SERPENTINIZATION CONSIDERED AS A CONSTANT-VOLUME METASOMATIC PROCESS[1]

T. P. Thayer, *U. S. Geological Survey, Washington, D. C.*

Abstract

The three classic arguments for major expansion of peridotite during serpentinization—(1) constant composition except for hydration, (2) internal deformation, and (3) lack of Mg- or Si-metasomatism in country rocks—are considered and found invalid in specific instances, and probably in general. Plots of about 350 analyses of fresh and serpentinized ultramafites show that major changes in the ratio of total bivalent oxides (MgO, FeO and CaO) to SiO_2 and oxidation of iron yield an end product essentially composed of serpentine and magnetite from either dunite or pyroxenite. Structural relations of serpentinized rocks with interlayered or included fresh rocks and minerals, such as serpentinized dunite with pyroxenite, anorthosite, and chromite, prove that no change in volume has accompanied serpentinization, on hand-specimen and outcrop scales. World-wide association of calcium-rich rodingite with serpentinite indicates: that Mg-metasomatism of the kind that forms chloritic "blackwall" with talc does not occur in the serpentine mineral stability range; that Mg, Si, and alkalies in excess of the amounts needed to form serpentine are relatively fugitive elements; and that diffusion between ultramafite and country rock must be very minor compared to fluid or gas transfer of Mg and Si. Failure to recognize the chemical changes accompanying serpentinization has led to serious exaggeration of the original pyroxene content of alpine peridotite.

Introduction

Recently three papers (Hess and Otalora, 1964; Green, 1964; Hostetler *et al.*, 1966) have given new impetus to the theory, also held by some Russians (Shteinberg, 1960), that serpentinization of ultramafic rocks is accomplished by minimal changes in composition except for addition of water, and is accompanied by major increase in volume. Decrease in density from about 3.2 to 2.6 g/cc and addition of 10–14 per cent water during the process present three alternatives: (1) removal of about 30 per cent of the original material in solution; (2) increase in volume by 35 to 40 per cent; (3) some combination of (1) and (2). Most geologists seem to argue either for alternative (1) or (2), with little inclination to compromise on (3). Because ultramafites of the alpine type commonly are more or less serpentinized and are widely believed to represent upper mantle material, possible changes in bulk composition during serpentinization have broader implications than many geologists realize.

The arguments for expansion during serpentinization arise primarily from the sheared nature of most serpentinite and from general absence of obvious related alteration in adjoining country rocks, but also, I believe, from inadequate study of critical rock relations and failure to consider fully available petrographic and chemical information. The aim of this

---

[1] Publication authorized by the Director, U. S. Geological Survey.

paper is to call attention to data that show serpentinization commonly does involve major changes in bulk composition and that, at least in some situations, constancy of volume can be proved. Volume-for-volume replacement of olivine and pyroxene by serpentine[1] or other minerals requires movement of large quantities of water or other solvents in an open system, but this concept is fundamental in genesis of many kinds of ore deposits. Refusal to apply the same concept to serpentinization, even though it involves unsolved problems, seems inconsistent.

A paper of this kind grows, like Topsy, largely from discussions between the author and his colleagues, who may serve as consultants, provide alternative hypotheses as targets, or do both. R. G. Coleman and P. B. Hostetler very kindly reviewed this paper at an early stage, loaned me a copy of their manuscript to which this is in part a rebuttal, and called my attention to Shteinberg's paper by providing a translation. C. Ervin Brown, C. L. Christ, G. T. Faust, P. W. Guild, Norman Herz, D. B. Stewart, and David Wones contributed critical advice and friendly counsel on many aspects of the complex problems touched upon in this paper. The San Jose Oil Company, Manila, kindly provided two analyses of combustible gas from seeps in the Zambales Complex, and permitted their publication.

NORMATIVE COMPOSITION OF SERPENTINIZED DUNITE AND SERPENTINE MINERALS

One way to illustrate the chemical changes effected by serpentinization is to compare the known original modal composition of an ultamafite with the normative pyroxene-olivine ratio of its serpentinized equivalent. Dunites are ideal for such comparisons: "As the serpentinization process is one of replacement by pseudomorphism, the relative proportions of replaced olivine and pyroxene may be readily determined, and . . . the rocks may be referred to as serpentinized dunite or . . . peridotite" (Bailey and others, 1964, p. 81) and the essential original mineral in dunite is olivine, which varies mainly in Mg:Fe ratio. In Table 1 the normative pyroxene-olivine ratios for a highly serpentinized dunite and the average of four completely serpentinized dunites are compared with that for the average of 15 analyses of serpentine minerals (Faust and Fahey, 1962, p. 18). In column B of the table the sum of pyroxene and olivine has been recalculated to 100 per cent from the CIPW norm. In column C pyroxene and olivine are recalculated by assigning all MgO, CaO, FeO and SiO_2 in the analyses to these minerals and recalculating

---

[1] In this discussion the serpentine-group minerals are referred to collectively as serpentine or serpentines, and rocks composed essentially of serpentine minerals are called serpentinite.

TABLE 1. CHEMICAL ANALYSES, NORMS AND NORMATIVE PYROXENE CONTENT OF SERPENTINIZED DUNITE, SERPENTINE MINERALS, AND SERPENTINITE

Chemical analyses and molecular equivalents

	1		2		3		4	
	anal.	mol.	anal.	mol.	anal.	mol.	anal.	mol.
SiO₂	40.12	669	33.10	552	40.65	677	38.2	637
Al₂O₃	.98	10	.72	7	1.60	16	2.0	20
Cr₂O₃	.28	2	.38	2	—	—	—	—
Fe₂O₃	6.52	41	5.54	34	2.80	18	6.0	38
FeO	1.21	17	2.30	32	1.34	18	2.3	31
MgO	35.78	895	40.37	1,009	38.71	968	36.9	923
CaO	.12	2	.31	5	.02	—	.5	9
Na₂O	.24	4	.31	5	none	—	.2	3
H₂O+	12.17	—	14.46	—	13.31[1]	—	12.4	—
Other	2.70	—	2.50	—	2.34[2]	—	1.5	—
Total	100.12		99.99		100.77		100.0	

Normative Composition

[A, calculated by C.I.P.W. method; B, olivine and pyroxene recalculated to 100 per cent from A; C, proximate composition calculated by method described in text; D, composition calculated on feldspar-free basis, modified after Shteinberg (1960)]

	1 A	1 B	1 C	1 D	2 A	2 B	2 C	2 D	3 A	3 B	3 C	3 D	4 A	4 B	4 C	4 D
fo	41.6	47.7	43.6	47.4	82.5	95.1	88.0	85.3	47.7	51.3	52.8	51.7	52.2	61.7	56.8	56.3
fa	45.7	52.3	1.2	7.1	—	—	4.1	11.7	45.5	48.7	1.0	3.5	32.4	38.3	2.6	8.5
en	—	—	53.5	37.8	3.7	4.3	6.7	—	—	—	44.6	39.4	—	—	37.4	26.2
fs	—	—	1.4	5.2	—	—	0.4	—	—	—	1.6	2.4	—	—	1.9	3.7
wo	2.5	—	.3	—	0.5	0.6	0.8	—	—	—	—	—	1.9	—	1.3	1.2
ab	.7	—	—	—	3.2	—	—	—	—	—	—	—	2.9	—	—	—
an	4.6	—	—	—	0.7	—	—	1.1[3]	4.9	—	—	—	8.4	—	—	—
mt	4.9	—	—	2.3[4]	9.0	—	—	1.9[4]	1.9	—	—	3.0[4]	1.3	—	—	4.1[4]
hm	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
c	.5	—	—	—	.4	—	—	—	—	—	—	—	.9	—	—	—
Total pyroxene	45.7	52.3	55.2	43.2	4.2	4.9	7.9	0	45.5	48.7	46.2	41.8	32.4	38.3	40.6	31.1

[1] Average of 10 determinations.
[2] Includes 2.00 per cent H₂O⁻, average of 8 determinations.
[3] Ca₂SiO₄.
[4] Chromian spinel.
1. Serpentinized dunite, Lizard, Cornwall. Green, 1964, p. 144.
2. Average of 4 serpentinized dunites, Mayaguez, Puerto Rico. Hess and Otalora, 1964, p. 158.
3. Average of 15 serpentines. Faust and Fahey, 1962, p. 18.
4. Average of 60 serpentinites containing more than 11 per cent H₂O+.

the total to 100 per cent. This approximate method minimizes the pyroxene content because no FeO is assigned to magnetite, and it ignores Al_2O_3, which in feldspar-free rocks is mostly in pyroxene, though some may occur in spinel. Calculation of Na_2O and K_2O as feldspar has two objections: no feldspar occurs in the mode, and determination of Na and K in ultramafic rocks seems to be uncertain (Steuber and Murthy, 1965; Hamilton and Mountjoy, 1965). In the CIPW calculation, Na_2O has a strong effect on the pyroxene-olivine ratio because one per cent of it ties up as much SiO_2 in albite as 3.9 per cent MgO in enstatite or 7.8 per cent MgO in forsterite; corresponding figures for FeO in ferrosilite and fayalite are 5.4 and 10.8 per cent, respectively. To avoid confusion, norms calculated by the simplified method will be referred to as proximate in this paper.

In column D the normative minerals have been calculated essentially by Shteinberg's method (1960). This method calls for doubling the molecular amount of Fe_2O_3 and adding it to the total of bivalent oxides (RO); then an amount of RO equivalent to Al_2O_3 and Cr_2O_3 is subtracted as spinel. The resulting molecular figure is designated $R\acute{O}$ and used as the basis for chemical discussions. This method is followed in essence also by Hess and Otalora (1964, p. 159) and Green (1964, p. 143) to determine the original composition of serpentinites.

Examination of Tables 1 and 2 shows that the normative pyroxene content of serpentinized dunite ranges from almost zero to about 45 per cent even when calculated by Shteinberg's method, and the normative pyroxene may exceed olivine. The proximate normative pyroxene in 15 serpentines from ultramafites (Faust and Fahey, 1962, p. 18) ranges from 20.8 to 81 per cent, but the average normative pyroxene:pyroxene plus olivine (100 px:px+ol) ratio of 48.7 (Table 1, no. 3B) (50.6 if Al_2O_3 is included) is remarkably close to the 50:50 ratio in theoretical serpentine ($H_4Mg_3Si_2O_9$). The very low normative pyroxene in the Mayaguez dunites is attributable partly at least to presence of brucite (Table 2).

Principal Chemical Changes Accompanying Serpentinization

The general trends of chemical variation with increasing serpentinization of ultramafites are shown in Fig. 1. There the silica and sums of the major bivalent constitutents in 165 analyses of samples from widely scattered regions have been plotted against content of H_2O+, if determined, or total H_2O. About 125 of the analyses, or three-fourths, are of alpine ultramafites (Joplin, 1963; Green, 1964; Mattson, 1964; Wilson and Ingham, 1959); 35 are from stratiform complexes, mostly the Great Dyke (Worst, 1958); and five are from concentrically zoned complexes (Ruckmick and Noble, 1959, p. 984). Analyses containing more than 0.5

per cent CO_2 and about 6 per cent Al_2O_3, or so much SiO_2 as to suggest presence of much talc or quartz were excluded.

The data plotted in Fig. 1 indicate that serpentinization of the average ultramafite is essentially complete when H_2O+ reaches about 11 per cent, a figure that agrees fairly well with a theoretical mixture of 90–95 per cent serpentine and 5–10 per cent magnetite and chromite. Oxidation of Fe^{2+} in olivine and pyroxene somewhat in excess of the amount needed to

TABLE 2. COMPARISON OF ORIGINAL MINERAL COMPOSITION, DEGREE OF SERPENTINIZATION, AND PROXIMATE NORMATIVE PYROXENE IN PERIDOTITE SAMPLES FROM THE AMSOC CORE HOLE NEAR MAYAGUEZ, PUERTO RICO

Sample No.	Rock Type	Per Cent serpentinized	Per Cent H_2O+	Per Cent pyroxene		
				Original[1]		Proximate normative[2]
				en	di	
A2	Harzburgite	90–95	12.41	5	5	35.5
A3	Harzburgite	80	10.97	10		37[3]
A6	Harzburgite	97	12.70	5	3	35.4[3]
A7	Dunite	100	14.02		3	8.7 (1.9)[4]
A8	Dunite	99–100	15.26		3	0 (2.7)[4]
A10	Harzburgite	100	12.41	5		32.4
A11	Harzburgite	80	10.00		5–10	37.4[3]
A13	Dunite	100	14.54		2	22.2[3]
A14	Dunite	99–100	14.10		2	3.9 (3.3)[4]
A18	Harzburgite	94	12.15	5	6	36.5[3]
A19	Harzburgite	75	11.13		25–30	33.3

[1] en, di: relict grains of and serpentine pseudomorphs after enstatite and diopside, respectively (Mattson, 1964, p. 17).

[2] Calculated by method described in text.

[3] Rock contains, or may contain, brucite.

[4] Weight percent of brucite in rock (Hess and Otalora, 1964, p. 154).

form magnetite, shown by hematite in the norm, appears to be a consistent chemical change (Table 1, col. 4A). The great variability of the $FeO:Fe_2O_3$ ratio in serpentine minerals (Faust and Fahey, 1962, p. 18) and general absence of modal hematite imply that the excess Fe_2O_3 over that assignable to normative magnetite is in the serpentine structure, but some may also be in magnesioferrite in solid solution with magnetite. Native FeNi alloys such as awaruite or josephinite seem to be quantitatively minor, and apparently formed during the later stages of serpentinization under exceptional reducing conditions (Krishnarao, 1964).

The MgO-FeO-CaO-SiO_2 part of the diagram may be divided into

T. P. THAYER
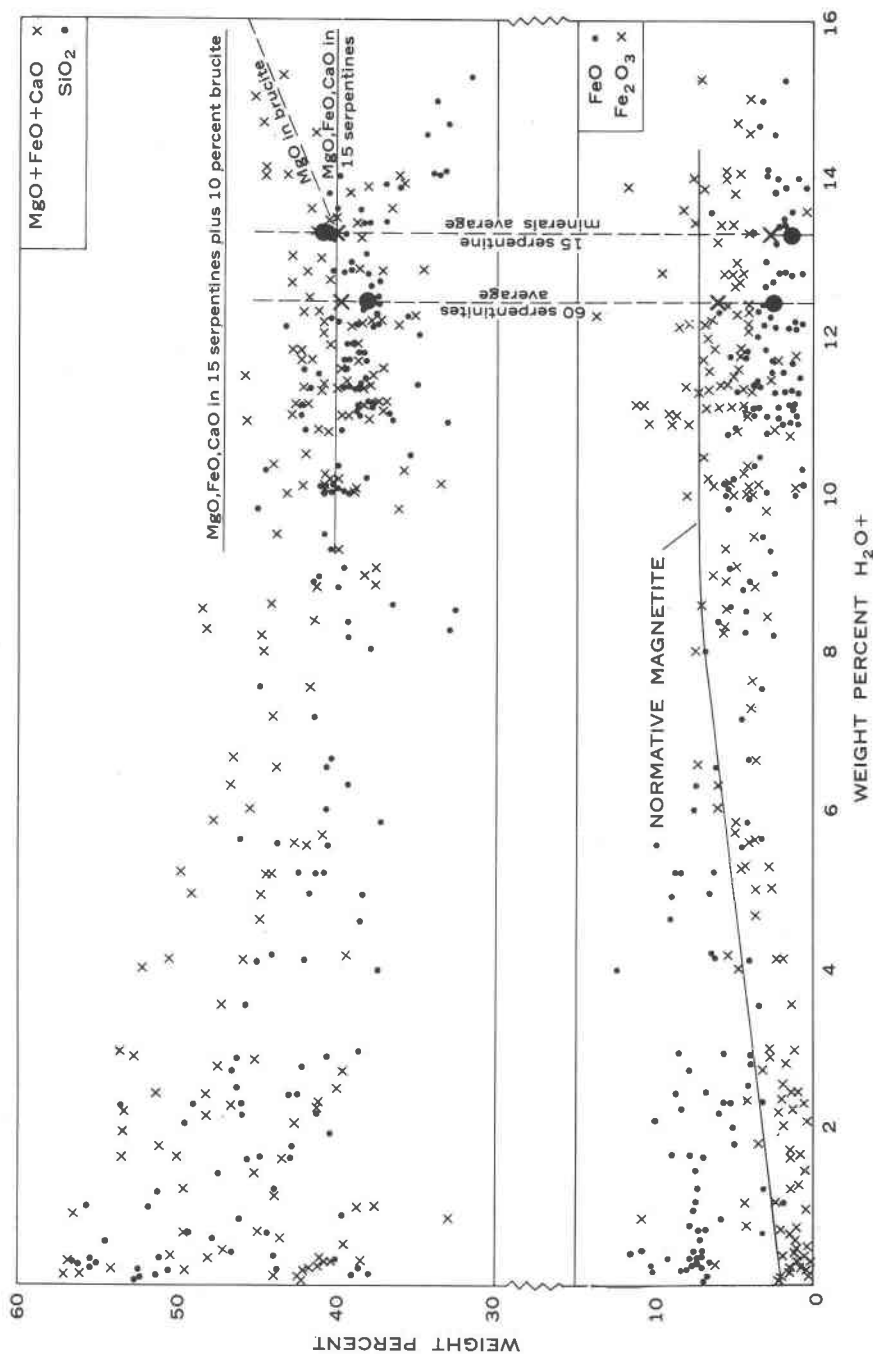
Fig. 1. Variation in composition of 165 ultramafites with content of H_2O+: above, total bivalent oxides (MgO, FeO, CaO) and SiO_2; below, FeO, Fe_2O_3, and approximate normative magnetite. Large symbols indicate averages of 15 serpentine minerals (Faust and Fahey, 1962) and 60 serpentinites containing more than 11 per cent H_2O+.
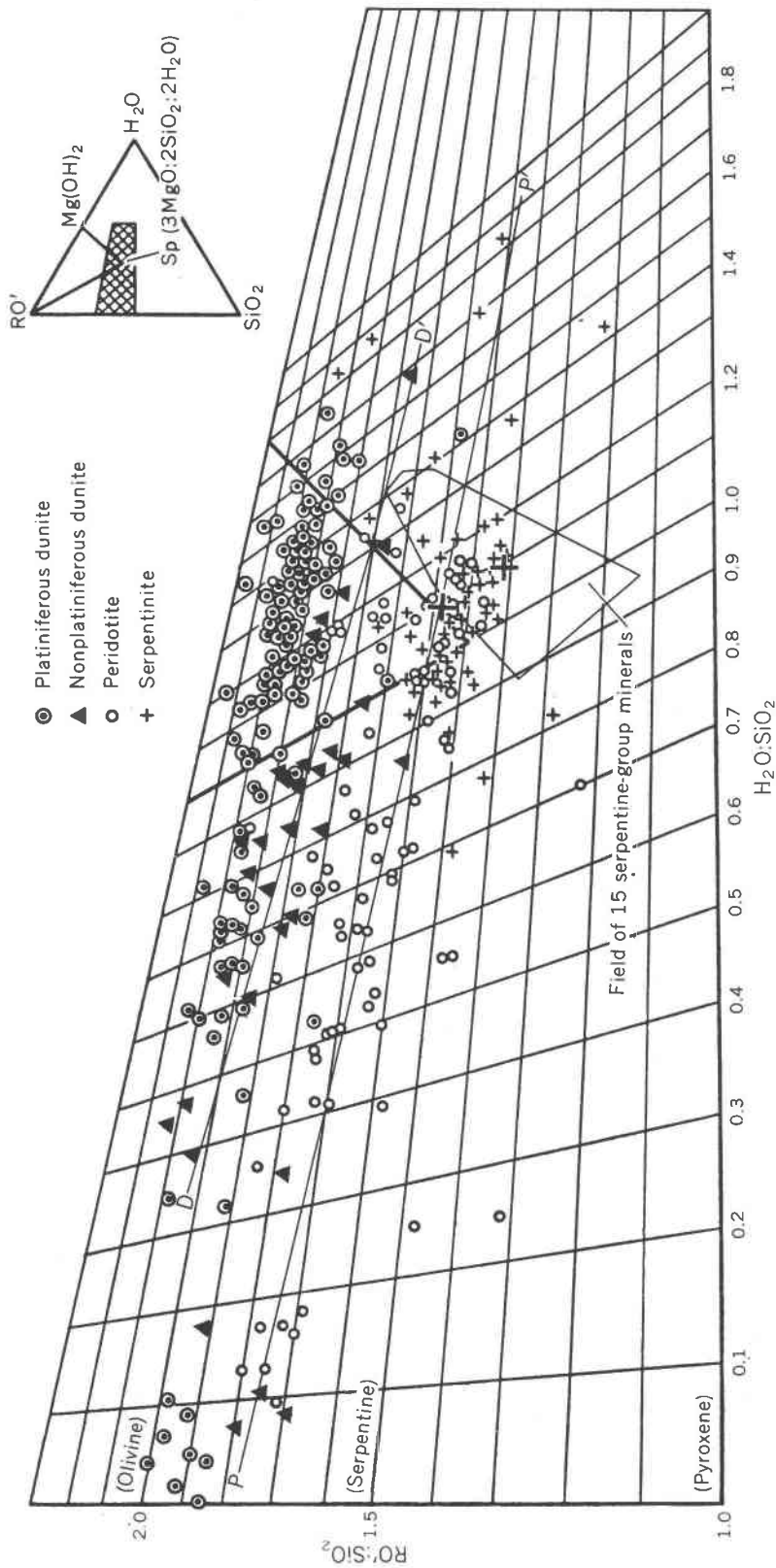
Fig. 2. Diagram showing molecular ratios of $RO':SiO_2$ and $H_2O:SiO_2$ in ultramafites of the Ural Mountains, after Shteinberg (1960). Trend lines for non-platiniferous dunites (D-D') and peridotites and serpentinites (P-P') added, with composition field of 15 serpentine minerals (Faust and Fahey, 1962) calculated by Shteinberg's method. Averages of 60 serpentinites shown by large crosses; upper cross calculated by Shteinberg method; lower cross, calculated with normative magnetite.

three segments according to H_2O+ content: (1) 0–1 per cent, (2) 1–10 per cent and (3) 10–16 per cent. The wide variation of the oxides in the first segment reflects samples of fresh rocks that range from dunite to pyroxenite. The segment from 1–10 per cent H_2O+ represents mixtures of primary and secondary minerals, in which the decrease of total MgO, FeO, and CaO is comparable to that of SiO_2 as the composition of serpentine is approached. The essentially horizontal trend of values between 10 and 14 per cent H_2O results principally from mixtures of secondary minerals: magnetite, serpentines of various compositions, and small amounts of brucite, talc, amphibole and carbonate. The presence of brucite (69 per cent MgO, 31 per cent H_2O) accounts for the high content of water and total bivalent elements and the low SiO_2 in at least three and probably in seven of the eight samples that contain more than 14 per cent H_2O. For comparison, three lines have been added to show the effect of brucite on total composition. The sloping line indicates increase in MgO and H_2O with increase in brucite; a reciprocal decrease in SiO_2 seems obvious. The lower horizontal line indicates the average bivalent oxide content of 15 serpentines (Faust and Fahey, 1962, p. 18); only one analysis deviates from this average by more than 2 percentage points. The upper line indicates the effect of adding 10 per cent brucite (6.9 per cent MgO) to the serpentine average. In most rock analyses much of the excess of the bivalent oxides over the serpentine average consists of FeO, probably combined in modal magnetite; only part of this excess is attributable to brucite. For example, subtraction of FeO in normative magnetite from the analyses of the brucite-bearing Mayaguez dunites (Table 2) gives calculated percentages (in parentheses) for brucite that compare with the determined values as follows: A-7, 1.9(1.2); A-8, 2.7(2.0); A-14, 3.3-(2.4). Even though it may be coincidental, such close agreement indicates that very few of the serpentinites plotted contain as much as 5 per cent brucite. CaO and Al_2O_3 seem to decrease irregularly with increasing water content, but not in constant ratio: the average CaO content drops from 1.34 per cent (22 analyses) in the range 8–10.7 per cent H_2O to 0.56 (56 analyses) with higher H_2O content; Al_2O_3 averages 2.71 per cent (25 analyses) between 8 and 10.7 per cent H_2O, and drops to 1.70 per cent (33 analyses) above 12 per cent H_2O. Although CaO and Al_2O_3 may be leached during serpentinization or fixed in hydrogrossularite as Hess and Otalora (1964, p. 155) suggest, comparison of modes and analyses of the Mayaguez cores indicates that occurrence of relict clinopyroxene, which is notably resistant to serpentinization, is a more important factor in the distribution of these two oxides in serpentinite.

Two conclusions may be drawn from the data in the two tables and

Fig. 1: (1) completely serpentinized ultramafites are, as they theoretically should be, mixtures of serpentine and magnetite, with other minerals in accessory amounts; (2) the serpentinization process is not uniform, but forms serpentines that differ widely in composition and normative px:ol ratio. The chemical differences between the serpentinized dunites from Mayaguez and Lizard must be due largely to the serpentinizing processes, because the composition of the original olivine in them was essentially the same: $Fo_{89-91.2}$ in Mayaguez (Hess and Otalora, p.153) and $Fo_{89.7-91.0}$ in Lizard (Green, 1964, p. 148).

Major differences in chemical and physical conditions of alteration are implied by variations in stability of chromite in the verde antique and "buckskin-weathering" varieties of serpentinite. In the verde antique variety, well described by Chidester (1962) lamellar or platy serpentine and antigorite form a felted fabric which makes the rock tough. Concentration of the magetite in grains of appreciable size commonly leaves the native green color of the serpentine unobscured when the rock is cut for ornamental use. In this rock chromite characteristically is attacked hydrothermally, and may be extensively replaced by chromian chlorite (Miller 1953; Thayer, 1956). The "buckskin-weathering" facies is named from its characteristic yellow-brown or brownish-red color on weathered surfaces and is very brittle. In this rock the serpentine forms a very characteristic mesh of minute cross-fiber veins along grain boundaries and fractures in olivine; much of the magnetite is extremely fine and dusty, imparts a sooty gray or black color on fresh fractures, and weathers readily to brown limonite. The magnetite in this kind of serpentinite commonly accretes on chromite to form simple sharply bounded rims (Du Rietz, 1956, fig. 25, 26; Thayer, 1956). In general, I believe that verde antique is associated with talc in foliated green-schist or amphibolite-faces country rocks and near younger dioritic or more silicic plutonic intrusions. The "bucksin-weathering" facies is preeminent in low-grade unfoliated country rock environments such as Cuba, Oregon, California, and Cyprus. Intermixing of both kinds of serpentinite in some places undoubtedly reflects a complex history of fluctuating conditions, as in the State Line district of Maryland and Pennsylvania. Little systematic work seems to have been done on this very interesting and promising problem.

Belief in essential immobility of Mg, Fe, Ca and SiO_2 during serpentinization seems to be founded on the common presence of brucite in partly or completely serpentinized dunite and on the assumption that recalculation of secondary magnetite back to FeO is a valid procedure. Shteinberg (1960) has plotted more than 300 Russian analyses of ultra-

mafites, recalculated by his method, to show the mutual relations of $RÓ$: SiO_2: H_2O. His diagram (Fig. 2) shows that in approximately 150 dunites the average $RÓ:SiO_2$ mole ratio falls between 1.8:1 and 2.2:1, and the extremes range between about 1.6:1 and 2.25:1. A ratio of 1.6:1 is equal to about one-third pyroxene in the norm, whereas 2.25:1 indicates a deficiency of SiO_2 equivalent to about 9 per cent of forsterite. Calculation of Mayaguez analysis A8 (Table 2) by this method yields an $RÓ:SiO_2$ ratio of 2.2, or SiO_2 deficiency equivalent to 7.2 per cent forsterite or 6 per cent brucite. Ratios of $RÓ:SiO_2$ exceeding 2:1, that of $RO:SiO_2$ in olivine, obviously cannot be interpreted rationally in terms of original olivine and pyroxene.

Shteinberg, I believe, oversimplifies interpretation of his data (Fig. 2), when he draws a rather sharp distinction between dunites in the range 1.9–2.1 $RÓ:SiO_2$, and peridotites and serpentinites between 1.4 and 1.8:1, even though he recognizes some transitional rocks. To compare my diagram with Shteinberg's I have added to his the composition field of the 15 serpentines from Faust and Fahey, and the average of the 60 serpentinites from Table 2, all recalculated by his method. The peridotites, though scattered, clearly trend from about 1.75 $RÓ:SiO_2$ when fresh to about 1.55:1 when serpentinized, and cluster with other serpentinites around the serpentine composition point (1.5 $RÓ:SiO_2$; $1H_2O:1SiO_2$). Of the 32 nonplatiniferous (alpine type) dunites, 28 follow a trend approximately parallel to the peridotites, from about 2.05 $RÓ:SiO_2$ and $0.4H_2O:SiO_2$ to 1.75 $RÓ:SiO_2$ and $1.7H_2O:SiO_2$. Similar relationships between dunite and pyroxene-bearing peridotites are suggested in my diagram by the upper staggered or double row of symbols for total bivalent oxides below about 8 per cent H_2O. Except for the platiniferous dunites, it seems to me that Shteinberg's and my diagrams, based on two different groups of analyses and different methods of calculation, agree surprisingly well. The platiniferous dunites, which are described as small bodies within coarse gabbro, appear to maintain essentially constant $RÓ:SiO_2$ ratios, and probably reflect a consistently different chemical environment related to their different occurrence. Support for this hypothesis is provided by two analyses of serpentinized dunite in Lizard (Green, 1964) which can be distinguished chemically from associated pyroxene-bearing peridotites only by 2–3 per cent more H_2O+, 1–3 per cent less Al_2O_3, and 1–2.5 per cent less CaO. These differences, of course, reflect variations in degree of serpentinization as well as original composition, and would be expected to decrease with further serpentinization of the mass as a whole.

Because oxidation of about two-thirds of the iron in silicates to form magnetite is a fundamental aspect of serpentinization, recalculation of all Fe_2O_3 as FeO is misleading. In the first place, it completely disregards the

actual mineralogic equilibria of the rocks and exaggerates the RÓ combined in the silicates. In fresh rocks the RÓ:SiO_2 ratio, when corrected for spinels, theoretically cannot exceed the 2:1 ratio in olivine. Ratios as high as 2.25:1 therefore indicate that the RÓ:SiO_2 ratio has been increased or that the method of calculation is invalid, or perhaps both. Correction for magnetite in the nonplatiniferous dunites in Shteinberg's diagram would increase the slope of the RÓ:SiO_2 trend line (D-D') by at least half, from about 2:1 in fresh rocks to 1.55:1 in the serpentinite equivalent, which is still higher than the 1.42:1 ratio in Lizard dunite. Similar adjustment of the peridotite and serpentinite analyses would bring many more into the composition field of the 15 serpentines. Application of the Shteinberg formula to the 60 serpentinite average (Table 1, 4D) has the same effect on total bivalent oxides as adding 7.8 per cent brucite. Shteinberg's method of calculation, however, must be used to determine possible changes in the ratio of Fe and Mg during serpentinization. His data indicate little or no change in Fe:Mg ratio despite the shifts in RÓ:SiO_2, and therefore imply significant removal of Fe.

Evidence of Volume Change During Serpentinization

Possible volume changes accompanying serpentinization must be determined by the physical evidence in the rocks themselves, regardless of theoretical arguments. I agree with Turner and Verhoogen's conclusion (1960, p. 318) that "microscopic fabric and field relations of undeformed serpentinites show clearly . . . that serpentinization is commonly accompanied by little or no increase in volume." Hostetler *et al.* (1966) argue that volume increases of 35 to 40 per cent are probably common even in rocks that originally contained essential pyroxene; Hess in 1955 (p. 403) suggested a 25 per cent volume increase in dunite, although earlier (1933) he had cited evidence of constant volume as an argument for hydrous ultramafic magma and autometamorphic origin of serpentine.

Volume increases of 35 to 40 per cent are equivalent to linear expansion of 11 to 12 per cent, and should be readily detectable in rocks under suitable conditions. The most obvious evidence for expansion consists of radial fractures in fresh feldspar surrounding serpentinized olivines in troctolite (Smith, 1958, pl. 5); in Cuba I have seen troctolites that weather to resemble cup corals because of this phenomenon. The freshness of the feldspar, however, suggests limited movement of solutions, and very slight expansion could cause the fractures. The highly sheared nature of most serpentinite is cited also, but this is at best questionable evidence in view of the notoriously unstable tectonic environments of alpine ultramafites; even large masses of associated gabbros normally are highly faulted and sheared. The real answer to the question must be found in

structural relations between serpentinized ultramafites and unaltered but related contemporaneous rock units, such as interlayered dunite and chromite or fresh pyroxenite, or disruption of features in large exposures. Most olivine-rich peridotites do not provide this kind of unequivocal evidence. Complete serpentinization of olivine lenses and layers in massive chromite and of olivine-rich peridotite interbanded with centimeter-thick layers of fresh anorthosite without any visible disruption of chromite or anorthosite, as specimens in Geological Survey collections show, is conclusive evidence of volume-for-volume replacement. Fragile chromite structures such as the nodules and crystals from the Guillermina mine in Cuba (Thayer, 1942, pl. 4; 1964, Fig. 3) would be completely disrupted by any significant expansion; on the contrary, they characteristically are found intact even though the olivine matrix is thoroughly serpentinized. Original features of peridotites, such as schlieren banding in chromite deposits, commonly are so well preserved and intact over distances of several feet in large outcrops (Smith, 1958, pl. 6, 7) that one cannot tell anything about the degree of serpentinization from inspection of the weathered surface; such undisturbed preservation after even 10 per cent of volume increase seems out of the question.

In thin-section studies, many features like granulation in olivine and kink-banding in enstatite, which actually are relict from earlier magmatic stages and are quite distinctive, have been wrongly attributed to deformation resulting from expansion during serpentinization. Hostetler *et al.* (1966) with regard to other microscopic criteria state:

"Preservation of olivine grain boundaries in mesh-structure serpentines and the presence of bastite-type pseudomorphs after enstatite is often cited as evidence for 'serpentine' replacement at constant volume. This evidence is ambiguous. Interconnecting 'serpentine' veins and the innumerable fine veinlets of 'serpentine' cutting through parent olivine grains which show optical continuity are, in the manner of septarian concretions, plausible evidence for expansion. Buse and Watson . . . noted a volume increase due to a 'spreading apart' of olivine grains along fractures during serpentinization."

The characterization of the evidence as "ambiguous," I would say, is conservative; other relations indicate that it may be delusive. The partly serpentinized matrix of chromite ore such as that from the Guillermina mine (Thayer, 1964, Fig. 3) shows all the features mentioned in mesh-structure serpentinites, but the continuity of structure in the chromite shows that there can have been no volume change whatever. A photomicrograph by Diller (1921, Pl. 1B) of chromite from Shasta County, California, shows an intact anastamosing network of chromite grains in partly serpentinized dunite that has an apparent "expansion" pattern. Such situations show that the accepted criteria for determining spatial relationships between cross-fiber chrysotile and olivine may be completely misleading.
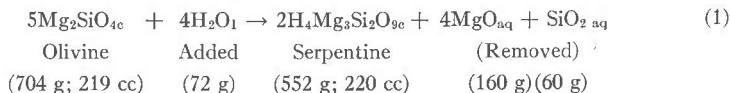
Diapiric movement during or after serpentinization has been proposed to account for the lack of Mg-metasomatism or silicification around some serpentinite masses (Hostetler *et al.*, in press), and has been appealed to as the solution of the volume problem. As Chidester (1962, p. 89) summarized the situation:

"The general lack of evidence for either increase in volume or expulsion of Mg and Si into the surrounding schist supports the idea that serpentinization did not occur while the ultramafic rocks were in their present positions."

It can be demonstrated, however, that no significant movement has accompanied the principal serpentinization of some large ultramafic masses. In the Canyon Mountain Complex (Thayer, 1963) the peridotite, as distinct from highly sheared marginal serpentinite, is probably 75 per cent serpentinized, and the gabbro is extensively altered to saussurite and rodingite. Post-gabbro dikes that cut the serpentinite are also extensively rodingitized. Perfect pseudomorphic preservation of igneous-intrusion features, absence of faults between gabbro and country rock, and interfingering of gabbro and peridotite eliminate the possibility of significant tectonic transport during or after serpentinization. As described by C. H. Smith (1958), relationships between country rock, gabbro, and ultramafites in the Bay of Islands Complex are essentially the same as those in the Canyon Mountain Complex; despite 60–99 per cent serpentinization of dunite (p. 29), layering in dunite and peridotite (pl. 6) and in interbanded peridotite and gabbro (pl. 7) is preserved perfectly. Clear distinction between border serpentinization during emplacement and later alteration probably is impossible in most masses, but I do not believe that we can seriously debate the evidence for large-scale constant-volume replacement of peridotite by serpentine *in situ*.

Reactions During Serpentinization and Movement of Materials

The main argument for volume increase during serpentinization seems to be the need, otherwise, for removal in solution of MgO and SiO_2 equal to 31 per cent of original dunite, according to the equation presented by Turner and Verhoogen (1960, p. 319):

$$5Mg_2SiO_{4c} + 4H_2O_l \rightarrow 2H_4Mg_3Si_2O_{9c} + 4MgO_{aq} + SiO_{2\ aq} \tag{1}$$

Olivine	Added	Serpentine	(Removed)
(704 g; 219 cc)	(72 g)	(552 g; 220 cc)	(160 g)(60 g)

The equivalent constant-volume equation for enstatite is

$$7MgSiO_{3c} + 4H_2O_l \rightarrow 2H_4Mg_3Si_2O_{9c} + MgO_{aq} + 3SiO_{2\ aq} \tag{2}$$

(700 g; 219 cc) (72 g) (552 g; 220 cc) + (40 g) (180 g)
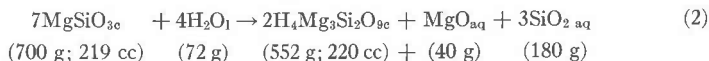
Addition of 10 per cent fayalite as in natural olivine changes equation (1) at atmospheric pressure to

$5(Mg_{.9}Fe_{.1})_2SiO_{4c} + 4.15H_2O_l$

(735 g; 221 cc)

$$\rightarrow 1.87(H_4Mg_3Si_2O_9)_c + 0.33\tfrac{1}{3}\,Fe_3O_{4c} + 3.4\,MgO_{aq} + 1.3\,SiO_{2\,aq} +\quad 0.4H_2 \tag{3}$$

(517 g; 206 cc)   (77 g; 15 cc)   (136 g)   (78 g)   (8,960 cc)g
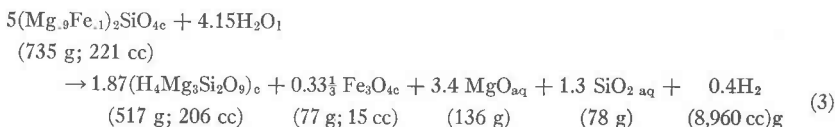
The comparable equation for natural enstatite is

$7(Mg_{.9}Fe_{.1})SiO_{3c} + 4H_2O_l$

(722 g; 219 cc)

$$\rightarrow 1.9(H_4Mg_3Si_2O_9)_c + 0.23\,Fe_3O_{4c} + 0.6\,MgO_{aq} + 3.2\,SiO_{2\,aq} +\quad 0.2\,H_2 \tag{4}$$

(524 g; 209 cc)   (54 g; 10 cc)   (24 g)   (192 g)   (4,480 cc)g
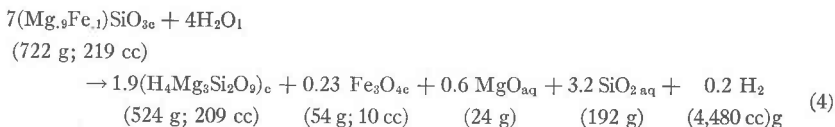
The four equations show that the weight of material that must be removed in solution during constant-volume serpentinization is about 30 per cent in both natural olivine and enstatite, and that, although presence of Fe reduces the amount of MgO to be removed in solution, it increases the SiO_2 reciprocally. From the solubility of brucite and SiO_2 in pure water some believe that unreasonable volumes of water would be required for their solution and transportation. However, as Bowen and Tuttle said (1949, p. 456), "The aqueous medium coming into the mass in nature would not be pure water."

Because ultramafites commonly are more highly serpentinized in low-grade geosynclinal rocks than in high-grade metamorphic terrains, connate water is now widely regarded as a probable major source of serpentinizing solutions. Of 24 oil-field waters and deep-well brines rich in $CaCl_2$ and NaCl listed by White and others (1963, p. F30–F33), 15 contained more than 500 ppm Mg, averaged 2,340 ppm, and ranged as high as 9,960 ppm of Mg. In the same samples Na averaged 46,420 ppm and Cl 83,000 ppm. None of the Mg-rich brines analysed for SiO_2 contained as much as 50 ppm of it. Connate waters of such compositions moving into a hot peridotite mass which is being serpentinized could be very effective carriers of Mg and Si. The contact zone would be marked by two opposite gradients: (1) rising temperature toward the intrusion: (2) decreasing water vapor or fluid pressure due to progressive combination of water in serpentine. The rising temperature in the contact zone would lead to formation of albite by reaction of NaCl in water moving toward the intrusion with kaolinite or other clay minerals at temperatures down to 300° C. or less (Hemley and others, 1961, p. D339). With a molar ratio of NaCl: HCl in the range of 1000:1 at 300° and 100:1 at about 450° C., solutions containing 50,000 ppm NaCl should be very active in serpentinizing peridotite. Magnesium would be highly soluble as $MgCl_2$. The mobility of silica in such an open system, after being freed in ionic form by decomposition of olivine or pyroxene, can be determined only by experiment, but $Na_2O\cdot nSiO_2$ might offer some interesting possibilities.

The hypothesis outlined is supported by presence of chlorine in serpentinites in Canada, and an unusual spring in California may be related to the problem. Earley (1958, p. 151) found that Precambrian serpentinized dunite in three drill holes in Ontario, at the corners of a triangle approximately 50 miles long and 30 miles across, averaged between 0.16 and 0.30 per cent Cl over intercepts of 150 to 650 feet; one sample from a depth of 1150 feet contained 0.7 per cent Cl. Associated unserpentinized peridotite and pyroxenite contained about 0.04 per cent Cl. Part of the chlorine is soluble in water, and most of it is readily soluble in cold H_2SO_4; the way in which the chlorine is held is not known. Kuroda and Sandell (1953) also reported 0.24 per cent Cl in serpentinized dunite from Newfoundland and 0.13 per cent in a serpentinized harzburgite. Earley suggests (1958, p. 148) "that the readily soluble chlorine was introduced into the rock during serpentinization by chloride-rich solutions from adjacent sediments and tuffs."

The relationship to this problem of a cold spring of unusually high pH and SiO_2 content is problematical but of interest. Water from Aqua de Ney spring, which appears to issue from highly sheared serpentinite along a fault zone in metavolcanic rocks near Mount Shasta, California (Feth *et al.*, 1961, p. 76) contains 3400–3970 ppm SiO_2, 8710–10,900 ppm Na, 4790–5560 ppm CO_3, 5950–7180 ppm Cl, and much smaller amounts of nitrogen in ammonia, SO_3, SO_4, Br, I, and B. The pH of the water is 11.6. The solutions are attributed to alteration of a mixture of entrapped sea water, from a thick sedimentary sequence believed to underlie the volcanic rocks, and a calcium-magnesium-sulfate-rich ground water.

The discussion of connate waters is not intended to imply that water or solutions of other origin are not equally important as agents of serpentinization. Serpentinization of large volumes of peridotite in high-grade metamorphic terrains and in large, apparently deep-seated plutons must require solutions from magmatic or deep crustal sources. A large pipelike serpentinized zone in the heart of the Troodos Complex, Cyprus (Wilson and Ingham, 1959), which intrudes sediment-free meta-volcanic rocks, is an example of this problem. The partial serpentinization of dunitic ultramafites in the southern Appalachians (Miller, 1953) probably occurred during the later stages of a metamorphic episode which in its earlier stages formed amphibole, corundum, talc and related minerals.

The source of oxygen for oxidation of the iron in silicates to form magnetite, or even in excess of the amount needed for that reaction, is an interesting aspect of serpentinization. Equations (3) and (4) imply generation of substantial amounts of hydrogen gas by decomposition of water and, accordingly, the presence of hydrogen in serpentinite would be evidence against serpentinization by meteoric water containing

dissolved oxygen. Serpentinite from Leupoldsgrün was found by Hahn-Weinheimer and Rost (1961) to contain 2–20 cc of hydrogen per 5 g of rock; they related the hydrogen to the formation of awaruite. Serpentinization now in progress is believed to be the source of hydrogen and methane gas that seeps from peridotite of the Zambales Complex in the Philippines; Stoll (1953, p. 167) described seeps about 5 miles east of the Coto mine, known by the local people as "los fuegos eternos," as follows:

"In an area of a few square rods there are about 18 separate orifices with yellow-orange flames . . . extending from 6 to 12 inches above. The flames are fed by a combustible natural gas escaping . . . with a slight whispering, rustling noise. There is no smoke. The orifices, where visible, coincide with tiny, tight cracks in the rock, which is pyroxene-peridotite. Where the flames are partly enclosed . . . the rocks are orange-hot. . . . The origin of the natural gas is obscure, as the country rocks for miles around are peridotites and gabbros insofar as is known."

Analyses by the San Jose Oil Company, Manila (personal communication, 1965) of two samples of gas from similar seeps in peridotite of the same complex, but south of Mt. Lanat several miles to the west, gave the following results, in mole per cent:

Sample No.	1A	1B
Hydrogen	41.4	45.6
Oxygen	0.5	0.2
Nitrogen (by difference)	5.5	0.4
Methane	52.6	53.8

Reaction of juvenile CO_2 with hydrogen would produce methane, and could form graphite like that Krishnarao (1964) found associated with most natural NiFe alloys, and Cady and others (1963, p. B39, B42) describe in Vermont. According to equations (3) and (4) the hydrogen released, at 400° C. and 1,000 atm., would equal about 10 and 5 per cent, respectively, of the volumes of olivine and pyroxene that were serpentinized.

IRREVERSIBILITY OF SERPENTINIZATION AS A PROCESS

Complete reversibility is a corollary of the hypothesis that, except for hydration, serpentinization is an isochemical process. Field evidence, however, shows that high-temperature metamorphism of serpentinite does not reproduce the primary mineralogy or textures of ultramafic rocks. Regenerated olivine as described by Durrell (1940), Gabrielse (1963) and Leech (1953) consistently contains much powdery magnetite, extinguishes uniformly, may have a granoblastic to porphyritic texture, and forms stringers and chains in serpentine. Talc, tremolite, hornblende, clinochlore and similar metamorphic minerals are associated with the

olivine, which in some instances appears to be nearly pure forsterite (Gabrielse, 1963). Gabrielse (p. 82) summarizes the mineralogic relations as follows:

"The unique texture and composition of the olivine, the unusual texture of the serpentine, and the environment in which these rocks are found, point to a metamorphic origin. . . .

"The widespread presence of dust magnetite in the regenerated olivine indicates that ferrous iron, released upon serpentinization of the original rock and subsequently oxidized, was not reincorporated into regenerated olivine. The extremely low iron content of the metamorphic olivine supports this belief.

" . . . the lack of talc in the regenerated dunites may be the result of reactions having taken place in an open system."

RODINGITE, A PARADOX OF SERPENTINIZATION

The association of rodingite, a suite of rocks composed essentially of hydrous calcium and calcium-aluminum silicates, with serpentinite is a paradox whose implications have not been fully recognized. The relationships of these two radically different suites of rocks, I believe, show that Ca-metasomatism of wall rocks on a very small scale, not Mg-metasomatism of the type that forms "blackwall" during steatization (Chidester, 1962; Cady *et al.*, 1963), accompanies serpentinization. In other words, it seems likely that those who postulate extensive Mg-metasomatism and silicification in country rocks as a corollary of serpentinization at constant volume look for something that does not exist. Phillips and Hess (1936), like Chidester, described "blackwall" as associated with and related to steatite; extrapolation of the reaction to the serpentinization process is pure inference. Perhaps we should consider two distinct but probably overlapping metamorphic or hydrothermal mineral facies: a low-temperature serpentine-rodingite facies and an intermediate-temperature, steatite-carbonate-blackwall facies. Definitions of these two facies are beyond the scope of this paper. Contact metamorphism of the kind described near Dillon, Montana by Heinrich (1963), in which serpentine forms during the last stages of a process that involves falling temperatures, would be in the intermediate-temperature facies of this classification.

Since its first identification as a distinct kind of rock by Marshall in New Zealand (Bell and others, 1911, p. 31), rodingite and similar rocks called by other names have been described in serpentinite, and only in serpentinite, practically all over the world. Rodingite consists essentially of the Ca-rich minerals hydrogarnet, prehnite, idocrase, zoisite and clinozoisite, diopside, edenite and xonotlite, with chlorite as the principal magnesium mineral. Rodingite occurs mainly as selvages on dikes and irregular inclusions and as border zones of country rocks against serpen-

tinite. Because of gradational relations, all students now agree that rodingite is an alteration product of many kinds of rocks ranging from keratophyre (Coleman, 1961) to dolerite (Bilgrami and Howie, 1960; Suzuki, 1953) and quartz-sericite-albite-chlorite schist (Cady *et al.*, 1963, p. B41). The width of altered zones ranges from an inch or two to several feet, but most commonly is between 6 inches and 3 feet.

The essential workings of the serpentinization process in forming rodingite, and the differences and similarities between it and the black-wall-forming process, are suggested by two diagrams from Cady, Albee
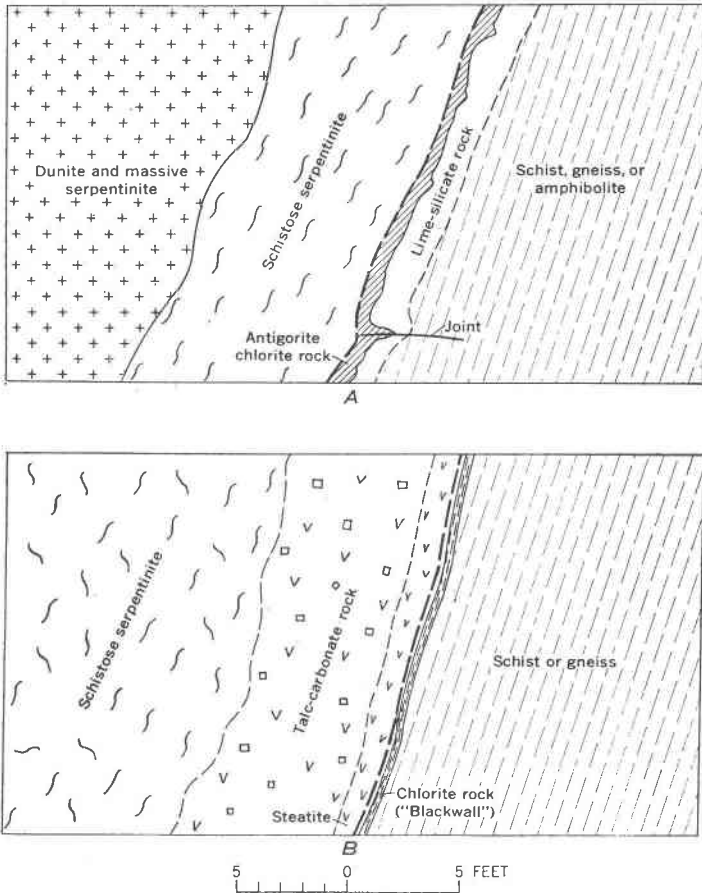

FIG. 3. Diagrammatic sections illustrating the relations of rodingite (lime-silicate rock) to serpentinite (A), and "blackwall" (chlorite rock) to steatite (B) in Vermont. After Cady, Albee, and Chidester, 1963.

and Chidester (1963, Fig. 2). (See Fig. 3.) They describe lime-silicate rock (rodingite) as gradational with the country rock schist, and antigorite-chlorite rock in turn replacing the lime-silicate rock, with a generally sharp irregular contact. In the field the contact between dark antigorite-chlorite rock and light-colored calc-silicate rock is much more prominent than the other two. We get the impression from Fig. 3A, accordingly, of two well-defined fronts, the outer one rich in Ca, the inner one rich in Mg, moving out from the serpentinite in the absence of talc. In the presence of talc, only a narrow zone of chlorite-rich "blackwall" develops along the country rock. Mutual incompatibility between rodingite and "blackwall" is implied in their discussion of genetic relations (Cady *et al.* p. B46) and the following statements (p. B36):

"The chlorite rock ('blackwall') appears to be restricted principally to places in which the calc-silicate rock is absent. It is invariably succeeded inwardly by steatite a few inches to a few feet thick."

Coleman (1963) has characterized development of rocks very similar to rodingite at contacts with serpentinite as due to "a relative enrichment of sodium accompanied by a Ca-Mg invasion from the serpentinites." Coleman's (1961) discussions of zoning in pods of jadeite and jadeite-albite schists in serpentinite in California indicate relations like those described by Cady, Albee and Chidester, but with the addition of local concentrations of Na and Al in jadeite ahead of the calc-silicate rocks. A jadeite zone of this kind would be analogous to the discontinuous albite-porphyroblast zones formed in schist outside of the "blackwall" zone around talc deposits in Vermont (Chidester, 1962). Coleman's analyses (1961, p. 231) of specimens taken 3 or 4 feet apart in an inclusion about 10 feet across show, from jadeite rock at the center to calc-silicate rock near the margin, the following changes (in weight per cent): decrease in SiO_2 from 57.1 to 37.2, in Al_2O_3 from 20.9 to 13.8, and in Na_2O and K_2O from 13.4 to 3.3; increase in MgO from 1.4 to 2.6, in CaO from 2.6 to 25.9, and in H_2O+ from 0.35 to 6.3. The contrast between doubling the small amount of MgO and a ten-fold increase in CaO, though extreme, is characteristic (Bilgrami and Howie, 1960; Grange, 1927, p. 165) of rodingite-type alteration. To form rodingite from normal Franciscan graywacke or meta-graywacke (Coleman, 1961, Table 8) the only essential changes are addition of 23–25 per cent CaO and 3 to 4 per cent H_2O+, and a concomitant decrease of 30–35 per cent in SiO_2 but only minor or insignificant changes in other oxides. In general, analyses (Baker, 1960, p. 29; Bilgrami and Howie, 1960, p. 795) indicate that rodingitization of dolerite and gabbro involves replacement of feldspar by calcium minerals, with removal of

alkalis and silica to balance; chloritization of mafic minerals may or may not be accompanied by some enrichment in magnesium.

The restriction of rodingite exclusively to serpentinites or closely related gabbroic rocks and its uniform mineralogy I regard as *prima facie* evidence of a close genetic kinship to serpentine minerals. Hydrogarnet pseudomorphs after bytownite in olivine gabbro apparently were formed by a single process together with serpentine after olivine and bastite after enstatite. Rodingitization of basaltic and dioritic dikes which have chilled margins against serpentinite and development of hornblendic and pyroxenic metamorphic rocks around ultramafic plutons (Smith and MacGregor, 1960; MacKenzie, 1960), show that rodingite cannot be magmatic or contact-metamorphic, as some geologists have suggested (Cady *et al.*, 1963; Turner and Verhoogen, 1960). The phenomenal enrichment of calcium in rodingite during serpentinization can have only one meaning: magnesium in excess of that needed to form serpentine, the alkalis, and excess SiO_2 are fugitive compared to calcium combined in hydrous silicates under identical conditions. Also, the narrowness of the zones in albitite-jadeite-rodingite inclusions and their sharp boundaries led Shido (1958, p. 599) to conclude that "the diffusion of silica appears to have been very limited within the concentric structure." Finally, the compositional contrasts and very limited thicknesses of rodingite indicate that diffusion and activity gradients of Mg and Si between ultramafites and other rocks are unimportant in comparison with fluid or gaseous transport during serpentinization.

ORIGINAL VERSUS NORMATIVE PYROXENE CONTENT OF SERPENTINIZED ALPINE-TYPE PERIDOTITES

Determination of the average primary composition of alpine peridotites is of major geologic interest because of the general belief that they constitute the upper part of the mantle and may be a source of basaltic magma. The ratio of pyroxene to olivine would be the principal limiting factor in possible generation of basaltic magma by direct fractional melting of peridotite. Because of the scarcity of fresh rocks, methods for determining the original composition of peridotites from their serpentinized equivalents should be rigorously tested. The following statement by Hess and Otalora (1964, p. 159) about the Mayaguez cores epitomizes the problem (italics added):

"Mattson's . . . estimates of the olivine-pyroxene ratio in the serpentinized rocks is considerably higher than ours. His is based on examination of thin sections and ours on the norms of the chemical analyses. *Before the chemical analyses were available we agreed with Mattson's estimate when we too were only examining the thin sections.* The water-free chemical

analyses of type C [harzburgite] are nearly identical to the olivine nodules. In the latter case the true mineral composition can be determined and agrees exactly with the norm; so there can be little doubt that the estimates based on chemical analyses are accurate and should be used in preference to the visual estimate."

Mattson's (1964) data indicate that the average pyroxene content of the Mayaguez core, including dunite, is about 8.9 per cent; Hess and Otalora's normative data with Fe_2O_3 recalculated to 1 per cent give a figure of 16.7 per cent; and the CIPW figures calculated feldspar-free are: magnetite-chromite 10 per cent, pyroxene 29 per cent, olivine 61 per cent.

Comparison of the original mineral composition with normative composition of most serpentinized ultramafites is uncertain because of lack of modal data. Although pseudomorphs after pyroxene generally are readily recognizable in unsheared periodotite (Bailey *et al.*, 1964), in reporting
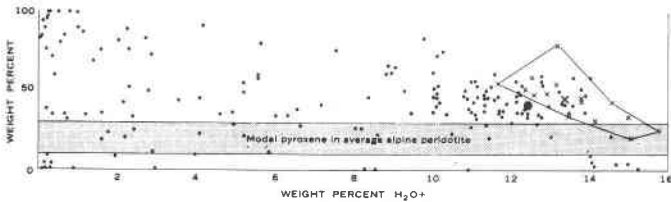

Fig. 4. Proximate normative pyroxene content of 165 ultramafites based on data shown in figure 1, in weight per cent; large dot indicates average of 60 serpentinites containing more than 11 per cent H_2O+. Composition field of 15 serpentine minerals (Faust and Fahey, 1962) indicated by small X's and average by large X. Probable average range of primary pyroxene in alpine peridotites (10–30 per cent) indicated by shaded strip.

modes most authors do not distinguish them from serpentine after olivine. Mattson's estimates (1964, p. 17) of the original pyroxene content of several Mayaguez core samples, as listed in Table 2, show that except for three samples which contain significant amounts of brucite, proximate normative pyroxene greatly exceeds the original mode. The Mayaguez rocks, it is generally agreed, are characteristic alpine peridotites, in which as a class over-all pyroxene content ranges from about 10 to 25 per cent (Bailey *et al.*, 1964, p. 81; Gabrielse, 1963, p. 69; Leech, 1953, p. 29; Smith, 1958, p. 29; Thayer, 1960, p. 251); the dunites, as usual, contain only traces of pyroxene. In Fig. 4 the situation appears to be similar; although most of the analyses containing more than about 10 per cent H_2O+ are of alpine-type serpentinites, very few of the proximate norms even approach the modal composition range of average alpine peridotite as indicated by the shaded strip. The average normative px:px+ol ratio in 60 serpentinites that contain more than 11 per cent H_2O+ ranges

somewhere between the CIPW figure 37.7 and 41.5, if CaO, Al_2O_3, and excess Fe_2O_3 are assigned to pyroxene as they would be in the fresh rock. Both figures are well within the range of norms for serpentine minerals and, therefore, are completely in accord with theory. The proximate normative pyroxene content (40.6 per cent) of the 60 serpentinites (Table 1, no. 4C), however, is about twice the original modal pyroxene of the average alpine periodotite. To reduce the proximate normative pyroxene to the alpine modal average of about 20 per cent would require addition of 5.4 per cent MgO in 7.3 per cent brucite, which would increase the H_2O+ to 13.7 per cent. These data confirm the findings of Hostetler *et al.* (1966), who identified brucite in only 31 of 102 samples of serpentinized alpine peridotites. Hostetler and others and Shteinberg all seem to have discounted the possibility that in open systems brucite forms in the presence of olivine as a more or less transitory phase during early stages of serpentinization, and may or may not be removed entirely by the time serpentinization is completed. Conversely, the presence of brucite in dunite is not in itself proof that no material has been removed from the system because, as in the Mayaguez cores, rocks other than dunite show that the original Mg:Si ratios may be changed significantly.

Exaggeration of apparent pyroxene content and the need for more accurate data on composition of alpine peridotites are exemplified by the figures cited by Ringwood *et al.* (1964) for pyroxene pyrolite as average upper mantle peridotite. Their figures are based on the average of 4 analyses of Green's "primary," "recrystallized anhydrous," and "recrystallized hydrous" facies of the Lizard peridotite (Green, 1964, table 1), and one analysis of fresh peridotite from Tinaquillo, Venezuela. The Lizard samples average 9.88 per cent H_2O+, so are about 80 per cent serpentinized;[1] their normative composition, calculated feldspar-free, is about 52 per cent pyroxene, 38 per cent olivine and 10 per cent magnetite, chromite, and spinel. Calculation of the norm on an Fe_2O_3-free anhydrous basis reverses the proportions of pyroxene and olivine, to about 56 per cent olivine and 42 per cent pyroxene. The Tinaquillo peridotite, whose analysis apparently was matched with the Lizard average on a water- and Fe_2O_3-free basis, consists of about 38 per cent normative pyroxene, 58 per cent olivine, and 3 per cent chromian spinel. These norms differ markedly from Green's statement (1964, p. 137) that the Lizard rock "is a true peridotite rarely having less than 20 per cent or more than 40 per cent pyroxene" and MacKenzie's description (1960, p. 303) of the Tinaquillo

---

[1] Theoretically, complete serpentinization of a rock containing 40 per cent SiO_2 would require 12 per cent H_2O.

peridotite as "more than 90 per cent . . . unserpentinized dunite . . . [which] . . . contains up to 10 per cent lamellae-bearing enstatites." On an overall basis, it would appear that the original modal composition of the Mayaguez and Tinaquillo ultramafites was very similar, with about 90 per cent olivine. It seems possible that even my estimate of 20 per cent, which is based largely on visual examination of outcrops where pyroxene weathers in relief, may be too high for the original pyroxene content of average alpine peridotite.

Conclusions

The available chemical and physical evidence leaves little room for argument, I believe, but that serpentinization is essentially a constant volume metasomatic process which requires removal of about 30 per cent by weight of the original bivalent oxides and SiO_2 in peridotite. The final equilibrium products of the process are dominantly magnetite and serpentine minerals whose composition varies widely and presumably reflects differences in temperature, pressure and pH. Brucite probably occurs in less than a third of partly serpentinized peridotites and serpentinites, and is quantitatively significant in very few serpentinites; it seems most likely to be an early transient phase formed in the presence of olivine or a late phase deposited from solutions of unusually high pH. Oxidation of Fe^{2+} in olivine and pyroxene during serpentinization probably releases significant amounts of H_2 as gas, making the process one of dehydrogenation as well as hydration. The association of rodingite with serpentinite shows that serpentinizing solutions remove alkalis and SiO_2 from feldspathic rocks, that calcium instead of magnesium is introduced into adjoining rocks during serpentinization, and that diffusion between serpentinite and country rocks or inclusions is limited to a few inches commonly, and at most to a few feet.

Surely, very large volumes of water must pass through ultramafites during serpentinization, but this problem is not new to geology. The wide differences of opinion now current show that laboratory investigations of the system olivine ($Fo_{90}Fa_{10}$)-serpentine-magnetite-$NaCl$-H_2O are urgently needed for even a rudimentary understanding of the equilibria involved in serpentinization. Connate waters rich in Cl^- from geosynclinal sediments probably are an important source of solutions, but magmatic or other deep-seated sources must be at least as important quantitatively. The belief in major volume increase during serpentinization, it seems likely to me, has grown more from absence of information on a number of related problems than from positive data that can be obtained from the rocks involved.

References

BAILEY, E. B., W. P. IRWIN AND D. L. JONES (1964) Franciscan and related rocks, and their significance in the geology of western California. *Calif. Div. Mines Bull.* **183**.

BAKER, G. (1960) Rodingite in nickeliferous serpentinite near Beaconsfield, northern Tasmania. *Geol. Soc. Australia Jour.* **6**, 21–35.

BELL, J. M., E DE C. CLARKE, AND P. MARSHALL (1911) The geology of the Dun Mountain subdivision, Nelson. *New Zealand Geol. Survey Bull.* **12**.

BILGRAMI, S. A. AND R. A. HOWIE (1960) Mineralogy and petrology of a rodingite dike, Hindubagh, Pakistan. *Am. Mineral.* **45**, 791–801.

BOWEN, N. L. AND O. F. TUTTLE (1949) The system $MgO-SiO_2-H_2O$. *Geol. Soc. Am. Bull.* **60**, 439–460.

CADY, W. M., A. L. ALBEE AND A. H. CHIDESTER (1963) Bedrock geology and asbestos deposits of the upper Mississquoi Valley and vicinity, Vermont. *U. S. Geol. Survey Bull.* **1122-B**, B1–B78.

CHIDESTER, A. H. (1962) Petrology and geochemistry of selected talc-bearing ultramafic rocks and adjacent country rocks in north-central Vermont. *U. S. Geol. Survey Prof. Paper* **345**.

COLEMAN, R. G. (1961) Jadeite deposits of the Clear Creek area, New Idria district, San Benito County, California. *Jour. Petrology* **2**, 209–247.

———— (1963) Serpentinites, rodingites, and tectonic inclusions in alpine-type mountain chains. *Geol. Soc. Am. Spec. Paper* **73**, 130.

DILLER, J. S. (1921) Chromite in the Klamath Mountains, California and Oregon. *U. S. Geol. Survey Bull.* **725-A**, 1–35.

DU RIETZ, TORSTEN. (1956) The content of chromium and nickel in the Caledonian basic rocks of Sweden. *Geol. Fören. Förh.* **78**, 233–300.

DURRELL, C. (1940) Metamorphism in the southern Sierra Nevada northeast of Visalia. *Calif. Univ. Pub. Geol. Sci.* **25**, 74–94.

EARLEY, J. W. (1958) On chlorine in serpentinized dunite. *Am. Mineral.* **43**, 148–155.

FAUST, G. T. AND J. J. FAHEY (1962) The serpentine-group minerals. *U. S. Geol. Survey Prof. Paper* **384-A**, 1–92.

FETH, J. H., S. M. ROGERS AND C. E. ROBERSON (1961) Aqua de Ney, California, a spring of unique chemical character. *Geochim. Cosmochim. Acta* **22**, 75–86.

GABRIELSE, HUBERT. (1963) McDame Map Area, Cassiar District, British Columbia. *Canada Geol. Survey Mem.* **319**.

GRANGE, L. I. (1927) On the rodingites of Nelson. *New Zealand Inst. Trans.* **58**, 160–166.

GREEN, D. H. (1964) The petrogenesis of the high-temperature peridotite intrusion in the Lizard area, Cornwall. *Jour. Petrology* **5**, 134–188.

HAHN-WEINHEIMER, P. AND F. ROST (1961), Akzessorische Mineralien und Elemente in Serpentinit von Leupoldsgrün (Münchberger Gneissmasse). Ein Beitrag zur Geochemie ultrabasischer Gesteine. *Geochim. Cosmochim. Acta* **21**, 165–181.

HAMILTON, WARREN AND WAYNE MOUNTJOY (1965) Alkali content and origin of ultramafic rocks of alpine type. *Geochim. Cosmochim. Acta.* **29**, 661-671.

HEINRICH, E. WM. (1963) Paragenesis of clinohumite and associated minerals from Wolf Creek, Montana. *Am. Mineral.* **48**, 597–613.

HEMLEY, J. J., CHARLES MEYER AND D. H. RICHTER (1961) Some alteration reactions in the system $Na_2O-Al_2O_3-SiO_2-H_2O$. *U. S. Geol. Survey Prof. Paper* **424D**, D338–D340.

HESS, H. H. (1933) The problem of serpentinization and the origin of certain chrysotile asbestos, talc, and soapstone deposits. *Econ. Geol.* **28**, 634–657.

———— (1955) Serpentines, orogeny, and epeirogeny. In *Crust of the Earth. Geol. Soc. Am. Spec. Paper* **62**, 391–408.

—— AND G. OTALORA (1964) Mineralogical and chemical composition of the Mayaguez serpentinite cores. In A study of serpentinite, the AMSOC core hole near Mayaguez, Puerto Rico. *Nat. Acad. Sci.-Nat. Res. Council Pub.* **1188**, 152–168.

HOSTETLER, P. B., R. G. COLEMAN, F. A. MUMPTON AND B. EVANS (1966) Brucite in alpine serpentinites. *Am. Mineral.* **51**, 75–98.

JOPLIN, G. A. (1963) Chemical analyses of Australian rocks. Part 1: Igneous and metamorphic. *Australia Bur. Min. Resources, Geol. Geophys., Bull.*, **65**.

KRISHNARAO, J. S. R. (1964) Native nickel-iron alloy, its mode of occurrence, distribution and origin. *Econ. Geol.* **59**, 443–448.

KURODA, P. K. AND E. B. SANDELL (1953) Chlorine in igneous rocks: *Geol. Soc. Am. Bull.* **64**, 879–896.

MACKENZIE, D. B. (1960) High-temperature alpine-type peridotite from Venezuela. *Geol. Soc. Am. Bull.* **71**, 303–318.

LEECH, G. B. (1953) Geology and mineral deposits of the Shulaps Range, southwestern British Columbia. *British Columbia Dept. Mines Bull.* **32**.

MATTSON, P. H. (1964) Petrography and structure of serpentinite from Mayaguez, Puerto Rico. In A Study of serpentinite, the AMSOC core hole near Mayaguez, Puerto Rico. *Nat. Acad. Sci.-Nat. Res. Council Pub. 1188*, 7–24.

MILLER, ROSWELL, III (1953) The Webster—Addie ultramafic ring, Jackson County, North Carolina, and secondary alteration of its chromite. *Am. Mineral.* **38**, 1134–1147.

PHILLIPS, A. H. AND H. H. HESS (1936) Metamorphic differentiation at contacts between serpentinite and siliceous country rocks. *Am. Mineral.* **21**, 333–362.

RINGWOOD, A. E., I. D. MACGREGOR AND F. R. BOYD (1964) Petrological composition of the upper mantle. *Carnegie Inst. Washington Year Book* **63**, 147–152.

RUCKMICK, J. C. AND J. A. NOBLE (1959) Origin of the ultramafic complex at Union Bay, southeastern Alaska. *Geol. Soc. Am. Bull.* **70**, 981–1018.

SHIDO, F. (1958) Calciferous amphibole rich in sodium from jadeite-bearing albitite of Kotaki Prefecture. *Geol. Soc. Japan Jour.* **64**, 595–600.

SHTEINBERG, D. S. (1960) New data concerning the serpentinization of dunites and peridotites of the Urals. *Inter. Geol. Cong.*, XXI SESS. *Dokl. Sovetskikh Geol.* Petrographicheskie Provintsii, Izverzhennye i Metamorficheskie Gornye Porody. *Izdatel'stvo Akad. Nauk. S.S.S.R. Moskva*, 250–260, (In Russian).

SMITH, C. H. (1958) Bay of Islands igneous complex, western Newfoundland. *Canada Geol. Survey Mem.* **290**.

—— AND I. D. MACGREGOR (1960) Ultrabasic intrusive conditions illustrated by the Mount Albert ultrabasic pluton, Gaspe, Quebec. *Geol. Soc. Am. Bull.* **71**, 1978.

STEUBER, A. M. AND V. RAMA MURTHY (1965) Strontium isotope and alkali element abundances in ultramafic rock. *Am. Geophys. Un. Trans.* **46**, 186.

STOLL, W. C. (1953) Natural fires in South Lawis River Valley, Zambales, P. I. *Philippine Geologist* **7**, 167.

SUZUKI, J. (1953), On the rodingitic rocks within the serpentinite masses of Hokkaido. *Hokkaido Univ. Jour. Fac. Sci.* **8**, 419–430.

THAYER, T. P. (1942) Chrome resources of Cuba. *U. S. Geol. Survey Bull.* **935-A**, 1–74.

—— (1956) Mineralogy and geology of chromium. *In* Chromium, *Am. Chem. Soc. Mon.* **132**, 14–52.

—— (1960) Some critical differences between alpine-type and stratiform peridotite-gabbro complexes. *Inter. Geol. Congress, 21st, Copenhagen 1960, Rept. pt.* **XIII**, 247–259.

—— (1963) The Canyon Mountain Complex, Oregon, and the alpine mafic magma stem. *U. S. Geol. Survey Prof. Paper* **475-C**, C82–C85.

—— (1964) Principal features and origin of podiform chromite deposits, and some observations on the Guleman-Soridağ district, Turkey. *Econ. Geol.* **59,** 1497–1524.

TURNER, F. AND J. VERHOOGEN (1960) *Igneous and Metamorphic Petrology. 2d edition, McGraw-Hill, New York, N. Y.*

WHITE, D. E., J. D. HEM AND G. A. WARING (1963) Chemical composition of subsurface waters, Data of geochemistry, 6th edition. *U. S. Geol. Survey Prof. Paper* **440-F,** Chap. F, F1–F67.

WILSON, R. A. M. AND F. T. INGHAM (1959) The geology of the Xeros-Troodos area, with an account of the mineral resources. *Cyprus Geol. Survey Dept., Mem.* **1.**

WORST, B. G. (1958) The differentiation and structure of the Great Dyke of Southern Rhodesia. *Geol. Soc. South Africa Trans.* **61,** 283–358.