ORIGIN OF A ROBERTS VICTOR SANIDINE-COESITE GROSPYDITE:
THERMODYNAMIC CONSIDERATIONS

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Abstract - A grospydite xenolith from the Roberts Victor kimberlite pipe in South Africa presents an unusual phase assemblage of clinopyroxene, garnet, kyanite, coesite, and sanidine. The rock as previously described (Smyth and Hatton, 1977) consists of 50% omphacitic clinopyroxene, 28% garnet ($Gr_{50}Py_{28}$ Alm_{22}), 9% kyanite, 6% coesite, and 1% sanidine (Or_{99}). Assuming the addition of three additional compatible phases (phlogopite, enstatite, and H_2O vapor) and a simplified chemistry of the phases present, a Schreinemaker's thermodynamic analysis was attempted in order to estimate the pressure and temperature of equilibrium of the rock.
   Four reactions involving six components are likely to have determined an invariant point for the assemblage.
   (1)   3 Kyn + 6 Cpx + Phl = San + 3 Gt + 6 En + H_2O
   (2)   6 Cos + 3 Gt + Phl = San + 3 Kyn + 6 Cpx + H_2O
   (3)   Kyn + 2 Cpx = Cos + Gt + En
   (4)   3 Cos + Phl = San + 3 En + H_2O
Using tabulated as well as estimated thermodynamic data for the phases, the calculated values for equilibrium temperatures and pressures for the reactions yield an invariant point for the assemblage at a depth of about 160 km (49 kbars) and a temperature of about 1060°C. This point likely represents a subsolidus recrystallization stage of origin.

INTRODUCTION

   Eclogite nodules are typical inclusions in many mantle-derived magmas and are generally considered to have equilibrated within the upper mantle. Smyth and Hatton (1977) recovered an unusual eclogite nodule from a kimberlite of the Roberts Victor Mine near Kimberly, South Africa. This eclogite nodule shown in Figure 1 is unusual because it contains crystals of sanidine and coesite. The principal phase assemblage consists of omphacitic clinopyroxene, pyrope to grossular-rich garnet, kyanite, coesite, and sanidine. This rock is a grospydite (Sobolev et al., 1968) of which several have been previously described from Roberts Victor by Hatton (1978), Rickwood et al. (1968), MacGregor and Carter (1970)[b], Lappin (1978), and Chinner and Cornell (1974). Free SiO_2 (Coesite — Coes, 1953) is rare in eclogitic inclusions from kimberlite, and potassium feldspar has been noted only in small amounts from diamondiferous eclogites and diamond inclusions (Reid et al., 1976; Prinz et al., 1975).

   Smyth and Hatton (1977) estimated a minimum pressure of equilibration of 29 kbar based on the quartz-coesite transition and a minimum temperature of equilibration of 900°C based on the high structural state of the sanidine. Ellis and Green (1979) have calibrated the Fe-Mg distribution coefficient as a
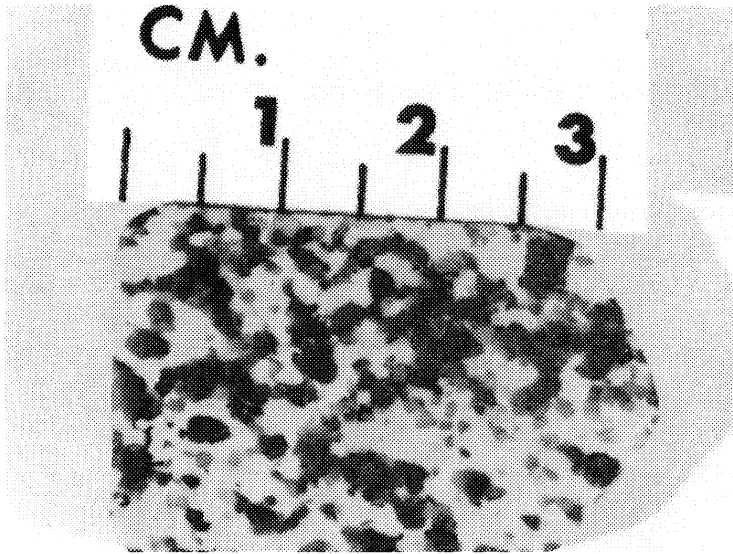
Fig. 1. Photograph of the sanidine-coesite grospydite collected at the Roberts Victor Mine, South Africa by, Smyth and Hatton (1977).

function of temperature, pressure, and Ca-content of garnet. Using their equation for this rock, we calculate temperatures of 1038°, 1067°, and 1097°C for pressures of 30, 40, and 50 kbar respectively. The large number of equilibrated phases in this nodule compared with other eclogite inclusions in kimberlites, however, permits the application of additional thermodynamic constraints to establish the conditions of equilibration. We have therefore attempted to determine a possible invariant point for the system from which this grospydite crystallized.

Table 1 lists the phases and their observed compositions in the grospydite (Smyth and Hatton, 1977). Six components ($CaO-MgO-K_2O-Al_2O_3-SiO_2-H_2O$) are considered to cover the range of compositions in this study. For simplification, the garnet ($Gr_{50}Py_{28}Al_{22}$) is assumed to be a grossular-pyrope solid solution, and the clinopyroxene, an average omphacite, is treated as diopside. Primary phlogopite may occur in related eclogites, and both phlogopite and enstatite are common secondary phases in kimberlitic eclogites from Bobbejaan (Caporuscio and Smyth, 1983). Enstatite, phlogopite, and water are additional phases assumed to accompany this rock in order to satisfy the phase rule.

The methods employed for analysis of the system are Schreinemaker's geometric approach (Zen, 1966), treatment of thermodynamic properties taken from various experimental works using the method of Fisher and Zen (1971), and data approximation methods from Wood and Fraser (1976).

TABLE 1

Compositions and assumed compositions of phases.

Phase Present	Composition	Assumed
1 % Sanidine	$KAlSi_3O_8$	$KAlSi_3O_8$
6 % Coesite	SiO_2	SiO_2
9 % Kyanite	Al_2SiO_5	Al_2SiO_5
28% Garnet	$(Gr_{50}Py_{28}Al_{22})$	$(Gr_{67}Py_{33})$
		$(Ca_2Mg)Al_2Si_3O_{12}$
56% Clinopyroxene	$(Ja_{50}Di_{50})$	$Ca\ MgSi_2O_6$
Additional Phases Assumed		
Vapor	H_2O	H_2O
Phlogopite	$K_2(Mg,Fe)_6(Al_2Si_6)O_{20}(OH)_4$	$KMgAl\ Si_3O_{10}(OH)_2$
Enstatite	$MgSiO_3$	$MgSiO_3$

THERMODYNAMIC DATA AND CALCULATIONS

With the exception of phlogopite and garnet, thermodynamic data from Robie and Waldbaum (1968), Robie et al. (1978), and Kelly (1960) are complete for the phases in this rock. Of interest for calculations are values at both 298 and 1000 K for Third Law entropies, enthalpies and free energies of formation from the elements, and molar volumes (Table 2).

Garnet

The garnet is assumed to be $Gr_{67}Py_{33}$. Since pyrope ($Mg_3Al_2Si_3O_{12}$) with lesser amounts of grossular ($Ca_3Al_2Si_3O_{12}$) and almandine ($Fe_3Al_2Si_3O_{12}$) is the

TABLE 2

Thermodynamic data* used in analyses

Phase	V Molar Volume (cal/bar)	$H_{f,T}$ Formation Enthalpy 298 K (Kcal/mole K)	1000 K	S_t° Third Law Entropy 298 K (Kcal/mole K)	1000 K	$G_{f,T}$ Formation Free Energy 298 K (Kcal/mole K)	1000 K	$S_{f,T}$ Formation Entropy 298 K (cal/mole K)	1000 K
Garnet $(Ca_2Mg)Al_2Si_3O_{12}$	2.89	-1554.2 (-1562.6)	-1577.9 (-1591.2)	62.7 (64.3)	186.6 (185.1)	-1469.0 (-1477.9)	-1290.9 (-1302.2)	-285.9 (-284.4)	-287.6 (-289.1)
Phlogopite $KMg_3AlSi_3O_{10}(OH)_2$	3.58	-1534.0 (-1560.0)	-1443.8 (-1469.8)	76.4	231.9	-1442.5 (-1460.0)	-1154.8	-307.9 (-337.0)	-289.4
Sanidine $KAlSi_3O_8$	2.61	-944.4	-944.5	56.9	134.7	-892.3	-768.7	-174.8	-175.8
Coesite SiO_2	0.49	-216.4	-215.7	9.65	26.61	-203.4	-172.7	-43.8	-42.9
Kyanite Al_2SiO_5	1.05	-619.9	-623.3	20.0	68.2	-584.0	-499.4	-120.6	-123.9
Clinopyroxene $CaMgSi_2O_6$	1.58	-767.4	-766.9	34.2	95.7	-725.8	-628.2	-139.5	-138.7
Enstatite $MgSiO_3$	0.75	-370.1	-371.4	16.2	46.1	-349.4	-300.6	-69.6	-70.8
Vapor H_2O	0.431	-68.32	-24.40	16.71	55.6	--	--	-39.02	-29.09

* Adjusted estimated values shown in parenthesis.

characteristic garnet of mantle-derived samples, it constitutes a very impor-
tant mineral system that has, until recently, been poorly understood. Maaløe
and Wyllie (1979) have determined pyrope-grossular stability at 30 kbar and
established subsolidus phase boundaries for these solid solutions. Haselton
and Newton (1980) reviewed previous studies on the pyrope-grossular join and
formulated the thermodynamic functions based upon a positive deviation from
ideality of mixing. In this study, we use a slightly different approach to
calculating garnet stability.

Data for grossular and pyrope are given in Robie et al. (1978), however,
pyrope data are estimated in part from oxide sums (Wood and Fraser 1976) for
use in the following mixing model. Newton et al. (1977) have found by using
solution calorimetry in lead borate that grossular-pyrope solid solutions show
a positive deviation from ideality in enthalpy which becomes smaller for
grossular-rich compositions. For the grossular-rich garnet in this study,
enthalpy of formation is calculated from heats of solution values given by
Newton et al. (1977) using oxide calorimetry data from Navrotsky and Coons
(1976) and Navrotsky and Kleppa (1968). The enthalpy obtained fits a Margules
type or subregular mixing model (Thompson, 1967):

$$\Delta H^{ex} = 3(x_{Gr}^2 x_{Py} W_1 + x_{Gr} x_{Py}^2 W_2) \tag{1}$$

where W_1 and W_2 equal 2.0 kcal/mole and 3.82 kcal/mole respectively (Newton et
al., 1977). Since deviation from ideality becomes small for grossular-rich
compositions, ideal mixing model is assumed for entropy of mixing:

$$\Delta S_{mix} = -nR(x_{Gr} \ln x_{Gr} + x_{Py} \ln x_{Py}) \tag{2}$$

where n is the number of positions in each formula unit in which mixing occurs
(3 for garnets with no substitution in the Al site) and R is the gas constant
(Wood and Fraser, 1976).

The heat capacity of pyrope has been discussed by Haselton and Westrum
(1980) and is estimated in this study by summing oxide values:

$$N = N_{ox} \frac{1 + (V/V_{ox})}{2} \tag{3}$$

where N represents constants a, b, or c of the heat capacity function summed
from constituent oxide values (Kelley, 1960). The volume of pyrope is calcu-
lated from unit cell measurements. Using the estimated heat capacity
function, Third Law entropy at a T of 1000 K can be calculated:

$$S_{1000}^{\circ} = S_{298}^{\circ} + \int_{298}^{1000} \frac{(a + bT + c/T^2)}{T} \, dT \tag{4}$$

where:

$$S_{298}^{\circ} = S_{ox} \frac{(1 + V/V_{ox})}{2} \quad .$$ (5)

Similarly, H_{298}° is:

$$H_{298}^{\circ} = H_{1000}^{\circ} + \int_{298}^{1000} (a + bT + c/T^2) \, dT$$ (6)

where H_{1000}° (pyrope) is calculated from formation from the elements (Navratosky and Coons, 1976). Estimated free energy values shown in Table 2 have been adjusted using tabulated pyrope data from Robie et al. (1978).

Phlogopite

Thermodynamic data available in Robie and Waldbaum (1968) for phlogopite are its molar volume and entropy at 298 K. Wood (1976)[a] has performed experiments with a reaction involving the dehydration of phlogopite establishing two equilibrium pressure-temperature points.

Phlog   Qtz   En   San   Water

$$KMg_3AlSi_3O_{10}(OH)_2 + 3SiO_2 \rightleftarrows 3Mg_2SiO_3 + KAlSi_3O_8 + H_2O.$$
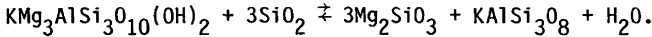
These two points were used in the method of Fisher and Zen (1971) to obtain an entropy for phlogopite where the free energy expressions for the two points are solved simultaneously yielding this expression at equilibrium:

$$0 = \Delta G_{1,solids} - \Delta G_{2,solids} - \Delta S_{solids}(\Delta T_1) + \Delta S_{solids}(\Delta T_2)$$

$$+ \Delta V_{1,solids}(\Delta P_1) - \Delta V_{2,solids}(\Delta P_2) + G_{T_1 P_1}^{*H_2O} - G_{T_2 P_2}^{*H_2O}.$$ (7)

The free energies of the solid components subtract out resulting in the following equation for S_f of the reaction.

$$\Delta S_f^{reac.} = [\Delta V(\Delta P_1 - \Delta P_2) + G_{T_1 P_1}^{*H_2O} - G_{T_2 P_2}^{*H_2O}]/(\Delta T_1 - \Delta T_2)$$ (8)

where P_1 = 385 bar, T_1 = 790°C, P_2 = 293 bar, T_2 = 750°C and $G_{T_1 P_1}^{*H_2O}$ and $G_{T_2 P_2}^{*H_2O}$ =

-33.79 kcal and -34.34 kcal respectively (Wood, 1976)[a]. The entropy change of this reaction equals the standard entropy of the solids minus the elements:

$$\Delta S_f^{reac.} = \Delta S°(solids) - \Delta S°(elements)$$ (9)

and the standard entropy of phlogopite is then:

$$S_{Ph}^{\circ} = 3(S_{En}^{\circ}) + S_{San}^{\circ} - 3S_{Qtz}^{\circ} + 1/2S_{O_2}^{\circ} + S_{H_2}^{\circ} - \Delta S_f^{reac.}$$ (10)

The value of standard entropy at 298°C obtained for phlogopite is too large by 14 kcal/mole compared to that given by Robie et al. (1978). This result

suggests that the error in experimental measurement in P and T is sufficient to give poor results in data estimation. The enthalpy of formation from the elements of phlogopite is calculated at 298°C by

$$H^\circ_{f,Ph} = G^\circ_{f,Ph} + T\Delta S^\circ_{f,Ph} \tag{11}$$

where, from Fisher and Zen (1971), we calculate

$$G^\circ_{f,Ph} = 3G^\circ_{f,En} + G^\circ_{f,San} - 3G^\circ_{f,Qtz} - \Delta S^{reac.}_f \cdot \Delta T_1 + \Delta V_1 \Delta P_1 + G^{*H_2O}_{T_1 P_1} \tag{12}$$

for the above dehydration reaction. S°_{1000} and H°_{1000} then can be calculated from heat capacity function estimated by Equation 3. The entropy of formation from the elements shown in Table 2 has been adjusted to fit the average range of free energies experimentally determined by (Wood, 1976)[a] which accordingly produce variations in H°_f and S°_f.
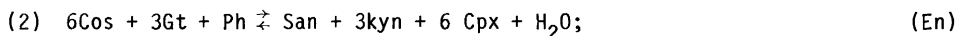
The free energy calculated for phlogopite from the Fisher-Zen equation is 4 kcal/mole less than that given for fluorophlogopite at 298 K (Robie et al., 1978). These two minerals should compare closely when considering the stronger bonding in fluorophlogopite due to higher electronegativity of fluorine.
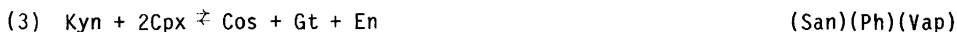
MINERAL REACTIONS

Four reactions can be written that involve the assumed phase assemblage. They are two univariant reactions: one with coesite absent,

(1) 3Ky + 6Cpx + Ph $\rightleftarrows$ San + 3Gt + 6En + H_2O (Cos)
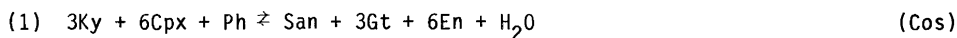
and the other with enstatite absent,

(2) 6Cos + 3Gt + Ph $\rightleftarrows$ San + 3kyn + 6 Cpx + H_2O; (En)

and two double-degenerate reactions: one with sandine, phlogopite, and vapor absent,

(3) Kyn + 2Cpx $\rightleftarrows$ Cos + Gt + En (San)(Ph)(Vap)

and the other with kyanite, clinopyroxene and garnet absent,

(4) 3Cos + Ph $\rightleftarrows$ San + 3En + H_2O. (Kyn)(Cpx)(Gt)

Each of these reactions are considered separately and molar volume changes, entropies, enthalpies, and free energies at 298 K and 1000 K for the reactions are calculated (Table 3). From these values, Clapeyron slopes, dP/dT = $\Delta S^\circ_T/\Delta V$, are calculated and equilibrium temperature points for the vapor containing reactions are found by extrapolating slopes calculated by the Fisher and Zen (1971) equation to zero reaction free energy:

$$\Delta G_{P,T} = \Delta G(solids) - \Delta S(solids)\Delta T + \Delta V(solids)\Delta P + G_{H_2O} = 0 \quad . \tag{13}$$

RESULTS

Using the tabulated as well as estimated thermodynamic data, we have determined an invariant point of 1330 K and 49 kbars. Several methods of P and T

TABLE 3

Thermodynamic data calculated for reactions.

Reaction	ΔV_r (bar/K)	ΔS°_{298} ΔS_{1000} (cal/mole K)		ΔH°_{298} ΔH°_{1000} (Kcal/mole K)		$\Delta S_{f,298}$ $\Delta S_{f,1000}$ (cal/mole K)		$\Delta G_{f,298}$ (Kcal/mole K)
1. (Cos)	0.029	17.54	15.5	163.6	-15.9	---	---	---
solids	-0.402	---	---	---	---	90.2	29.9	126.9
2. (En)	0.438	16.5	17.9	44.2	31.5	---	---	---
solids	0.007	---	---	---	---	83.9	29.9	97.7
3. (San)(Phl)(Vap)	-0.068	3.3	-1.84	13.90	-7.8	0.3	30.5	---
4. (Kyn)(Cpx)(Gt)	0.234	17.2	16.7	60.3	7.8	---	---	---
solids	-0.197	---	---	---	---	85.9	29.9	112.5

determination for the reaction curves were attempted. These included extrapolation of P-T values at standard state of 1 bar and 298 K by Clapeyron slopes with a correction for the activity of water when present and the Fisher-Zen equation (11). The Fisher-Zen equation produced the most consistent results for the reactions involving water for which the adjusted values of $S_{f,298}$ and $G_{f,298}$ for phlogopite were used.

Reaction (1) Solutions to the Fisher-Zen equation give temperature values of about 1315 to 1325 K for a nearly vertical reaction slope. When extrapolated to 50 kbar by calculated Clapeyron slopes of 0.5 kbar - K^{-1}, a temperature of 1330 K is obtained.

Reaction (2) Temperatures of near 1088 K and 1230 K were obtained for pressures of 25 kbar and 40 kbar respectively. These values are extrapolated by a Clapeyron slope of 100 bar-$^\circ K^{-1}$ to a point at 50 kbar near 1330 K.

Reaction (3) The results of calculations for this reaction produce constraining values because it is the only one in which water is absent as is phlogopite for which data are considered least reliable. The Clapeyron slope is 30 bar -$^\circ K^{-1}$. Using the expression for equilibrium free energy at 1 bar:

$$0 = \Delta G_{f,1bar} - \Delta H_{f,1bar} - T\Delta S_{f,1bar} - (P-1)\Delta V \qquad (14)$$

a temperature of -240 K is obtained that when extrapolated to 40 kb:

$$T_{40kb} = T_{1bar} + (P-1)(dT/dP) \qquad (15)$$

is in the range of 1050 to 1090 K.

Reaction (4) Consistent results for the Fisher-Zen equation and Clapeyron slopes were obtained using the estimated phlogopite data for all values except $S_{f,298}$ for which the adjusted value was used. The Clapeyron slope of the reaction curve is 70 bar -$^\circ K^{-1}$ at both 298 and 1000 K. Results of the Fisher-Zen equation showed points at P = 5 and 40 kbar and T = 1050 and 1320 K respectively.

The near vertical slope calculated for the coesite absent reaction (1) places the most reliable constraints on the invariant point temperature.

Simultaneous solution of the Fisher-Zen equation for the two univariant reactions yields an invariant point at 1330 K and 49 kbar. Reaction (3) to which the problems of estimated phlogopite data do not contribute has the lowest P-T slopes and therefore places the strongest constraint of P at the invariant point.

In order to establish the sequence of reaction curves about the invariant point, we use Schreinemakers' geometric approach (Zen, 1966). Two univariant reactions (1 and 2) of six components and seven phases each and two double-degenerate reactions (3 and 4) of five phases each exist. Each double-degenerate reaction may be considered as three separate, identical reactions each identified by one of the three missing phases (e.g., reaction (3) comprises three reactions of the same slope, one with sanidine absent and the others with phlogopite and vapor absent respectively). Stable-to-stable projections through the invariant point then can be constructed in order to satisfy Schreinemaker's criteria (Figure 2). Curvature of reactions is predicted from variation of Clapeyron slopes with temperature as well as the existence of water as a volatile phase in reaction products.

DISCUSSION

The position of the invariant point (Fig. 2) at 1060°C and 49 kbars appears to be a likely environment of equilibration for the sanidine-coesite grospydite and is supported by the following arguments. The quartz-coesite transition passes through 1186 K at about 30 kbars as determined by Boyd and England (1960) and Akella (1973), which suggests that this rock likely equilibrated at depths greater than 100 km. Smyth and Hatton (1977) used cell parameters determined by x-ray precession photographs to verify that the feldspar present is sanidine, a high-temperature disordered structure. Previous studies of feldspar (Smith, 1974; Orville, 1967) demonstrating Al-Si-disorder to be a function of temperature and pressure led Smyth and Hatton (1977) to conclude that equilibration must have occurred at temperatures greater than 900°C. Further evidence cited by Smyth and Hatton (1977) includes their measured value for K_d of 6.04. This value for Fe-Mg distribution between co-existing garnet and clinopyroxene corresponds to a temperature of 1038°, 1067°, and 1097°C at pressures of 30, 40, and 50 kbar respectively when applied to P-T curves generated by Ellis and Green (1979).

Harte and Gurney (1975)[a] suggest an initial cumulate origin for grospydites from Roberts Victor. Their evidence is the layered textures and similar compositions of related eclogites. However, subsolidus recrystallization textures are evident and Lappin (1978) recognizes three stages in the textural evolution involving clinopyroxene and garnet in a grospydite from Roberts Victor. Because we use an ideal clinopyroxene composition in our
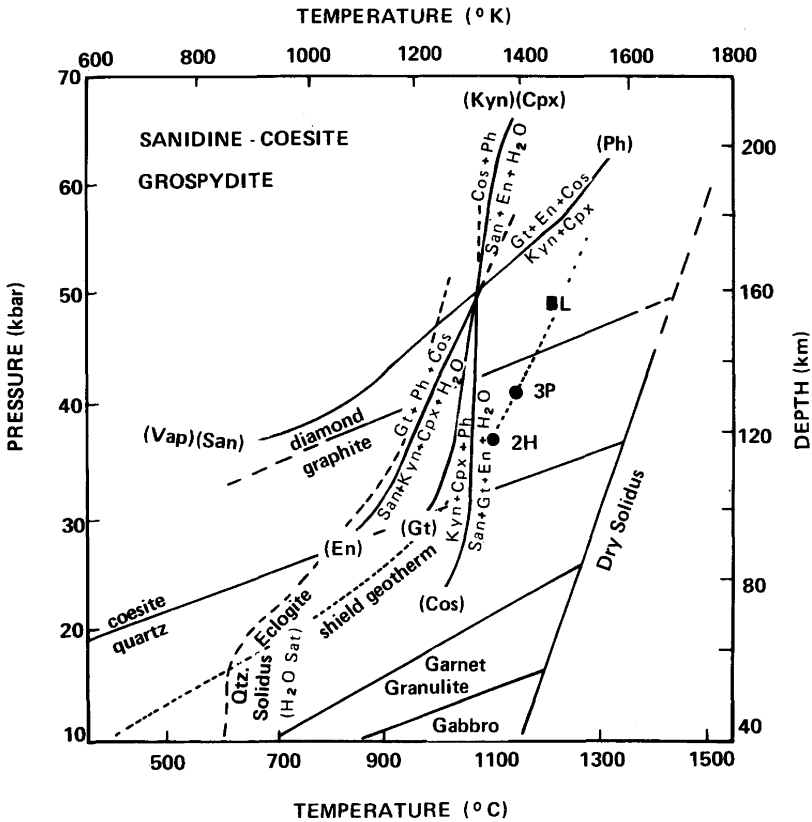
Fig. 2. Pressure-temperature diagram showing the invariant point for the grospydite; stable and metastable projections of two univariant reactions, coesite absent (Cos) and enstatite absent (En), two sets of degenerate reactions, sanidine and vapor absent (San) (Vap) extending through the invariant point to the phlogopite absent reaction (Ph), and garnet absent (Gt) extending to the kyanite and clinopyroxene absent reaction (Kyn) (Cpx). The quartz-coesite transition shown is taken from Akella (1973), the quartz eclogite melting curve from Merril et al. (1970). The relationship of this invariant point is shown with respect to the shield geotherm and gabbro-eclogite-liquid fields (Green and Ringwood, 1967)[a]. The points labeled 2H and 3P are the inferred equilibration conditions of two corundum grospydites from Bobbejaan studied by Smith et al. (1982). The point, L, corresponds to conditions of subsolidus recrystallization of the grospydite from Roberts Victor studied by Lappin (1978).

thermodynamic treatment and those of Roberts Victor grospydites are often non-stoichiometric and hyperaluminous (Smyth, 1980; Gasparik and Lindsley, 1980), we can not confidently relate the above mineral reactions to an equilibration P-T path for this rock. Initial coprecipitation of kyanite and clinopyroxene without garnet followed by further kyanite formation as T decreased and P increased (Lappin, 1978) may involve a reaction similar to reaction (1).

Figure 2 shows the invariant point plotted on a P-T diagram with the equilibrium curves for each reaction. The point is shown in relationship to the gabbro-eclogite-liquid stability field of Green and Ringwood (1967)[a], the shield geotherm, and the quartz eclogite melting curve in water-saturated systems (Merril et al., 1970). The invariant point lies below the shield geotherm which does not agree with "hot spot" theories of magma generation but possibly may be explained by the presence of water in the system, especially if its activity is unity. The point however is above the minimum melting curve of a water-saturated quartz eclogite suggesting that this rock was not water-saturated. The water and phlogopite are assumed phases and, in fact, Smyth and Hatton (1977) found no hydrous phases present in the rock. Carswell (1982) suggests that the phlogopite (1 volume percent) he found in garnet lherzolites indicates depths of origin from 100 to 150 km. Due to the ideal nature of assumed and estimated phase compositions used in the thermodynamic analysis, the P-T conditions of equilibration of the grospydite likely occur in one of the divariant regions around the invariant point. For example, reaction (3) places the strongest constraint on the pressure of the invariant point. Variation of garnet's Third Law entropy by less than one percent of its absolute value results in an invariant pressure near 40 kbar.

CONCLUSIONS

Thermodynamics provides a method that can be a powerful tool for understanding the origin of rocks. Of course, the method cannot be reliably used unless accurate thermodynamic data are available for the phases involved in the system being studied. Still, when data are incomplete, reasonable estimates can be made to yield approximate results. As with a sanidine-coesite eclogite, incorporation of estimated data in a thermodynamic study results in finding an invariant point of origin for the rock at 1060 K and 49 kbars. This finding is consistent with other petrologic evidence and yields several interesting implications about the upper mantle: (1) the existence of free silica is in the form of coesite at depths greater than 100 km; (2) that alkali concentration within the mantle results in the formation of K-feldspar where the melt is silica-saturated but little water is present; and (3) a violent eruption mechanism is indeed probable in the formation of diatremes and kimberlite pipes.