

Metasomatism in the Wairere Serpentinite, King Country, New Zealand

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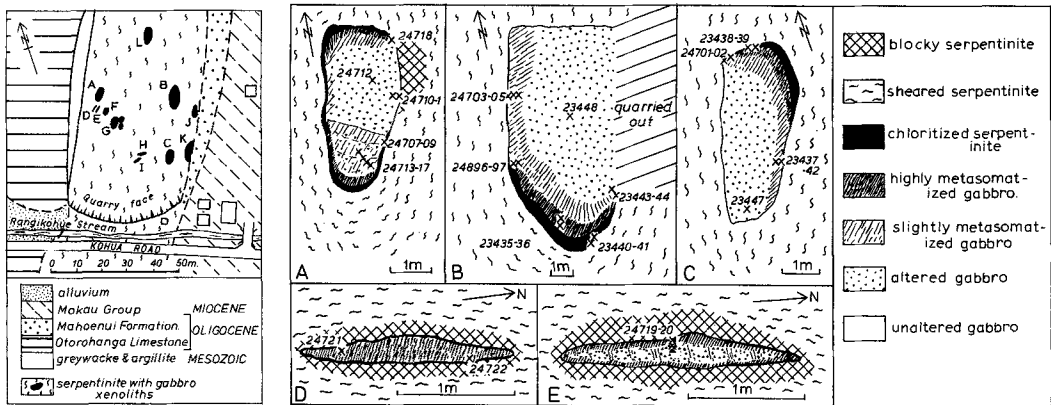
SUMMARY. Metasomatic zones formed at the borders of various mafic inclusions in the Wairere Serpentinite, central North Island, New Zealand, show eucritic and hornblende gabbros grading through distinct zones of altered gabbro (hydrogarnet-free) to coarse and fine-grained rodingites (hydrogarnet-bearing). The hydrated, calcium-rich, aluminium-silicate mineral assemblages of each reaction zone change between the zones, with one mineral phase being altered to another at each replacement front. Initial alteration of the gabbros albitized, prehnitized, and epidotized plagioclase and chloritized hornblende and clinopyroxene. Continuing metasomatism garnetized prehnite and generated secondary amphibole and pyroxene while the original host harzburgite was highly serpentinized and, adjacent to the inclusions, the serpentinite was chloritized so as to form a further distinct zone between peridotite and gabbro. These mineral replacement reactions are reflected in the bulk chemistry of the reaction zones, which show that increasing alteration of the gabbro is accompanied by a marked increase in Ca and H₂O, a possible small gain in Mg, and depletion in Si, Al, and alkalis. These trends are balanced in the host peridotite by Si enrichment and Ca loss upon serpentinization. Clinopyroxenes and hornblendes of the zones show an increase in Ca and Mg and a decrease in Si with increasing metasomatic alteration. Garnets also decrease in Si but chlorites show an increase in both Si and Mg. Additional minerals analysed from both primary and altered rocks include olivine, orthopyroxene, biotite, plagioclase, pectolite, rosenhahnite, sphene, and chrome spinel. The zones are regarded as the result of reaction between the inclusions and Ca- and Al-rich solutions derived, in turn, by action of alkaline, CO₂-poor solutions, which percolated through fractures in the original host peridotite and, in the process of serpentinization, released Mg and enhanced Ca and Al levels. At the contact of the mafic inclusions, chemical gradients were generated down which various chemical species diffused to different levels forming the zonation. The reactions probably took place in the vicinity of 260 to 350 °C, 2 to 3 kb, and at constant volume. Cataclasis and brecciation of the outer zones indicate more than one metasomatic episode.

THE Wairere Serpentinite has been described by O'Brien and Rodgers (1973a; 1974). Ca meta-

somatism at the contacts between serpentinite and included eucritic gabbro pods was briefly reported on by the same authors (1973b). This account is a far more comprehensive study of the metasomatic rocks and minerals and is based on samples collected from the active quarry in 1973-4. Fig. 1 shows the main serpentinite quarry area as it was in those years (cf. O'Brien and Rodgers, 1973a, fig. 2).

Localities B, J, K, and L are eucritic-gabbro pods, which were partially quarried out and stood, *in situ*, in sheared serpentinite. C and G were similar gabbros that had been totally blasted but lay on the quarry floor. All these pods had smooth, slickensided outer surfaces. Locality A was a relatively unaltered hornblende gabbro pod, *in situ*, close to the western contact of the serpentinite. The pod consisted of a highly jointed and fractured block in contact with a more massive segment. The contacts with the highly sheared serpentinite were smooth and slickensided. A zone of chloritized serpentinite irregularly bounded the pod. Locality D proved to be a highly metasomatized gabbro; locality E, an altered hornblende gabbro. Both were interpreted as dyke fragments. H and I were rodingite veins, one containing hornblende and the other pyroxene, occurring in blocky serpentinite. The hornblende rodingite was heavily mantled with a hard white hydrogrossular zone. In addition to these localities, a blocky, *in situ*, serpentinite pod F, unusually rich in relic harzburgite minerals, was collected.

Five pods (fig. 2) were studied in detail. In each, three major metasomatic reaction zones were well developed: altered gabbro, rodingite, and chloritized serpentinite. For the purpose of this study, the term *reaction zone* is used for all metasomatized rocks within the Wairere Serpentinite while *rodingite* is used for that metasomatic phase containing garnet derived by metasomatism (cf. O'Brien and Rodgers, 1973b). *Altered gabbro* defines those portions of the gabbroic inclusions that have undergone some metasomatism but do not contain garnet.



FIGS. 1 and 2: FIG. 1 (left). Map of the main quarry area of the Wairere Serpentinite as in 1973-4. (Surrounding geology after O'Brien and Rodgers, 1973a.) Capital letters refer to pod localities, discussed in text. FIG. 2 (right). Field sketches of the various inclusions that were investigated in detail showing sample numbers referred to in text.

Sample numbers used are those of the University of Auckland rock and mineral collection and are usually cited by way of example only.

Petrographic summary

Details of the petrography of the metasomatized rocks are in the Miniprint section of this journal, pp. M8-11.

All eucritic gabbro pods were highly altered. Initially, alteration has albitized the plagioclase, followed by conversion to prehnite and clinzoisite. Original clinopyroxene and hornblende have been altered to chlorite. Skeletal leucoxene (probably after ilmenite) is common. The original igneous texture is largely destroyed but was probably subophitic.

More intense metasomatism results in the garnetization of prehnite and the production of secondary clinopyroxene and amphibole yielding a rodingite reaction zone about the altered gabbro pod. Both fine-grained rodingites, up to a metre in thickness, and coarse-grained varieties, about 20 cm thick, are present. The former is regarded as the result of more intense metasomatism than produced the latter. Adjacent to the contacts, the hydrogarnet content of the rodingite increases and is probably the end-product of rodingitization. Hard white zones of pectolite and prehnite commonly cut the coarser rodingites.

The original harzburgite host has been highly serpentinitized and, at the contact with the gabbroic inclusions, the serpentinite has been altered to a blue-green chlorite zone.

The borders of the gabbros exhibit cataclasis and brecciation, indicating strong tectonic movements before being emplaced in their present position.

The rodingites show evidence of more than one metasomatic episode and this may well be related to the tectonic history of the ultramafic assemblage.

Hornblende gabbro inclusions vary in their degree of alteration but the pattern of metasomatism is essentially similar to that found in the eucritic gabbros but differs in the presence of abundant, accessory sphene in both altered and unaltered varieties, in an abundance of late-stage serpentinite veins cutting the reaction zones, and in the absence of the prehnite-pectolite zones.

Numerous pyroxene-bearing rodingite veins, 6 to 8 cm wide, occur throughout the quarry cutting the blocky, mesh-textured serpentinite. Essentially they consist of diallage, diopside, brown garnet, and chlorite set in a panidiomorphic-granular texture but asymmetrical compositional layering exists parallel to their contacts. Mica is occasionally present.

Rarer, hornblende-bearing, rodingite veins also occur in the serpentinite where they are mantled by hard white hydrogarnet zones sometimes associated with an orthopyroxene zone, although the mineralogy of the contact zone is variable.

Mineral chemistry

Optical, X-ray, and microprobe studies of the different mineral assemblages show changes in mineral chemistry associated with increasing alteration. Microprobe analyses cited in the Tables in the Miniprint section (pp. M12-15) are by way of example only and have been numbered continuously through those Tables to avoid repetition of Table and sample numbers in the text.

Olivine (Table I; 1). Relic olivine is not common at Wairere. Analyses of grains from both compara-

tively unsheared serpentinite of the main rock body and from serpentinite immediately adjacent to rodingite showed all olivines to be richer in FeO (range, FO_{83-75}) than is typical of olivines from alpine-type ultramafics (Loney *et al.*, 1971; Rodgers, 1976).

Orthopyroxene (Table I; 2-4). Relic, serpentinized harzburgite orthopyroxenes are typically bronzites of the 'Bushveld type' exhibiting abundant exsolution lamellae of clinopyroxene parallel to (100). They average En_{86} in composition and CaO is low and Al_2O_3 is high. Comparable pyroxenes have been reported from the Lizard, Dawros, and New Caledonian peridotites (e.g. Green, 1964; Rodgers, 1976).

In an orthopyroxene-rich zone adjacent to a hornblende rodingite vein and separating mesh-textured serpentinite from a white hydrogrossular zone, the orthopyroxenes adjacent to the serpentinite contain no exsolution lamellae and have lower MgO and Al_2O_3 and higher FeO contents (av., En_{77}) than those of the harzburgite. This trend continues towards the hydrogarnet zone so that the pyroxenes adjacent to this latter zone are hypersthene (av., En_{65}) rather than bronzites.

Clinopyroxene is the most abundant mineral in all the various zones of metasomatism associated with the eucritic gabbros and variations in its composition are believed to reflect the chemical changes that have taken place. Typical analyses of the mineral from different zones are given in Table I (5-16) along with analysis of a relic grain from the host serpentinite (17). This last analysis is comparable to that from the primary peridotite of the Lizard (Green, 1964) and of the endiopsides of Red Mountain (Challis, 1965a) although alpine-type peridotite clinopyroxenes are frequently richer in Ca (e.g. Loney *et al.*, 1971; Rodgers, 1976).

Most clinopyroxenes of the altered gabbros and the associated rodingites are augites with a few plotting as endiopsides. In passing from altered eucrite to fine-grained rodingite there is a definite trend in substitution of $(Fe^{2+} + Mn)$ for $(Ca + Mg)$ (fig. 3). An initial Ca enrichment occurs from altered gabbro to rodingite followed by an Mg enrichment with increasing rodingitization. The clinopyroxenes analysed from the altered gabbros are probably secondary; they were quite fresh and in sharp contrast to the highly chloritized augites found in the centres of the gabbro pods.

Augites from rodingite veins are richer in Ca than those of the gabbro pods. Those from the border of the hornblende rodingite vein and the hibschite zone plot as sahlites but all rodingite clinopyroxenes analysed here are far richer in iron than those from rodingite dykes described by Bilgrami and Howie (1960) and by Larrabee (1969).

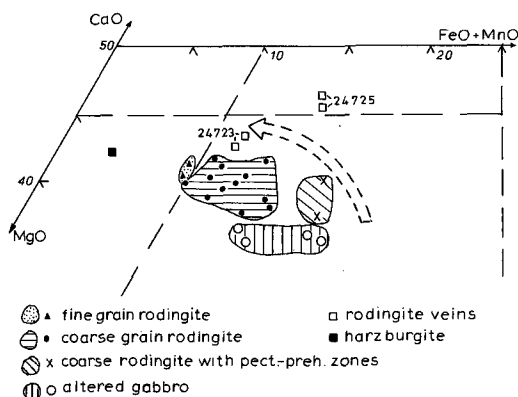


FIG. 3. CaO-MgO-(FeO+MnO) diagram of Wairere clinopyroxenes displaying the chemical variation, which occurs with increasing metasomatism as shown by the arrow.

Al_2O_3 (1.53-3.89%) and TiO_2 (0.0-2.83%) contents are quite variable in the pyroxenes. Al increases with increasing alteration and this may parallel a decreasing silica activity (cf. Verhoogen, 1962). In all the altered gabbros Ti must be assigned to tetrahedral positions if such sites are to be regarded as being fully filled and it is found that most of the rodingite clinopyroxenes plot close to a line with a slope of $Ti:Si = 0.5:1$ suggesting a substitution of the type $Mg_2^{2+} + 2Si_2^{4+} \rightleftharpoons Ti_2^{4+} + 2Al_2^{3+}$. However, augites from the coarse-grained, pectolite and prehnite-bearing rodingites, with the highest Ti content, deviate from this trend as do those from the rodingite veins. Various substitution schemes can be postulated, e.g. $Mg_2^{2+} + Si_2^{4+} \rightleftharpoons Al_3^{3+} + Al_3^{3+}$ as a result of the introduction of the acmite molecule in vein pyroxene.

All clinopyroxenes are low in Cr and Mn.

Amphiboles display the greatest variation in composition with increasing metasomatism of any of the mineral groups examined. All samples that were probed proved to be reasonably homogeneous. Typical results are given in Table II where the structural formulae have been calculated for both the minimum and maximum oxidation values of iron that are in keeping with stoichiometry. The calcic amphiboles of the unaltered hornblende gabbro dykes are actinolitic hornblendes; those of the rodingite vein and altered gabbro pods are magnesio-hornblendes.

A decrease in Si and an increase in *mg* occurs with increasing metasomatism while the CaO content varies little (11.1-12.0%). The atomic percents of Mg, Fe, and Ca are comparable in the hornblendes from both the unaltered dyke and the altered pod. Al^{IV} increases also with increasing metasomatism and the over-all substitution trend

appears to be $(\text{Mg}, \text{Fe}^{2+}) + \text{Si}^{\text{iv}} \rightleftharpoons (\text{Al}^{\text{vi}}, \text{Fe}^{3+}) + \text{Al}^{\text{iv}}$. This trend may be compared with that of calcic amphiboles from the metasomatized gabbro-peridotite plutons of the Urals, which also display an over-all loss of Si and an increase in the ratio $\text{Al}/(\text{Mg} + \text{Fe})$ with increasing alteration (Kolesnik and Guletskaya, 1970). 'A' site occupancy increases with decreasing silicification— $\text{Si}^{\text{iv}} \rightarrow (\text{Na}, \text{K})^{\text{A}} + \text{Al}^{\text{iv}}$ —as does the content of the octahedral cations, $\text{Si}^{\text{iv}} \rightarrow (\text{Al}^{\text{vi}}) + (\text{Al}^{\text{vi}}) + \text{Fe} + \text{Ti}$. Kolesnik and Guletskaya regarded the latter type of substitution as a diffusion process, characterized by a low mobility of Si at low pressures.

The occurrence of the orthopyroxene-rich zone at the contact of the hornblende rodingite vein and the serpentinite may be related to the desilification process. Kolesnik and Guletskaya suggested that a decrease in the ratio Si/Al can occur in the system $(\text{Mg}, \text{Fe})\text{-Si-Al}$ according to the reaction $\text{En} + \text{Hb}_{\text{Al} < n} \rightleftharpoons \text{Hb}_{\text{Al} = n}$. If enstatite components migrate from the rock during rodingitization the reaction shifts to the left so as to increase the Al content of the amphibole with accompanying loss of Si.

The chemistry of the Wairere amphiboles appears to support the contention of Kolesnik and Guletskaya that the mobility of silica governs its involvement in isomorphous substitution of metasomatic amphiboles with enhanced mobility and release from the lattice occurring at greater degrees of metasomatism.

Chlorites from the coarse-grained rodingite of the eucritic gabbros were low-birefringent (1st order grey) chlorites; those of the highly metasomatic gabbros were medium-birefringent (1st order blue) and pseudomorphous after clinopyroxene; those of the chloritized serpentinite had the highest birefringence (1st order orange). Recalculation of analyses of these chlorites

(Table III) indicates that all iron is in the ferrous stage.

Two types of substitution appear to occur in these chlorites. Dominant is $\text{Fe}^{2+} \rightleftharpoons \text{R}^{2+}$ ($\text{R} = \text{Fe}^{2+} + \text{Ca} + \text{Mg} + \text{Mn}$) with the ratio $\text{Fe}^{2+}/\text{R}^{2+}$ decreasing from coarse-grained rodingites, through finer-grained varieties to the chloritized serpentinite zone. The second type, $\text{Si}^{\text{iv}} + \text{R}^{2+} \rightleftharpoons \text{Al}^{\text{iv}} + \text{Al}^{\text{vi}}$, is of lesser importance and is represented by a slight increase in silica in successive zones moving out from a pod centre. A plot of $\text{Fe}^{2+}/\text{R}^{2+}$ vs. Si (Foster, 1962) shows that the chlorites of the coarse-grained rodingites are diabantites, those of the chloritized serpentinites are pennines, while those of the fine-grained rodingites fall in a distinct field between the other two, some plotting as diabantites, some as pennines. (Chlorites from rodingite veins plot as ripidolites, brunsvigites, and diabantites.) Thus each main metasomatic zone has its own characteristic chlorite, the major compositional variations being an increase in Mg and a decrease in Al and Fe outwards towards the chloritized zone (fig. 4). It may be noted that these trends are paralleled by an increase in Si that is the converse of the Si loss found in the amphiboles and clinopyroxenes. But whereas the chlorites of the coarse-grained rodingites may be directly related to the rodingitization process, the chlorites of the other two zones are pseudomorphous after diopside and serpentine and may possibly be the result of later processes.

In none of the chlorites examined in this study did Cr_2O_3 exceed 0.1%. O'Brien and Rodgers (1973b) described a pink chlorite from a rodingite vein, which, on the grounds of its physical properties, they concluded was Cr-bearing. An analysis of a similar chlorite (24723) from a similar setting proved it to be a pennine. Chlorite from the

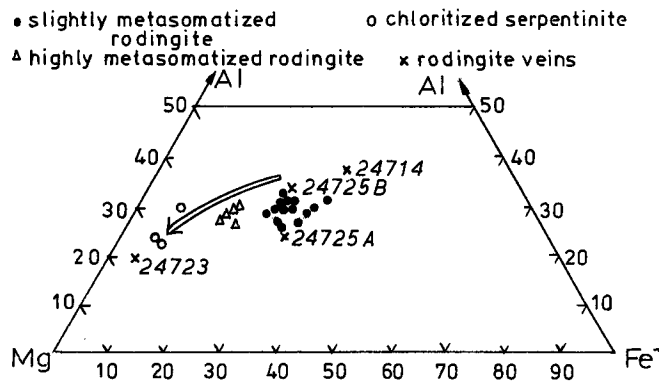


FIG. 4. Changes in composition in the system Al-Mg-Fe for the Wairere chlorites. The arrow indicates the progression in zones from the centre of the gabbro pods to the encasing chloritized serpentinite zones.

hornblende rodingite veins (24725A and B) varies from a Si-rich diabantite near the contact with serpentinite to a Si-poor brunsvigite in the centre of the vein. A deep-green chlorite associated with prehnite and serpentine zones transecting the hornblende gabbro pod is a ripidolite with a high degree of Al substitution for Si and a relatively low Mg content.

Biotite. An analysis of biotite from the centre of the hornblende gabbro dyke is given in Table III, no. 35. The structural formula is calculated on a basis of total iron as FeO. The dominant octahedral ions, Mg and Fe²⁺, are present in sub-equal amounts with Fe/(Fe + Mg) = 0.52.

Garnet is used in this study to distinguish *altered gabbro* from *rodingite*. Analyses of this mineral from a variety of environments are given in Table IV. No inhomogeneity or compositional zoning was detected.

Two types of calcium-rich garnet occur in the Wairere rodingites. As opposed to the preliminary report of O'Brien and Rodgers (1973*b*) based on physical observations, hydrogrossular (*a* 11.83 Å) proves to be the most common type in a variety of rodingite types. Andradite-grossular is confined to pyroxene rodingite veins. Hydrogrossular is the most frequently reported garnet from rodingites. Andradites have been reported occasionally (Seki, 1965; Challis, 1965*a*; Duffield and Beeson, 1973). The present grandites have a grossular/andradite ratio from 22/78 to 29/71, which lies outside the limits reported by Seki (1965) for serpentinite environments. This suggests that the temperature of formation must have been such as to close the miscibility gap between andradite and grossular (> 300 °C, Seki, 1965).

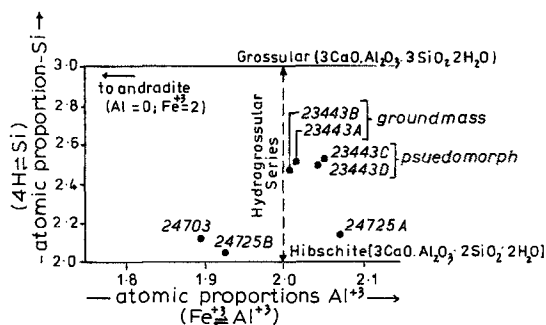


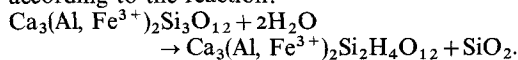
FIG. 5. Wairere hydrogrossulars plotted on a diagram of atomic proportion of Al versus Si.

The chemistry of the Wairere hydrogrossulars is summarized in fig. 5. In contrast to the findings of Duffield and Beeson (1973), the present hydrogrossulars were not confined to forming as pseudomorphs after plagioclase, but are also found in

groundmass settings. The groundmass garnets are slightly lower in Al and are intermediate members of the grossular-hibschite series, whereas the pseudomorphous varieties plot closer to the hibschite end-member. Groundmass hydrogrossulars from the hornblende rodingite are also lower in Al, and hence display a higher andradite component than the white hydrogrossular of the border zone. Garnets from this zone have an XRD pattern very close to that of hibschite.

The pyralospite content of all the analysed garnets is small and is largely almandine (up to 5%; analysis 38). The pyrope component is less than 1% except for analysis 37 while the spessartine component is always less than 0.2%.

The water content of the hydrogrossulars was not determined directly, but was estimated from the atomic proportion of Si. Seki (1965) attributes the formation of hydrogarnet to desilicification according to the reaction:



This suggests that the formation of hydrogrossular in the Wairere rodingites is due to a greater chemical potential of water and, or, lower activity of silica than is present in the altered gabbros.

Plagioclase. The primary plagioclase of the least-altered eucritic gabbros is calcic (An₇₆₋₈₃, O'Brien and Rodgers, 1973*b*). Analyses given in Table V are of bent and fractured, partially prehnitized and saussuritized, highly albitized, relic grains.

Plagioclase from the hornblende gabbro is zoned normally from a bytownite core (An₇₀₋₈₄) to a distinct andesine rim (An₆₀). The cores have higher FeO contents (0.37-0.47%) than the rims (0.12-0.16%). In all plagioclases the orthoclase component is less than 1.5 mole%.

Calcium silicates. O'Brien and Rodgers (1973*b*, p. 234) gave physical and chemical data for xonotlite, which they found 'separating the slickensided rodingite from serpentinite' and in veins cutting the altered gabbros. The pod from which they collected their samples has since been blasted and removed as quarry fill. Samples collected from white marginal zones and cross-cutting veins of six pods present in the quarry in 1973-4 all proved to be compact aggregates of pectolite and prehnite and, in one instance, rosenhahnite (Leach and Rodgers, 1977). Imai *et al.* (1972) found one vein of xonotlite in albitite adjacent to serpentinite; all other veins proved to be pectolite. Similar pectolite zones and veins have been reported by other authors from serpentinites, e.g. Parsons (1924), Francis (1955), Coleman (1961), Kolesnik (1974*a*).

As noted by Coleman (1961), it was difficult to identify pectolite in thin section, largely because of its fibrous nature, which made it difficult to obtain

an adequate interference figure. XRD patterns of the bulk white zones or veins could not be satisfactorily interpreted as the major X-ray peaks of pectolite and prehnite interfered, while pectolite reflections vary in intensity due to preferred orientation. Concentrates, prepared with a micropanner, were positively identified as pectolite by powder photographs.

Microprobe analyses of two pectolites, one from a marginal zone and the other from a vein, are given as analyses 47 and 48. Recalculation on an anhydrous basis gives a formula of $\text{Ca}_{3.9}\text{Na}_{1.9}\text{Si}_{6.0}\text{O}_{16.9}$. Addition of 3% water gives a hydrous formula of $2(\text{Ca}_{2.0}\text{Na}_{1.0}\text{H}_{1.1}(\text{SiO}_3)_3)$ (cf. the theoretical formula $\text{Ca}_2\text{NaH}(\text{SiO}_3)_3$).

The occurrence of rosenhahnite in one of the brecciated pectolite zones at Wairere has been reported elsewhere (Leach and Rodgers, 1977).

Titanite (Sphene) is the most abundant accessory mineral in both unaltered and altered hornblende gabbros. It occurs as small veinlets (24716, 24720), as large, partially resorbed crystals in chlorite veins (24714), as elongated granules in the matrix of rodingites (24713), both replacing plagioclase (24720) and being replaced by ilmenite (24707). In most instances the mineral is strongly pleochroic from pink-orange to pale yellow but it is colourless in the matrix of the rodingites.

Sphene was analysed from both a metasomatic chlorite zone (analysis 51), where it was associated with prehnite, and from the unaltered hornblende gabbro dyke (49 and 50). No significant compositional variation was found between these two, primary and secondary occurrences. Up to 1.87% Al_2O_3 is present and a step-scan across crystals showed a sympathetic variation of Al with Ti, but not with Fe, indicating the substitution $3\text{Ti}^{4+} \rightleftharpoons 4\text{Al}^{3+}$.

Chrome spinels. Chrome spinels from unshered mesh-textured serpentinite containing a small

amount of relic olivine, orthopyroxene, and clinopyroxene (analysis 52) plot in the field typical of alpine-type serpentinites (Irvine, 1965; Rodgers, 1973). Analysis 53 is from a mesh-textured serpentinite 2 cm from a pyroxene-rich rodingite vein. The two spinels differ in respect of Cr/Al and $(\text{Fe}^{2+}/\text{Fe}^{3+})_{\text{calc}}$ but a similar range in composition has been found in Mg-rich chrome spinels from comparable alpine-type harzburgites (Bevan and Rodgers, 1977).

PETROCHEMICAL TRENDS

Eighteen new analyses have been made of the metasomatic zones and associated rocks from the Wairere Serpentinite (Table VI). The altered gabbros display the relatively low Si and comparatively

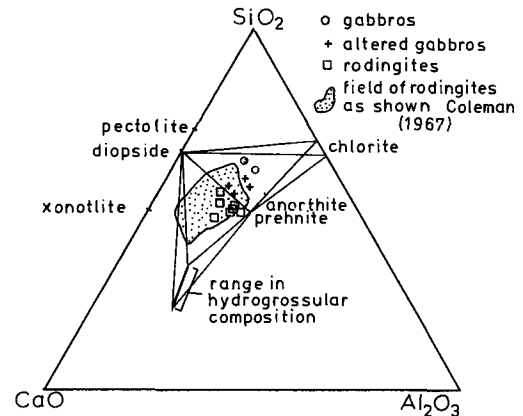


FIG. 6. Analyses of gabbros (○), altered gabbros (+), and rodingites (□) from the Wairere Serpentinite plotted in the diagram $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$. Shaded area is the field of rodingites as given by Coleman (1967).

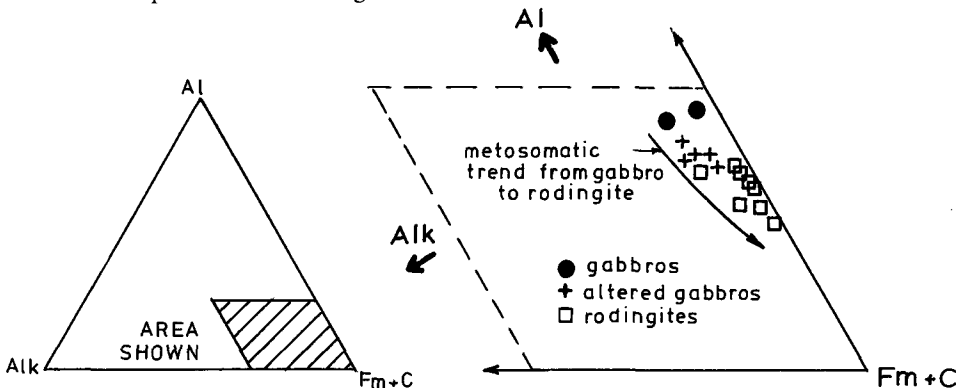


FIG. 7. The metasomatic trend of the Wairere mafic rocks as shown by Niggli's diagram. Symbols as for fig. 6 (cf. Coleman, 1966, p. 85, fig. 57B).

high Ca typical of metasomatically altered mafic rocks associated with serpentinized peridotite (fig. 6). The rodingites are comparable to those from other serpentinites (e.g. Coleman, 1967) although a little higher in Al than some. A depletion in Si and an enrichment in Ca, with respect to Al, is evident in passing from gabbro to rodingite. All Wairere rodingites plot in the three-component triangle diopside-prehnite hydrogrossular; most altered gabbros lie in the larger diopside-chlorite-prehnite field. The petrographic distinction between altered gabbro and rodingite, based on the presence or absence of hydrogrossular, is therefore supported by chemical data.

Niggli's diagram (fig. 7) shows that increased metasomatism of the gabbros involves depletion in alumina and alkalis and an increase in the (FeO + MgO + CaO) component. Coleman (1966) reported this same trend in other serpentinite-associated metasomatic rocks from New Zealand.

ACF plots (fig. 8) show that most commonly there is an initial increase in Ca from gabbro to altered gabbro to rodingite, 20 cm from contact, but a reversal occurs at the contact. Ca falls and Al increases with a minor enrichment in Mg and Fe. It is suggested that this chemical reversal is expressed mineralogically by the chloritization of diopside in the rodingites adjacent to the contact. The coarse-grained rodingites of pod B, which are considered to be less metasomatized than the finer variations, do not display this trend. Specimen 23443 lacks hydrogrossular while 23444 does not show chlorite pseudomorphous after diopside.

PROGRESSIVE METASOMATISM

Plots of element variation across the different types of reaction zones (fig. 9) illustrate the progressive nature of the metasomatism at Wairere. An average pyroxene hornblende gabbro (Nockolds, 1954) and a New Zealand harzburgite (Challis, 1965a) have been included in this figure as indicating the approximate, pre-alteration composition of the rocks.

Silica decreases with increasing alteration of both eucritic and hornblende gabbros, whereas serpentinization of harzburgite appears to involve some silicification followed by a slight decrease on chloritization of the serpentine. In the eucritic gabbro pods the fine-grained (more highly metasomatized) rodingites display a greater Si loss 20 cm from the contact than do coarse-grained rodingites. *Calcium*, over all, increases with increasing alteration but this trend is not prevalent throughout all the rodingites. The fine-grained varieties show a fall in CaO adjacent to the contacts whereas the same

oxide reaches a maximum in coarse-grained types at the chlorite-gabbro contact. The ultramafics exhibit a marked loss in lime upon increased serpentinization. *Alumina* is initially slightly lost from both gabbro types but with increased metasomatism and the formation of rodingites there is substantial increase. Chloritization of serpentinite is accompanied by some increase in Al from nil in massive serpentinite to 4.2% in the chlorite zone adjacent to the gabbros. *Magnesia* falls on initial alteration but increases on rodingite formation. Serpentinization of the harzburgite involves loss in MgO. *Alkalis* are initially enriched by albitization of the calcic plagioclase of the gabbros, but upon rodingite formation Na₂O is depleted, the loss being more pronounced in the finer-grained rodingites. Potash shows a similar trend. *Water*. All alteration processes at Wairere involve increasing hydration (cf. O'Brien and Rodgers, 1974). *Other elements*. The distribution of Fe, Mn, and Ti is irregular in the various metasomatic zones and these elements do not appear to be mobile components during metasomatism except in the hornblende gabbros where titania may be involved in rodingitization. It may be noted that the P₂O₅ concentration of all the rocks analysed here is much less than in those cited by O'Brien and Rodgers (1973b) who also reported the presence of apatite, not observed in the present study. (The analyst was the same in both cases but the method has changed from colorimetry to XRF.)

Limestone. Two samples of Otorohanga limestone (Oligocene) were analysed (Table VI, analyses 17-18). There is little difference between that 40 m from the contact and that adjacent to the serpentinite apart from a slight difference in Al. The carbonate level (95% CaCO₃) is typical of this limestone, in this region.

MINERALIZATION

The chemical trends within the Wairere reaction zones reflect the various mineral-replacement reactions that have occurred. These processes are discussed here in the order in which they appear to have occurred.

Albitization of the primary calcic plagioclase is reflected in the initial Na₂O enrichment of the altered gabbros. The origin and nature of hydrothermal solutions producing this alteration is speculative. Němec (1966) concluded that the albitization in lamprophyre dikes is autometasomatic, occurring in the late stages of magmatic consolidation. Alternatively, an influx of sea-water could supply the system with excess Na and flush out the excess Ca (Spooner and Fyfe, 1973). O'Brien and Rodgers (1973b) linked albitization

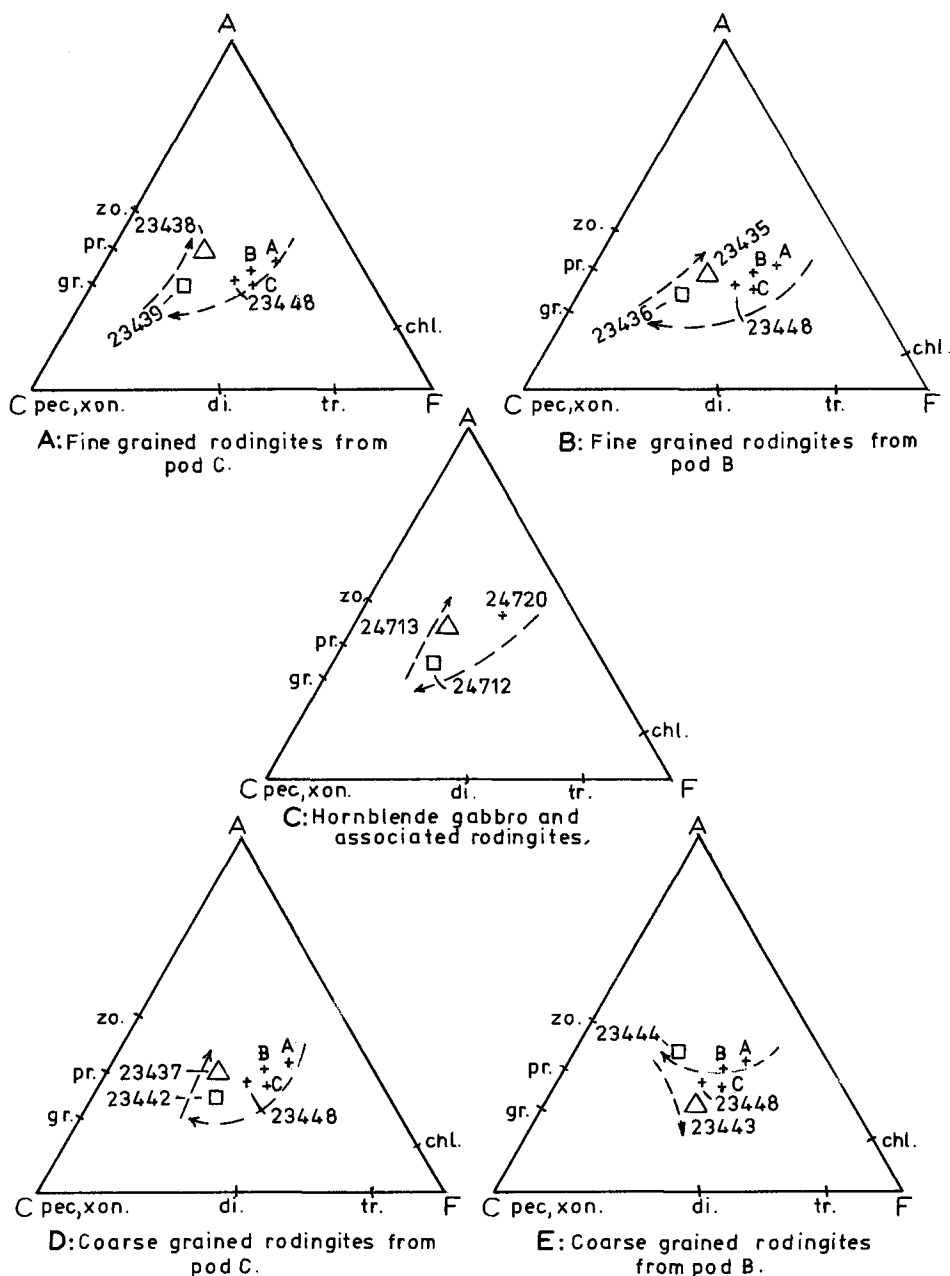


FIG. 8. ACF plots of Wairere mafic rocks showing the trends (arrowed) occurring with increasing metamorphism. + = gabbro and altered gabbro; □ = rodingite, 20 cm from outer margin; Δ = contact rodingite. A, B, and C refer to analyses of the least altered portion of the pods. Zo = zoisite, pr = prehnite, gr = grossular, pec = pectolite, xon = xonotlite, di = diopside, tr = tremolite, chl = chlorite.

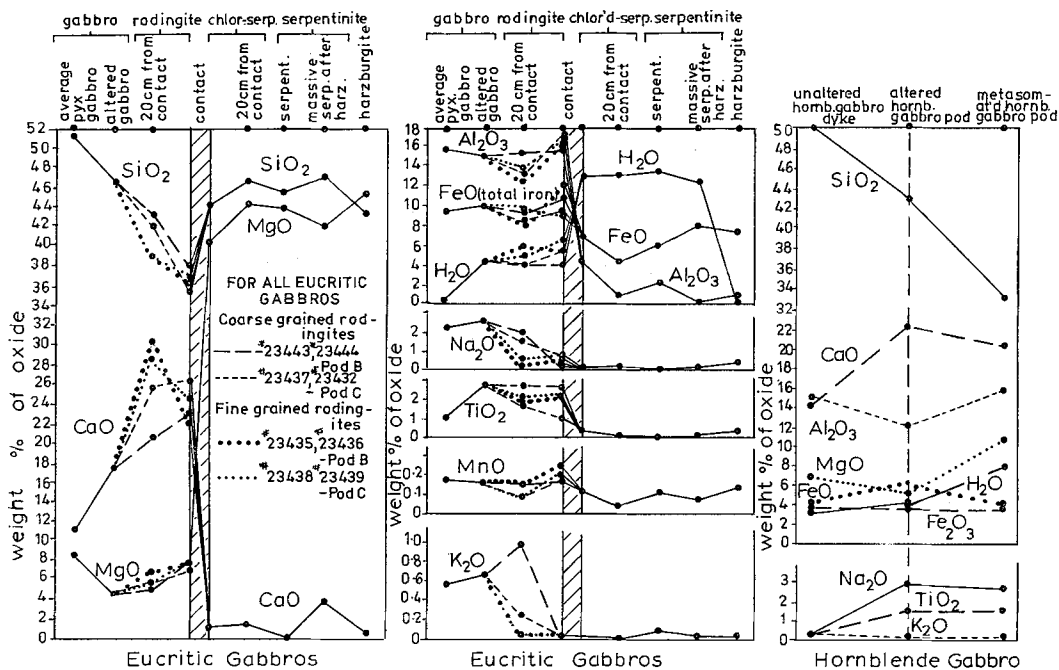
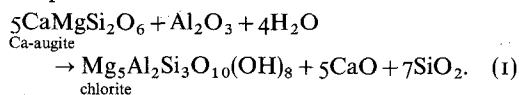


FIG. 9. Variation diagram showing chemical trends with progressive metamorphism across eucritic and hornblende gabbro reaction zones in the Wairere Serpentinite.

with rodingitization, stating that the albite content of the feldspar increases from the centre of a xenolith to the serpentinite contact. This link now seems unlikely as the new analyses show the soda content of the bulk rock to decrease towards the contact, i.e. the reverse of albitization. It appears then that alteration of calcic plagioclase is a separate process from serpentinitization and rodingitization at Wairere, perhaps occurring before the mafics are included in the peridotite as perhaps suggested by the presence of the fresh bytownites in the hornblende gabbro dyke.

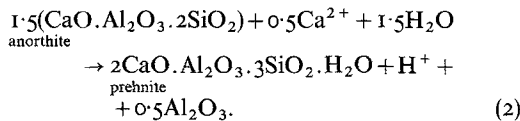
The turbid appearance of the albites indicates that albitization of calcic plagioclase is accompanied by the formation of calcium-rich cryptocrystalline by-products and Némec (1966) suggested that the decomposition products are granular inclusions of the zoisite-epidote group and prehnite. The process leading to plagioclase alteration also affects the augites and hornblendes, producing swirls of colourless to green chlorite by the possible reaction:



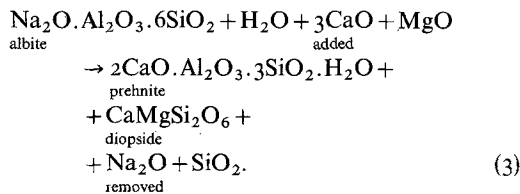
Challis (1965b) proposed that the Ca released upon chloritization is flushed out in solution.

Prehnitization and saussuritization. Albitization of plagioclase is followed by prehnitization and saussuritization. Only a few relic albites remain in the core of the gabbro pods, the majority being replaced by prehnite (in the eucritic gabbros) and epidote and zoisite-clinozoisite (in the hornblende gabbro).

Coleman (1967) suggested that prehnite is derived from the alteration of calcic plagioclase by the reaction:

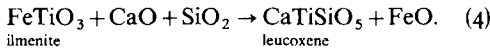


However, evidence from this study shows that secondary diopside (and in some cases hornblende) and prehnite (pseudomorphing albite) were formed from the alteration of the sodic plagioclase as described by Watson (1953):

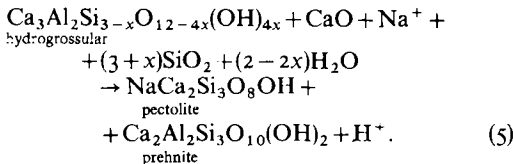


Similar reactions can be written for the saussurization of albite, forming zoisite-clinozoisite and epidote.

Reactions (1) and (3), with the addition of lime and water, and loss of Si and alkalis, parallel the metasomatic trends for alteration of gabbros to rodingites, and were probably related to the same process. Similarly, primary ilmenite is altered to leucoxene by the introduction of additional calcium and silica:



Formation of pectolite-prehnite zones. Bilgrami and Howie (1960) envisaged a replacement origin for wide xonotlite zones derived from hydrogarnet. A similar genesis would apply to the pectolite-prehnite zones that run parallel to the contact of the Wairere gabbros according to the following reaction:



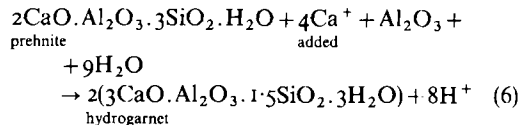
However, Challis (1965*b*) described veins of wollastonite, which may be regarded chemically as dehydrated xonotlite, being replaced by pectolite and hydrogrossular. In the same manner the pectolite-prehnite zones at Wairere may have replaced the wide xonotlite zones described by O'Brien and Rodgers (1973*b*). Both these possibilities are supported by Kolesnik (1974*b*), who concluded that pectolite in outer zones of gabbroic inclusions was formed by the 'washing' of calcium silicates by aqueous solutions. He stated that Na silicates are more soluble than Ca silicates, therefore, washing by neutral or weakly alkaline solutions increases the alkali-ion content, which reacts with components such as hydrogrossular and xonotlite to form pectolite.

The pectolite and prehnite veins that radiate from the contact and cut the centres of the altered gabbros are probably formed by the reaction of Si- and Na-rich metasomatic phases percolating inwards. A similar origin for pectolite in albite pods within serpentinites was proposed by Francis (1955).

Large jadeite and albite deposits characteristic of contacts in some serpentinite bodies (e.g. Coleman, 1962) are absent from the Wairere Serpentinite. The presence of pectolite in the gabbroic inclusions at Wairere indicates that this mineral, rather than jadeite or albite, is the product of soda released upon albitization.

The absence of xonotlite in all gabbro inclusions sampled in 1973-4 could be due to replacement reactions. It should be noted that the gabbro containing xonotlite (O'Brien and Rodgers, 1973*b*) also contained calcic plagioclase in the central regions. In this study only albite was found in the altered gabbros. It is possible therefore that the rocks analysed here have undergone a greater degree of alteration than that containing xonotlite. On the other hand, Miyashiro (pers. comm. Honnerez and Kirst, 1975) proposed that the absence of xonotlite or wollastonite could be caused by compositional differences in the original gabbro. The xenoliths studied here may therefore have had a higher initial Al/Ca ratio than the xenolith containing xonotlite.

Garnetization. Hydrogrossular is the most abundant and widespread mineral present in all rodingites, and appears to be the final product of rodingitization. Coleman (1962) stated that the composition of rodingites is approximated by the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$, which approaches that of hibschite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The garnetization of prehnite involves the addition of calcium and alumina:



assuming chlorite does not take part in the reaction. This reaction is probably responsible for the increase in Ca and Al content between altered gabbros and rodingites. The groundmass hydrogarnet is probably derived from the alteration of zoisite-epidote by the addition of calcium and water and the release of silica.

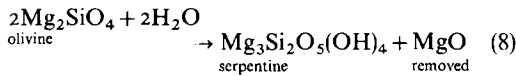
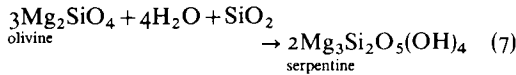
Honnerez and Kirst (1975) suggested that the change from grossular to hydrogrossular involves the removal of silica as well as the addition of water. Therefore the occurrence of hydrogrossular, instead of grossular, may be due to the relatively low activity of silica during rodingitization.

The presence of andradite garnets in the pyroxene rodingite veins possibly indicates high iron activity with respect to calcium at the time of alteration. This may be related to the degree of serpentinization, or to the low lime content in the original mafic rock.

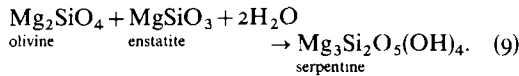
Serpentinization. The discussion will be restricted to aspects of volume changes and the origin of the solutions as these apply to the formation of the metasomatic zones.

Thayer (1966) described serpentinization as a process of replacement by pseudomorphism; the

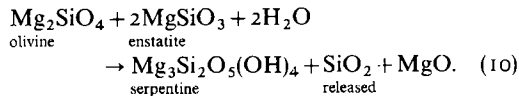
major change being the transformation of anhydrous into hydrous magnesium silicates. If brucite or magnesite is present in the serpentinite, then a constant volume replacement of the peridotite requires only the introduction of water and, or, CO₂ (Hostetler *et al.*, 1966). Brucite occurs only in small quantities in the Wairere Serpentinite (O'Brien and Rodgers, 1974), therefore the alteration of olivine may require the introduction of silica or the removal of magnesia by the reactions:



resulting in the expansion of the original peridotite. Since pyroxene is present in harzburgites, some silica may be introduced from enstatite:

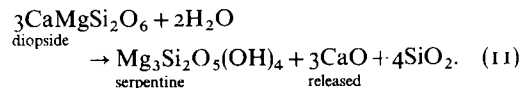


At constant volume, serpentinitization may also require the removal of large quantities of MgO and SiO₂:



However, the gabbroic inclusions exhibit a decrease, not addition of silica thereby favouring reactions (7), (8), and (9).

Natural peridotites and hydrothermal systems cannot be adequately described by a three-component system. With the introduction of other elements such as FeO, Fe₂O₃, CaO, Al₂O₃, and alkalis, the system becomes exceedingly complex. Iron released upon serpentinitization often forms magnetite (Gresens, 1969). Barnes and O'Neil (1969) have shown that partially serpentinitized ultramafics release fluids that contain unusually high concentrations of Ca and Al. Ca is probably released upon serpentinitization of clinopyroxene by the reaction:

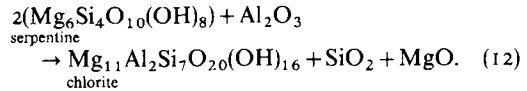


Condie and Madison (1969) have shown that the degree of serpentinitization of a dunite could not be related to Ca or Al content. However, peridotites containing pyroxenes such as the South Island harzburgites and the massive serpentinite after harzburgite in Wairere contain up to 3% CaO, whereas serpentinites rarely contain over 0.2%

CaO (e.g. Wairere serpentinite from Henderson and Ongley (1923) contains 0.19% CaO).

Chloritization occurs at different intervals during metasomatism. For example, chlorite may form contemporaneously with albitization of plagioclase, but its occurrence in the rodingites adjacent to the contact, where a colourless chlorite pseudomorphs endiopside, post-dates the rodingitization and reverses the calcium enrichment trend characteristic of rodingite formation.

Chlorite (and in some cases amphibole) zones, separating serpentinite from rodingite, have been reported from most reaction zones in the literature. Some authors (e.g. Chidester, 1962; Černý, 1968) believe that the chlorite zones develop from adjacent siliceous rocks. However, in the Wairere Serpentinite, the chlorite is an alteration product of the highly sheared serpentinite, as shown by the increasing occurrence of chlorite in the serpentinite adjacent to the xenoliths. The chlorite is probably formed by the introduction of Al and the release of Si and Mg:



This agrees well with the chemical trends exhibited between serpentinite and chloritized serpentinite.

Most authors believe that formation of the chlorite zones is closely related to serpentinitization. Černý (1968) considers that the degree of serpentinitization determines whether rodingites or chlorites are produced (i.e. whether the products are Mg-, Ca-, Al-rich, and Si-poor; or Mg-, Al-, and Si-rich). Coleman (1966) interprets the chlorites as an equilibration product contemporaneous with the release of silica and magnesia from the mafic rocks and of water and magnesia from the serpentinites. However, Martin and Fyfe (1970) point out that on completion of serpentinitization Mg²⁺-HCO₃ meteoric waters such as those described by Barnes and O'Neil (1969), could produce chlorite from a serpentinite. This possibility appears most applicable in Wairere since chloritization post-dates both serpentinitization around the gabbroic bodies and rodingite alteration of the mafic bodies.

ORIGIN OF REACTION ZONES

Magmatic origin. Early investigators (e.g. Marshall, 1907; Finlayson, 1909; and Bell *et al.*, 1911) considered rodingites to be products of a Ca- and Mg-rich magma that had resulted from differentiation of a basic magma. Recently, Bassaget *et al.* (1967) proposed that rodingites were a magmatic member of the ophiolite suite, and Kolesnik (1974a) suggested that the source of Ca for the rodingites

arose by dissociation of clinopyroxene derived from a spinel-lherzolite magma:



The resulting metasomatic solutions he regarded as reacting with gabbros to form rodingites composed of the high-temperature minerals garnet, clinopyroxene and, less commonly, wollastonite and pectolite, while serpentine, chlorite, prehnite, zoisite, epidote, and carbonates are formed later. A similar suggestion has come from MacKenzie (1960) who, in a study on altered rocks in Venezuela, concluded that Ca and Mg metasomatism occurs when hot solutions emanating from peridotites percolate into colder country rocks forming pseudogabbros.

However, rodingites only occur in association with, and in contact with, serpentinites (Thayer, 1966), thus conclusively relating rodingite formation and serpentinization (O'Brien and Rodgers, 1973*b*). Bowin (1966) and De (1972) related the magmatic origin of rodingites to serpentinization by regarding the sequence gabbro \rightarrow rodingite as reflecting gradational environments of increasing water pressure and, or, decreasing temperature. The absorption of water from serpentinized peridotite by a mafic magma would inhibit early crystallization of lime-rich minerals (anorthite and hornblende), thus releasing calcium to form rodingites in the late stages of the melt. These later lime-rich phases would be concentrated locally, depending on the *P-T* conditions. However, relic textures, gradational pseudomorphic replacements, and extensive Ca-rich veining that characterize the Wairere rodingites do not support any theories involving a lime-rich melt, rather, the evidence overwhelmingly suggests action by hydrothermal solutions.

Ca-rich solutions. De (1972) believed that insufficient lime is produced from the serpentinization of Ca-rich pyroxenes to facilitate rodingite formation, particularly as there was no change in mineral assemblages of rodingite dykes that cut through both pyroxene peridotites and dunite. Baker (1959) regarded the alteration of ferromagnesian minerals and plagioclase in the mafic inclusions as providing the necessary Ca and Al, but on the other hand, Bloxam (1954) suggested that neither alteration of mafics nor serpentinization provide a sufficient source of Ca and invoked Ca- and CO₃-rich solutions, which post-date serpentinization to produce both the alteration of gabbroic inclusions and local carbonization of the serpentinite. Barnes and O'Neil (1969) have discovered that post-serpentinization fluids are rich, not in CaO, but in MgO.

At Wairere, the massive serpentinite after harzburgite contains up to 3% CaO; thus, because of the large volume of serpentinite as compared to the altered gabbros, there would have been potentially sufficient Ca present in the ultramafic body to produce the calc-silicate rocks. Within the gabbro itself, most of the Ca released upon albitization of the plagioclase formed cryptocrystalline prehnite and zoisite. Ca released by chloritization of primary gabbroic augites might have been transported to the contacts but there would be insufficient lime produced to form the volume of rodingites found.

The majority of authors (Grange, 1927; Watson, 1953; Bilgrami and Howie, 1960; Schlocker, 1960; Suzuki, 1953; Coleman, 1961, 1962, 1966, 1967; Kaiser *et al.*, 1969; Larrabee, 1969; Barnes *et al.*, 1967, 1969, 1972; Ashley *et al.*, 1971; O'Brien and Rodgers, 1973*b*; Rubenach, 1974; Honnorez and Kirst, 1975) consider rodingite and serpentine formation to be two concomitant and complementary metasomatic processes. Serpentinization at Wairere has released Ca, Al, and Mg, which is available to react with the mafic rocks, while alteration of the gabbros has removed Si and alkalis into the host peridotite. All chemical, petrological, and mineralogical data from this study suggest that chemical exchange of these elements has produced the metasomatic reaction zones in the Wairere Serpentinite. The uniformity of all mineral assemblages that make up rodingites (Coleman, 1967) suggest a similar origin, the variations present being primarily due to variations in the initial rock composition.

NATURE OF METASOMATIC FLUIDS

Hydrothermal solutions are generally rich in alkali and alkaline earth chlorides as well as gases such as CO₂ and H₂S, and Vidale (1969) has shown that such salt solutions readily react with minerals and rocks; especially, they can dissolve out bivalent ions such as Mg²⁺ and Ca²⁺. Serpentine is unstable in the presence of CO₂ (Johannes, 1969), thus the role of carbon dioxide in the Wairere metasomatic processes is likely to be minimal. Strong brines have been reported from two possible environments of alteration: geosynclinal sediments (Gresens, 1969), and oceanic crust (Spooner and Fyfe, 1973). However, in an open, highly sheared system of serpentinization, a continuous flow of fluids could pass through the ultramafics. Hence alkaline chloride solutions are not necessary to dissolve and carry the migrating elements since there would be a replenishing supply of solutions. The composition of the fluid could change as the ultramafic became progressively serpentinized (cf.

Martin and Fyfe, 1970), and would thus be capable of producing different metasomatic effects at different times.

Various investigations have been made on compositional changes during progressive serpentinization. Condie and Madison (1969) revealed that as FeO and Mg decrease, Si and Na increase with increasing serpentinization of dunite. Coleman and Keith (1971) concluded that serpentinization is accompanied by introduction of only water and loss of CaO. However, Hess and Otlara (1964) had deduced that with increasing serpentinization there is a decrease in Al_2O_3 and CaO; and this was supported by Barnes and O'Neil (1969), who reported that meteoric waters issuing from partly serpentinized ultramafics are highly alkaline (pH 11–12), containing unusually high quantities of Ca^{2+} and Al^{3+} , and were low in Fe^{2+} , Mg^{2+} , Mn^{2+} , Cr (total), $\text{SiO}_{2(\text{aqueous})}$, $\text{CO}_{2(\text{aqueous})}$, CO_3^{2-} , HCO_3^- , Na^+ , Cl^- , F^- , and B. These waters were believed to be the product of modern serpentinization.

Thayer (1966) stated that pyroxene (especially Ca pyroxene) is the last of the ultramafic phases to serpentinize. O'Brien and Rodgers (1974) showed that at Wairere, the susceptibility to serpentinization was in the sequence olivine > orthopyroxene > clinopyroxene. Therefore, with progressive serpentinization the level of Ca (and Al) released into solution will increase.

The hydrothermal fluids that formed the metasomatic zonations at Wairere were probably carbonate-poor and probably (but not necessarily) rich in alkali chlorides. These solutions would have effected transport of Si and Na from gabbro to ultramafic and increasing amounts of Ca and Al (and perhaps Mg) from the ultramafic to gabbro. Once serpentinization is complete, the solutions could revert to the $\text{Mg}^{2+}\text{-HCO}_3^-$ composition recorded by Barnes and O'Neil (1969), producing chlorite at the mafic-ultramafic contacts and carbonate veining within the Wairere Serpentinite.

FORMATION OF METASOMATIC ZONATION

The most characteristic feature of metasomatic formations is their zoning (Korzhinskii, 1968), which directly results from the reaction of chemical species in solution on existing rocks and minerals. A combination of infiltration and diffusion (Korzhinskii, 1965) is believed to have produced vein-wall rock and metasomatic alteration of both the gabbroic inclusions and adjacent serpentinite at Wairere.

Bimetasomatism is the most common type of alteration at Wairere. The process was probably initiated by the juxtapositioning of the two rock types in chemical disequilibrium, i.e. the ultramafic

host and the more siliceous, gabbroic, inclusions. Large volumes of water, whether geosynclinal, meteoric, magmatic, or oceanic in origin, percolated through fissures in the original peridotite. The resultant serpentinization released certain species into solution, which flowed down pressure gradients to the gabbro-peridotite contacts. Here, chemical gradients were established and the components then diffused through the mafic rocks down activity gradients established between the serpentinite solution and the gabbros. A summation of the processes for the eucritic gabbro pods is illustrated in fig. 10.

Serpentinization, both as a constant volume and as a volume-expansion reaction, may have occurred within the Wairere ultramafic body (cf. O'Brien and Rodgers, 1974). Initial alteration, with the addition of only water (cf. equations (7) and (8)), released Mg and small quantities of Al and Ca into solution. These reactions could only have been temporary, for if Mg was released constantly during serpentinization of the harzburgite, then Mg-metasomatism would have exceeded Ca-metasomatism, whereas the reverse is the case (cf. Challis, 1965*b*; Černý, 1968). Upon subsequent alteration of the gabbros, Si moved down the activity gradient into the percolating solution, serpentinizing the harzburgite with addition of H_2O and Si, and releasing increasing amounts of Ca and Al. A similar mechanism was proposed by Seki *et al.* (1960) for serpentinities in the Sambagawa belt of Japan.

The zonal boundaries in fig. 10 represent the extreme penetration of each chemical species, with sharp limits of replacement on one of the minerals at each front. Since local reactions were more rapid than diffusion, local equilibrium was approached between the pore fluid and solid in each zone (Vidale, 1969). Diffusion of components through the rock-pore solution proceeded much slower than the levelling of temperature. Therefore, gradients in temperature can be neglected for these processes (Korzhinskii, 1968). The reaction systems are assumed to have been subject to the conditions of constant total pressure ($P_{\text{H}_2\text{O}} = P_{\text{total}}$). However, in natural systems the zoning may be affected by gradients in fluid pressure (Vidale, 1969; Vidale and Hewitt, 1973).

The zonation is therefore regarded as forming by the differential mobility of chemical species in response to an activity gradient, which was maintained by the constant flow of fresh solutions supplied by the open environment of serpentinization. The mineral species that are replaced or formed from the pore fluids may depend on either the activity of the individual species or the free energy of the reaction.

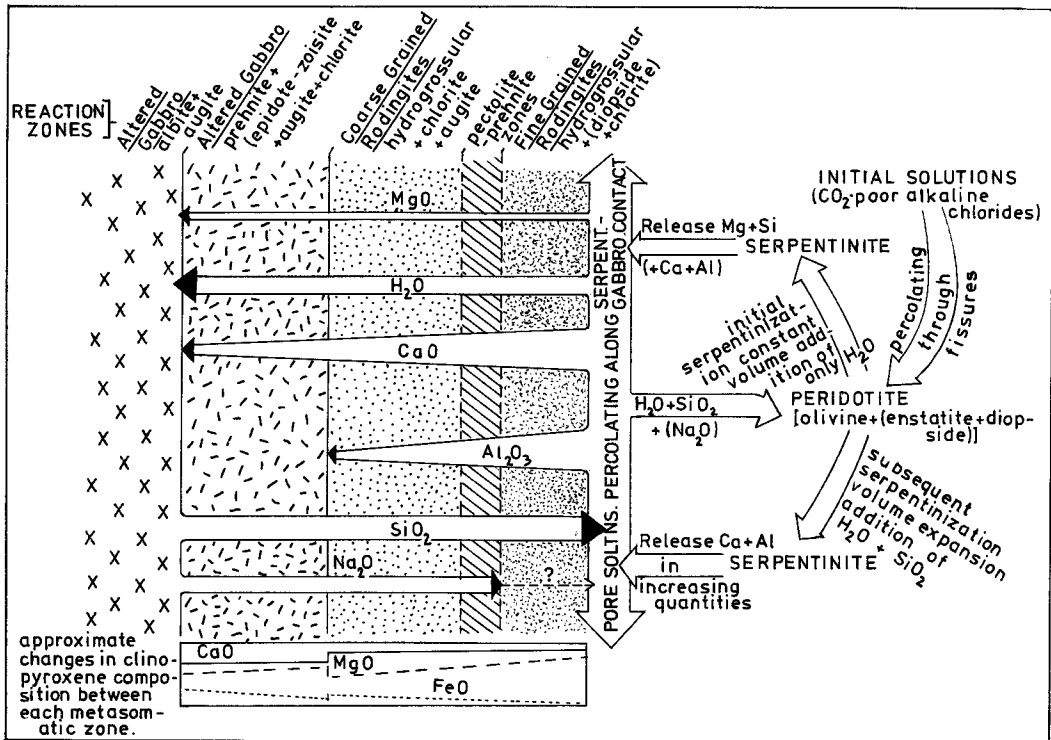


FIG. 10. Formation of reaction zones in the Wairere eucritic gabbro pods and possible modes of serpentinization of the original host harzburgite.

Coleman (1967) devised activity diagrams illustrating possible fields of stability for the minerals present (fig. 11). Here albite may be replaced by either zoisite or prehnite depending on the activities of Al_2O_3 and SiO_2 . Thus, in the altered hornblende gabbros, zoisite rather than prehnite is present due to higher $a_{\text{Al}_2\text{O}_3}$ and a lower a_{SiO_2} than in the eucritic gabbros. Hornblende formed instead of diopside in rodingite veins because of a higher silica activity present. As suggested earlier, xonotlite may be absent in the pods studied because of a low $a_{\text{Ca}}/a_{\text{Al}}$ ratio present during formation of the metasomatic zones. The rodingites at the border of the hornblende gabbro pod contain chlorite instead of either diopside or hornblende, possibly due to a low a_{Mg} and a low $a_{\text{Ca}}/a_{\text{Al}}$ ratio.

The reaction that involves the largest negative change in free energy will occur at each replacement front and will depend on the free energies of both the solids and the solvated species as well as the concentration levels (Carswell *et al.*, 1974). Thus, for example, at the hydrogrossular replacement front, the free energy required to release Al from solution to form garnet from prehnite is less than that required to produce zoisite from prehnite. A replacement front is therefore formed where the

activity level, dictated by the assemblage, is sufficiently low to prevent that species from taking part in any further reactions. Carswell further suggested that the relative width of the zones depends on the concentration gradient and diffusion coefficient of the individual species.

Upon cessation of serpentinization, Barnes and O'Neil (1969) and Barnes *et al.* (1972) showed that the percolating fluids may revert to $\text{Mg}^{2+} - \text{HCO}_3^-$ solutions capable of creating chlorite zones in the serpentinite and facilitating the pseudomorphing of endiopside in the rodingites. This change in solution composition is recognized both in the reversal in chemical trends and in the composition of chlorites in the various zones. The calcite and aragonite veining in the serpentinite and the formation of aragonite crystals at the serpentinite-limestone contact (O'Brien and Rodgers, 1974) probably formed from these later, near surface, carbonate solutions. Černý (1968) proposed that the Mg metasomatism was an earlier deep-seated alteration, which took place prior to Ca metasomatism; however, the chlorites near the contact were obviously a later feature than the formation of the calc-silicate zones and serpentinization of the harzburgite.

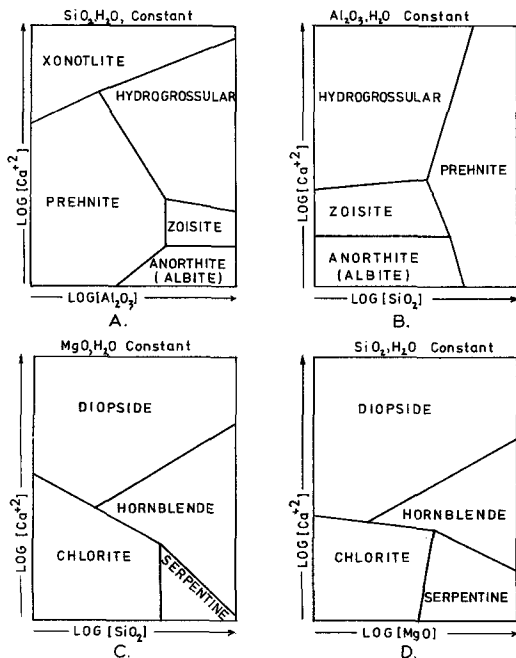


FIG. 11. Activity diagrams of minerals that make up calcium aluminosilicate reaction zones (after Coleman, 1967).

The diffusion nature of the metasomatism is demonstrated in two ways. The alteration is restricted to a few metres from the borders of the inclusions since, in diffusion alteration, the chemical gradients are only maintained over short distances. Secondly, a graded change in mineral composition is established within the zones. This is illustrated schematically for clinopyroxene in fig. 10 where there is gradual increase in Mg and Ca content within the rodingitic augites, and a sharp Ca enrichment at the hydrogrossular-prehnite front. Hornblendes, on the other hand, exhibit a sharp increase in magnesium content at the hydrogrossular front. The chlorite composition changes because of an abrupt change in the metasomatizing solution to an Mg-rich fluid.

The fine-grained rodingites, which are restricted to the apices of the gabbro pods, were possibly formed by channelling of the percolating solutions. The increase in flow would have increased the activity gradients between the gabbro and the serpentinite fluids, thus forming an almost monomineralic hydrogrossular zone.

Vein-wall rock alteration. This type of metasomatism is primarily restricted to the hornblende gabbros at Wairere where late serpentine veins have percolated through fissures. These veins, which would have been in equilibrium with the

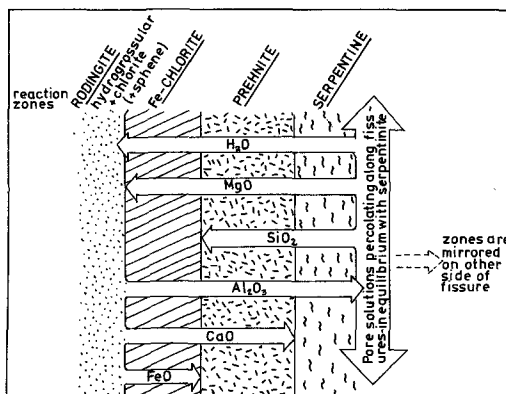


FIG. 12. Local equilibria established in hornblende gabbro between successive minerals and pore fluid.

serpentinite, have created small asymmetric rodingite zones in the unaltered hornblende gabbro dyke. At the borders of the hornblende gabbro xenolith, monomineralic zones of serpentine, prehnite, and chlorite are formed. A summation of the possible local equilibria between pore fluid and successive zonal minerals is given in fig. 12. Assuming the late serpentine veins reflect the composition of solutions similar to those previously mentioned (Mg^{2+} - HCO_3^- -rich), then a reversal to the activity gradients shown in fig. 10 was established between the percolating solution and the rodingite. Thus Ca, Al, and, perhaps, Fe would have migrated from the rodingites (with alteration of hydrogrossular) and silica and magnesium would have diffused into the rodingite.

Metasomatic zonation is also established at the contact of the hornblende rodingite vein and the serpentinite, forming monomineralic orthopyroxene and hydrogrossular zones and a Ca-rich sahlite zone is initiated. The diffusion nature of this alteration is illustrated in the compositional

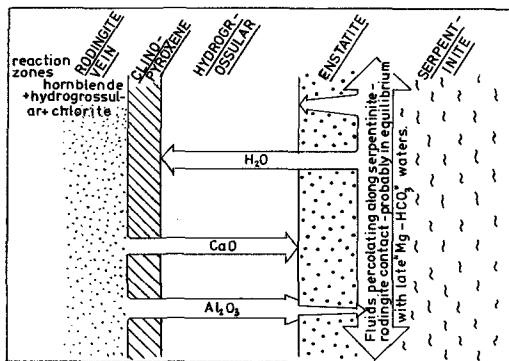


FIG. 13. Possible pore-fluid-wall-rock reactions occurring between hornblende rodingite vein and serpentinite.

variation of the orthopyroxenes, which exhibit a decrease in Mg content away from the serpentinite contact. A sketch of the possible pore fluid-wall rock reactions is illustrated in fig. 13.

ENVIRONMENT OF METASOMATISM

The metasomatic alteration of the gabbroic rocks has probably taken place both contemporaneous with and after serpentinization, but, because a wide range in conditions is possible for serpentinization (e.g. Bowen and Tuttle, 1949; Weiner and Taylor, 1973; Barnes *et al.*, 1969, 1972; Campbell, 1975) it is necessary to examine the stability fields of the minerals that make up the rodingites to determine the conditions of metasomatism.

Liou (1971) proposed that the appearance of prehnite in discrete patches or veins in hydrothermally altered gabbroic rocks can be used as a geothermometer. Maximum temperatures of prehnite crystallization are 403 °C at 3 kb and 393 °C at 5 kb. However, the presence of CO₂ lowers the dehydration curve and prehnite probably forms at much lower temperatures.

Hydrogrossular affords a geothermometer that is independent of pressure. Experimental work in the system CaO-Al₂O₃-SiO₂-H₂O (Yoder, 1950; Carlson, 1956) shows that the temperature of hydrogrossular crystallization increases with increasing Si content, from 220–226 °C for a fully hydrated species, to 800 °C for an anhydrous grossular. The compositions of the hydrogrossulars analysed in this study give a temperature range of 260 to 320 °C; however, these temperatures are only an approximation because of the unknown effect of trivalent ions other than Al³⁺. Seki (1965) concluded that garnets in rodingites were formed below 300 °C because the associated minerals were formed in the greenschist facies or lower. Coleman (1966) suggested that the New Zealand hydrogarnets formed between 290 and 450 °C and the California ones in the range 240 to 360 °C. O'Brien and Rodgers (1973*b*) suggested that the Wairere hydrogrossulars formed at between 430 and 580 °C, although lacking chemical data.

O'Brien and Rodgers (1973*b*) reported the presence of xonotlite in some gabbros in the Wairere serpentinite. Buchner *et al.* (1960) showed experimentally that xonotlite is stable between 260 and 400 °C at 500 lb in.⁻² (0.03 kb) and between 220 and 470 °C at 3000 lb in.⁻² (0.21 kb). O'Brien and Rodgers (1973*b*) concluded that the rodingites formed in the higher pressure range because of the effect of strong tectonic compression on the serpentinite. The evidence provided by rosenhahnite has been discussed by Leach and Rodgers (1977).

It seems probable therefore that the formation of the reaction zones may have occurred in the temperature range of 260 to 350 °C; however, it is difficult to estimate the pressure at the time of alteration. The presence of anhydrous garnet in the rodingites suggests a moderate to high pressure, while, as in the case of rosenhahnite, the pressure indicated by aragonite, which occurs on the shear planes at the limestone-serpentinite contact, is considered unreliable (O'Brien and Rodgers, 1973*b*, 1974). From the stability fields experimentally determined for prehnite and chlorite, it appears possible that the reaction zones formed at pressures between 2 and 3 kb. The load pressure prevailing during the formation of hydrogrossular was probably very low (Seki, 1965), and because of the high water content of these rocks it may be assumed that $P_{\text{total}} = P_{\text{H}_2\text{O}}$.

It has been proposed that the formation of calcisilicate zones occurs with a decrease in volume, since the alteration of plagioclase to hydrogrossular involves a loss of 20% by volume (Coleman, 1966). However, this is probably compensated for by the addition of water. If volume changes did occur then there would be fracturing between the different zones and shearing and fracturing within the zones, whereas neither of these two features are widely present. It is probable, therefore, that alteration of the gabbros approximates a constant volume process.

The presence of native copper in the rodingite dyke gives an estimate of the sulphur activity present during formation. From sulphide reactions plotted by Barton and Skinner in Barnes *et al.* (1967), the sulphur activity at 250 to 360 °C would be very low ($a_s = 10^{-19}$ – 10^{-22}).

TECTONIC SETTING

The tectonic emplacement of the Wairere Serpentinite as a cold diapir intruding Mesozoic and Tertiary sediments along the Waipa fault has been described by O'Brien and Rodgers (1973*a*, 1974). They have stressed the highly sheared nature of the serpentinite and the probable high compressional regime. The slickensided and grooved surfaces of the gabbroic inclusions as well as the cataclastic and brecciated nature of some contacts is evidence that the petrogenesis of the gabbros and rodingites was associated with strong tectonic movements of the serpentinite.

The general term, alpine ophiolite complex, has been applied to describe these peridotite-gabbro assemblages in orogenic zones (Coleman, 1971). The similarities between the oceanic crust and underlying mantle and the ophiolite suite suggests that the latter represents oceanic crust, generated at the oceanic ridges, and orogenically emplaced at

consuming plate margins (Thayer, 1969; Bird and Dewey, 1970, 1971; Gresens, 1970; Coleman, 1971).

The mineralogy, petrology, and geological setting of rodingites within these ophiolites is restricted to serpentinites and is unique, not being found in any other geological environment. Serpentinization of peridotites and rodingite alteration of gabbros could have taken place at the oceanic ridges. Honnorez and Kirst (1975) proposed that the gabbroic melt intruded ultramafic rocks in the upper mantle where basaltic magmas are generated. The metasomatism of both the peridotites and gabbros took place concomitantly in the lower oceanic crust and then moved diapirically upwards through fracture zones. Bird and Dewey (1971) and Coleman (1971), however, envisaged the metasomatic process to have occurred during the emplacement of the ophiolites into the continental margins.

The formation of double reaction zones and serpentinite veins cutting rodingites suggests that there has been more than one period of rodingitization and serpentinization at Wairere. Coleman (1967) proposed that reaction zones have been sheared off during the movement of the serpentinite and other reaction zones formed. It is probable therefore, that metasomatism has occurred at various intervals, possibly at the oceanic ridges and during emplacement into the geosynclinal sediments. O'Brien and Rodgers (1974) postulated that emplacement of the Wairere Serpentinite was intermittent and Honnorez and Kirst (1975) proposed the same type of movement for oceanic serpentinites and rodingites. Serpentinization would therefore occur at intervals with the influx of solutions of different compositions. All these factors greatly complicate the interpretation of the metasomatic formation of the reaction zone.

The different degrees of alteration exhibited by the various gabbro bodies within the Wairere Serpentinite could be caused by three factors: selective channelling of metasomatic fluids; introduction of mafic rocks at different periods of serpentinization; metasomatism of more altered rocks prior to juxtapositioning with the serpentinite.

The first postulate is unlikely because of the proximity of the unaltered hornblende gabbro dyke to the similar, but completely metasomatized dyke. Both inclusions have almost identical shapes and both are set in massive serpentinite, therefore channelling of solutions should have occurred equally along the contacts of both bodies. Various episodes of mafic inclusion are possible since Miyashiro (1975) has proposed the formation of ophiolites at island arcs while other authors have supposed formation at oceanic ridges. The mixing

of altered and unaltered gabbros could occur during consumption and ascent of the oceanic crust at plate margins or during diapiric intrusion at the ridges. The serpentinite therefore may leave behind original gabbroic contacts, incorporate additional tectonic inclusions and form new metasomatic contacts (Coleman, 1967) during the migration of the ultramafic body from its formation at the oceanic ridges to its emplacement at the continental margins. It is, however, not possible to distinguish between the other postulates from the existing evidence at Wairere.

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M12 Leach: The Wairere Serpentinite

THE PETROGRAPHY OF METASOMATIC ROCKS FROM
THE WAIRERE SERPENTINITE, KING COUNTRY,
NEW ZEALAND

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THE WAIRERE Serpentinite has been described by O'Brien and Rodgers (1973a, 1974) and calcium metasomatism occurring at contacts between serpentinite and included gabbro pods was briefly reported on by the same authors (1973b). In the course of a more comprehensive chemical and mineralogical study of the metasomatic rocks and minerals the opportunity was taken to make detailed petrographic examinations of all metasomatic and altered rocks exposed by active quarrying in 1973-74. Details of localities, referred to here by University of Auckland, Geology Department sample numbers, will be published in a full account of the chemistry and mineralogy elsewhere in this journal.

Eucritic gabbros, invariably highly altered, are the dominant type of included block. Hornblende gabbros occur rarely and vary from highly altered to relatively unaltered. Around each pod, three main metasomatic reaction zones were well developed. For the purpose of this study, the term reaction zone for all the rocks of the Wairere Serpentinite, while *rodingite* is used for that metasomatic phase containing garnet derived by metasomatic process (cf. O'Brien and Rodgers, 1973b). *Altered gabbro* defines those portions of the gabbro inclusions that have undergone some metasomatism but do not contain garnet.

Eucritic gabbros and their reaction zones

Altered gabbro All pods sampled were highly altered with the least altered sample (23448) being a grey, medium-grained rock cut by prehnite and pectolite veins. Secondary augite and skeletal leucoxene (probably after ilmenite) are set in a fine-grained aggregate of prehnite and saussurite and swirls of colourless chlorite. Rare, bent and fractured, albified plagioclase and fragmented augite suggest the original texture was subophitic. Elsewhere, the plagioclase is prehnitized and the augite completely chloritized.

Rodingite The rodingite reaction zones vary in thickness from about a metre, being very fine-grained and a light grey brown, to about 20 cm where they are a coarse-grained dark grey rock. The fine-grained variety is regarded as a result of a higher degree of metasomatism, than that which produced the coarse.

Coarse-grained rodingite (23443) has a pseudomorphic-granular texture of coarse-grained equant, colourless augite, dark-brown euhedral leucoxene and hydrogarnet laths pseudomorphous after plagioclase, set in a matrix of fine colourless to dark brown hydrogarnet and swirls of colourless to orange-tinted chlorite. Chlorite and serpentine veins transect the rock both parallel and perpendicular to the contact.

The contact with the serpentinite consists firstly, of a 7-8 mm cataclastic zone of fine-grained, rounded augite, and elongated rodingite fragments set in a laminated cryptocrystalline dark-brown matrix. Small calcite veins parallel the contact. This zone gives way to a thin brecciated zone of subhedral fine-grained augite and large rounded to angular fragments of dark-brown hydrogarnet partially altered to green chlorite; and this brecciated zone in turn grades into chloritized serpentinite consisting of minor magnetite and accessory equant leucoxene in a matrix of sheared clinoclase.

There is an abrupt change from coarse rodingite to altered gabbro 20 cm from the contact, marked by the disappearance of both groundmass and pseudomorphic hydrogarnet (23444).

A medium-grained equivalent of these rodingites is common in some pods (23437). However, in this case the contact between the chloritized serpentinite and the rodingite is sharp with green chlorite pseudomorphing augite up to 2 cm into the gabbro. Leucoxene is absent in such rocks and the rodingite extends up to 35 cm from the outer margin.

In all the eucritic gabbros the coarse and medium-grained rodingites are locally intersected by hard white zones of colourless acicular pectolite, radiating from zone borders, and matted by rosettes of lath-like prehnite which are the major constituent in central regions. These zones run sub-parallel to the contact and are very irregular, attaining 7-8 cm in thickness (23701) and pinching out to a few millimetres in width (24702). In one locality two such zones were present. The outer zone (24703) is chalky due to intense weathering, and in some segments is pink in colour.

The lower portion of this zone is brecciated, containing rounded fragments and subhedral crystals of colourless lath-like rosenblutite. The inner zone (24705) is separated from the outer by a dark grey, medium-grained, partially brecciated rodingite containing flakes of prehnite and pectolite and green chlorite-filled vugs.

Fine-grained rodingite is located only at the apices of the xenoliths (23435, 23436, 23438, 23439). These rocks have a porphyritic texture with colourless euhedral endopside phenocrysts set in a very fine-grained matrix of chlorite and hydrogarnet. The contact with a monomineralic, fine-grained penninite zone is sharp but irregular, with rounded fragments of rodingite being incorporated in the outer chloritic zone (24697). These rodingites show both textural and compositional gradations. Near the contact there is a sharp boundary where endopside is pseudomorphed by green chlorite (penninite-dianite) and is set in a matrix of up to 95% very fine-grained brown hydrogarnet. Such rodingites are a milky green-grey colour. Further into the gabbro, the matrix becomes a little coarser grained with an increase in chlorite content and the appearance of groundmass diopside. At the inner edge of this rodingite zone, the rock is medium-grained (24700) and is similar to that found associated with the coarse-grained varieties.

The brown patchy appearance of most fine-grained rodingite is due to concentrations of either chlorite or garnet in the matrix. Large vugs filled with colourless diabantite are rimmed by a chlorite-rich rodingite. Some, rare, large garnets pseudomorphing plagioclase are scattered throughout 23438. Chlorite veins occur parallel and perpendicular to the contact with some cutting, and being cut, by diopside phenocrysts.

Chloritized serpentinite occurs as a dark blue-green zone adjacent to the gabbro contact and extends a few centimetres to a metre from the xenoliths. The highly sheared, platy serpentinite is cut by calcite veins and is altered to a fine-grained, green penninite, primarily around these veins, with minor alteration elsewhere (23441). Chloritization and calcite veining increases near the contact (24696) and in places the chlorite forms a thin, dark-green, monomineralic zone (24697). Magnetite is also concentrated near contacts.

Hornblende gabbros and their reaction zones

Altered gabbro Near the centre of the hornblende gabbro xenolith, the rock is hard, grey, highly altered, fine-grained and cut by numerous chrysotile and prehnite veins (24712). There is no primary plagioclase. Rare, primary, euhedral and subhedral, green hornblendes are bent, fractured and partially chloritized and are set in a fine-grained matrix of clinzoisite, prehnite, 2-3X magnetite and accessory titanite. Subhedral brown titanite and green chlorite form rare veins. In places the rock is highly sheared with hornblende fragments set in a foliated matrix of prehnite, chlorite and elongated granular titanite.

Rodingite At the contact with the serpentinite, the hornblende gabbro has been altered to a very fine-grained, hard, light-brown rodingite (24713) consisting of granular, light-brown hydrogarnet and colourless chlorite containing up to 10% titanite and minor (1-2%) opaques. Titanite grains are elongated parallel to the jointing, giving the rock a schistose character. The rodingite has a patchy appearance (24714, 24715) due to concentrations of either hydrogarnet (white in hand specimen), or colourless chlorite (brown in hand specimen) or purplish-brown magnetite patches (24716). In some cases these patches exhibit flowage.

Late stage serpentinite veins cut the rodingite and are bordered by a 5-7 mm zone of lath-like prehnite crystals which, in turn, is mantled by a dark-green chlorite (ripidolite) zone containing large euhedral to subhedral titanite grains.

Elsewhere ripidolite, again associated with titanite, is found in veins (24716) that cut through the rodingite and along joints. In (24717) fragmented basaltic grains and serpentinite fragments are also present. Prehnite flakes are concentrated around some veins (24717) and also may occur in the rodingite matrix (24714).

The contacts between chloritized serpentinite and rodingite are irregular and varied. In 24718, the contact is sharp with a large white zone of impure, dark brown hydrogarnet and fine-grained serpentinite separated from the chloritic zone by a pink-brown rodingite. In places this zone is sheared and brecciated; fragments being found in an inner hydrogarnet and the outer serpentinite zone. In 24709 the contact is gradational with the chloritized serpentinite containing patches of white hydrogarnet passing into fine-grained rodingite.

All these reaction zones are cut by a network of late serpentine veins, ranging from coarse translucent green serpentine (24716) to fine chrysotile veinlets. Relic altered gabbro is present within the rodingites, as greyish-black blocks consisting of bent and fractured green to blue-green hornblende, set in a fine-grained intergranular matrix of clinzoisite and titanite.

Chloritized serpentinite Adjacent to the gabbro is usually a zone up to 30 cm wide of highly sheared serpentinite that has been almost completely chloritized to green penninite and is cut by 5-7 cm clear chrysotile veins that are most numerous near the contact (24707). Euhedral to granular, yellow-orange, pleochroic titanites occur some 6 cm from the rodingite and show partial replacement to an opaque, probably ilmenite. In 24709 this titanite has been granulated by shearing. Elsewhere (24709) the chloritic zone encloses partially chloritized basaltic grains. In places the chloritic zone is absent (24710), with unaltered blocky serpentinite, exhibiting mesh texture, in direct contact with altered hornblende gabbro (24711).