

## The Thermodynamic Regime of Metamorphism in the Ancient Subduction Zones

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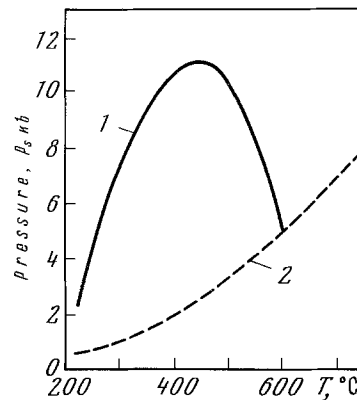
**Abstract.** Based on mineralogical themometry and barometry and computation of mineral reactions modelling metamorphic sequence, a geotherm for metamorphic belts of the subduction zones has been deduced. Relatively low  $PT$ -values (3 kbar/200°C) correspond to zeolite and prehnite-pumpellyite meta-sediments and at higher pressures and temperatures (10 kbar/400°C) lawsonite-glaucophane assemblages become unstable. The  $PT$ -curve achieves maximum at 11 kbar and 470°C to drop down to normal geotherm (Perchuk 1977). High concentration of  $H_2O$  in the metamorphic fluid has been revealed, the difference between  $P_{fl}$  and  $P_{H_2O}$  being less than 2 kbar. Consideration has also been given to specific thermodynamic regime of zeolite and prehnite-pumpellyite zones of the younger island arcs, where lawsonite-glaucophane zones are absent. Here the geotherm has been found to rise from 0.2 kbar/120°C up to 4 kbar/350°C and  $P_{H_2O}$ -regime similar to that of glaucophane schists formations.

### Introduction

The metamorphism of the subduction zones is believed to have taken place at an early stage of the evolution of geosyncline complexes ("protogeosynclines") at the continental boundaries and at the beginning of island-arc development. Both zoning and the geological position of zones within the general tectonic structures have been established accurately by petrologic and geological methods (Ernst 1971; Miyashiro 1973; Dobretsov 1974; Perchuk 1973 and others).

Both the geothermic and barometric determinations (Perchuk 1973, 1977) of mineral equilibria in

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**Fig. 1.** Variation of temperature with pressure in glaucophane schist provinces (curve 1) and the ancient geothermal gradient in the developed metamorphic areas (curve 2) according to Perchuk (1977, p. 336)

the zones have revealed certain  $P$  and  $T$  distribution patterns across the zoning, the maximum  $P$  being at 400–450°C (Fig. 1). The right-hand part of the curve in Fig. 1 is based on numerous  $PT$ -measurements for natural assemblages. The purpose of this paper is to ascertain the shape of the left side of the curve.

### Methods of Calculations

The calculations were based on the gas-mineral reactions involving  $CO_2$  and  $H_2O$  at low temperatures. The minerals and their thermodynamic properties are given in Table 1. Data for Ab, An, Arg, Jd, Chl, Qz, Cal, Tr,  $H_2O$ , and  $CO_2$  were taken from Karpov's compilation (Karpov et al. 1976), the  $H_2O$  fugacity coefficients ( $\gamma_i$ ) for high  $T$  and  $P$  were from Burnham et al. (1969) and those for  $CO_2$  from Perchuk (1977). The zoisite free energy and entropy (Aranovich 1977; Perchuk and Aranovich 1979) are in good agreement

**Table 1.** The indexes of minerals and their thermodynamic properties

N	Mineral, formula	Index <sup>a</sup>	$-\Delta G_{f,298}^0$ cal/mole	$S_{298}^0$ cal/mole ·grad
1	Albite (low), NaAlSi <sub>3</sub> O <sub>8</sub>	Ab	883.340	50.20
2	Analcime, H <sub>2</sub> NaAlSi <sub>2</sub> O <sub>7</sub>	Anc	736.450	56
3	Anortite, CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	An	955.662	48.4
4	Aragonite, CaCO <sub>3</sub>	Arg	269.727	21.2
5	Wairakite, CaAl <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·2H <sub>2</sub> O	War	1,457.421	112.64
6	Glaucofane, Na <sub>2</sub> Mg <sub>3</sub> Al <sub>2</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	Gl	2,685.874	128.09
7	Jadeite, NaAlSi <sub>2</sub> O <sub>6</sub>	Jd	676.579	31.9
8	Calcite, CaCO <sub>3</sub>	Cal	269.980	22.2
9	Quartz, SiO <sub>2</sub>	Qz	204.644	9.88
10	Lawsonite, CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ·2H <sub>2</sub> O	Law	1,071.956	55.88
11	Laumontite, CaAl <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·4H <sub>2</sub> O	Lam	1,596.868	117.03
12	Prehnite, Ca <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	Pr	1,390.6	60.15
13	Pumpellyite, Ca <sub>4</sub> MgAl <sub>5</sub> Si <sub>6</sub> O <sub>23</sub> (OH) <sub>3</sub> ·2H <sub>2</sub> O	Pum	3,203.551	212.6
14	Tremolite, Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	Tr	2,778.420	131.200
15	Chlorite, Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	Chl	1,974.851	118.3
16	Zoizite, Ca <sub>2</sub> Al <sub>3</sub> Si <sub>3</sub> O <sub>12</sub> (OH)	Zo	1,552.892	67.79
17	Water vapor, H <sub>2</sub> O	—	54.641	45.11
18	Carbon dioxide, CO <sub>2</sub>	—	94.261	51.07

<sup>a</sup> Besides that, the following indexes will be use in the paper: Act: Ca amphibole; Cpx: clinopyroxene; Ep: epidote; Hm: hematite; Ru: rutile; Sph: sphene

**Table 2.** Basic experimental data for calculations of thermodynamic properties of minerals used<sup>a</sup>

N	Reaction <sup>a</sup>	The equil. temp.	Bar	$X_{CO_2}^{fl}$	Reference
1	0.5Lam = 0.5War + H <sub>2</sub> O	282	2,000	0	Liou, 1971
		297	3,000	0	
		327	6,000	0	
2	0.5Law + Qz + H <sub>2</sub> O = Lam	210	3,000	0	Liou, 1971
		250	3,200	0	
3	0.5War = 0.5An + Qz + H <sub>2</sub> O	372	2,000	0	Liou, 1970
		392	5,000	0	
4	1.5Pr + CO <sub>2</sub> = Zo + Cal + 1.5Qz + H <sub>2</sub> O	315	2,000	0.05	Gurevich Ivanov, 1976
		328	2,000	0.032	
5	3.75Pum + 2.25Qz + CO <sub>2</sub> = 6.25Zo + 0.75Tr + Cal + 9.25H <sub>2</sub> O	350	2,000	0.05	Plyusnina, Ivanov, 1977
		380	2,000	0.005	

<sup>a</sup> Indexes of the minerals and their chemical formulas are placed in Table 1

with Perkins et al. (1977) data. The  $\Delta G_{f,298}^0$  and  $S_{298}^0$  values for Lam, Pr, Pum, Law, and War have been calculated from the experimental data (Table 2).

The glaucofane  $\Delta G_{f,298}^0$  value (Table 1) has been calculated from natural paragenesis using the phase correspondence method (Perchuk 1977) and is very close to that from Chen (1975). Let us consider the calculation procedure in detail.

Reaction 17 (Table 3):



is widespread in glaucofane schists and is very important because it does not involve H<sub>2</sub>O. The entropy of reaction (17)  $\Delta S_{298}^0$  is  $-117.6 \text{ cal K}^{-1} \cdot \text{mole}^{-1}$ , and the volume change is  $-3.234 \text{ cal} \cdot \text{bar}^{-1}$  (Karpov et al. 1971). For calculating the position of equilibrium (17) it is vital to know the *PT*-parameters at least for one point. This can be done using mineralogical thermometers and barometers.

Coleman and Lee (1962, 1963) described the following parageneses of type III glaucofane schists of the Franciscan formation (Cazadero area): Cl + Gl + Law + Ar + Qz, Gl + Law + Gr + Mu + Qz, Gl + Law + Gr + Qz etc. Using their analytical data on the coexisting minerals, we have determined the equilibrium temperatures as being 275°–300° C. Taylor and Coleman (1968) used the O<sup>18</sup>/O<sup>16</sup> method to obtain similar results for the same rocks. Lee et al. (1966) described the assemblage  $\text{Gr}_{0.117}^{0.567} + \text{Gl}_{0.544} + \text{Chl}_{0.52} + \text{Act}_{0.65} + \text{Ep}^{0.2} + \text{Pum} + \text{Mu}$  in the high temperature zone (type IV) of the same formation.

Using mineralogical thermometers, we have got the following temperatures for this assemblage: 395° (Am-Gr thermometer), 440° C (Chl-Gr thermometer), the average temperature being about 420° C. The glaucofane schists from this metamorphic zone (type IV) contain garnet and omphacite. The mole fraction of pyrope in the garnet (specimen 56-CZ-59, Coleman and Lee, 1963) is 0.116. The omphacite composition corresponding to  $X_{Mg}^{Cpx} = 0.55$  at 420° C has been estimated (not obtained from the analytical data) by means of amphibole-pyroxene diagram (Perchuk 1969) according to the known amphibole composition  $X_{Mg}^{Am} = 0.63$ . From these data we can calculate the MgO distribution coefficient between Cpx and Gr to estimate the pressure conditions:  $K_D = 0.1$  and  $P = 10.4 \text{ kbar}$  (Perchuk 1968).

Although in Cazadero aragonite often occurs in rocks of type I–III it is replaced by calcite in that of type IV, where Gl + Law assemblage also disappears. Consequently, reaction (17) takes place in the aragonite field at 370°–410° C and  $P \approx 10 \text{ kbar}$ , but is close to the calcite-aragonite transition curve in this *PT*-range. Taking 400° C as the equilibrium tempera-

**Table 3.** The standart Gibb's free energies, entropies and molar volumes of some important reactions

N	Reactions	$\Delta G_{298}^0$ cal/mole	$\Delta S_{298}^0$ cal/mole·grad	$\Delta V_s$ cal/bar
1	0.5Lam=0.5Lam+Qz+H <sub>2</sub> O	+3,171	+23.35	-0.702
2	0.429Lam+0.143Chl+1.214Pr=0.714Pum+1.5Qz+H <sub>2</sub> O	3,503	71.822	-1.097
3	3Lam+8.5Pr+Chl=5Pum+4.5Qz+H <sub>2</sub> O	17,521	355.36	-3.470
4	Pum+0.6Qz=0.6Zo+1.4Pr+0.2Chl+H <sub>2</sub> O	-1,849	21.79	0.342
5	1.071Pum+CO <sub>2</sub> =1.643Zo+0.214Chl+0.857Qz+Cal+2.071H <sub>2</sub> O	-6,300	18.03	0.228
6	3.75Pum+2.25Qz+CO <sub>2</sub> =6.25Zo+0.75Tr+Cal+9.25H <sub>2</sub> O	3,237	90.99	-1.465
7	Lam+Cal=Pr+Qz+3.5H <sub>2</sub> O+CO <sub>2</sub>	13,413	139.76	-1.851
8	Law+Cal+Qz=Pr+CO <sub>2</sub> +H <sub>2</sub> O	7,078	68.37	-0.448
9	1.5Pr+CO <sub>2</sub> =Zo+Cal+1.5Qz+H <sub>2</sub> O	-4,318	23.63	-0.285
10	0.5Law+0.25Pr=0.5Zo+0.25Qz+H <sub>2</sub> O	1,380	38.50	-0.294
11	0.5Law=0.5An+H <sub>2</sub> O	+3,506	41.37	-0.006
12	0.58Law=0.29Zo+0.14Ky+0.14Qz+H <sub>2</sub> O	1,558	36.82	-0.208
13	3Law+Cal=2Zo+5H <sub>2</sub> O+CO <sub>2</sub>	12,598	222.36	-1.623
14	2Zo+CO <sub>2</sub> =3An+Cal+H <sub>2</sub> O	8,434	25.86	1.584
15	Jd+Qz=Ab	-2,118	8.42	0.406
16	Arg=Cal	-153	1.00	0.406
17	2Law+5Gl=Tr+10Ab+2Chl	+11,760	117.6	3.234
18	0.857Law+0.357Gl=0.714Ab+0.214Chl+0.5Qz+0.429Zo+H <sub>2</sub> O	1,046	46.67	0.069
19	0.107Tr+0.643Law+0.357Ab=0.179Gl+0.5Qz+0.429Zo+H <sub>2</sub> O	3,892	29.12	-0.287
20	0.429Tr+0.643Chl+3.57Ab=1.786Gl+0.429Zo+0.5Qz+H <sub>2</sub> O	-3,947	-3.72	-1.326
21	Anc+Qz=Ab+H <sub>2</sub> O	3,112	29.43	-0.480
22	0.1Tr+0.2Chl+Anc+Qz=0.2Law+0.5Gl+H <sub>2</sub> O	1,937	17.67	-0.803
23	2.273Law+Arg+0.182Tr=0.909Pum+0.545Qz+1.545H <sub>2</sub> O+CO <sub>2</sub>	8,761	168.58	-0.807
24	0.5Lam=0.5War+H <sub>2</sub> O	5,083	42.915	-0.158
25	0.5War=0.5An+Qz+H <sub>2</sub> O	2,406	32.75	-0.505
26	1.353Law+0.118Chl+0.471Qz+Cal=0.588Pum+CO <sub>2</sub> +1.118H <sub>2</sub> O	9,140	110.16	+0.203
27	0.373Pum+0.03Chl+0.133Qz=0.642Zo+0.104Tr+H <sub>2</sub> O	1,328	15.19	+0.236

ture (at 10 kbar), we have calculated  $\Delta G_T^0$  for reaction (17):

$$\Delta G_T^0 = \Delta G_{298}^0 - \Delta S_{298}^0(T-298) + \Delta V_s P. \quad (1)$$

Knowing  $\Delta V_s = -3.234 \text{ cal} \cdot \text{bar}^{-1}$  and  $\Delta S_{298}^0 = -117.6 \text{ cal/K}$ , it is easy to find  $\Delta G_{298}^0 = -11,760 \text{ cal}$  and  $P_s = -4,545.5 + 33.364 t(^{\circ}\text{C})$  for equilibrium (17). The reactions involving H<sub>2</sub>O and CO<sub>2</sub> were calculated assuming the ideal model of the gas mixture:

$$\begin{aligned} \Delta G_T^P &= \Delta G_{298}^0 - \Delta S_{298}^0(T-298) + \Delta V_s P_{f1} \\ &+ RT(\Delta n_{\text{H}_2\text{O}} \ln X_{\text{H}_2\text{O}} + \Delta n_{\text{CO}_2} \ln X_{\text{CO}_2}) \\ &+ \Delta n_{\text{H}_2\text{O}} \int_1^{P_{f1}} V_{\text{H}_2\text{O}} dP_{\text{H}_2\text{O}} + \Delta n_{\text{CO}_2} \int_1^{P_{f1}} V_{\text{CO}_2} dP_{\text{CO}_2}, \end{aligned} \quad (2)$$

where  $\Delta G_{298}^0$  is Gibbs free energy of a reaction,  $\Delta S_{298}^0$  is entropy effect,  $\Delta V_s$  is volume change of a reaction,  $\Delta n_{\text{H}_2\text{O}}$  and  $\Delta n_{\text{CO}_2}$  are H<sub>2</sub>O and CO<sub>2</sub> changes;  $P_{f1} \approx P_s = P_{\text{CO}_2} + P_{\text{H}_2\text{O}}$  is fluid pressure.

Ernst (1971, 1977) and Dobretsov (1974) established the following four metamorphic zones in the glaucophane schist formation:

- 1) zeolite,
- 2) prehnite-pumpellyite,
- 3) green and blue schists,
- 4) garnet amphibolites with eclogite lenses.

The  $P$  maximum corresponds to zone 3, where glaucophane schists are well developed. As the boundaries of zones 1, 2 and 3 have not yet been determined, it seems reasonable to calculate the boundary reactions in the  $P_{f1}$ - $T$ - $P_{\text{CO}_2}$ - $P_{\text{H}_2\text{O}}$  coordinates.

To this end, a general topological diagram was constructed in the  $P_s$ - $T$ - $P_{\text{H}_2\text{O}}^{\text{fl}}$  and  $P_{\text{CO}_2}^{\text{fl}}$ - $P_{f1}$ - $T$  coordinates to delineate all stable reactions, from which only reactions that determined the mineral facies boundaries were selected.

The  $\Delta G_{298}^0$ ,  $\Delta S_{298}^0$  and  $\Delta V_s$  of the reactions are given in Table 3. According to Eq. (2):

$$\Delta G_T^P = \Delta G_T^0 + \Delta G^{P_s} + \Delta G^m = 0, \quad (3)$$

where

$$\Delta G_T^0 = \Delta G_{298}^0 - \Delta S_{298}^0(T-298); \quad (4)$$

$$\Delta G^{P_s} = \Delta V_s P_{f1}; \quad (5)$$

$$\begin{aligned} \Delta G^m &= G_T^m + G_P^m = RT(\Delta n_{\text{H}_2\text{O}} \ln X_{\text{H}_2\text{O}}^{\text{fl}} + \Delta n_{\text{CO}_2} \ln X_{\text{CO}_2}^{\text{fl}}) \\ &+ \Delta n_{\text{H}_2\text{O}} \int_1^{P_{f1}} V_{\text{H}_2\text{O}} dP_{\text{H}_2\text{O}} + \Delta n_{\text{CO}_2} \int_1^{P_{f1}} V_{\text{CO}_2} dP_{\text{CO}_2}. \end{aligned} \quad (6)$$

The isobaric ( $P_{\text{CO}_2}^{\text{fl}} = 20 \text{ bar}$ ) section of the  $P_{f1}$ - $T$ - $P_{\text{CO}_2}$  diagram is given in Fig. 2, where the reaction boundaries delineate the following mineral facies:

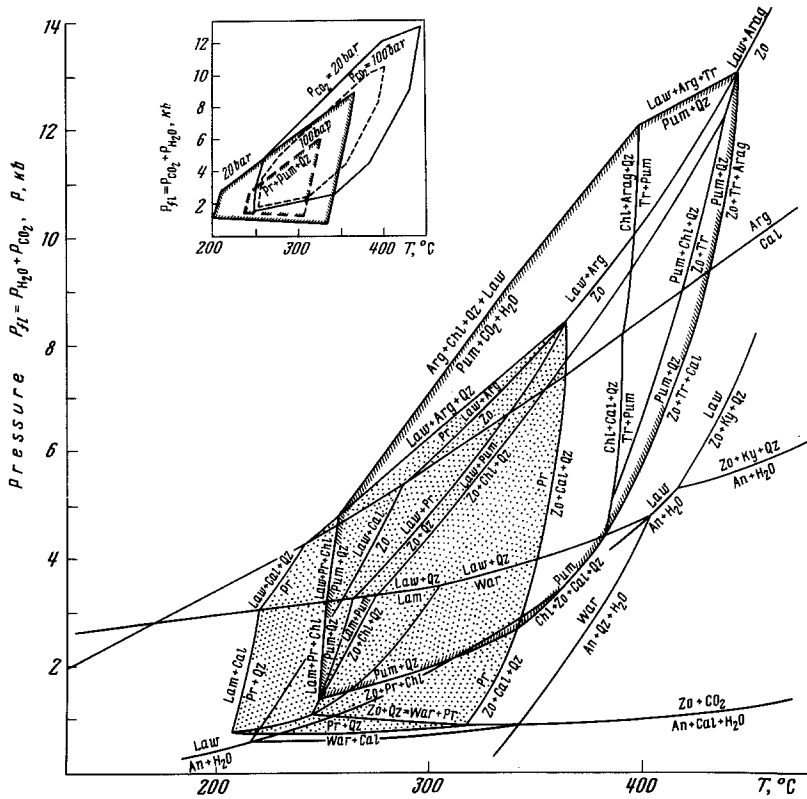


Fig. 2. The most important metamorphic facies in some ancient areas with high  $dP/dT$ -gradient in the  $P_{H_2O}$ - $T$  diagram

1. pumpellyite ( $\pm$ Qz)
2. prehnite ( $\pm$ Qz)
3. zeolite:
  - a) laumontite subfacies
  - b) wairakite subfacies
4. lawsonite ( $\pm$ Qz)
5. zoisite ( $\pm$ Qz).

Prehnite field overlaps that of pumpellyite (with or without Qz). The area of overlapping of these fields defines virtually the prehnite-pumpellyite metamorphic facies.

The increase in the  $\text{CO}_2$ -pressure up to 100 bars will lead to a sharp constriction in the  $\text{Pum} \pm \text{Qz}$  and  $\text{Pr} \pm \text{Qz}$  stability fields in the  $P_{H_2O}$ - $T$  coordinates. As a result, a much smaller area is occupied by the prehnite-pumpellyite facies which is substituted by the blue and green schists assemblages. These relations are shown in the upper part of Fig. 2.

On the contrary, the  $\text{Law} + \text{CaCO}_3$  field becomes larger with the increase of  $P$  and  $T$ .  $\text{Law} + \text{CaCO}_3$  is replaced by  $\text{Zo}$  with increasing  $T$  but in the absence of  $\text{CaCO}_3$ .  $\text{Law}$  is stable up to  $T > 400^\circ\text{C}$ . In quartz-bearing assemblages, the reaction  $\text{Law} + \text{Qz} = \text{Lam}(\text{War})$  is a natural pressure boundary for  $\text{Law}$ , i.e.  $\text{Law} + \text{Qz}$  assemblages are not stable at pressures lower than 2.5 kbar.

The diagram in Fig. 2 was constructed assuming two-component ( $\text{H}_2\text{O} + \text{CO}_2$ ) fluid model. Although natural fluids contain a number of components, these

two are the most important. In the general case, the  $\text{CO}_2$  mole fraction could be determined from the diagram in Fig. 2. But it was of particular interest to estimate the  $\text{H}_2\text{O}$  influence on the boundaries of the established mineral facies.

Therefore, the  $P_{\text{H}_2\text{O}}$  isobaric sections have been constructed (Fig. 3). They reflect the mineral facies relationships at  $P_{\text{CO}_2}^{\text{fl}} = 20$  bar and  $P_{\text{H}_2\text{O}}^{\text{fl}} = 1,000, 5,000$  and  $8,000$  bars. The diagram reveals a striking effect of  $P_{\text{H}_2\text{O}}$  on the  $\text{Pr} \pm \text{Qz}$  stability limits. Under the high-pressure conditions ( $P_s \approx 8.5$  kbar and  $P_{\text{H}_2\text{O}}^{\text{fl}} \approx 8$  kbar), prehnite becomes unstable and therefore the occurrence of  $\text{Pr}$  in the high-pressure rocks suggests relatively high-temperature conditions of metamorphism ( $\sim 350^\circ\text{C}$ ). On the other hand, the  $\text{Pum} \pm \text{Qz}$  stability boundaries change little with increasing  $P_{\text{H}_2\text{O}}$  but strongly depend on  $P_s$ , so that the replacement of the prehnite zone by the pumpellyite one in metamorphic belts with high  $dP/dT$  gradient reflects the increase in  $P_s$ . Under the low  $dP/dT$  gradients, the relations between the subfacies in the prehnite-pumpellyite zone may become more complicated and eventually result in the disappearance of the pumpellyite zone.

The metamorphic zoning mentioned above agrees well with the mineral facies sequences in diagram of Figs. 2 and 3. In other words, the pressure ( $P_s$ ) factor plays the dominant role in the development of the complexes. In fact, the zeolite field is replaced by the

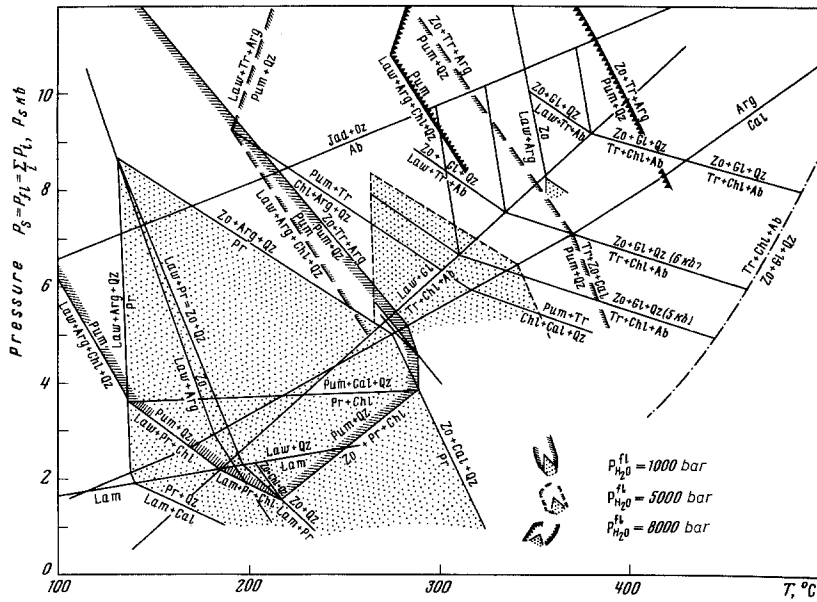
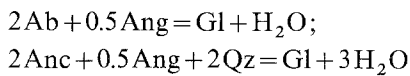


Fig. 3. The most important metamorphic facies in some zones of high  $dP/dT$ -gradient in the  $P_s$ - $T$  diagram with water isobaric lines of mineral equilibria

prehnite and pumpellyite ones; decomposition of Pr yields common green schist assemblage Zo + Cal + Qz. With pressure increase the glaucophane schist assemblage Ep(Zo) + Gl + Qz appears instead of the green schist assemblage Law + Tr + Ab in albite-bearing rocks.

In the diagram of Fig. 3 the lawsonite-glaucophane mineral facies is restricted by reaction (17). In the low-temperature region, the Gl stability is restricted by the wellknown reactions between Ab (or Anc) and antigorite (Ang):



but unfortunately, lack of reliable Ang constants prevented the computation. Although reaction (17) doesn't depend on  $P_{H_2O}^{fl}$ , there is a direct connection between the lower  $P_s$  stability boundary for the Law + Gl paragenesis and reaction 21 (Table 3):  $Ab + H_2O = Anc + Qz$ . The higher value of  $P_{H_2O}^{fl}$  the higher is value of  $P_s$ , required for the paragenesis Law + Gl to form. The phase relations of these minerals are shown in Fig. 4.

The basis of the thermodynamic regime is the correlation between temperature and pressure during metamorphism in the subduction zones. Recent investigations have shown that in these regions pressure can not be strictly correlated with the depth of metamorphism, owing to the development of "over pressure zones". The attempts were made to explain the pressure increase by subduction of the oceanic plate under the continental one (Perchuk and Ushakov 1973).

Using the diagrams in Figs. 2 and 3, it is possible to ascertain the position of the left-side part of the

curve in Fig. 1. For this purpose, more than 20 assemblages with known temperatures have been selected, covering the whole span from prehnite-pumpellyite to glaucophane schist facies (Table 4). After that, the  $PT$ -gradient curve (Fig. 5, compare curves 1 and 3) has been drawn which shows a good agreement with the previous curve (Perchuk 1977). Another curve (line 2) is shown in Fig. 5 for the  $PT$ -gradient in the zeolite and prehnite-pumpellyite metamorphic facies of the developed island arcs. We have not enough data to expand the curve into the high-temperature and high-pressure region. The line is likely to reflect a gradient which corresponds to the metamorphic conditions of medium pressure complexes (Miyashiro 1973, p. 71). In any case glaucophane was not found in these rocks (see Table 4). On the other hand, there are no data on the  $PT$ -parameters of mineral equilibria in the zeolite and prehnite-pumpellyite zones from the blue schist formations (see zoning on page 4), and it has been difficult to extrapolate curve 1 in Fig. 5 low pressure.

$PT$ -estimates (Table 4) have been obtained in different ways. Temperatures not marked with asterisks are taken from the literature - they were estimated either by the oxygen isotope thermometry (Taylor and Coleman 1968; Platt 1976), or by other methods. Pressures were derived from these temperature values and the diagrams in Figs. 2-4. Arrows in Fig. 5 indicate a lower pressure limit for the given assemblage. For example, in assemblage No. 11 (Table 4) there coexist Law + Gl + Qz + Arg + Pum + Gr. The low pressure stability limit for Law + Gl (at 285°C) is about 5.8 kbar. Therefore,  $P_{fl}$  in Table 4 is  $P_{fl} \geq 6$  kbar. This value is unlikely to be considerably lower because this paragenesis contains aragonite, that

**Table 4.** The parageneses and thermodynamical parameters of mineral equilibria in some metamorphic rocks

N <sup>a</sup> Sample	Paragenesis	t °C	P <sub>fl</sub> kbar
<i>Middle pressure metamorphism</i>			
1 -	Lam + Anc + Ab + Qz	65	0.4
2 -	Lam + Cal	160	1
3 -	Anc + Ab + Qz	120	1.5
4 -	Pum + Lam + Anc	200	1.6
5 9b	Chl + Ep + Hm + Pum + Pr + Cal + Ab + Qz	250	2
6 8.9	Pum + Pr + Cal + Ep + Chl + Qz	225	2
7 -	Ab + Pr + Lam + Anc	165	2-3
8 Bb34903	Gr <sup>0.67</sup> + Chl + Ep <sup>0.23**</sup> + Qz + Cal + Pr	340	3-5
9 H35347A	Gr <sup>0.43</sup> Chl + Ep <sup>0.03</sup> + Act + Ab + Qz + Pum	370	3-5
<i>High pressure metamorphism</i>			
10 50-CZ-59	Law + Gl + Gr + Qz	275	5.8
11 51-CZ-59	Law + Gl + Qz + Gr + Arg + Pum	285	6
12 201H	Law + Gl + Gr + Qz + Mn	300	6.4
13 -	Gl + Law + Ep + Ab + Chl + Pum + Cpx	300*	6.4
14 1A	Ab + Jd + Act + Gl <sub>0.96</sub> <sup>***</sup> + Ep + Law + Pum + Chl + Gr <sub>0.15</sub>	300	6.4
15 84M	Law + Gl + Ab + Qz + Chl + Sph + Cal(Arg) + Pum + Cpx <sub>jd</sub>	300	6.4
16 829	Cpx <sub>0.05</sub> + Gl <sub>0.355</sub> + Tr <sub>0.573</sub> + Chl + Law + Mu	350*	8.2
17 37	Cpx <sub>0.116</sub> + Gl <sub>0.143</sub> + Chl + Ep + Mu + Law + Sph	390*	9.6
18 56-CZ-59	Gl + Qz + Gr <sub>0.116</sub> + Cpx <sub>0.43</sub>	420*	10.4
19 H-3393	Gl <sub>0.544</sub> + Act <sub>0.65</sub> + Chl <sub>0.52</sub> + Gr <sub>0.117</sub> + Ep <sub>0.2</sub> Mu + Pum <sub>0.45</sub>	440*	10.7
20 TPY6833	Gl + Ab + Chl + Ep + Act <sub>0.53</sub> + Gr <sub>0.12</sub> <sup>**</sup>	450*	11
21 79-69A	Gl <sub>0.58</sub> + Cpx <sub>0.6</sub> + Gr <sub>0.1</sub> + Chl + Ep + Ab + Qz + Ac4	400*	10.4

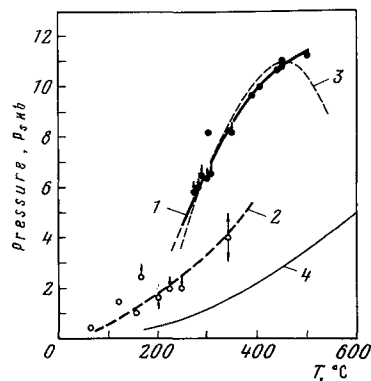
\* The temperatures have been estimated using geothermometers and geobarometers (Perchuk 1969, 1977; Perchuk and Aranovich 1979)

\*\* The overline values correspond to  $X_{Fe} = Fe^{3+}/Fe^{3+} + Al$

\*\*\* The underline values correspond to  $X_{Mg} = Mg/(Mg + Fe + Mn)$

<sup>a</sup> Sources of data: 1: Read, Eisbacher 1974; 2: Zen, Thompson 1974; 3: Iijima, Utada 1971; 4: Liou 1977; 5: Zen 1974; 6: Papezic 1974; 7: Surdam 1973; 8, 9: Coombs et al. 1977; 10, 11, 18: Taylor, Coleman 1968; 12, 19: Lee et al. 1966; 13: Roever et al. 1976; 14: Hermes 1973; 15: Platt et al. 1976; 16, 17: Dobretsov 1974; 20: Liou et al. 1975; 21: Ghent, Coleman 1973

changes to calcite at ~5.5 kbar ( $t=285^{\circ}C$ ). Pressures were estimated by several authors. For example, the *PT*-conditions of zeolite parageneses were measured directly in the drills (Zen and Thompson 1974; Read and Eisbacher 1974; Iijima and Utada 1971; Surdam 1973). These values for assemblages 13-16 are given in Table 4. The origin of the zeolite rocks is associated with the modern hydrotherms in the active



**Fig. 4.** *PT*-gradients during metamorphism of volcanic-silica sediments. The points are plotted according to Table 4. 1: for glaucophane schist provinces; 2: for zeolite and prehnite-pumpellyite rock complexes; 3 and 4 are the same as 1 and 2 in Fig. 1 correspondently

**Table 5.** The thermodynamic parameters of metamorphic processes in ancient subduction zones

N in Table 4	t °C	P <sub>fl</sub> kbar	P <sub>H<sub>2</sub>O</sub> <sup>fl</sup> kbar	The reactions (number in Table 3) which have been used for estimation of P <sub>H<sub>2</sub>O</sub> <sup>fl</sup>
1	65	0.4	0.4	21
2	160	1	1	7
3	120	1.5	0.8	21
4	200	1.6	0.95 <sup>a</sup>	-
5	250	2	1.4	4.9
6	225	2	1.2	4
7	165	2-3	1.4	21
8	340	3-5	3.7	9
9	370	3-5	4.0	27
11	285	6	4.5	18
13	300	6.4	4.8	18
14	300	6.4	4	18
15	300	6.4	5.2	26
16	350	8.2	6.8	18
19	440	10.7	8.4	20
20	450	11	9	20
21	400	10	8.6	20

<sup>a</sup> The Lam + Pum stability at 200°C and  $P_2=1.6$  kbar is limited by the water pressure:  $0.8P_{H_2O}^{fl}$  1.1 kbar

volcanic areas confined to the ocean-continent transition zones.

To estimate the  $P_{H_2O}^{fl}$  regime of the metamorphism in question we have selected some univariant reactions corresponding to the given paragenesis. For instance, assemblage No. 21 (Table 4): Gl + Chl + Ab + Ep + Qz + Tr + (Gr + Cpx) corresponds to equilibrium reaction (20) in Table 3:



At  $t=400^{\circ}C$  and  $P_{fl}=10$  kbar this univariant curve intersects the equilibrium line for Gl + Law

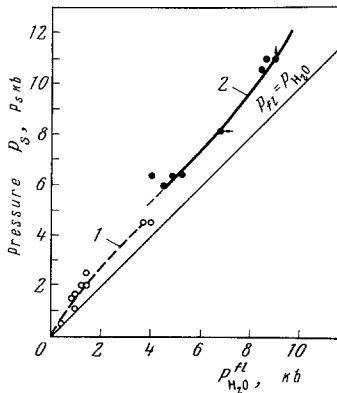


Fig. 5. The  $H_2O$  regime in the metamorphic rocks of subduction zones. 1: zeolite and prehnite-pumpellyite zones; 2: green and blue schist zones

= Tr + Ab + Chl at  $P_{H_2O}^{fl} \approx 8,6$  kbar, and it is this value that is presented in Table 5.

The  $P_{H_2O}^{fl}$  values, estimated by this method for different assemblages, are given in Table 5 and shown in Fig. 5. The diagram (Fig. 5) reveals a positive correlation between fluid pressure and partial  $H_2O$  pressure in the fluid. Thus, the higher  $P_{fl}$ , the greater the difference between  $P_{fl}$  and  $P_{H_2O}^{fl}$ ,  $P_{fl} - P_{H_2O}^{fl}$  approaching 2 kbar at  $P_{fl} = 11$  kbar. But the difference is not so important as the  $H_2O$  mole fraction in the fluid. For zeolite and prehnite-pumpellyite rocks  $X_{H_2O}^{fl}$  is about 0.75 that differs from that for glaucophane schists, where  $X_{H_2O}^{fl} \approx 0.8$  (the average for 4 samples). Thus, the  $H_2O$  regime of metamorphism in different zones is the same in character ( $P_{H_2O}^{fl}$  is increased with  $P_{fl}$ ) but distinct in  $X_{H_2O}^{fl}$  values.

### Concluding Remarks

Inevitably, further work is required for more complete understanding of the thermodynamic regime concerned in this paper. Our calculation model does not take into account the effect of solid solutions on the position of reaction curves. In some cases this effect is probably negligible (as for Pum-Tr and Chl-Tr relations; Plusnina, Ivanov 1977), but in others it is almost certainly of first-order importance (as for Ep; Perchuk, Aranovich 1979). Also, the uncertainties may have arisen from the assumption of ideal mixture of  $H_2O$  and  $CO_2$  in the fluid phase. But it seems reasonable that the main features of the thermodynamic regime, outlined above, would be valid.

This work has confirmed that the metamorphic pressure is greater than the downward pressure of the upper rocks. It means that subduction mechanism creates overpressure at the ocean-continent boundaries (Ernst 1971, 1977; Perchuk and Ushakov 1973).

It is in these zones of the Earth's crust that a specific geotectonic regime has given rise to a specific thermodynamic regime to produce mineral assemblages like Jad + Qz, Pr + Arg + Qz, Pum + Gl + Qz peculiar to metamorphism of blue schists kind ("embryonal metamorphism").

*Acknowledgements.* We would like to express our appreciation to V.S. Sobolev, F.J. Turner, and H.C. Helgeson for their constructive reviews of the manuscript and helpful suggestions for improvement.

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Received December 20, 1979; Accepted November 26, 1980