

# The iron-rich blueschist facies minerals: I. Deerite

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**SUMMARY.** The mineral deerite is restricted in occurrence to blueschist facies meta-ironstones. From the ideal formula of  $\text{Fe}_{12}^{2+}\text{Fe}_6^{3+}\text{Si}_{12}\text{O}_{40}(\text{OH})_{10}$  there are a limited range of substitutions: Ti and V for  $\text{Fe}^{3+}$  and Mn on the  $\text{Fe}^{2+}$  site. In the present survey of deerite compositions from the majority of deerite localities the maximum substitutions have been 2Ti and 3Mn in the above formula. There is an at present unexplained anomaly in the totals of a number of the analyses indicating that there may be variations away from the ideal formula towards increased hydroxyl and decreased cation contents.

From differences between the mineral compatibilities of deerites from the higher-grade Franciscan exotic block blueschist localities and those from more conformable Alpine blueschists, in conjunction with previous work on the experimental stabilities of the low-pressure/low-temperature hydrous iron silicate minerals, it has been possible to map the form of the low-pressure deerite stability field involving reactions of greenalite or minnesotaite or grunerite with magnetite and quartz. Within the deerite stability field, further deerite-forming reactions involve the breakdown of riebeckite and the hydrous incompatibility of magnetite with quartz; both are very dependent on the activity of sodium. A low-pressure stability to 4 kb at 200 °C and 6 kb at 300 °C are estimated from these low-temperature breakdown reactions. This fits in well with the high-pressure deerite stability determinations of Langer *et al.* (1977).

THE mineral deerite is now recognized as being of considerable importance within meta-ironstones of the blueschist facies. It has been found in suitable metamorphics from: the Franciscan terrain (both in exotic blocks and in more coherent formations), Oregon, Washington State, the Alps, Corsica, Turkey, Greece, and New Caledonia, such that it can now be considered a normal blueschist facies indicator. The total, so far, of eighteen reported localities is listed in Table I. The absence of deerite from some (higher-temperature) blueschist terrains (such as Japan), and its presence in boundary facies (as at Shuksan, Washington State) indicate that its stability range is not quite the same as that of the normal facies indicators: glaucophane-crossite and lawsonite.

Deerite is a ferrous-ferric hydrous iron silicate

TABLE I. *Deerite localities*

1.	Laytonville Quarry, Mendocino County, California: Agrell <i>et al.</i> (1965).
2.	Ward Creek, Cazadero, Sonoma Co., California: Coleman and Lee (1963).
3.	Panoche Pass, San Benito Co., California: Ernst (1965).
4.	Pacheco Pass, California: Ernst <i>et al.</i> (1970).
5.	Burn's Flats, Mendocino Co., California: Agrell (unpubl.).
6.	Covelo, Mendocino Co., California: Muir Wood (1977).
7.*	Beauregard Creek, Santa Clara County, California: Muir Wood (1977).
8.	Wild Horse Lookout, Curry County, Oregon: Coleman (1972).
9.	Powers Quarry, Coos County, Oregon: Coleman (pers. comm.).
10.	Finney Creek, Shuksan Unit, Washington State: Brown (1974).
11.	Termignon, Haut Savoie, France: Bocquet (1971).
12.	Salbertrand, Piedmont, Italy: Agrell and Gay (1970).
13.	Beth e Ghinivert, Piedmont, Italy: Bocquet and Forette (1973).
14.	Cervione, Corsica: Collected by Essene (unpubl.).
15.	Sifnos, Greece: Schliested (1978).
16.	Sübren-Karaalan, Eskisehir County, Turkey: Taylan Lünel (1966).
17.	Diahöt Valley, New Caledonia: Black (1973).
18.	Ouegoa Koumec, New Caledonia: Coleman (1967).

\* Preliminary identification.

with an accepted ideal formula of (half-cell contents)  $\text{Fe}_{12}^{2+}\text{Fe}_6^{3+}\text{Si}_{12}\text{O}_{40}(\text{OH})_{10}$ . It can be present within iron-enriched rocks of a wide range of intermediate oxidations.

Deerite was discovered twenty years before being recognized as a new mineral, by Lacroix (1941) who mentions a grunerite-magnetite-quartzite with riebeckite, from Diahot, New Caledonia (a rock re-examined by Black, 1973) in which 'ces amphiboles sont accompagnées de grenat almandin rose renfermant des aiguilles opaques d'un mineral qui semble

être de la goethite' (p. 71). These unidentified black needles were shown by Black to be deerite. In Ellenberger (1958) there is a description of 'un mineral presque opaque' (pl. 18, text p. 261) within iron-rich concretions from near Termignon, France (identified as deerite by Bocquet, 1971); and Coleman in 1959 noted the presence of a mineral, referred to as a 'black ortho-amphibole' in material from Cazadero (published as Coleman and Lee, 1963). All these various unidentified black needles were found to be 'deerite' as the result of investigations on material collected from a small roadside quarry south of Laytonville, Mendocino County, California (subsequently referred to as the Laytonville Quarry) that was studied by Agrell in 1963, presented at a meeting of the Mineralogical Society in May 1964 (Agrell *et al.*, 1964) and subsequently published as an abstract (Agrell *et al.*, 1965), along with descriptions of the accompanying new mineral species, howieite and zussmanite.

**Structure.** The presence of pervasive submicroscopic diad twinning of the  $P2_1/a$  cell has thwarted several attempts at structure determination, and has led to at least one spurious published solution (Wenk *et al.*, 1976). The structure finally conceived by Fleet (1977) was from an untwinned deerite edge of a crystal from material collected by R. M. W. at Panoche Pass, California (specimen PC65). The octahedral ribbons of the structure form a kind of honeycomb, with chains of  $\text{Si}_6\text{O}_{17}$  single-linked rings (as in howieite) running through the cavities. Hydroxyl sites and the positions of the various octahedral ions remain to be ascertained. Three groups of octahedral ion sites had, however, already been identified from magnetic susceptibilities and Mössbauer work (Carmichael *et al.*, 1966; Bancroft *et al.*, 1968; Frank and Bunbury, 1974). A series of small-scale phase transformations discovered in the above work and also found in DTA investigations (R. C. MacKenzie, unpubl.) suggest that problems of relative adjustment between the ribbons of this compact structure are critical. A similar imposition on structural flexibility is suggested by the constancy of cell dimensions despite variable substitution of Mn and Al (Langer and Schreyer, 1970; Bocquet and Forette, 1973).

**Chemistry.** Through the limitations of the electron-probe-determined compositions, the chemistry of deerite has been imprecisely treated in the literature. There are only a few wet chemical compositions: seven from Laytonville Quarry (in which the water content has been determined in four) and one from Cazadero (Coleman and Lee, unpubl.). All of these have been of deerites that are easy to separate and these are all from the simpler manganese-poor assemblages. Other authors who

have published deerite compositions have found separation impossible and have chosen to present electron-probe analyses corrected according to one of the wet chemical ones. Thus, Agrell and Gay (1970) and Bocquet and Forette (1973) apply the same ferrous/ferric ratio as was found in the wet chemical analysis of the deerite from specimen 93727 (Laytonville Quarry), which is relatively manganese-enriched. A more realistic recalculation of their analyses is presented in Appendix 3.

The deerite analysis of Agrell and Gay (1970), using the 93727 water content of 4.25 wt%, sums to only 96.36 wt% oxides. Similarly Brown (1974) (who inverted the method and assumed  $(\text{OH})_{10}$  in the final formula: 4.12 wt%  $\text{H}_2\text{O}$ ) obtained for his Shuksan deerite a total of 97.3 wt% oxides. Both of these analyses on recalculation to 30 cations and 90 charges (see Appendix 2) have a problem, that is common to a number of the analyses listed in this study, of containing about 5% too much silicon in the recalculated unit cell. It seems possible that the ideal formula, particularly with regard to hydroxyl content and octahedral cation vacancies, is not without variance.

The chemistry of deerite is relatively simple in terms of the recognizable substitutions of octahedrals; manganese, magnesium, aluminium, vanadium, and titanium may all substitute for iron. Of these, manganese is the most significant with a maximum of 3 Mn ions being incorporated into the half-cell formula. Both magnesium and aluminium are trace impurities (except in the synthetic alumino-deerite, Langer and Schreyer, 1970). Vanadium is scarce in most Laytonville Quarry deerites except those from PA10, 102454, and B153 in which  $\text{V}_2\text{O}_3$  may be as high as 2.8 wt%. In PA15, a vanadium-rich assemblage that includes a new vanadous form of aegirine with 15 wt%  $\text{V}_2\text{O}_3$ , it is likely to be still higher, but the deerites are too small to analyse (Abraham has obtained values as high as 4 wt%  $\text{V}_2\text{O}_3$  from Laytonville Quarry deerites—pers. comm.). All these assemblages are reduced and graphite-rich; vanadium substitutes direct for ferric iron. The only other vanadium-enriched deerites are those found in Alpine assemblages. At Beth e Ghinivert (Bocquet and Forette (1973) failed to analyse for either vanadium or titanium) the deerite in specimen R10 contained about 1 wt%  $\text{V}_2\text{O}_3$  and those from Termignon were all vanadium-enriched with up to 2.54 wt%  $\text{V}_2\text{O}_3$  in T6.

Titanium concentrations may be still higher; Ti substitutes for ferric iron but for charge-balancing it must be accompanied by a divalent ion, generally ferrous iron, so lowering the oxidation state of the mineral:  $\text{Fe}^{2+}\text{Ti} = 2\text{Fe}^{3+}$ .

Thus it is found enriched in deerites from the

more reduced rocks, unlike the vanadium, which is enriched in the rock as a whole through reduction-precipitation in the original sediment. Titanium enters deerite instead of forming a mineral of its own: rutile, sphene, or mangano-ilmenite (characteristic of blueschist facies meta-pelites), which in rare instances may individually coexist with deerite. The maximum recorded  $\text{TiO}_2$  content is 7.21 wt% in B153 from Laytonville Quarry, but moderate concentrations are common in many of the accompanying rocks as well as those of Panoche and Cazadero; the average being around 1 wt%  $\text{TiO}_2$ . Within the Alpine localities the deerites from R10 (Beth e Ghinivert) and all the Termignon specimens are titanium-enriched as well as containing up to 0.65 wt%  $\text{Cr}_2\text{O}_3$ .

All these substitutions, particularly the manganese, show susceptibility to local chemical conditions; the Alpine deerites are all manganese-poor as the assemblages in which they occur are lithologically distinct from the oceanic iron-manganese sedimentary facies of the Franciscan. The effect of divalent ion substitution, as with manganese, raises the internal oxidation state (the ratio of ferric iron to total iron), that of trivalent and tetravalent ion substitution lowers it: see fig. 1.

Chemical zoning has not been observed in deerite; along with stilpnomelane it is the only mineral within the iron-rich blueschist facies rocks that has a potential for solid solution, but does not zone. Instead the deerites within one rock or one probe section may be of differing compositions along a regular trend of manganese enrichment with decreasing total iron and manganese, the deficiency being filled by titanium. Such trends can be seen on fig. 2. This balance of manganese and titanium substitution is remarkably close to the constant oxidation state substitution ratio of 5:1 Mn:Ti. Other composition plots for deerites from the individual localities are presented in figs. 3 and 4.

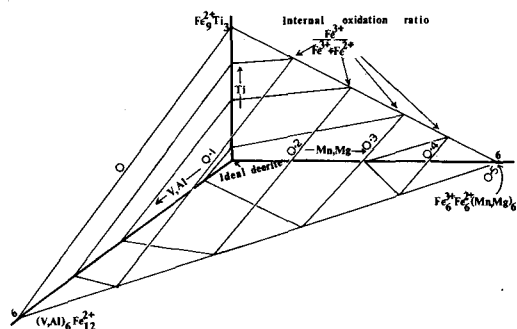


FIG. 1. Variation of internal oxidation state  $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$  of deerite for the principal chemical substitutions.

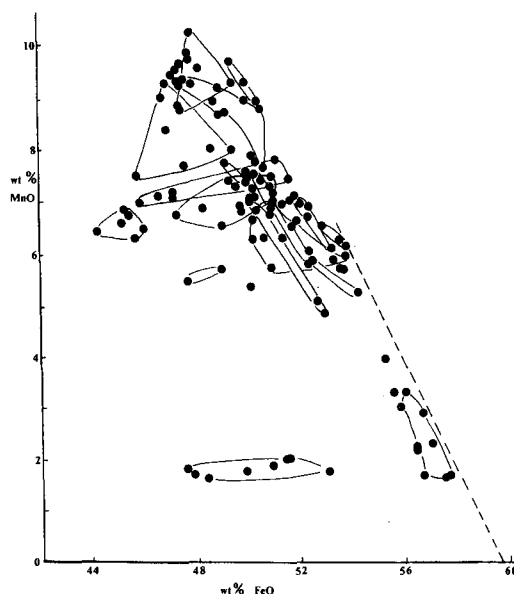


FIG. 2. Compositions of deerite from Laytonville Quarry, California. Wt% FeO v. wt% MnO. (All iron recalculated as ferrous.)

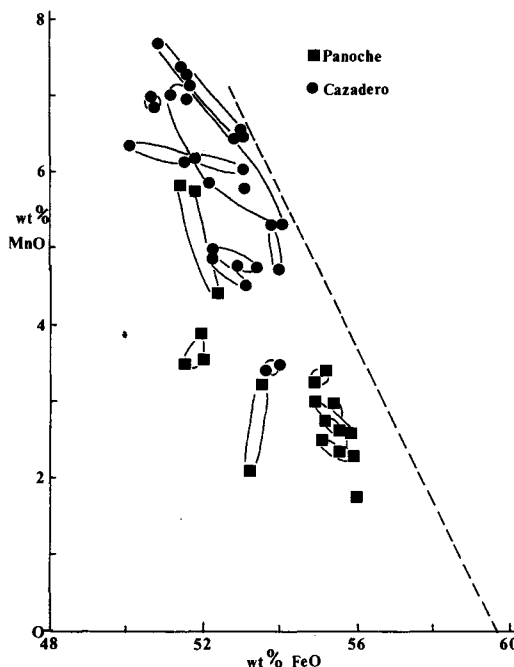


FIG. 3. Compositions of deerite from Panoche Pass and Ward Creek, Cazadero, California. Wt% FeO v. wt% MnO. (All iron recalculated as ferrous.)

As compositional annealing is most unlikely, it appears that the homogeneous deerite crystals grew from a latently supersaturated environment in which the partition coefficients for component cations between the minerals and the immediate chemical environment have been approximately unity. In many of the Franciscan assemblages it is clear that deerite has not developed to its full potential within an assemblage; many minerals that are beginning to resorb remain essentially intact when their component chemistry could readily be assimilated into the deerite. These partial reactions, which are so convenient for the identification of former mineral assemblages, are a result of the restricted entry of water; all the

deerite-forming reactions for the Franciscan involve hydration. Thus the mineral has been latently supersaturated and once water is present, grows rapidly, homogeneously, and at the control of the immediate chemistry. As the activity of water declines, the mineral returns to its latency. The concentration of manganese in deerite, stilpnomelane, and background is generally identical. Some deerite textures are illustrated in fig. 5.

Within the Alpine deerite localities studied it is less simple to find the assemblage that existed prior to the appearance of deerite, but at Termignon it is clear that deerite has arrived through the isochemical replacement of its hydrous precursors. Zoning would be anticipated, but the deerite crystals are too small to permit a compositional traverse. A simplified analysis of the deerite-forming reactions is presented in the next section.

At the Laytonville Quarry, the entry of deerite into assemblages formerly composed of aegirine, grunerite, garnet, and manganese-iron carbonates is roughly contemporaneous with that of the appearance of zussmanite, but pre-dates the formation of riebeckite, howieite, and stilpnomelane. The gap in compositions of deerites between 3–5 wt% MnO appears to reflect a difference in these earlier assemblages between the manganese poor ones, in which the ferrous iron must have been contained within hydrous silicates such as greenalite or early riebeckite (now largely missing) and the manganese-enriched assemblages in which the deerite coexists with iron-manganese carbonates. Controls imposed by a former mineralogy appear to have interrupted the continuum of secondary mineral compositions. At Panoche and Cazadero there is no such gap, but also an absence of carbonates (in all but a few of the Cazadero manganese-enriched assemblages). Deerite at these localities is associated with an episode of hydrous intrusion that also produced howieite. A breakdown and analysis of the mineral and metamorphic histories of these assemblages will appear in forthcoming papers.

*Paragenesis.* Attempts to synthesize deerite have recently met with some success; Langer *et al.* (1977) have produced the ferric end-member after previously manufacturing more aluminous forms of the mineral (Langer and Schreyer, 1970) when trying to form almandine (Keesman *et al.*, 1971) (a solid solution has been shown to exist between end-member deerite and 20 mol% of a hypothetical aluminous end-member). Langer *et al.* found that the ferric end-member could only be synthesized with a Ni/NiO oxygen buffer, but it is clear from natural assemblages of deerite that this restriction is not general. The breakdown products that they obtained (ferrosilite + magnetite + quartz) are likely to be metastable variants on the anticipated

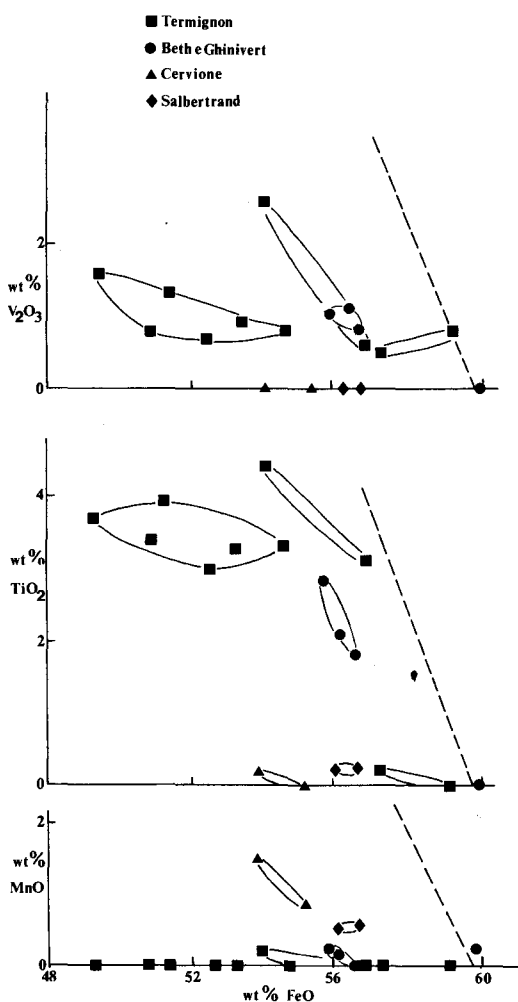


FIG. 4. Alpine deerite compositions. Wt% FeO v. wt% MnO, TiO<sub>2</sub>, and V<sub>2</sub>O<sub>3</sub>. (All iron recalculated as ferrous.)



FIG. 5. Deerite textures:  $\times 30$ . *a*, 'Franciscan' deerite. (Laytonville Quarry specimen 102520.) Explosion texture of radiating deerites from a single spherule of quartz within an aegirinite. *b*, deerite resorption. (Laytonville Quarry specimen 109784.) Unzoned deerite fragmented on replacement by quartz, concomitant on near-by howieite growth. Adjacent aegirines are atollated. *c*, 'Alpine' deerite. (Termignon specimen T3.) Minor amount of small deerite crystals imbedded in calcite associated with reaction between chlorite and magnetite.

grunerite + magnetite + quartz product (grunerite breakdown temperatures of  $650^{\circ}\text{C}$  were found experimentally (Ni/NiO buffer) by Forbes, 1977). Langer *et al.*'s work was performed at pressures in excess of 15 kb (ferrosilite breaks down to fayalite and quartz below 13 kb) and there are some problems in extending their metastable breakdown curves to more realistic blueschist  $T$ - $P$  regimes.

The position of deerite within the hydrated iron silicate system is represented in fig. 6: the  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  quaternary system. The low-temperature stabilities of the low-pressure hydrous iron silicates are themselves poorly known. The overlapping greenalite and minnesotaite stabilities of Flaschen and Osborne (1957) were partly

resolved by Grubb (1971) who found greenalite reacted to minnesotaite at  $150^{\circ}\text{C}$  although more recently Floran and Papike (1975) have discovered solid solution between them. Minnesotaite reacts to grunerite between  $270$  and  $300^{\circ}\text{C}$  (Forbes, 1971) and siderite reacts with chert between  $350$  and  $400^{\circ}\text{C}$  (French, 1968, 1973). The composition of the accompanying fluid is the single most important determinant in all these dehydration or decarbonation reactions. Under the appropriate chemical conditions they can all be said to be stable (Garrels and Christ, 1965), so it is only through the generalized equivalence of fluid behaviour during low-grade metamorphism that these minerals may be used to determine isograds (e.g. French, 1973 or

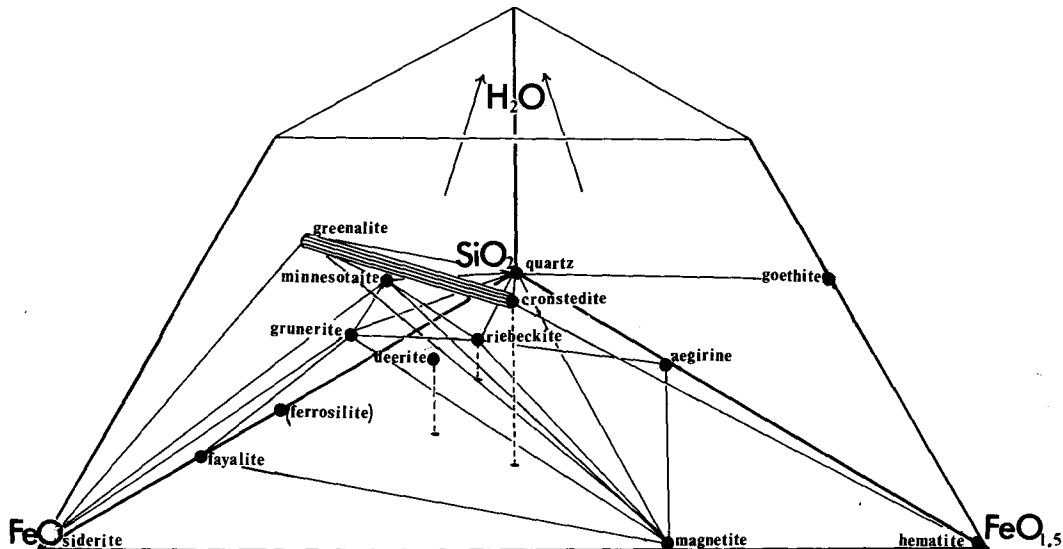


FIG. 6. The position of the deerite composition within the low-pressure hydrated iron silicate compatibilities:  $\text{FeO}-\text{Fe}_{1.5}\text{O}-\text{SiO}_2-\text{H}_2\text{O}$  quaternary system.

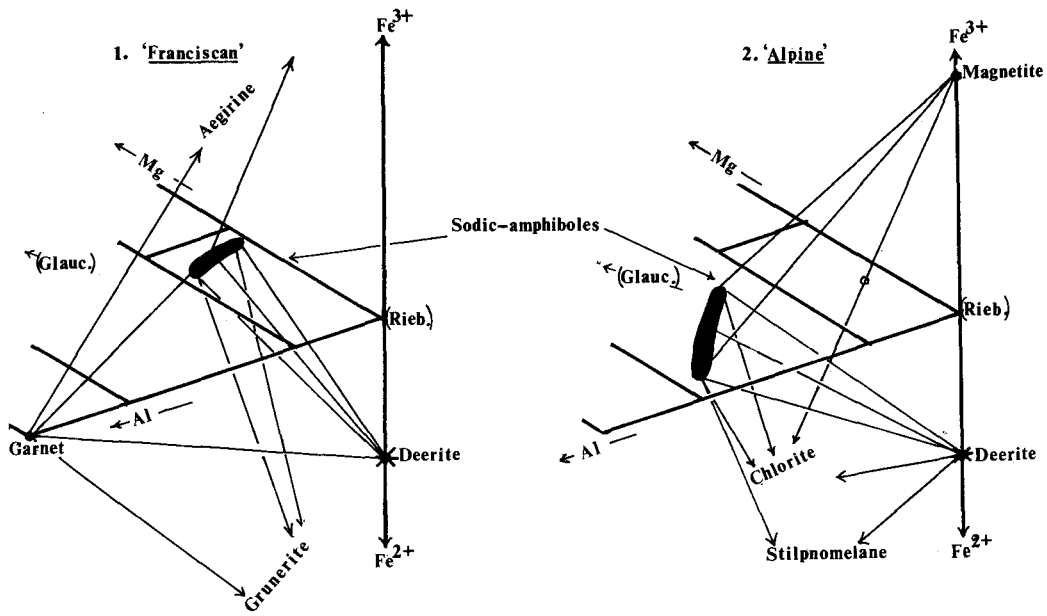


FIG. 7. Alternative high-grade 'Franciscan' and low-grade 'Alpine' compatibilities. Simplified  $Fe^{2+}$ - $Fe^{3+}$ -Mg-Al hydrous silicate system centred on the sodic amphibole plane of compositions.

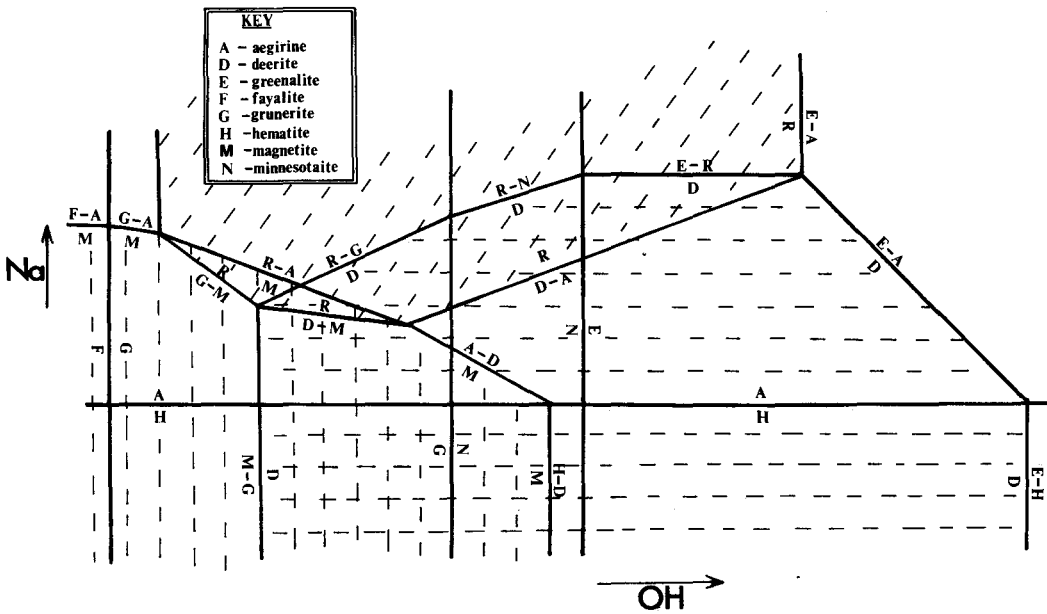


FIG. 8. The relative stabilities of the iron silicates at high pressure-low temperature: for  $\mu Na^+$  plotted against  $\mu OH^-$ .

Burt, 1973) that can even be extended to include the sodic and potassic species, crocidolite and stilpnomelane (Ayres, 1972).

Deerite must fit into the high-pressure side of these low-pressure iron silicate stabilities. Reactions are:

$3/4$  Greenalite + 3 magnetite + 6 silica = deerite + 3 water.

$9/7$  Grunerite + 3 magnetite +  $12/7$  silica +  $17/7$  water = deerite.

$3/2$  Minnesotaitite + 3 magnetite + 2 water = deerite.

$9/2$  Fayalite + 3 magnetite +  $15/2$  silica + 5 water = deerite.

From the 25 °C, 1 atmosphere pressure, cell dimensions, recalculated for the formula unit (magnetite  $73.98 \text{ \AA}^3$ , Deer *et al.*, 1962; quartz  $37.65 \text{ \AA}^3$ , Deer *et al.*, 1962; greenalite  $763.99 \text{ \AA}^3$ , Steadman and Youell, 1958; grunerite  $459.5 \text{ \AA}^3$ , Finger and Zoltai, 1967; minnesotaitite  $484.76 \text{ \AA}^3$ , Gruner, 1944; fayalite  $77.03 \text{ \AA}^3$ , Deer *et al.*, 1962; deerite  $926.5 \text{ \AA}^3$ , Bown and McKie, unpubl.) it is possible to gain a rough estimate of volume changes.

The dehydration of greenalite to form deerite involves a loss of volume (excluding water) of 10%; the hydration of minnesotaitite-magnetite also involves a loss of volume of about 5%; thus the formation of deerite from this reaction, on increasing pressure, will tend to attract water into the rock (!). The reaction from grunerite-magnetite-silica involves hydration and a solid volume increase (neglecting the volume of water) of a little over 5%, though for both this reaction and for the hydration of the fayalite-magnetite-quartz there is an *over-all* density increase for the production of deerite when the volume of water is included in the calculations.

The greenalite-minnesotaitite transformation and the minnesotaitite-grunerite transformation will both intersect the deerite stability field and mark sudden changes in the  $P$ - $T$  gradients of the deerite boundary reactions. At the lowest pressures of deerite stability the maximum temperature should be around 350 °C (the intersection of the minnesotaitite-grunerite boundary). The lower-pressure stability is more difficult to estimate, but the presence of deerite in blueschist/greenschist boundary facies, as at Shuksan (Brown, 1974) suggests its stability range parallels that of lawsonite, which extends to slightly lower than 5 kb fluid pressure.

Deerite-formation reactions within the meta-ironstones are confused by the presence of additional phases. From the evidence of the Franciscan, riebeckite (which has a very similar composition to deerite) is no longer stable, the assemblage deerite-aeigrine-quartz taking its place. Magnetite, missing

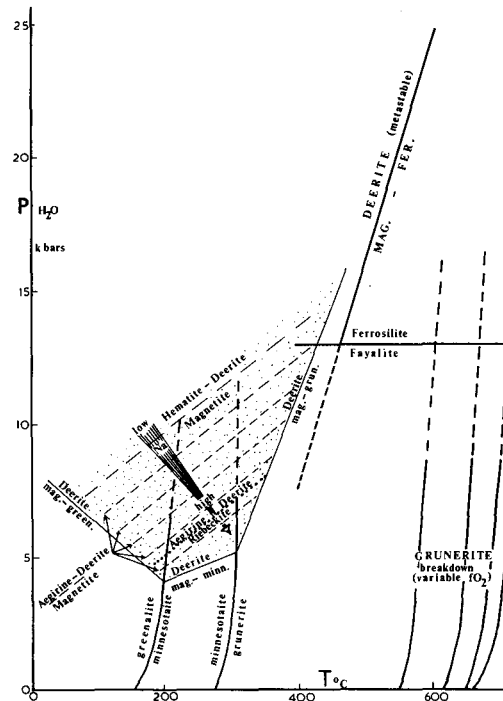


FIG. 9. The relative stability of the iron silicates, particularly deerite:  $P_{\text{H}_2\text{O}}$  v.  $T$ .

from the Laytonville Quarry (and nearly all Franciscan) assemblages, is, however, found in the Alpine meta-ironstones coexisting with deerite. The breakdown reactions for magnetite (with quartz) and for riebeckite are very dependent on the activities of sodium and water. The differences between the mineralogy coexisting with deerite in Franciscan exotic block assemblages and those from Alpine localities are represented in fig. 7. The relative importance of the fluid concentrations for blueschist facies mineral stabilities is plotted in fig. 8.

Through a combination of information extrapolated from the high-pressure experimental deerite breakdown reactions of Langer *et al.* (1977), from the low-pressure stabilities of the hydrous iron silicates, and from the theoretical topology of reaction, partly gained from the actual blueschist facies mineral assemblages, fig. 9 is constructed to indicate the position of deerite within blueschist facies  $P$ - $T$  conditions.

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