.04$	$93.22^{a}\pm0.42$	$-2,590,025^{g}\pm1,640$	16.60^{d}	2.84^{e}
corundum	$25.575^{a}\pm0.007$	$50.92^{a}\pm0.10$	$-1,675,700^{a}\pm1,300$	6.44^{d}	0.93^{c}
jadeite	$60.4^{a}\pm0.1$	$133.47^{a}\pm1.25$	$-3,024,270^{b}\pm4,180$	17.15^{d}	4.52^{c}
albite	$100.43^{a}\pm0.09$	$221.6^{g}\;\pm2.5$	$-3,922,170^{g}\pm4,300$	27.21^{d}	15.94^{c}
paragonite	$131.98^{g}\pm0.05$	$276.0^{g}\;\pm4.6$	$-5,943,160^{g}\pm4,490$	43.40^{f}	15.86^{c}
H_2O	–	$188.83^{a}\pm0.04$	$-241,814^{a}\pm40$	–	–

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*    Data sources:
a    Robie et al. (1978)
b    Robie et al. (1978), Hlabse and Kleppa (1968)
c    Birch (1966), muscovite used for paragonite
d    Skinner (1966)
e    Brace et al. (1969)
f    Takeda and Morosin (1975), fluorphlogopite data
g    This study and Chatterjee (1970, 1972)
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** *Error limits.* Because of the large number of brackets, and the interdependence of the data among the six reactions, the thermodynamic data can only be made consistent with the experiments within very narrow limits. The errors introduced from the imprecision of the $P-T$ measurements are negligible when compared with the calorimetric uncertainties on the data accepted from the literature and are neglected here. Errors on the thermal expansions and compressibilities have minimal effect on the derived enthalpy and entropy quantities and are ignored

side of the above expression against T for the brackets of reaction (1) yields a straight line with ΔS_{298}^0 as slope and $\Delta_f H_{298}^0$ as intercept at $T=0$ K. This procedure was repeated for the following reactions, determined experimentally by Chatterjee (1970, 1972):

$$NaAl_3Si_3O_{10}(OH)_2$$
$$\text{paragonite}$$

$$\rightleftharpoons NaAlSi_3O_8+ \quad Al_2O_3 \quad + \quad H_2O \tag{2}$$
$$\text{albite} \qquad \text{corundum} \quad \text{vapour}$$

$$NaAl_3Si_3O_{10}(OH)_2$$
$$\text{paragonite}$$

$$\rightleftharpoons NaAlSi_3O_8+ \quad Al_2SiO_5 \quad + \quad H_2O \tag{3}$$
$$\text{albite} \qquad \text{andalusite} \quad \text{vapour}$$

$$NaAl_3Si_3O_{10}(OH)_2+ \quad SiO_2$$
$$\text{paragonite} \qquad\qquad \text{quartz}$$

$$\rightleftharpoons NaAlSi_3O_8+Al_2SiO_5+ \quad H_2O \tag{4}$$
$$\text{albite} \qquad \text{kyanite} \quad \text{vapour}$$

Taking heat capacities, entropies, volumes, thermal expansions, and compressibilities from Table 2, the entropy of paragonite can be estimated from reactions (1), (2), and (3) as $277\pm10\,J/K$, $263\pm13\,J/K$ and $278\pm9\,J/K$ respectively. The entropy derived from reaction (1) is the most reliable as it does not involve any assumptions regarding the amount of Al/Si disorder, and hence entropy, of synthetic albite.

The entropy of albite listed in Table 2 was itself derived from tight reversals of the author (in preparation) on the reaction

$$NaAlSi_2O_6+ \quad SiO_2 \quad \rightleftharpoons NaAlSi_3O_8 \tag{5}$$
$$\text{jadeite} \qquad \text{quartz} \qquad \text{albite}$$
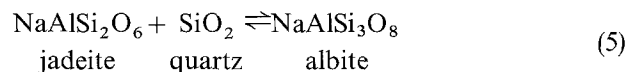
performed in the range 600–1,200° C. The additional entropy above that of low albite is slightly less than that predicted by assuming the full configurational entropy of disorder, but is in excellent agreement with the disordering entropy calculated by Holm and Kleppa (1966) from the observed tetrahedral site populations in low and high albite. The entropy for paragonite derived from reaction (3) is marginally consistent with that from (2) but is in perfect agreement with that from (1). Reaction (4) does not constrain the estimates well and was not used. A value of 276 J/K is considered the best estimate consistent with reactions (1) to (4).

It is instructive to compare this entropy value with those estimated by Ivanov and Gusynin (1970), Chatterjee (1970, 1972), and Zen (1972), 280.3 J/K, 283.7–300.4 J/K, and 279.9 J/K respectively. The last two estimates were linked to high albite and derived from Chatterjee's experiments (reactions (2), (3), (4)). Paragonite entropy can be estimated from tabulated entropies for muscovite, low albite, and microcline. Applying a volume correction to the result, ignoring any Al–Si disorder in mica, we arrive at the value 281 J/K which agrees very well with that estimated

here and with estimates from the literature. The implication is that although muscovite may be characterised by considerable Al – Si disorder (Chatterjee and Johannes, 1974) it appears that paragonite is not. The smaller Na ion in the dioctahedral mica structure causes the tetrahedral framework to distort (Papike and Cameron, 1976), which could conceivably produce a certain amount of ordering of Al and Si on different tetrahedral sites. It is also possible that paragonite is partially disordered, but with an anomalously low third law entropy. Measurement of the low temperature heat capacities is clearly needed to resolve this problem.

(b) Enthalpy Quantities

Enthalpies from Robie et al. (1978) for corundum, α-quartz, and H_2O were used in the construction of Table 2. Entropies except for paragonite and albite (discussed above) were also taken from this source. The enthalpy of andalusite was determined from reactions (2) and (3) by difference. Kyanite enthalpy was derived from the equilibrium

$$Al_2SiO_5 \rightleftharpoons Al_2SiO_5$$

$$\text{kyanite} \quad \text{andalusite} \tag{6}$$

as studied by Richardson et al. (1969) and Holdaway (1971). Thus the values for the aluminosilicates are tied to the enthalpy of formation of corundum. They are in excellent agreement with the enthalpy of solution measurements for these phases by Anderson and Kleppa (1969), Newton et al. (1974) and Anderson et al. (1977). The enthalpy of jadeite was determined from the new measurement of the heat of solution of low albite (Hemingway and Robie, 1977) combined with the calorimetric work of Hlabse and Kleppa (1968) on the enthalpy of reaction (5) involving low albite. The experimental brackets of reaction (5), performed on a mixture containing high albite, were used to derive the enthalpy of synthetic albite used in these runs. The value derived predicts a slightly lower disordering enthalpy than that found by Holm and Kleppa (1968), but agrees well with recent measurements of heats of solution of low and high albite (R.C. Newton, personal communication). The "best" enthalpy of paragonite was derived from the data of reactions (1) to (4). The $P - T$ curves for reactions (1) to (6) have been recalculated from the data in Table 2 and are plotted in Fig. 1. The degree of internal consistency among the six reactions is evident. It was only possible to obtain this consistency of the thermochemical data by using compressibilities and thermal expansions of the solid phases in the calculations.
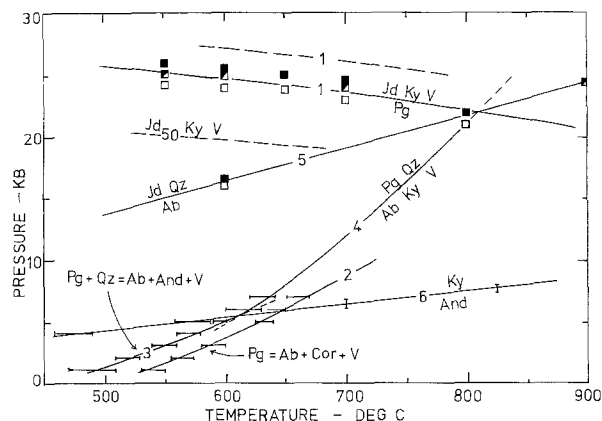
Fig. 1. Experimental brackets pertaining to paragonite and paragonite + quartz stability. Curves are numbered in accordance with reactions described in the text. Brackets for reactions (2), (3), and (4) are from Chatterjee (1970, 1972) and Ivanov and Gusynin (1970). Brackets for reaction (6) are from Richardson et al. (1969) and Holdaway (1971). Brackets for reaction (1) are from this study, and for reaction (5) from this study and from Holland (in preparation). The curves are all calculated from the data in Table 2 using the H_2O data of Delany and Helgeson (1978) above 10 kb, and Burnham et al. (1969) below 10 kb. Curve 1 has also been calculated using the MRK equation for H_2O (*dashed line*). The stability of omphacite ($jd_{50}di_{50}$) with kyanite and H_2O vapour has been calculated from the brackets for reaction (1) with the assumption of ideal mixing in the pyroxene

(c) H_2O Fugacities at High Pressures

There are currently two sets of data used widely in the literature for calculating the fugacity of H_2O at pressures in excess of 10 kb. The first is based on shock wave determination at very high pressures and the second is an extrapolation from the measured range (0–10 kb) of $P - V - T$ data for water by using the Modified Redlich Kwong equation (MRK). Delany and Helgeson (1978) presented a polynomial, based largely on the shock wave data, from which the fugacity of H_2O can readily be calculated at pressures from 10 to 100 kb. Holloway (1977) has popularised the MRK equation and published coefficients which fit the measured $P - V - T$ data for H_2O (Burnham et al., 1969) remarkably well, but yield significantly higher fugacities than the shock wave data at high pressures. The discrepancy increases with pressure above 10 kb.

The six reactions discussed above have all been determined over a similar temperature interval (500–700° C) but over a wide range of pressures (1–26 kb) in the same temperature range, and are particularly well suited to discriminate between the two differing sets of H_2O data. Reaction (1) can be calculated by combining the thermodynamic data for reactions (4) and (5) which have themselves been made entirely consistent with reactions (2), (3), and (6). The calculat-

ed position of reaction (1) depends strongly on the H$_2$O fugacities used. Figure 1 clearly shows that the experimentally determined brackets of reaction (1) discriminate against the MRK data.

It must be stressed that this is a very stringent test for the H$_2$O fugacity data. The fact that the calculated $P-T$ curve for reaction (1) passes through all the reversed brackets argues overwhelmingly for the validity of the Delany and Helgeson (1978) fit to the shock wave data. The MRK equation predicts unreasonably low compressibilities for CO$_2$ (Haselton et al., 1977, 1978) and H$_2$O (this study) at high pressures and does not appear to be a suitable equation, with its present coefficients, for extrapolation to high pressures.

Geological Applications

The geological occurrences of paragonite were briefly reviewed by Chatterjee (1970). Mineral assemblages of eclogites from the eastern Alps that have not suffered retrograde metamorphism contain the phases garnet, omphacite, kyanite and quartz, together with paragonite (Holland, 1979). Paragonite is associated texturally with kyanite (which it occasionally replaces) and omphacite, and occurs also as abundant inclusions trapped within garnet crystals. Omphacite, kyanite and paragonite are all in mutual contact and presumably have coexisted since growth of the garnets. The conditions of equilibration of this assemblage can be calculated by determining the effect of 50 mol% diopside in solid solution with jadeite coexisting with paragonite, kyanite and vapour.
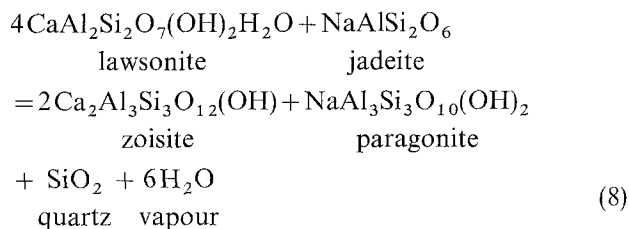
Low temperature omphacites in the composition range considered sometimes show cation ordering (Clark and Papike, 1968; Matsumoto et al., 1975) and consequently lower symmetry (P2/n, P2/c, and P2 space groups, Carpenter, 1968) than synthetic C2/c omphacites involved in experimental phase equilibrium studies. The applicability of such experimental results to natural eclogitic pyroxenes might therefore be questioned until it could be shown that the pyroxenes initially crystallized in the disordered form. Introduction of long range order, such as alternating Al and Mg on the M1 sites with partial ordering of Na and Ca on the M2 sites, will greatly reduce the entropy of mixing, but this will be largely compensated by a negative heat of mixing term due to the tendency towards compound formation. Short range ordering maintaining local charge balance, not detectable by X-ray methods (Whittaker, 1977) will have similar effects on the stability of the pyroxene. It is not known whether such ordering occurs in high temperature experiments (Wood, 1976; Newton, 1977).

Recent studies (Champness, 1973; Yokoyama et al., 1976; Carpenter, 1978) discuss observed antiphase domains in omphacites from low temperature blueschists and eclogites and conclude that the omphacites originally crystallized with the disordered C-lattice and have gained their primitive lattice by cooling through the transition temperature, estimated to be around 300–400° C (Champness, 1973; Yokoyama et al., 1976). Therefore the crystallization of omphacites at temperatures in excess of this transition will involve at least largely disordered structures similar to those from experimental studies, and any deductions from such phase equilibrium work will be applicable to natural omphacites. Complete disorder corresponds to a high entropy of mixing, but this effect is commonly offset in pyroxenes (Newton, 1977) by a positive heat of mixing. The combined result produces quasi-ideal pyroxenes (Wood, 1976) characterized by having activity nearly equal to mol fraction. Available experimental work on omphacites suggests that this is the case on the join jadeite-diopside.

It can be deduced from the work of Kushiro (1969), Bell and Davis (1969), and Ganguly (1973) that diopside-jadeite mixtures at high temperatures conform closely to a "one-site" ideal solution (activity equals mol fraction). Reversals of omphacite compositions coexisting with albite and quartz in 600° C-hydrothermal runs also show that the activity of jadeite in omphacite is approximately equal to the mol fraction (unpublished results of the author). An omphacite with 50 mol% jadeite (as in the Austrian eclogites: Miller, 1974; Holland, 1979) will coexist with paragonite and kyanite some 5 kb lower than would a pure jadeite. The calculated $P-T$ curve for this assemblage is given in Fig. 1 and implies a minimum pressure of 19.5 kb for the Austrian eclogites if temperatures of around 600° C are accepted (Holland, 1979). Temperatures were estimated on the basis of (a) the distribution of Fe^{2+} and Mg between garnet and clinopyroxene, (b) the presence of zoisite +kyanite+quartz instead of lawsonite, and (c) the absence of evidence for melting in a fluid saturated environment. The arguments in support of an aqueous fluid accompanying the eclogite crystallization have been presented in detail elsewhere (Holland, 1977, 1979) and are based upon the abundance of veins and mineral segregations of quartz + omphacite ±kyanite, the presence of aqueous fluid inclusions trapped within omphacite and zoisite, and on calculated isopleths for X_{H_2O} and X_{CO_2}. Chinner and Dixon (1973) argue persuasively for aqueous metamorphism in the formation of omphacite+kyanite assemblages from the Allalin gabbro, Switzerland. On the basis of available experimental data they con-

cluded that a minimum of 15 kb was required to produce the observed assemblages; an additional 3–5 kb may now be added to their minimum pressure estimate. Such pressures, while high in magnitude, are consistent with recent reports of jadeite coexisting with quartz, which give pressures of 20 kb in the Western Alps (Reinsch, 1977) and a minimum of 14 kb at Sifnos, Greece (Okrusch et al., 1978).

Pseudomorphs of paragonite and clinozoisite after lawsonite led Bearth (1973) to postulate the reaction:

$$4CaAl_2Si_2O_7(OH)_2H_2O + NaAlSi_2O_6$$

$$\text{lawsonite} \qquad \text{jadeite}$$

$$= 2Ca_2Al_3Si_3O_{12}(OH) + NaAl_3Si_3O_{10}(OH)_2$$

$$\text{zoisite} \qquad \text{paragonite}$$

$$+ SiO_2 + 6H_2O \tag{8}$$

$$\text{quartz} \quad \text{vapour}$$

This reaction is readily calculated, using the method of Fisher and Zen (1971), from the experiments on lawsonite breakdown (Newton and Kennedy, 1963) and the results of this study. This reaction and a number of further equilibria among the phases paragonite, jadeite, kyanite, albite, quartz, chloritoid, almandine, lawsonite, and zoisite have been calculated and are shown in Fig. 2. The breakdown of lawsonite + albite and lawsonite + jadeite is characteristic of the change from blueschist into higher grade conditions, and places an upper temperature limit to the typical glaucophane-lawsonite schist facies.

The alteration of chloritoid to paragonite in blueschist metabasites (e.g. Bearth, 1963) may be due to a reaction such as

$$3FeAl_2SiO_5(OH)_2 + 2NaAlSi_2O_6 + 2SiO_2$$

$$\text{chloritoid} \qquad \text{pyroxene} \quad \text{quartz}$$

$$= 2NaAl_3Si_3O_{10}(OH)_2 + Fe_3Al_2Si_3O_{12} + H_2O \tag{11}$$

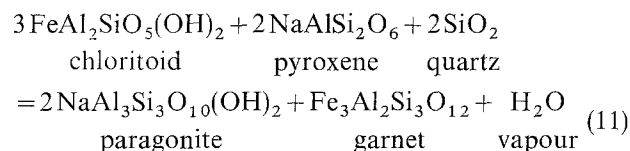$$\text{paragonite} \qquad \text{garnet} \qquad \text{vapour}$$

Figure 2 shows that this curve lies at lower temperatures than the inferred lawsonite pseudomorphing reaction and both reactions could have proceeded during progradation from blueschist into high pressure greenschist facies conditions. The exact location of this latter curve will depend largely on the pyroxene composition and not so strongly on the chloritoid or garnet compositions as these phases tend to have similar Fe:Mg ratios. That this curve lies at lower temperature than reaction (8) suggests that the lawsonite + almandine-rich garnet assemblage should occur in nature. The demonstration of lawsonite pseudomorphs within garnets from the Eastern Alps (G.T.R. Droop, personal communication 1977) and
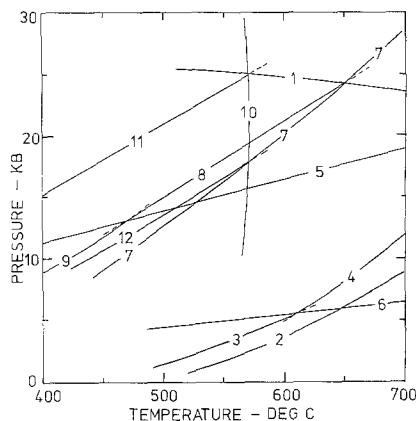

Fig. 2. Some calculated equilibria in the system $Na_2O - Al_2O_3 - CaO - FeO - SiO_2 - H_2O$ involving the phases paragonite (pg), jadeite (jd), kyanite (ky), albite (ab), quartz (qtz), andalusite (and), lawsonite (lws), zoisite (zo), chloritoid (ctd), almandine (alm) and H_2O (v). Reactions (1) to (6) are described in the text. (7) 4 lws = 2 zo + ky + qtz + 7 v, from Newton and Kennedy (1963). (8) 4 lws + jd = 2 zo + pg + qtz + 6 v, from (7) and (1). (9) 4 lws + ab = 2 zo + pg + 2 qtz + 6 v, from (8) and (5). (10) 3 ctd + 2 qtz = alm + 2 ky + 3 v, from Ganguly (1969) and data in Table 2. (11) 3 ctd + 2 jd + 2 qtz = alm + 2 pg + v, from (1) and (10). (12) 8 lws + alm = 4 zo + 3 ctd + 4 qtz + 11 v, from (7) and (10). All curves were calculated using the Fisher and Zen (1971) approximation $\Delta_f C_{p_s} = 0$

from Sifnos, Greece (Okrusch et al., 1978) confirms this conclusion.

Conclusions

The upper pressure stability of paragonite has been reversed in hydrothermal runs in the range 550–700° C. The experiments, yielding a value for the entropy of paragonite independent of the ordering state of albite, are thermochemically consistent with the lower pressure stability relations studied by Chatterjee (1970, 1972).

The experimental brackets are sufficiently precise to discriminate against the Modified Redlich Kwong equation of state for H_2O at high pressures in favour of the H_2O fugacities, presented recently by Delany and Helgeson (1978), derived from the shock wave data.

The experiments allow determination of the stability in the presence of aqueous fluids of important high-pressure assemblages which include combinations of the phases lawsonite, omphacite, jadeite, kyanite, chloritoid, paragonite, albite, and almandine.

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