Mineralogy and phase relations in the blueschist facies of the Black Butte and Ball Rock areas, northern California Coast Ranges

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Abstract

Microprobe study of minerals in rocks of the blueschist facies from the Black Butte and Ball Rock areas of the South Fork Mountain Schist, Northern California Coast Ranges, is the basis in this report for analysis of reactions and phase relations among lawsonite, pumpellyite, epidote and associated minerals. Observed assemblages are intermediate in a progression from those observed elsewhere in high P-low T schists of the Franciscan (e.g., Panoche Pass) where lawsonite is present in nearly all lithologies, to the relatively low Phigh T assemblages of the Shuksan blueschist (Washington) where epidote is ubiquitous. Two successive reactions in this sequence, in order of increasing temperature, are:

- (1) lawsonite + Na-amphibole = epidote + quartz + albite + chlorite + H_2O ;
- (2) Na-amphibole + pumpellyite + quartz = epidote + Ca-amphibole

+ albite + chlorite + H_2O .

The pressure of metamorphism for the Black Butte and Ball Rock areas is estimated from the jadeite content of pyroxene and from the stability of aragonite to have been approximately 7 kbar; temperature estimates are not tightly constrained by mineral equilibria but are suggested to be in the range of 250 to 300°C.

Introduction

Schists in the Black Butte area, northern California Coast Ranges (Fig. 1), contain minerals diagnostic of the blueschist facies (Ghent, 1965, see definition of Turner, 1981, p. 321). Preliminary consideration of the phase relations, without the benefit of mineral compositions, and comparison with other blueschist terranes suggested that the Black Butte rocks have mineral associations intermediate between the high pressure, jadeite-bearing assemblages of parts of the Franciscan Complex and lower pressure/higher temperature blueschists which are transitional to the greenschist facies, as in the Shuksan Suite, Washington (Brown, 1977). In this paper we report mineral compositions and re-examine the phase relations in the Black Butte and neighboring Ball Rock regions (Fig. 1). Results of the study are relevant to the general problem of formulating a P-T grid for the blueschist facies, and pertain also to the regional problem of P-T gradients and interpretation of causes of blueschist metamorphism in the Northern California Coast Ranges.

Schists of the Black Butte and Ball Rock areas are part of a narrow metamorphic belt extending some 200 km in northern California, bounded to the northeast by the Coast Range Thrust and to the southwest by less recrystallized Franciscan metagreywackes (Fig. 1). This belt, considered to be part of the Franciscan Complex, is named the South Fork Mountain Schist (Blake and others, 1967). Protolith materials were greywacke, mudstone and basic volcanic rock; metamorphism has mostly obliterated protolith textures, however relict bedding, pillows and igneous clinopyroxene grains are locally observable (e.g., Ghent, 1965). Various aspects of the field setting, texture and structure of the South Fork Mountain Schist are described in published reports by Ghent (1965), Blake and others (1967), Wood (1971), Suppe (1973), Irwin and others (1974), Bishop (1977), and Worrall (1981). A recent assessment of radiometric dates by Lanphere and others



Fig. 1. Index map for studied localities, from Jenkins, 1977.

(1978) suggests an Early Cretaceous age of metamorphism (115-120 m.y.).

Mineral assemblages

The fine-grained nature of the rocks (grain diameters are dominantly less than 20 μ m) creates difficulty for mineral identification by petrographic microscope and such determinations were augmented in the present study by X-ray diffraction analysis and electron microprobe study.

Maximum phase mineral assemblages are given in Table 1, and assemblages in specific rocks containing analysed minerals in Table 2. Metasedimentary rocks in the Black Butte and Ball Rock areas are composed predominantly of the assemblage quartz + albite + chlorite + phengite + lawsonite, with sporadic occurrence of aragonite and epidote. The common assemblage in basic schists at Black Butte is quartz + albite + epidote + chlorite + pumpellyite + crossite + sphene. Actinolite is uncommon and does not coexist with epidote or crossite. Aragonite, stilpnomelane, phengite and aegerine-rich pyroxene are rare additional phases. Lawsonite occurs in some basic schists, but not in association with amphibole. In the Ball Rock area, assemblages of basic schists are in all respects similar to those of Black Butte with the notable exceptions that (1) lawsonite is present in a high percentage of specimens (17 of 27 examined), where it coexists with Na-amphibole, and (2) epidote is less common (present in 9 of 27 samples). Some basic schists contain the assemblage: quartz + albite + epidote + lawsonite + pumpellyite + chlorite + crossite + sphene (Table 1).

Textural relations in rocks containing all above mentioned assemblages may be interpreted to indicate stable coexistence of the minerals; grains of different minerals can be found in contact and grain boundaries do not show

obvious signs of reaction. Obvious disequilibrium features are present also; relict igneous clinopyroxene abounds, epidotes and amphiboles are typically zoned. Our interpretation, however, is that these features do not preclude an approximate domain equilibrium among the metamorphic minerals occurring within a few millimeters of one another (considering rims on zoned grains).

Mineral compositions

A variety of rocks were selected for analysis of minerals in order that mineral compositions could be established for certain critical phase assemblages, and to document the composition range of each mineral. Chemical analyses of minerals were performed by electron microprobe at the University of Calgary (E. D. Ghent, analyst) and at Cambridge University (E. H. Brown, analyst, with assistance by P. J. Treloar). Accuracies and procedures for these two labs have been presented in other publications (Calgary: Ghent, 1970; Cambridge: Sweatman and Long, 1969, and Statham, 1976). Representative mineral compositions are listed in Table 3; Figures 2 to 5 display various aspects of mineral composition and are discussed below.

Pumpellyite

Pumpellyite in the Black Butte and Ball Rock areas ranges rather widely in composition, but corresponds generally to pumpellyite from other blueschist or pumpellyite-actinolite facies assemblages and does not range to

		6	LACK BUT	TE		BALL ROCK			
QUARTZ	x	х	x	X	х	х	х	х	
ALBITE	Х	Х	Х	Х	Х	х	Х	Х	
EPIDOTE	(rare)	Х		Х	Х		Х		
LAWSONITE	Х			X		х	Х	Х	
PUMPELLYITE			Х	Х	Х		Х	х	
CHLORITE	Х	χ	Х	Х	Х	Х	Х	х	
PHENGITE	Х	Х	Х	Х		Х	Х	х	
ACTINOLITE			Х						
CROSSITE		Х			Х		Х	Х	
Na-PYROXENE					Х			Х	
STILPNOMELANE	(rare)					(rare)			
ARAGONITE	Х		(rare)			Х	Х	(rare)	
SPHENE		Х	Х	Х	Х			х	
LITHOLOGY	QFS	BS				QFS	BS		

Table 1. Maximum phase mineral assemblages

QFS = quartzofeldspathic schist

BS = basic schist

	BLACK BUTTE AREA						BALL ROCK AREA						
	BB- 1	BB- 9	BB~ 17	88- 20	BB- 23B	515- 17	515- 226	SF- 1	SF- 3	SF- 16B	SF- 19	SF- 21	
Quartz	X	Х	х	Х	Х			Х	х	Х	х		
Albite		Х		Х	Х	х		Х	х		Х	Х	
Epidote	х	х	х	Х	Х			Х					
Lawsonite					Х			Х		Х	Х	Х	
Pumpellyite	Х		Х	Х	Х	х	Х	Х			Х		
Chlorite	Х	Х	Х	Х	Х	х	Х	Х	х	X			
Phengite		Х	Х		Х			Х		Х	Х	х	
Ca-Amphibole						Х							
Na-Amphibole	х	Х		х				Х	Х		х	Х	
Na-Pyroxene				Х					Х	Х	х	Х	
Aragonite						x		Х				Х	
Sphene	х	х	х	x	Х		х	х	Х	х	х	Х	

Table 2. Mineral assemblages in rocks for which microprobe analyses of minerals have been carried out

high Fe content as do pumpellyites from the zeolite facies (Fig. 2, and Coombs and others, 1976). As will be shown in a later section, the pumpellyite composition in the investigated rocks varies with mineral assemblages (bulk chemistry) and does not reflect variation in metamorphic grade.

An estimate of Fe^{3+}/Fe^{2+} in pumpellyite is necessary for the analysis of phase relations carried out in a following section of the paper. To this end, Figure 3 shows that Fe_{total} varies antithetically in pumpellyite relative to Al, and that Mg is nearly constant. These observations suggest that the observed compositional

Table 3. Representative electron microprobe analyses of minerals from the Black Butte and Ball Rock areas, northern Coast Ranges, California

	515-17 amph	515-17 pump	515-17 chl	BB-20 amph	BB-20 pump	BB-20 ep	BB-20 px	SF21 amph	SF21 px	SF1 Iws	
Si0,	53.28	37.8	27.16	54.54	37.4	37.9	53.84	53.07	54.38	38.7	
TiO2	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.04	b.d.	0.4	b.d.	
A1203	1.90	25.8	18.35	5.84	22.2	21.9	3.72	9.66	5.79	31.8	
Fe0	14.18	3.8	20.78	21.46	7.7	16.0 ^a	18.95	22.89	20.65	1.56	
MgO	15.42	3.0	19.01	7.73	3.0	0.08	4.44	4.40	1.49	.64	
CaO	12.42	23.4	b.d.	0.96	22.7	23.8	8.76	0.84	4.59	16.6	
Na ₂ 0	0.33	b.d.	b.d.	6.91	b.d.	b.d.	9.06	6.95	11.77	b.d.	
Total	97.53	93.8	85.30	97.44	93.0	99.68	98.81	97.81	99.07	89.4	
Number of	Cations:										
Si	7.66 ^b	5.99 ^b	2.87	7.80 ^b	6.06 ^b	2.99	2.00 ^b	7.65 ^b	2.00 ^b	2.01	
Ti							0.00		0.01		
Al	0.33	4.83	2.29	0.98	4.23	2.04	0.16	1.64	0.25	1.95	
Fe ³		0.20		1.20	0.76	0.95	0.49	0.85	0.59		
Fe ²	1.71	0.30	1.84	1.36	0.29		0.10	1.91	0,05	0.07	
Mg	3.31	0.70	2.99	1.65	0.71	0.01	0.25	0.95	0.08	0.05	
Ca	1.92	3.97		0.15	1.99	2.02	0.35	0.13	0.18	. 92	
Na	0.10			1.92			0.65	1.94	0.84		

a = total Fe as Fe_20_3

 $b = Fe^{2+}$ and Fe^{3+} estimated according to formula constraints, see text for discussion.

b.d. = below detection limit



Fig. 2. Al-Fe-Mg plot of pumpellyites in the Franciscan Complex. Ortigalita data are from Echeverria (1978) and Ward Creek from Brown (unpublished). Types II and III refer to the designations of Coleman and Lee (1963). Composition fields for the zeolite and pumpellyite-actinolite facies in New Zealand are from Coombs and others (1976).

variation is due to $Fe^{3+} \rightleftharpoons Al$ isomorphism, and that Fe^{2+} is nearly constant. The distribution of data points on Figure 3 fit closely to lines representing cation distributions in the idealized pumpellyite formula of:

$$Ca_4(Mg, Fe^{2+})(Al, Fe^{3+})Al_4Si_6Si_6O_{22}(OH)_7$$

Wet chemical analysis of FeO in pumpellyite BB-17 (M. Stout, Calgary, analyst) together with microprobe analysis yields a formula with Mg + Fe²⁺ = .90, Al + Fe³⁺ = 5.14, based on a cationic charge of 49. These compositions are somewhat lower in Fe²⁺ + Mg and higher in Al



Fig. 3. Plot of Fe_{total} vs. Al and Mg in pumpellyites from the Black Butte and Ball Rock areas. Ions calculated on the basis of cationic charge = 49, and all iron as Fe²⁺. Mg is nearly constant in all pumpellyites, at a value of 0.68. Al + Fe^{total} is close to 5.32 in all pumpellyites. Thus, the ideal formula of Ca₄(Fe²⁺,Mg) (Al,Fe³⁺)Al₄Si₆O₂₂(OH)₇ is closely approximated.

+ Fe³⁺ than that of the ideal formula; other pumpellyites, shown in Figure 3, depart equally from the ideal composition in the opposite sense. For treatment of phase relations, we calculate pumpellyite formulas according to the above model, setting Fe²⁺ = 1.00 - Mg. The possibility of departures on the order of $\pm .10$ for the values of Fe³⁺ and Fe²⁺ is recognized.

Lawsonite

The composition of lawsonite closely approaches that of the end-member (Table 3); measurable impurities are Fe and Mg, the sum of the oxides of which typically comprise about 2% of the analysis.

Epidote

For epidote, all iron is assumed to be ferric. The composition range is limited; $Fe^{3+}/(Fe^{3+}+Al)$ in epidotes from three Black Butte rocks is high, in the range of .28–.33. The birefringence of epidote in other rocks from both Black Butte and Ball Rock indicates a regional absence of aluminous epidotes in all lithologies. This observation is in contrast with the range of epidote composition in the greenschist facies (*e.g.*, Brown, 1967).

Amphibole

Formulas for amphibole, and calculation of $Fe^{2+} vs$. Fe³⁺, are based on the asumption that the total cation charge is 46 and that all cations except Na and Ca sum to 13. Plots of Na–amphiboles on the Miyashiro diagram, as in Figure 4, are subject to a fairly large degree of uncertainty due to combined effects of analytical error and departures of mineral formulas from the stoichiometric constraints used for partition of iron into ferric and



Fig. 4. Plot of Na-amphiboles on Miyashiro diagram. BB = Black Butte, SF = Ball Rock. Estimated range of uncertainty based on analytical uncertainty and departure of minerals from formula constraints used in calculating Fe^{3+} and Fe^{2+} . G = glaucophane, FG = ferroglaucophane, R = riebeckite, MR = magnesioriebeckite.

ferrous states. Based on these considerations, a rough estimate of this uncertainty is given on Figure 4.

Pyroxene

Formulas of pyroxenes, and partition of iron in ferric and ferrous states, were calculated on the basis of a total cationic charge = 12, and, in order to estimate Fe^{2+} and Fe^{3+} , by three different schemes: (a) normalization of cations to 4; (b) assumption that the pyroxene consists of the end members: NaAlSi₂O₆ (jadeite), NaFe³⁺Si₂O₆ (acmite) and Ca(Mg,Fe²⁺)Si₂O₆ (diopside-hedenbergite), then Fe³⁺ = Na - Al; and (c) the Bradshaw (1978) statistical determination. Of these methods, (c), developed primarily for omphacites, gives formulas with the largest departures from ideal pyroxene stoichiometry; (a) and (b) give mutually similar results. (b) is used here and preferred because it limits the effect of analytical error on Fe³⁺ determination to analyses of Na and Al.

The pyroxenes are relatively poor in jadeite (10-30%) and rich in acmite (50-75%) as shown on Figure 5. The jadeite content of the pyroxenes is notably lower than that of the omphacites and impure jadeites found in other parts of the Franciscan (*e.g.*, Essene and Fyfe, 1967).

Phase relations

Phase relations in the Black Butte area can be depicted on a ternary graph with Al-Ca-Fe³⁺ at apices, on which phases are projected from a constant subassemblage of quartz, albite, chlorite and H₂O fluid. Components accounted for in this projection are Si, Al, Fe³⁺, Fe²⁺+Mg as one component, Ca, Na, and H (explained more fully by Brown, 1977). Variations in the (Fe²⁺+Mg)/Al ratio of chlorite from one assemblage to another are slight and do not significantly affect the phase compatibilities derived in this projection. The diagram (Fig. 6) portrays the following features:



Fig. 5. Metamorphic pyroxenes from the Black Butte (BB) and Ball Rock (SF) areas plotted on an acmite-diopside + hedenbergite-jadeite diagram.



Fig. 6. Phase relations in the Black Butte area depicted on an Al-Ca-Fe³⁺ plot. Phases are projected from a constant subassemblage of quartz + albite + chlorite + H_2O + CO_2 . Laws = lawsonite, pump = pumpellyite, ar = aragonite, Ca-amph = Ca-amphibole, Na-amph = Na-amphibole, ep = epidote.

(1) Lawsonite + pumpellyite + epidote are a stable assemblage; the epidote has a maximum Al content;

(2) Iron-rich pumpellyite coexists with epidote and Naamphibole, iron-poor pumpellyite with actinolite (or lawsonite);

(3) Epidote and Ca-amphibole are not a stable pair;

(4) Lawsonite and Na-amphibole are not a stable pair. Mineral assemblages in the Black Butte area corre-

spond to Figure 6 without exception in our experience, although the lawsonite + pumpellyite + epidote assemblage is rare (Ghent, 1965). Some phases present in the area are not treated in the projection. Phengite occurs as a manifestation of K-content, stilpnomelane where Fe²⁺/Mg is particularly high, and Na-pyroxene in some rocks rich in Fe³⁺ and Mg. This last relation is displayed on Figure 7, a projection from quartz, albite, chlorite, pumpellyite and H₂O onto an acmite-diopside-hedenbergite ternary diagram. BB-20, which contains all the projection phases, as well as crossite + Na-pyroxene + epidote, is shown. Actinolite from 515-17 is also plotted. The amphiboles and pyroxenes are separated on the diagram; Fe²⁺/Mg partitioning between the Na-pyroxene and Na-amphibole allows the stable coexistence of these two phases, together with the projection assemblage.

Assemblages in the Ball Rock area do not correspond well to the phase relations of Figure 6, the departure being the common occurrence of lawsonite + Na-amphibole. Our best interpretation of phase relations in these rocks is that they are transitional between those of Black Butte and lower *T*-higher *P* rocks, as occur in other parts of the Franciscan, *e.g.*, Panoche Pass (Ernst, 1965). Schists at Ball Rock contain the full reaction assemblage for the equation: 1.7 lawsonite + 1.0 crossite = 0.8



Fig. 7. Phase relations among pyroxenes and amphiboles depicted on an acmite-diopside-hedenbergite plot, projected from quartz, albite, chlorite, pumpellyite, and H_2O .

epidote + 0.9 quartz + 1.9 albite + 0.3 chlorite + 1.4 $H_2O\pm$ pumpellyite. The reaction coefficient of pumpellyite may be positive or negative depending on the composition of phases used in balancing the equation; for other coefficients, variations in phase composition affects the size but not sign. The reaction as balanced above is based on treatment of Fe²⁺ and Mg as a single component. Crossite and chlorite, the minerals in which this component resides, both exhibit wide variability of Fe²⁺/Mg and little fractionation relative to one another; however, the fractionation may be sufficient to allow the reaction a *P*-*T* divariance.

A reaction relation between Black Butte and the higher T or lower P Shuksan terrane, Washington, can be inferred, as discussed in Brown (1977): 1.1 crossite + .8 pumpellyite + 1.3 quartz = 1.0 epidote + .5 actinolite + 2.2 albite + .3 chlorite + 1.4 H₂O. In some parts of the South Fork Mountain schists, near Tomhead Mountain (as observed in our reconnaissance sampling, and by Clark Blake, 1981, pers. comm.), both the crossite + pumpellyite and epidote + actinolite assemblages can be found in close mutual proximity; such rocks presumably represent P-T conditions where the above reaction is divariant.

Pressure and temperature of metamorphism

A summary of pressure-temperature sensitive mineral equilibria relevant to interpetation of metamorphic conditions in the South Fork Mountain Schist is given in Figure 8. The assemblage lawsonite + albite limits temperatures to less than 350° at 6 kbar and 400° at 9 kbar (Holland, 1979; Heinrich and Althaus, 1980). The presence of aragonite indicates pressures greater than 5.5 kbar at 200°C and greater than 7 kbar at 300°C. According to

experimental studies of the rate of inversion of aragonite to calcite by Carlson and Rosenfeld (1981), the preservation of aragonite in schist indicates a metamorphic geothermal gradient of approximately 9°C/km or less (P/T > 30 bars/deg).

The assemblage albite + pyroxene + quartz occurs both in the Black Butte and Ball Rock areas. Assuming that these phases were in equilibrium, one can make use of the relation, albite = jadeite + quartz, to set limits on the *P*-*T* conditions of metamorphism. Using the experimental data from Newton and Smith (1967), we have for albite = jadeite + quartz

$$O = -86 + 7.73T - 0.414P + RT \ln k$$

where T is the temperature in degrees Kelvin, P is the pressure in bars, R is the gas constant in calories and K is the activity product (= activity of jadeite in pyroxene/activity of albite in plagioclase). The jadeite component of the pyroxenes ranges from 10 to 30% (Fig. 5). The activity-composition relations of jadeite solid solutions have been reviewed by Ganguly (1973) and jadeite-diopside solutions have been studied thermochemically by Wood and others (1980). Using an ideal molecular solution model ($X_{padeite}^{PX} = a_{padeite}^{PX}$, where X is mole fraction



Fig. 8. Interpreted P-T conditions of metamorphism at Black Butte (BB). Sources of mineral equilibria and other data relevant to the interpretation: (1) Newton and Smith, 1967; (2) calculated, see text; (3) lowest P/T allowed for aragonite preservation, Carlson and Rosenfeld (1981); (4) Johannes and Puhan, 1971, Crawford and Hoersch, 1972; (5) Holland, 1979, Heinrich and Althaus, 1980; (6) estimated P-T of Shuksan based on pyroxene composition and oxygen isotope fractionation, Brown and O'Neil (1982).



Fig. 9. Summary of P-T estimates and phase relations.

and a is activity), and jadeite contents of 0.2 and 0.3, we estimate pressures of 5 to 6 kbar at 200°C or 6 to 7 kbar at 300°C. These pressure estimates are somewhat less than that predicted from the presence of stable aragonite. Part of this disagreement may be due to an inaccurate solution model, but it should be noted that the jadeite content of the pyroxenes varies widely even though the mineral assemblage is constant, suggesting that the rock system departed from equilibrium during metamorphism.

The oxygen isotope fractionation between quartz and magnetite in a sample from the Yolla Bolly quadrangle, near the Tomhead area (Fig. 1) is reported by Taylor and Coleman (1967). Using the Bottinga and Javoy (1973) calibration, the temperature of this rock is 330°C. (Taylor and Coleman, 1967, report 290°C based on a different calibration.) In terms of phase relations, the Tomhead rocks are transitional to the low-grade parts of the Shuksan Suite, and can be interpreted to have formed at slightly lower temperature and/or higher pressure. Estimated pressure and temperatures for Shuksan rocks, based on the jadeite-content of pyroxene, the stability of pumpellyite and lawsonite, and oxygen isotope fractionation in quartz-magnetite pairs (Bottinga and Javoy, 1973, calibration) are: T = 330 to $400 \pm 15^{\circ}$ C, $P \approx 7$ kbar (Fig. 8) after Brown and O'Neil (1982). The 330°C temperature for the Tomhead rocks is in good agreement with Shuksan temperatures. The estimated temperatures for Black Butte and Ball Rock metamorphism should, from phase relations, be slightly less than those of Tomhead; values in the range of 250 to 300°C seem probable. Following this argument, temperatures suggested by the preservation of aragonite a maximum of 230°C at 7 bars

(Carlson and Rosenfeld, 1981), seem too low. However, the calibration of the oxygen isotope geothermometer, upon which the higher temperatures are so strongly based, is uncertain (*e.g.*, Friedman and O'Neil, 1977).

Summary

Temperature-pressure estimates and interpreted phase relations are combined on Figure 9 to provide a summary of the major conclusions of the paper. By this scheme, the South Fork Mountain Schist is interpreted to have undergone metamorphism at temperatures ranging from 270 to 310°C at pressures of approximately 7 kbar. It contains assemblages representing reactions which with progressive decrease in P/T destroy lawsonite and produce epidote as the common Ca-Al silicate phase. Assemblages at Black Butte lie in the middle of this progression. Those at Ball Rock are transitional to the higher P/T parts of the Franciscan (*e.g.*, Panoche Pass) where lawsonite is ubiquitous, and assemblages at Tomhead Mountain are transitional to those of the lower P/T Shuksan terrane where epidote predominates.

The derived reaction relations should be applicable to isogradic mapping in the South Fork Mountain Schist, and in this sense can contribute a new constraint to solving the puzzle of the tectonic origin of the terrane.

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372