The Laytonville Quarry (Mendocino County California) exotic block: iron-rich blueschist-facies subduction-zone metamorphism

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ABSTRACT. The Laytonville Quarry exotic block contains a series of deep-ocean sediments of varying Fe:Mn, Fe:Al and $Fe^{2+}:Fe^{3+}$ contents, but all enriched in Fe–Mn carbonates. These sediments have a complex metamorphic history that has involved the early development of aegirine and garnet, followed by various phases of 'secondary' mineral growth, all of which required the addition of water to the metamorphic assemblages under high-P, low-T conditions. During the course of an early hydration episode deerite formed within most of the ironstones, and zussmanite in certain Fe-rich, Mn-poor pelites. At a later, and apparently lower pressure period in the metamorphic history, howieite, riebeckite, stilpnomelane, and a more manganous variety of zussmanite (ZU2) have overtaken much of the earlier mineralogy. Subsequent to this, and contemporaneous with the development of the tremolite–talc exotic block rind assemblage, there is a minor development of minnesotaite and ekmanite. During the course of the metamorphism the ironstones have become enriched in K and Na, necessary to form the blueschist meta-ironstone mineralogy. Such rocks therefore have the potential to reveal details of fluid expulsion within the subduction zone.

THE Laytonville Quarry exotic block is the type locality for the minerals deerite, howieite, and zussmanite (Agrell et al., 1965). Situated 8 km south of Laytonville (Mendocino County, California), the exotic block, originally 40 m in diameter has been halved in size by quarrying. The coarse-grained metamorphics of the block contrast with the surrounding sheared greywackes, but as the block arrived at its present position, 50 m above a nearby stream-bed, amongst landslides, field relations are insignificant. The block is rimmed with the remains of a metre-thick foliated and distorted tremolite rind. Through the centre of the block there is a fault that separates metabasites above from metasediments that show primary sedimentary layering and schistosity parallel to the fault plane. Small tight isoclinal folds have formed within the more incompetent Fe-rich horizons while the accom-

panying quartzites have become boudined. A view of the exposed geology of the block is shown in fig. 1.

In contrast to the apparent uniformity of the overlying fault-bounded metabasites, the sediments include a wide variety of compositions; most are Fe-rich, but with very variable additional amounts of Mn and Al. Their total exposed thickness does not exceed 15 m. Some of the middle horizons are graphite-rich and one of these was found to be vanadiferous. Towards the base of the sediments there are quartzites containing spherical nodules of Mn–Fe carbonates up to 50 mm in diameter. The ironstones pass sharply into underlying metabasites across a contact only exposed for a few metres at the base of the wall above the road.

Mineralogy

For details of analytical procedure used to obtain the data for Table I and the analysis recalculation, see the Appendix.
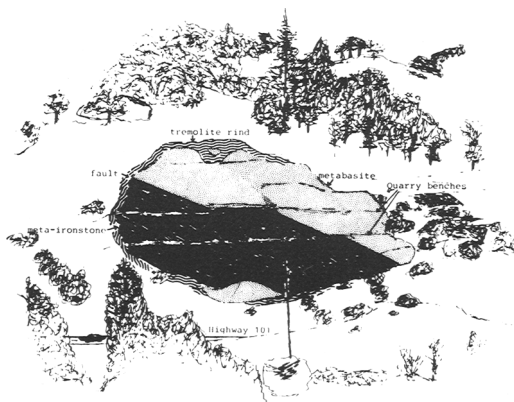

FIG. 1. Lithology of the Laytonville Quarry exotic block, viewed from the west.

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TABLE I. Selected meta-ironstone mineral compositions, from Laytonville Quarry (LQ), Ward Creek (WC), Panoche Pass (PC) and Powers Quarry (PQ)

Specimen	Calderitic garnet from PC83 (PC).	Vanadic- aegirine PA15 (LQ)	Mn-rich aegirine C307 (WC)	Ilvaite P8 (PQ)	Unknown A2131 (LQ)	Ekmanite (Nagy) C58 (LQ)	High-Mg stilpnome- lane,C44(LQ)	High-Mn(LQ) stilpnome- lane,102519	Trem/Act C82 (LQ)	Mg-rich riebeckite C130 (LQ)	Grunerite A2119 (LQ)
SiO_2	35.84	54.87	53.52	28.27	39.91	36.42	45.62	46.12	53.24	52.94	49.39
TiO_2	–	–	–	0.20	–	–	–	0.15	–	–	–
Al_2O_3	8.85	3.62	2.10	–	–	0.13	5.52	4.97	3.13	0.99	0.13
Cr_2O_3	–	0.19	–	–	–	–	–	–	–	–	–
V_2O_5	–	14.45	–	0.15	–	–	–	–	–	–	–
FeO*	19.46	12.27	18.88	46.61	24.71	37.31	19.01	25.33	11.40	25.10	33.76
MnO	29.78	–	3.70	4.48	25.08	11.37	3.88	9.85	3.11	1.33	8.90
MgO	–	–	3.69	–	0.27	4.52	9.72	1.71	15.24	5.27	4.64
CaO	5.83	1.05	8.06	11.73	–	0.14	0.28	0.11	11.78	0.98	0.45
Na_2O	–	13.44	9.34	–	–	–	1.33	–	1.45	6.10	0.20
K_2O	–	–	–	–	–	–	3.79	0.51	0.09	0.24	0.01
Total	99.65	99.88	99.29	91.45	89.98	89.96	89.14	88.76	99.44	92.43	97.46
Recalculated Cell											
Si	3.05	4.05	3.99	4.01	7.83	12.08	15.95	16.44	7.53	8.00	7.98
Ti	–	–	–	0.02	–	–	–	0.04	–	–	–
Al	0.89	0.31	0.18	–	–	0.04	2.27	2.08	0.52	0.18	0.02
Cr	–	0.01	–	–	–	–	–	–	–	–	–
V	–	0.85	–	0.02	–	–	–	–	–	–	–
Fe^{3+}	1.01	0.65	1.18	1.91	–	–	–	–	0.46	1.65	–
Fe^{2+}	0.37	0.11	0.02	3.71	4.05	10.34	5.56	7.57	0.89	1.60	4.56
Mn	2.15	–	0.23	0.54	4.17	3.19	1.15	2.97	0.38	0.17	1.22
Mg	–	–	0.41	–	0.08	2.23	5.07	0.90	3.22	1.21	1.12
Ca	0.53	0.08	0.64	1.78	–	0.04	0.11	0.04	1.78	0.17	0.08
Na	–	1.92	1.35	–	–	–	0.90	–	0.40	1.83	0.06
K	–	–	–	–	–	–	1.69	0.23	–	–	–
Total	8.00	7.98	8.00	11.99	16.13	27.92	32.70	30.27	15.18	14.81	15.04
O	12.00	12.00	12.00	17.00	24.00	40.00	96.98	95.35	46.00	46.00	46.00

* All iron listed as ferrous.

Garnet. Laytonville garnets are almandine-spessartines with the more almandinic compositions enriched in grossular and some of the spessartines with high calderite ($Mn_3Fe_2^{3+}Si_3O_{12}$) concentrations. According to Saxena (1968) the Ca content
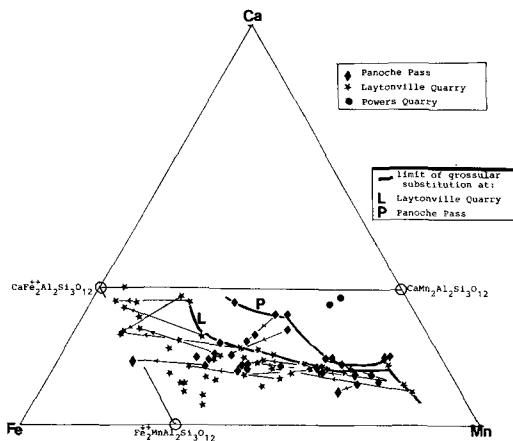

FIG. 2. Garnet compositions: the ternary grossular–almandine–spessartine system. Arrows indicate core–rim zoning vectors.

is a product of low temperature and is dependent on the presence or absence of an alternative Ca–Al phase such as lawsonite or epidote; grossular itself does not occur in blueschists. The maximum Ca/$(Ca + Mn + Fe^{2+} + Mg)$ is 1/3, see fig. 2.

Some of the more manganous ironstones contain myriads of tiny garnets that (inferentially) once contained calderitic centres but that have all subsequently been atolled; their cores can only be analysed where the garnets have been preserved intact within subsequent pyrite crystals (see Table II). Such calderitic garnets are only found in assemblages lacking aegirine.

In contrast garnets in reduced ironstones are large (0.5 mm across), but now skeletal, apparently having suffered resorption during the formation of adjacent zussmanites to leave almost homogeneous almandine–spessartines. Garnets from the meta-basites are almost Mn-free and are also far lower in pyrope than those that might be expected from a blueschist eclogite.

Pyroxene. All the Laytonville Quarry aegirines are zoned with cores more enriched in augite and rhodonite (see fig. 3). Several quartzitic assemblages contain remnant acmite-rich islets of the margins
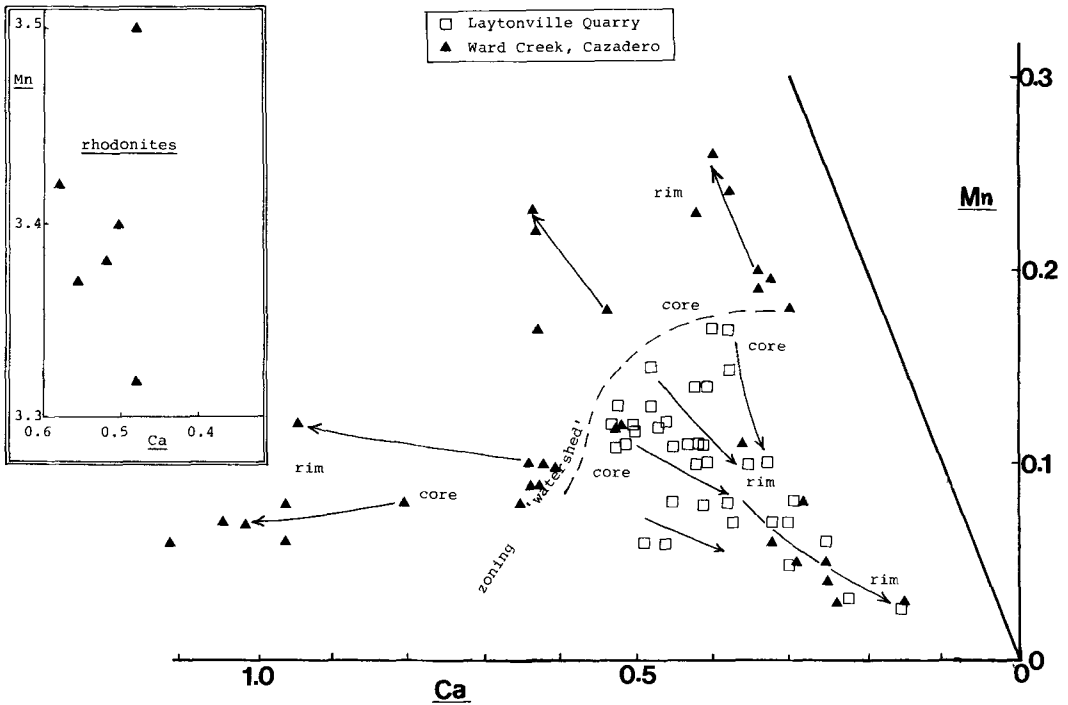
FIG. 3. Pyroxene compositions: the Mn *vs.* Ca system. Arrows indicate core–rim zoning vectors. 'Zoning watershed' marks boundary between zoning directions.

of atolled aegirines that have been largely replaced by quartz. One highly vanadiferous rock (PA15) contains vanadous aegirine with a chemistry that tends towards a V: $(Fe^{3+} + Al)$ ratio of $1:1$, see fig. 4. The combination of Fe and V has produced a startling 'traffic-light' red–orange–green pleochroism.

Amphiboles. The blueschist ironstone amphiboles are predominately sodic although grunerites are common in the reduced manganiferous assemblages. The sodic forms have a simple chemistry with almost negligible Al^{4+}, a vacant A site and very low Ca.

Late-stage amphiboles from the ironstones are all highly riebeckitic. In the more magnesic deerite-containing assemblages there are large primary amphiboles with riebeckitic rims but with cores of compositions close to $1:1$ riebeckite:magnesioriebeckite that appear to have formed contemporaneous with adjacent deerite. In Fe-rich metapelitic quartzites, crossite porphyroblasts, zoned from Fe^{3+}-rich cores to Al-rich rims, have been atolled, and their cores replaced by stilpnomelane and quartz (sometimes with chlorite), as described in Muir Wood (1980*a*). Metabasite amphiboles are Fe^{2+}-rich glaucophanes.

Gruneritic amphiboles, all with between one and two Mn atoms in the recalculated half unit-cell formula, are common in association with Mn–Fe carbonates. All the grunerite–deerite assemblages show a partial topotactic replacement of the rims of the grunerite by riebeckite in crystallographic continuity with the original crystal but with a sharp chemical discontinuity.
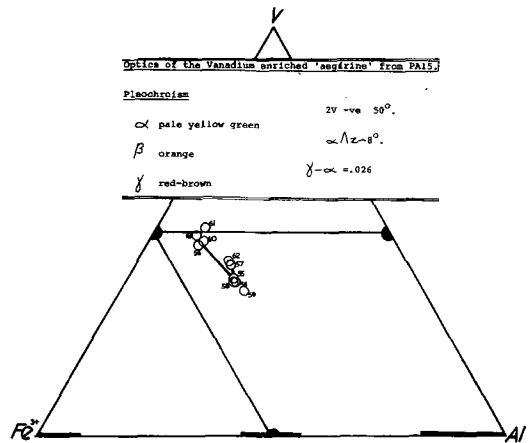

FIG. 4. Compositions of the vanadiferous aegirines from PA15, Laytonville Quarry, plotted on the ternary V–Al–Fe^{3+} system.

Calcic amphiboles are not important constituents of the ironstones but are found in the marginal replacement mineralogy close to the exotic block's rind.

Deerite. The chemistry and general phase relations of the characteristic blueschist meta-ironstone mineral deerite, that is so plentiful at the Quarry, were detailed in Muir Wood (1979a).

Howieite. The chemical, morphological and optical variants of howieite were detailed in Muir Wood (1979b). Massive well-crystallized howieites all have compositions around $NaMn_3Fe_8^{2+}(Mg, Al)Si_{12}O_{29}(OH)_{14}$.

Zussmanite. The zussmanite group of minerals was described in detail in Muir Wood (1980b). A new mineral, provisionally coded ZU2, with a similar cell-size to zussmanite, and with a comparable chemistry except for a greater Mn content, has been found to be of considerable importance in many of the late-stage replacement assemblages. Zussmanite, as originally defined is an important rock-forming mineral within Fe^{2+}-rich, Mn-poor pelitic assemblages. Mangano-minnesotaites (that also appear to be structurally related to zussmanite; Muir Wood, 1980b) are found as late-stage replacement minerals in a few assemblages.
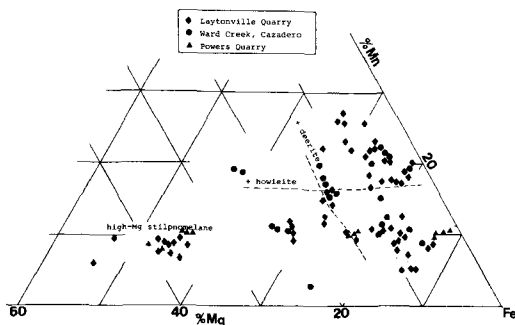
FIG. 5. Stilpnomelane compositions plotted on the Fe-Mn-Mg ternary system. Boundary lines mark coexistence with deerite and howieite.

Stilpnomelane. Stilpnomelane is found abundantly developed in almost all assemblages, principally consuming garnet and amphibole. The compositions appear to fall into two independent groups: normal low-Mg and rare high-Mg (see fig. 5); the former with a far wider range of Mn to Fe solid solution than the latter in which Mn/(Mn + Fe + Mg) is between 1:10 and 1:20. While all low-Mg stilpnomelanes produce K_2O totals (adjusted for microprobe beam diffusion) between 1 and 2 wt. % K_2O, the high-Mg stilpnomelane contains up to 5 wt. % K_2O. Although the high-Mg

and low-Mg forms have not been found coexisting there appears to be a compositional gap separating the two forms.

While the high-Mg form is invariably green and unoxidized, many of the low-Mg stilpnomelanes are oxidized, and as reported in Muir Wood (1980a) the quasi-isochemical (K for Na) replacement of crossite cores by stilpnomelane is impossible unless the stilpnomelane forms partially oxidized. All of the ferric-iron-rich assemblages also contain late-stage oxidized stilpnomelane and unless reduction was *always* superseded by oxidation it seems practical to consider that ferri-stilpnomelane is a stable blueschist-facies mineral.

Stilpnomelanes are generally massive, having grown in bow-tie clusters up to 10 mm in length, in sufficient profusion to give many of the rocks an anthracitic appearance.

Ekmanite. There is a divergence of usage whereby Shirozu (1964) applies 'ekmanite' to a stilpnomelane-type Mn-enriched, Al-poor calcic mineral that Matsueda and Hirowatari (1974) showed has a layer spacing of 12.7–12.8 Å. This contrasts with the 12.08 Å layer spacing found by Nagy (1954) in the Mn–Fe hydrous silicate from the type locality in Sweden. In several Laytonville assemblages the Mn-rich carbonates have been replaced by a fine-grained aggregate of ekmanite (Nagy). The intergrown clusters of platy crystals show yellow to green pleochroism and a birefringence of 0.025; otherwise they resemble chlorite. Their chemistry is simple; they are Fe–Mn hydroxy silicates with, in C58, moderate amounts of Mn (see fig. 6). The Fe is assumed to be all ferrous; on oxidation the mineral browns.
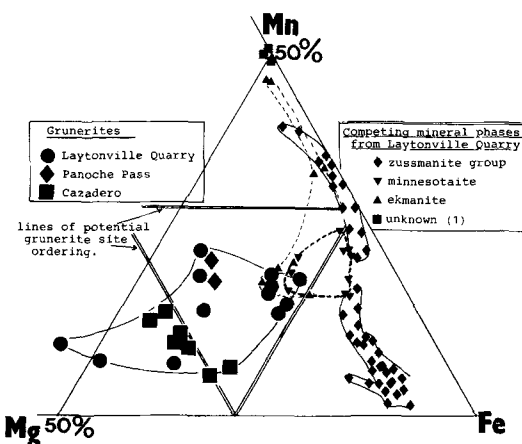
FIG. 6. Grunerites and associated hydrated iron silicates plotted on the $Mg–Mn–Fe^{2+}$ ternary system. Lines of 'potential site ordering' are 2:5 Mn:Fe+Mg, 2:5 Mg:Fe+Mn , and 2:5 Fe: Mn+Mg.

Chlorite. Chlorite is found as a late-stage replacement mineral in some of the more aluminous and basic assemblages.

Unknown. Within the most Mn-enriched of the assemblages (A2131) moderate sized clusters of a prismatic, colourless mineral with a simple hydrated silicate composition (Fe = Mn; Si/(Fe + Mn + Mg) = 8/8 − 8/9), have consumed an earlier texture of quartz and oligonite that is already partly pseudomorphed by ekmanite.

Carbonates. Carbonates are very plentiful in the quarry ironstones; their compositions lie close to the Mn–Fe and Mn–Ca edges of the Mn–Ca–Fe ternary system, see fig. 7. Their inter-relations are extraordinarily complex; there are six independent compositional clusters; oligonite, kutnahorites, two varieties of mangano-calcites with separate degrees of Mn-enrichment, one set of near end-member calcites, and aragonites (or the pure calcite pseudomorphs). The oligonites are the primary carbonates and are found unrecrystallized within the nodules at the base of the meta-sediments. At the rims of these nodules the carbonates have recrystallized to a more sideritic composition that is associated with garnet and quartz. Within most rocks oligonite is well crystallized, occurring as large rhombs.
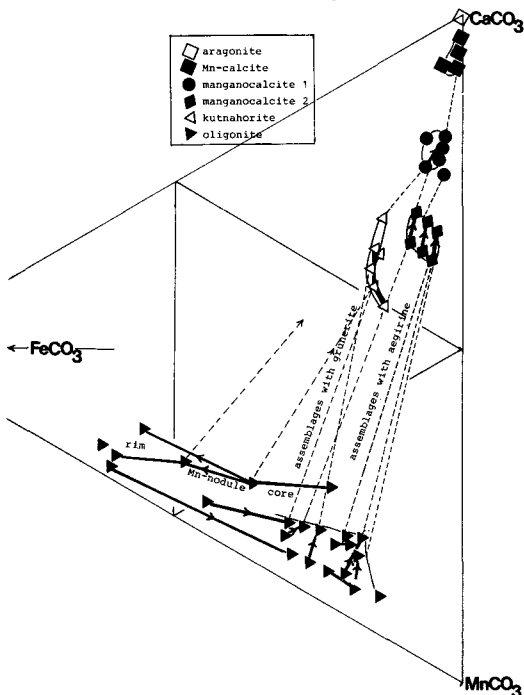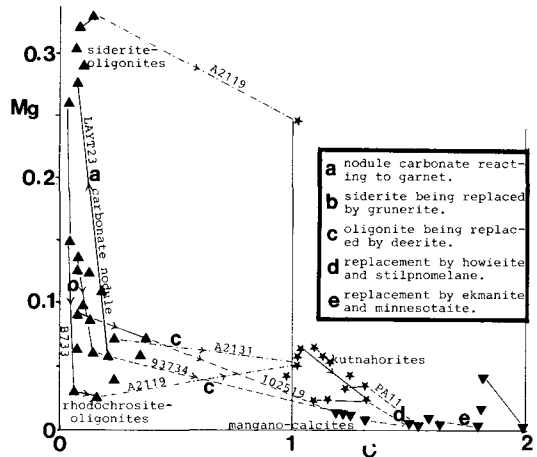

FIG. 8. Laytonville Quarry carbonates: Mg *vs.* Ca for the $M_2(CO_3)_2$ formula. Arrows and continuous lines indicate core-rim zoning vectors. Arrows and broken lines indicate one carbonate recating to another. Letters indicate associated and presumably causative recations.

The compositional zoning of these carbonates is dependent on the associated mineralogy: those that accompany garnet have rims enriched in siderite (garnet having a higher Mn/Fe partition coefficient); those that accompany only grunerite have rims enriched in rhodochrosite; those found in the more oxidized assemblages coexisting with aegirine are restricted to higher Mn/Fe ratios. Many of these earlier oligonites have gained subsequent poorly crystallized margins of more calcitic carbonates; those from the oxidized assemblages passing to mangano-calcite; those from the reduced assemblages passing to kutnahorite. The overlap in tie-lines seen on the Fe–Mn–Ca system only becomes disentangled when the extra componental dimension of Mg is introduced (as in fig. 8). During late-stage hydration oligonites, kutnahorites, and Mn-rich mangano-calcites all undergo partial decomposition leaving a more calcitic remnant. Howieite attack, for example, leaves an Mn-poor mangano-calcite; whilst ekmanite consumes all but the calcitic component. None of these late-stage reactions has, however, produced aragonite.

Ti-minerals. In many of the assemblages studied there is sufficient Ti to form a specific mineral; only deerite amongst the associated mineralogy can tolerate high TiO_2 (up to 7 wt. %). The Ti-containing minerals are sphene, rutile and mangano-ilmenite.

Sphene is common in the metabasites and in some of the ironstones, sometimes enclosing remnant fragments of rutile. Tiny irregular plates of mangano-ilmenite are restricted to Fe^{2+}-rich
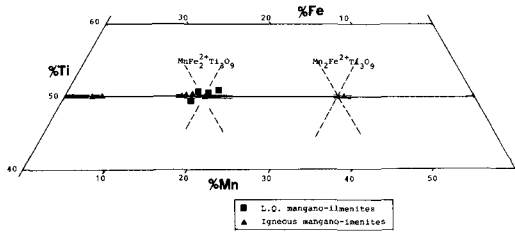

FIG. 7. Laytonville Quarry carbonate compositions: the Mn–Fe–Ca ternary system. Solid lines indicate continuous zoning profiles, broken lines indicate new carbonate phase rimming old carbonate phase.

FIG. 9. Mangano-ilmenite compositions: the Mn–Fe^{2+}–Ti ternary system.

pelitic stilpnomelane schists and have compositions almost identical to those found in acid igneous intrusions clustering around MnFe$_2^{2+}$Ti$_3$O$_9$, see fig. 9.

Fe oxides. These are completely absent from the Quarry rocks apart from a few lamellae of magnetite within degrading crossites (Muir Wood, 1980a).

Sulphides. Pyrite and chalcopyrite are scattered throughout the assemblages, but only become major rock-forming minerals in some of the graphite–quartzites. Both minerals have in general remained inert to the passage of metamorphism but in one rock (C130) chalcopyrite is being consumed by the late-stage zussmanite-type mineral ZU2. Significant quantities of Zn and Co have been found within inclusions in the chalcopyrites.

Graphite. Graphitic material occurs in some of the more reduced meta-ironstones.

Apatite. In general no more than an accessory mineral, but in one assemblage (1C2482) deerite and zussmanite are being replaced by thick apatite veins.

The metamorphic assemblages

Almost all the assemblages studied contain some sequential mineral development, a characteristic of blueschist metamorphics (Muir Wood, 1979c). Through stripping away the palimpsest minerals it is often possible to retrieve the series of compatible minerals that existed during earlier periods of the rock's history. The procedure involved is illustrated in the above paper. In order to avoid a

TABLE II. Laytonville Quarry metamorphic assemblages

	Rock chemistry	Fe^{3+}-ironstone	Mn-Fe^{3+}-ironstone	Mg-Fe^{3+}-ironstone	Fe^{2+}-Fe^{3+}-ironstone	Fe^{2+}-ironstone	Mn-Fe^{2+} pelitic ironstone
M	Primary	Qtz-Hem/Goe					Oli-Qtz-?
E	Early	Aeg-Qtz-Alm	Aeg-Qtz-Spe/ Alm-Rho-Gru	Aeg-Qtz-MgRie		Alm-Qtz	Alm/Spe-Sid
T	Middle	Dte	Dte-MCa	Dte	Rie-schist Dte-schist	Zus-Ara-(Gra)-(Dte)	
A	Late	Rie-Sti	Rie(1)-Sti-How(2)-ZU2	Rie-Sti	Sti	Sti-Rie	Sti-Ekm MnMinn(3)
M							

	Chemistry (cont.)	Mn-Fe^{2+}-ironstone	V-Fe^{3+}-ironstone	Pelite	Pelitic quartzite	Mg-pelite	Basic	Rim
O								
R								
P	Primary							
H	Early	Rho-Gru-Cal Cal/Alm	VSp-VAeg- Gra-Qtz		Phe-Alm- Qtz-Cro(5)	MgGru	Epi-Alm- (Omp?)	
I	Middle	Kut-Dte(4)	Dte	Cro-schist	Fer		Gla-Law- Mus-Alb- Ara(6)	
S								
M	Late	How-Ekm- Unk	Sti	Sti-schist (Act)	Sti-(Chl)	Sti	Act-Alb- Chl-Sti- Ara	Chl-Tre-Tal- Mus(7)

Notes. Laytonville Quarry meta-ironstones are remarkable for their late-stage mineralogy, for the large size of individual crystal clusters, the widespread replacement, and the several periods of fluid infiltration. The metamorphism (in combination with the chemistry) must represent some kind of extreme, as zussmanite still has a unique locality.
(1) Stilpnomelane and howieite grow as large radiating crystal clusters and cause the resorption of adjacent deerites and aegirines; the aegirines atolling, the deerites fragmenting.
(2) K and Na appear to have been available throughout the development of the late-stage mineralogy.
(3) Mangano-minnesotaite partly consumes the stilpnomelane.
(4) Calderite centres of garnets dissolved during formation of deerite.
(5) Massive crossite porphryoblasts with ferroglaucophane overgrowths from partial decomposition of adjacent almandine have suffered late-stage atolling with the amphibole cores replaced by stilpnomelane and quartz.
(6) Albite replaces some lawsonite and both albite and aragonite replace garnet. Away from such veins garnets suffer late-stage attack from chlorite and stilpnomelane.
(7) Rocks adjacent to the rim have suffered pronounced Mg metasomatism; almandine garnets are partly replaced by highly magnesic chlorite and talc, and sodic amphiboles by tremolite, except the most carbonate-rich rocks where talc and aragonite take the place of calcic amphibole.
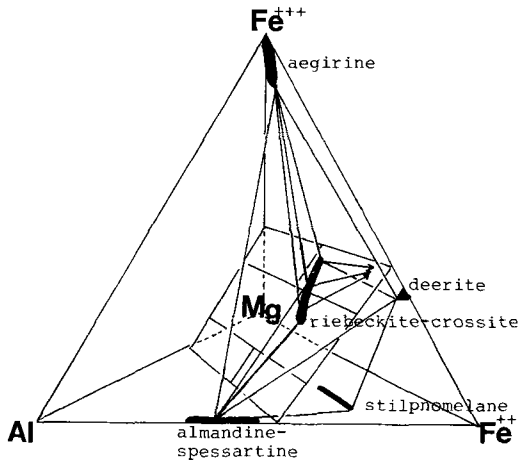
FIG. 10. The essential Laytonville Quarry meta-ironstone compatibilities for the middle stage of metamorphism: the Fe^{2+}-Fe^{3+}-Mg-Al quaternary system.

terminology that includes the concepts of meta-morphic culmination and retrogression that may be misleading for high-P, low-T metamorphics (see Muir Wood, 1979d), the periods of mineral formation have been classed in Table II as being simply 'early', 'middle' or 'late' relative to one another.

In order to display the phase information contained in Table II it is necessary to choose component diagrams that are both sufficiently expanded to separate diverse assemblages and sufficiently compact to be readily comprehended. Through testing various alternative plotting strategies it was discovered that the alkalis (Na, K and Ca) were responsive to the major Mg, Fe, Al, and Mn chemistry. Thus, through ignoring alkalis, no ambiguities of phase assemblage are introduced. This remarkable result is discussed below. Silica is always in excess, leaving the five components Fe^{2+}, Fe^{3+}, Al, Mg, and Mn to be the true determinants of assemblage mineralogy for a given stage of the metamorphic history. Unlike the blueschist meta-basites there is no standard mineralogy (such as lawsonite–albite) from which the rest of the assemblage may be plotted. Thus the componental diagrams are illustrative rather than exact plots of phase chemistry. The standard mineralogy for the Mn-free assemblages for both the middle stage of metamorphism is illustrated in fig. 10. Assemblages from the middle stage of metamorphism are plotted to include Mn in the quaternary Mn–Fe^{2+}–Fe^{3+}–(MgAl) system in fig. 11.

In order to place the Laytonville Quarry assemblages in some chemical and metamorphic context, material was collected from a number of other blueschist meta-ironstone localities. The most im-

portant of these were Ward Creek, Cazadero, Sonoma County, California (see Coleman and Lee, 1963), Panoche Pass, San Benito County, California (see Ernst, 1965) and Powers Quarry, Coos County, Oregon. Both the Ward Creek and Panoche Pass localities although structurally complex, have not been considered by their respective mappers to be exotic. At both localities there are, however, distinct and separate eclogite knockers. The Powers Quarry is a large exotic block approximately 200 m across, that like the Laytonville locality has provided material for road-stone. Very small quantities of meta-ironstones have been found as rubble at the base of the exposure—the bulk of the material is blueschist metabasite.
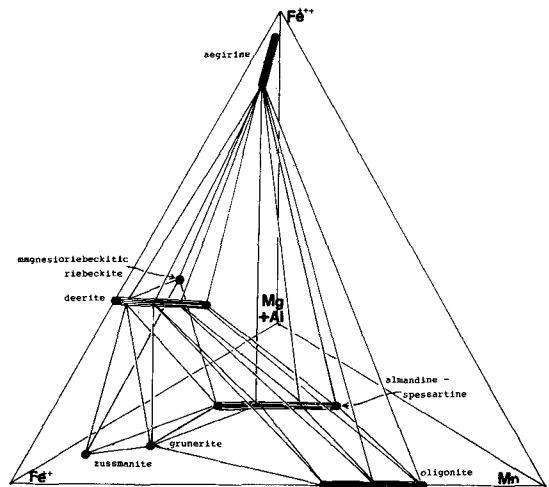

FIG. 11. Laytonville Quarry meta-ironstone compatibilities for the middle stage of metamorphism: the Fe^{2+}-(MgAl)- Fe^{3+}-Mn quaternary system.

The simplest assemblages are found at Panoche Pass where the rocks are predominantly granular garnet–aegirine gneisses with thick layers of apatite that have become pervasively veined with deerite and riebeckite. Only one rock, a manganese nodule embedded in meta-ironstone, was found to contain howieite. Other ironstones are quartzitic; none contain any carbonate. Some of the Ward Creek meta-ironstones are identical to those from Panoche Pass. Others are more manganous, containing rhodonite, manganese oxide, spessartine, and mangano-aegirine with replacement mangano-howieite. Several of the assemblages contain minor oligonite carbonate. Stilpnomelane is rare at Panoche Pass and of minor importance at Ward Creek, the rocks never gaining the anthracitic appearance of those from Laytonville.

The Powers Quarry assemblages are remarkable for containing no deerite but instead abundant ilvaite [ideal formula $CaFe_2^{2+}Fe^{3+}Si_2O_8(OH)$], with associated howieite in the more manganous assemblages. Fragments of almost unmetamorphozed greenalite chert are found in some of the ironstones and the general metamorphic grade as indicated by the degree of recrystallization is low. Replacement mineralogy in some of the ironstones includes riebeckite, aegirine, aegirine augite and even minor quantities of ZU2 in the most manganous assemblages. Pelitic ironstones consist of high- or low-Mg stilpnomelane partially replaced by actinolite. The metabasites are epidote-glaucophane-phengite assemblages with late-stage veins of lawsonite, pumpellyite, and chlorite. Metabasites which preserve a doleritic texture contain minor omphacite formed, it is presumed, from the topotactic alteration of augite. The ironstone assemblages are represented in fig. 12.

Mineral stabilities

In order to construct a blueschist meta-ironstone P-T grid it is necessary to compile the relevant information on mineral stabilities.

Deerite. The simplest ideal deerite-formation reactions are, in order of increasing temperature, from: magnetite + greenalite + silica; from magnetite + minnesotaite + water; and from magnetite + grunerite + silica + water. The P-T slopes of these theoretical reactions have been plotted in Muir Wood (1979a). In general, however, deerite formation is inter-related with the breakdown of riebeckite and magnetite; reactions dependent on the local a_{Na+}:

1. riebeckite + water = magnetite + deerite + silica + Na$^+$
2. riebeckite + water = aegirine + deerite + silica + Na$^+$
3. riebeckite + water = deerite + crossite + silica + Na$^+$
4. magnetite + water + silica + Na$^+$ = aegirine + deerite.

Some of these ideal blueschist-facies reactions between the various Fe-oxides and silicates are plotted for $a_{(OH)-}$ *vs.* a_{Na+} in fig. 8 of Muir Wood (1979a). In real rock systems it is very rare to find ironstones entirely free of Al and Mg, when reaction (3) becomes important. Crossite-deerite assemblages are found at all deerite localities. The importance of rival sodic mineralogy limits the use of deerite as a critical T-P indicator.

Ilvaite. The reaction between deerite and ilvaite,

5. deerite + calcite = ilvaite + CO_2 + water

prevents deerite forming under certain blueschist-facies conditions in the presence of a very low P_{CO_2}.

Howieite. The howieite stability field can only be estimated from the associated mineralogy. Attempts to synthesize howieite (Lattard, pers. comm.) have failed.

Zussmanite. From mapping the theoretical and actual phase relations it is possible to show a stability field for zussmanite between the high-temperature stilpnomelane breakdown reaction to grunerite + biotite and the minnesotaite breakdown to grunerite. The exclusivity of zussmanite to Laytonville suggests that zussmanite, chemically very similar to stilpnomelane, must be restricted by very high pressures (see Muir Wood 1980b).
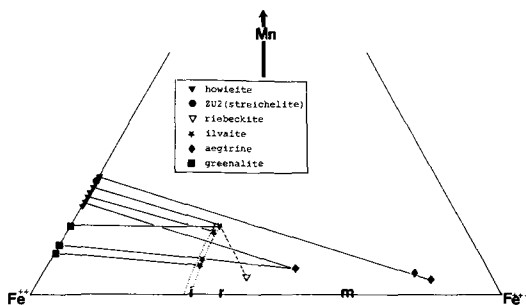

FIG. 12. Powers Quarry meta-ironstone assemblages: the Mn-Fe^{2+}-Fe^{3+} ternary system. (Ideal end-member mineral compositions of ilvaite 'i', riebeckite 'r', and magnetite 'm'.)

Grunerite. The Mn-enrichment of the blueschist grunerites probably extends the amphibole's stability range down from the end-member metamorphic minimum of 350-400 °C (French, 1968) towards 300 °C.

Sodic amphiboles. The stability fields of the sodic amphiboles were considered in Muir Wood (1980a). As a simplification, the increase in Al is a function of pressure, that of Mg a function of temperature; only riebeckite is stable at low-T and low-P, but breaks down within the blueschist facies to allow the uninterrupted compatibility of deerite and aegirine.

Carbonates. Through the extrapolation of known experimentally determined phase relations (Goldsmith, 1959, and Goldsmith and Graf, 1957 and 1962) and with the assumption that the divalent ion carbonate solvi are essentially congruent, it is possible to construct the complete rhodochrosite to calcite solvus (see fig. 13). Such phase relations are assumed to be effectively pressure invariant.
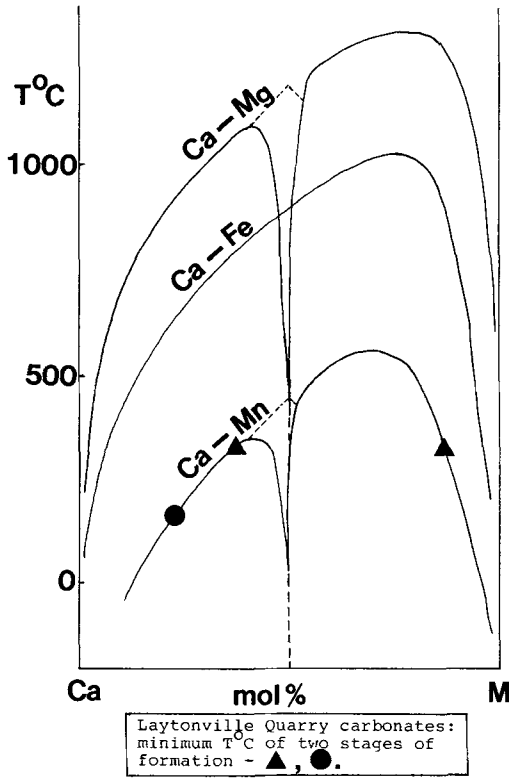
FIG. 13. Limits of the Laytonville Quarry carbonate solid solutions plotted on the rhodochrosite to calcite solvus. (Solvus derived from extrapolation and congruency with $FeCO_3$–$CaCO_3$ and $MgCO_3$–$CaCO_3$ solvii.)

Although it is possible to construct an approximate P-T grid for deerite (see Muir Wood, 1979a) in order to map the P-T history of the Laytonville Quarry exotic block it is necessary to consider the nature of the episodes of fluid infiltration.

(i) The relative $CO_2/H_2O/CH_4$ concentrations of the fluid. The stability of ilvaite relative to deerite + calcite in the Ca–Fe^{2+}–Fe^{3+} system becomes interrelated with the stability of the calcic amphibole, and within the extended Na–Ca–Fe^{2+}–Fe^{3+} system, with the augite solid-solution of aegirine. Under normal blueschist facies conditions only high Mg/Fe^{2+} calcic amphiboles are stable, and even under these conditions it may be in competition with the rival aragonite + talc assemblage, as found in certain Laytonville quartzites adjacent to the tremolite rind. Only at Powers was the P_{CO_2} sufficiently low to allow actinolite to form within the iron-enriched stilpnomelane schists.

The pyroxene solid solution is dependent on the competition from the rival carbonate Ca(Fe,Mg,

Mn)$(CO_3)_2$ (ankerite). Thus for the highest P_{CO_2} assemblage (Laytonville) the aegirine has the lowest augite component. At Powers Quarry (the lowest P_{CO_2} locality) 1:1 aegirine–hedenbergite is stable. The rival assemblage mineralogies for the extremes of P_{CO_2} are plotted in fig. 14.

The partition of Ca between carbonate and garnet reduces those spessartines coexisting with carbonates at Laytonville to low grossular contents. For more ferrous-iron-rich rock compositions in which siderite + quartz has been replaced by some hydrated Fe^{2+}-silicate (such as zussmanite) the garnet composition can extend to higher Ca-levels (see fig. 15). Only at Powers are grossular-rich spessartines stable (see fig. 2).

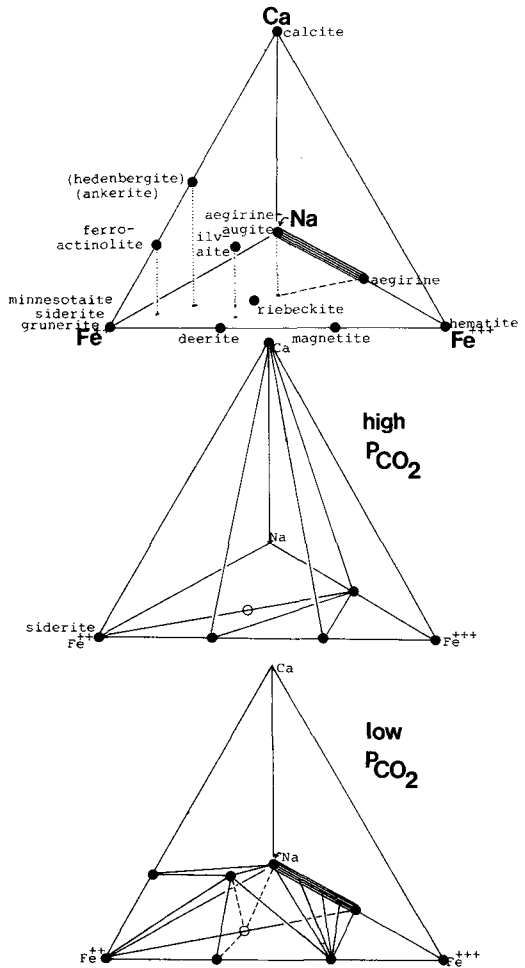Although components such as CH_4 may have had an important effect as dilutants within the

FIG. 14. Influence of P_{CO_2} on pyroxene, amphibole, and ilvaite/deerite stability: the Fe^{2+}–Fe^{3+}–Na–Ca quaternary system.
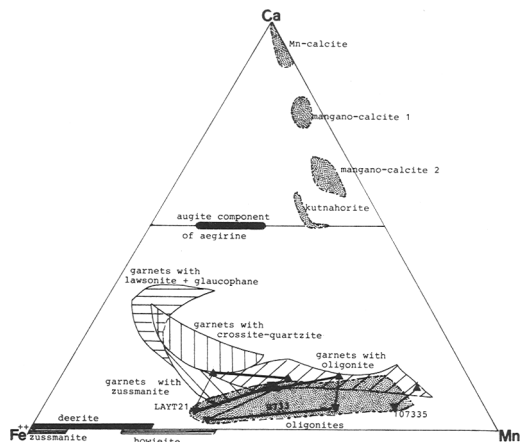
FIG. 15. Relationship between Laytonville Quarry garnet and carbonate compositions. Narrow lines represent phase compatibilities, thick lines represent continuous zoning profiles.

graphitic meta-ironstones, the extremely low δD values of deerite and howieite (Magaritz and Taylor, 1976) indicated that the fluid associated with the formation of these minerals never equilibrated with any such species.

(ii) The ability of the Fe-rich sediments to alter composition during metamorphism was first noted by Miyashiro (1967): goethite chert becomes recrystallized as aegirinite. The extraordinary ubiquity of this process (there are no relict iron oxides or hydroxides at Laytonville) was accounted for in Muir Wood (1977) as a product of the catalytic intervention of a fluid in order to allow recrystallization to take place at all. The composition of this metamorphic fluid need not be out of the ordinary to maintain an adequate background activity (and supply) of sodium to produce aegirine and, or, riebeckite, from the earlier iron oxide or hydroxide and silica phases. The existence of metamorphic sodic and potassic iron-enriched minerals and the alkali-free nature of most sedimentary ironstones makes such rocks 'alkalisponges' during the course of burial. The high early enrichment of Na in the Franciscan ironstone assemblages has provided a 'pool' from which late-stage howieite and riebeckite can abstract their requisite alkali. Through this ability to absorb externally-derived alkalis, ironstones are capable of recording incidents of fluid infusion in a way that would be impossible for a metabasite. Thus the K needed to form the late-stage stilpnomelane 'bloom' at Laytonville must have been externally derived as the only pre-existing potassic minerals (zussmanite and phengite) are of relatively minor

importance. At the Covelo meta-ironstone locality (see Muir Wood, 1979b) the sodic mineral howieite has extended its solid-solution range to cover compositions that would otherwise be contained by stilpnomelane. Evidently the fluid that determined this late-stage development of hydrous minerals was somehow K-depleted.

The introduction of Ca into the rocks is only of importance at Powers Quarry where actinolite and ilvaite have developed.

(iii) There is considerable divergence in style of fluid intervention between the two exotic blocks (Laytonville and Powers Quarries) and the two more conformable Franciscan formations (Ward Creek and Panoche Pass). At the two latter localities the entry of water to form deerite and riebeckite was restricted to sheet-like planar zones, spaced 5 to 20 mm apart in the foliated schists and gneisses, but distributed more irregularly within the more plastic formations. At Powers both fluid infiltration and deformation were more penetrative; the schists are permeated along numerous fissile lines and the quartzites have suffered fine-scale fracturing. At Laytonville the gneissic rocks have maintained integrity and the fluids have passed through almost all rocks without any restriction to specific zones.

Although at Powers there is no evidence for discriminating between the various episodes of hydrous mineral formation (ilvaite, howieite, actinolite), at Laytonville the first episode that formed deerite and zussmanite was clearly well separated in $P-T$ from the second episode in which howieite, stilpnomelane, riebeckite and ZU2 were produced. This second stage might be continuous with a third stage in which tremolite and talc flourished within the metabasites, and ekmanite and minnesotaite developed in the meta-ironstones.

Magaritz and Taylor (1976) found that the Laytonville metacherts, in parallel with those from Ward Creek, were markedly lowered in ^{18}O during metamorphism, and have approached homogenization with the accompanying metabasites. The Laytonville meta-ironstones, however, showed some of the most extreme deuterium partition values with deerite $\delta D = -102$ and howieite $\delta D = -98$, whilst much higher values (-53 to -61) were found within accompanying metabasites. Such low values within the Fe-rich minerals could only have formed through hydration reactions that have introduced water into the rocks during metamorphism. Such reactions were proposed on petrographic grounds (Muir Wood, 1979c) to account for the increasing water content of the blueschist meta-ironstone minerals, with regard to their remnant antecedent mineralogy.
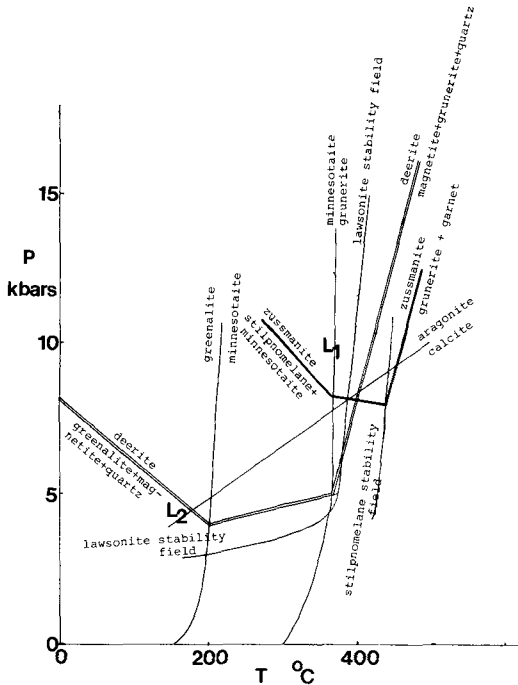
FIG. 16. Blueschist facies reaction grid with approximate positions of the 'middle' (L_1) and 'late' (L_2) stage conditions of the Laytonville Quarry metamorphism.

Fig. 16 is an attempt to locate the various phases of the Laytonville Quarry exotic block $P-T$ journey on the metamorphic grid as presented in Muir Wood (1979a, 1979c, 1980a, and 1980b).

Origin of the ironstones

All four of these Fe–Mn sediment localities occur in close proximity to basalts; at both Laytonville and Powers the sediments actually rest on basalts. All four localities also have $(Fe + Mn)/Al$ and Fe/Mn values typical of East Pacific Rise spreading ridge sediments (Edmond et al., 1979). The Panoche Pass ironstones are more oxidized than those from Laytonville, contain abundant apatite, no carbonate and a single manganese oxide nodule (PC53). The Powers Quarry sediments are similar though more reduced, having precipitated in the form of Fe–Mn silicates. The presence of baryte in one specimen and the absence of carbonates make Powers along with Panoche, typical of modern spreading ridge deposits.

The variations in Laytonville Quarry chemistry include: fluctuations in the oxidation state of the ironstones from hematite-goethite cherts to carbon-rich sediments; high V concentrations, and the almost ubiquitous Fe–Mn carbonates. The

carbon precipitation necessitates anaerobic sedimentation; under such reduced conditions the V would be precipitated directly out of solution passing from V^{5+} to V^{3+}. The quantity of carbonate within the sediments suggests a local source beyond that which could be supplied by bottom waters alone. The inverse relation between Al and Mn concentration suggests that Mn was precipitated out of solution before it could enter into some potential sheet silicate. Modern deep-ocean sediments only show rhodochrosite saturation within buried pore fluids (Lynn and Bonatti, 1965).

The Franciscan

The sediments of the Franciscan can be divided into a pre-subduction group that formed on ocean-crust, and a group of trench sediments. While the former group may become subducted or scraped off the down-going slab, the latter sediments become deeply piled and may suffer a lowered geotherm, but are unlikely to get truly 'subducted'. Some of the deep-ocean sediments, particularly the limestones, appear to become disconnected from their associated ocean-crust almost as a matter of course. The ironstones, being small in volume, resting directly on the basalts, and being relatively dense, are likely to be subducted.

The most easily identified orientation of the piled mélange units of the Northern Coast Ranges Franciscan is provided by long stringers of serpentinite that tend to outcrop along a NW–SE orientation that becomes interrupted by the San Andreas Fault and its imbricated parallel faults.

The intrusion of these faults marks a change in the pattern of serpentinite intrusion in the surface Franciscan outcrop, from the less disturbed Diablo Range, southeast of San Francisco, to the dissected belt around San Jose, San Francisco and within Marin and Sonoma counties. The most complex pattern lies to the north of the Russian River in Sonoma County where a series of wedges of blueschists have become uplifted into younger and largely unmetamorphosed subduction complex material. It is in this region that there is the greatest development of eclogite blocks, and also where the line of eclogites moves inland (to the north) away from the San Andreas Fault (see fig. 17).

The Franciscan eclogites are restricted to the west of the Cretaceous subduction zone complex following, within the North Coast Ranges, the outcrop of the Cenomanian-Turonian Laytonville Limestone. Metamorphic ages of the eclogites have been obtained from late-stage mineralogy and thus have given only minimum ages: around 150 Ma for phengites and glaucophanes (Lee et al., 1964). One age from an omphacite of 174 Ma might
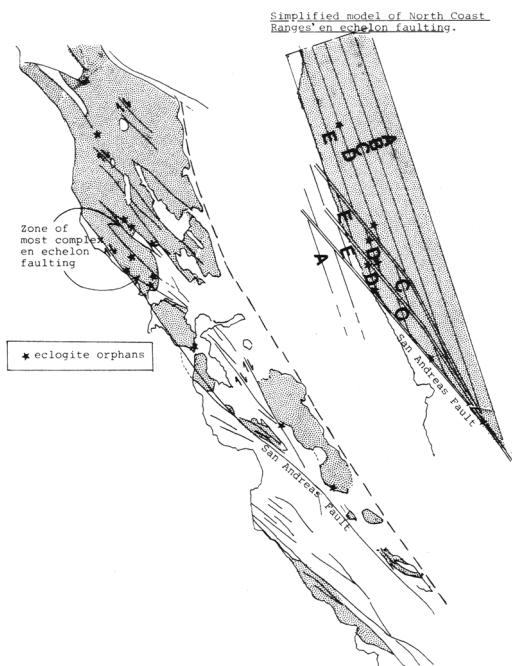
FIG. 17. En echelon offsets in the San Andreas Fault zone and the outcrop of eclogites in the North Californian Franciscan.

represent the actual date of eclogitization. Suppe and Armstrong (1972) obtained an age of 145 ± 3 Ma from late-stage mica from Laytonville Quarry metabasites that is compatible with the other age dates for Laytonville Mélange Unit exotic blocks of between 138–153 Ma (Gucwa, 1975), ages that are older than the associated mélange material.

Many of the eclogite blocks, in common with the Laytonville Quarry block, have remnant segments of a coarse-grained matted and lineated tremolite rind enveloping them. At some stage in these blocks' history they were immersed in a mobile, highly magnesic, hydrated medium, such as serpentinite. This period of immersion must also account for their having been brought from the subduction zone, up to the surface, within serpentinite diapirs.

Conclusion

The Laytonville Quarry exotic block has been carved out of a presumably oceanic section of ironstones resting on, and enclosed by, basalts. The ironstones formed under sporadically anaerobic, CO_2-rich conditions, that endured sufficiently to allow a finely banded series of layers to form of at least 15 m total thickness. Such conditions could

only have been maintained within some trap or downfaulted sea-floor depression. The fault that separates the ironstones from overlying metabasites may have come into operation during the first stages of lithosphere bending associated with subduction and thus ensured that the ironstones were incorporated into the basaltic crust. Boudined quartzites and carbonate nodules reveal that the sediments were undergoing tensional shear after consolidation but before the earliest period of metamorphic aegirine and garnet mineral growth. Movement was principally concentrated along sedimentary discontinuities and may have been associated with actual subduction; only quartz and calcite have grown within the fractures formed at this period.

The strangest chapter in the history of these rocks is their failure to continue down into the Mantle. Instead the rocks have suffered considerable hydration while buried at least 15–20 km underground, during which period deerite and zussmanite were formed within the meta-ironstones. This segment of ocean crust acted as a channel for escaping fluid that was emerging from deeper dehydration reactions. For all these exotic blocks the sampling process that brought the metamorphics to the surface is likely to have determined much of the latest stage of the metamorphic history. The serpentinite eroded around the ironstones leaving them sandwiched between two layers of metabasites.

Whilst travelling within the serpentinite the block was rounded and sheafed in a thick tremolite rind that formed out of the partial decomposition of the metabasite and that wrapped around the whole block, even those zones bordered by meta-ironstone. To one end of the block, now the upper end, this tremolitic material developed into a massive bulge that enclosed a fragment of metabasite that appears to have become detached from the major unit—one small incident in the process of abrasion has been frozen.

The subsequent history of where the block remained and how it became included within the 90 Ma subduction zone complex is unknown. That the age and the degree of metamorphism of the Franciscan exotic blocks is somehow related does, however, suggest a more continuous process of overturning whereby only the most deeply buried material from the earliest period of subduction along the Western American plate boundary, has a chance of survival.

work would have been impossible without the opportunities to work on rocks collected by Dr S. O. Agrell. The whole project has been very dependent on the rapid analysis facilities available in the former Department of Mineralogy and Petrology and grateful acknowledgement is made to the sectioners, polishers, and microprobe assistants.

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APPENDIX

The mineral analyses were all obtained on two electron microprobes in the Department of Mineralogy and Petrology, Cambridge: a Cambridge Instrument Geoscan wavelength-dispersive system, using individual element standards; and an energy dispersive system, using a cobalt standard and a St. John's olivine sample for quality control.

The failure of the electron microprobe to resolve the Fe^{2+} and Fe^{3+} spectral lines has been compensated for by analysis recalculation with the assumption of the two simultaneous equations that are considered inherent within the nature of the crystal structure: charge balance, and site occupancy. For some minerals this method is straightforward, and the results appear to be reliable: garnet has 24 (+) charge, and 8 cations; pyroxene has 12 (+) charge and 4 cations; ilvaite has 17 (+) charge and 6 cations. For some of the silicates studied there appears to be essentially no ferric iron: zussmanite, chlorite, ekmanite, greenalite. For other minerals variable site occupancy patterns complicate the recalculation procedure and require some additional equations and assumptions: for amphiboles, see Appendix 1 of Muir Wood (1980a). The recalculation of deerite (Muir Wood, 1979a) has not been highly satisfactory often providing an excess of 'Si'. Both stilpnomelane and howieite have additional problems in that the two equations are not independent. Both minerals have been recalculated here as if they are Fe^{2+}-rich forms; because of variable potassium count rate during analysis the stilpnomelane formula has been recalculated on the basis of 30 cations excluding the alkalis (approximately a 1/4 unit cell). The oxidation state of the iron in these minerals can only be estimated from phase compatibility and colour.