BRUCITE IN ALPINE SERPENTINITES

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ABSTRACT

X-ray diffraction tracings of 102 serpentinized and partially serpentinized Alpine-type ultramafics from the circum-Pacific orogenic belts show that brucite commonly forms during pervasive serpentinization of dunites and high-olivine peridotites. Characteristically, such brucite is fine-grained and intimately intergrown with lizardite. Microprobe analyses indicate that the lizardites contain less iron, and the brucites more iron, than the parent olivines and pyroxenes, although the brucites show broad variations in iron content.

Extensive brucite formation during serpentinization indicates maximum temperatures of about 400° C. and, unless massive amounts of both magnesia and silica are removed from the ultramafic mass, volume increases of about 40 per cent. Field evidence supporting such migration is generally lacking. The ellipsoidal, fault-bounded configurations typical of Alpine ultramafics suggest that large volume changes do not result from complete serpentinization *in situ;* rather, serpentinization probably results from incremental additions of water derived from country rocks during the tectonic ascent of the ultramafic mass through the earth's crust.

Reaction of brucite with CO_2-bearing groundwater at depth is probably responsible for much of the magnesite associated with serpentinites. In a surface oxidation environment, iron-bearing brucite is converted directly to pyroaurite or coalingite, or reacts with percolating groundwater to form hydromagnesite and artinite.

INTRODUCTION

X-ray diffraction studies by the authors of a large number of serpentinized and partially serpentinized dunites and peridotites have revealed that pervasive serpentinization commonly produces significant quantities of brucite, in addition to serpentine-group minerals[1] and magnetite. In this paper some typical brucite-"serpentine" assemblages are described in detail and corollary implications of serpentinization are discussed concerning:

(1) the transfer of magnesia and silica, (2) volume increase, and (3) maximum temperatures.

[1] Usage of the terms serpentinite, "serpentine", and serpentine-group minerals follows that given by Faust and Fahey (1962). Where the phases in a specimen have been identified, they are named, as clinochrysotile, lizardite, or antigorite. Where the phases were not identified, or are referred to collectively, they are called serpentine-group minerals. Appropriate rocks are called serpentinites. There still remain occasions in which it is desirable to use the term "serpentine" (in quotes), but only where the meaning cannot be misconstrued.

In addition, the conversion of brucite to hydrous magnesium carbonates during the oxidation and weathering of serpentinite bodies is discussed.

As long as serpentine-group minerals of nearly constant composition, together with accessory magnetite, are regarded as the sole products of serpentinization of Alpine ultramafics[1] which vary significantly in their original proportions of magnesia and silica, serpentinization must imply substantial changes to the initial proportions of magnesia and silica. Serpentinization is also commonly regarded as a process occurring at constant volume. According to Turner and Verhoogen (1960, p. 318), "microscopic fabric and field relations of undeformed serpentinites show . . . that serpentinization is commonly accompanied by little or no increase in volume." Because of the difference in densities between serpentine and the primary anhydrous silicates, such a concept can be accounted for only by a substantial subtraction of material.

In their pioneering experimental study of the $MgO-SiO_2-H_2O$ system, Bowen and Tuttle (1949) showed that the maximum stability limit of chrysotile serpentine is very close to 500° C. The specific reaction studied was that between clinochrysotile and forsterite, talc, and water vapor. For talc, however, one may substitute enstatite, quartz, or a vapor phase preferentially enriched in silica and thereby modify somewhat the stability limit of chrysotile serpentine. This reaction, in what we might call its "expanded form", can thus account for the exclusive formation of the serpentine-group minerals from a variety of starting materials, and the reaction may be accompanied by a variety of assumed volume changes including no volume change at all. It is not surprising then, that such a reaction has been commonly adapted by petrologists who have also accepted a temperature of 500° C. as characteristic of the reaction (the pressure-temperature curve shown by Bowen and Tuttle is very nearly independent of pressure, passing through 500° C. at 2000 psi water vapor pressure, and about 510° C. at 40,000 psi).

Bowen and Tuttle (1949) also showed that the minimum temperature for the breakdown of forsterite to yield clinochrysotile plus brucite in the presence of 15,000 psi water vapor pressure is 365° C. This reaction, however, has been thought to be of little petrological significance because brucite has not been generally recognized to be a product of serpentinization. Bowen and Tuttle themselves minimized its importance, for they stated (p. 452): "Olivine does appear to suffer a change in rocks whereby only serpentine remains in the rock." The formation of brucite during serpentinization implies both a sizeable drop in the maximum tempera-

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[1] The term Alpine ultramafics is used here in the sense propounded by Benson (1926) and Thayer (1960), that is, those ultramafics occurring astride the axes of mobile orogenic zones.

ture of serpentinization and a larger volume increase than would result if excess magnesia had been removed in solution from the area of serpentinization.

We have found that brucite not only is a common constituent of serpentinites but that it accompanies serpentine-group minerals at the earliest stages of alteration. Actually, there have been a number of descriptions in the literature of brucite occurrences in serpentinites. One large group of descriptions (Ferrari *et al.* 1950; Meixner, 1938, 1956; Fenoglio, 1930, 1933; Allakhverdiev, 1958; Serdyuchenko, 1949) is concerned with the mineralogical occurrence of brucite with some of the more exotic magnesium hydroxycarbonate minerals (hydromagnesite, pyroaurite, artinite) in serpentinites. The association of fibrous brucite (nemalite) with chrysotile fibers has been reported from Alaska (Fackler, 1945), Switzerland (Eckhardt, 1956), and Quebec (Allen, Gill, and Koski, 1957). Van Biljon (1960) describes thin veinlets and grains of brucite in a massive serpentinite sample from Swaziland, S. Africa. According to Sakomato (1959) the serpentinites around Kochi City, Japan, contain brucite in an intimate mixture with "serpentine." Massive serpentinite at Leopoldsgrün, W. Germany, (Hahn-Weinheimer and Rost, (1961) contains numerous small veinlets of brucite and magnetite. Shteïnberg (1960) has shown that brucite is an important constituent in serpentinized dunites in the Urals. According to Hess and Otalora (1964) modest percentages of brucite are scattered through much of the serpentinite taken from the AMSOC core hole near Mayaguez, Puerto Rico.

The cumulative weight of these references supports our observation that brucite is not uncommon in serpentinites, but their cumulative petrologic importance is diminished by the fact that in only two cases (Hahn-Weinheimer and Rost, 1961; and Shteïnberg, 1960) has any attempt been made to relate genetically the formation of brucite with the overall process of serpentinization. Hahn-Wienheimer and Rost (1961) do not believe that the brucite at Leopoldsgrün was formed during an initial, pervasive serpentinization stage, but rather they believe it was formed during a later stage of metamorphism and antigoritization. In our opinion the formation of fibrous brucite or brucite associated with magnesium hydroxycarbonate minerals is probably not related to initial serpentinization processes, but rather, is the result of reprecipitation or later reworking of the initial serpentinite.

Normative calculations from chemical analyses are an indication of the possible presence of brucite in serpentinites. Shteïnberg (1960) pointed out that magnesium carbonates were not present in significant amounts in most of his samples, and therefore the excess magnesia, for rocks whose initial MgO/SiO_2 ratio was greater than $3/2$, must be pres-

ent as brucite. Detailed x-ray, optical, and thermogravimetric analysis (Shteĭnberg, 1960) of a serpentinized dunite, two partly serpentinized dunites, and a partly serpentinized peridotite confirmed the presence of significant brucite in all but the peridotite.

Thus it seems that serpentinites often contain brucite, but to our knowledge Shteĭnberg (1960) was the first to associate brucite formation with the process of serpentinization. Occurrences of brucite in serpentinite undoubtedly have been overlooked in the past, indicating that identification of such brucite in thin-section is difficult.

GEOLOGIC OCCURRENCES

The bulk of this investigation rests on the evidence of x-ray diffraction tracings of 102 serpentinite samples from a number of Alpine ultramafic localities in the circum-Pacific orogenic belts. All the samples were collected by the authors, although none was collected with the specific idea in mind of determining the distribution of brucite-bearing serpentinites.

Eight serpentinite samples were collected over an 80-mile interval of the Great Serpentine Belt of New South Wales, as described by Benson (1913–1918). These samples were selected to represent the most intense areas of shearing and serpentinization. Eight more samples were taken from several of the isolated, partially serpentinized, periodotite masses in New Caledonia. The ten selected New Zealand samples are part of a larger study by Coleman on petrologic relationships in the Great Ultramafic Belt of New Zealand. Eighty of the samples were collected at numerous localities in Washington, Oregon, and California and are part of a continuing study on problems associated with serpentinization within the Pacific Coast ultramafic belts.

Preliminary mineralogical determinations were made on the basis of x-ray diffraction charts. Most of the samples (eighty-seven) were found to be completely serpentinized and generally contain a mixture of the polymorphs lizardite and clinochrysotile. Brucite was detected in thirty-one samples, and, as would be expected, the proportion of brucite to serpentine-group minerals varied widely, but in no case was a sample found in which the molar percentage of brucite exceeded that of the "serpentine." The fifteen samples of partially serpentinized ultramafic rocks contained olivine, or olivine plus orthopyroxene. Brucite was found in ten of these samples. The initial olivine/orthopyroxene ratio obviously controlled the brucite formation in these samples, for it was greater than $1/1$ (mol) in each of the ten samples containing brucite, but near $1/1$, or less, in three of the five samples devoid of brucite. The other two contained only olivine and serpentine-group minerals, but were taken from

weathering surfaces where, as will be discussed subsequently, brucite is demonstrably unstable. Thus the data from partially serpentinized dunites and pyroxene-poor periodotites implies that formation of brucite is to be expected during initial serpentinization of these rocks.

Mineralogy and Petrology.

1) *Petrography.* Detailed study to determine the characteristics and habitat of the brucite was restricted to five samples selected from the original one hundred and two (Table 1). These represent dunites in various stages of alteration to serpentine. In three of the samples (Dun Mtn., Twin Sisters, and Burro Mtn.) more than 40 volume per cent of the sample still consists of olivine and, in the case of the Burro Mountain sample, minor pyroxene. On the basis of any rock classification, the rocks represented by these samples would be considered dunites; in fact, the Dun Mountain material is representative of the type dunite described by Hochstetter (1859). The remaining two samples are presumed originally to have been dunites also, but now consist primarily of serpentine-group minerals. In hand specimen, unweathered surfaces of serpentinized portions of these ultramafics are black, whereas unaltered dunite is a light gray.

Microscopic examination of these samples reveals textures characteristically encountered in partially serpentinized ultramafic rocks. The olivines are in an advanced stage of replacement by serpentine-group minerals with individual grains separated one from the other by "serpentine" mantles and veinlets. Fracture patterns and crystal boundaries appear to have controlled the initial alteration of the olivine, and these boundaries are often preserved by trains of fine-grained, secondary magnetite. Progressive replacement of olivine grains from the rim inwards contributes to the typical mesh structure characterizing serpentinized dunites. Along these same original crystal boundaries brucite is commonly present as fine-grained veinlets. In other instances, particularly in the Dun Mountain and Burro Mountain specimens, the brucite may form a central core within a completely serpentinized olivine grain, or as a rim around those grains not yet completely altered. More typically, brucite occurs as an extremely fine-grained intergrowth with "serpentine." Optically, brucite may be distinguished from "serpentine" if individual grains exceed 0.05 mm due to its higher birefringence and indices of refraction. In the case of the New Idria material, brucite has formed large rectangular plates (up to 0.5 mm square) that are more easily recognized in thin section. The coarse-grained brucite, however, may be confused with chlorite, because, like chlorite, the brucite has anomalous reddish-

brown interference colors resulting from dispersion, and because the uniaxial positive character of the brucite could easily be mistaken for a chlorite with a small 2V.

In order to characterize more fully the brucite and coexisting serpentine-group minerals by optical, x-ray and chemical techniques, each of the five samples was crushed and sized to obtain a 200–325 mesh fraction suitable for centrifuging in heavy liquids. The density of brucite is given as 2.39 g/cc (Deer, *et al.* 1962, v. 5, p. 89) and lizardite and clinochrysotile as 2.55 (Deer *et al.* v. 3, p. 170); therefore liquids with densities of 2.40–2.50 g/cc were used to attempt a separation of brucite from serpentine-group minerals. This was not successful because the serpentine-group minerals and brucite were found to have overlapping densities, due probably to substitution of iron in the brucite. The brucite-"serpentine" mixtures were carefully purified so that the primary silicates and spinels were completely removed. These purified separates were used to obtain the x-ray and chemical information given in this paper. The refractive index, ϵ, for each brucite sample was measured as $1.580 \pm .004$, except for the Burro Mtn. sample ($1.585 \pm .004$).

2) *X-ray.* X-ray diffraction studies were made using a Norelco High Angle Diffractometer and Ni-filtered CuKα radiation. Powdered samples were sedimented on glass slides and x-rayed from 2° to 68°2θ at a scanning rate of 1°/minute. The x-ray diffraction data for the brucite in the five separates described above was sensibly identical to the ASTM standard brucite (card 7–239) for the spacings (001), (101) and (102); d (110) ranged from 1.580 to 1.583 as compared with 1.573 for standard brucite.

Figure 1 is an overlay comparison of six diffraction charts of:

(1) pure brucite, (2) whole rock from the Dun Mountain sample, (3) "serpentine"-brucite fraction of the Dun Mountain sample, (4) lizardite plus minor clinochrysotile, (5) clino-chrysotile, and (6) antigorite.

The whole rock from Dun Mountain (Fig. 1, line 2) contains approximately 20 mol per cent (5 weight per cent) brucite, and the (001), (101), (102) and (110) reflections of brucite are all plainly visible on the diffractometer chart. If the molar percentage of brucite in a whole rock sample is approximately 10 per cent or less, the (001) reflection at 18.6° 2θ may be the only observed peak. Density separation of a "serpentine"-brucite fraction from the primary silicates will yield a positive identification for brucite by eliminating interfering olivine peaks and by increasing the relative amount of brucite in the sample.

The normally difficult x-ray diffraction identification of specific ser-

pentine-group minerals is made even more complex by the presence of olivine, since strong reflections of olivine overlap the critical lines of lizardite and chrysotile. As seen in the whole rock Dun Mountain sample, the indicative (202) reflections of lizardite and chrysotile at 36.0° and 36.8° 2θ, respectively, are masked by the strong (131) and (112) reflections of olivine. When the olivine fraction is removed from the sample, identification is made much easier, and, from the pattern of the brucite-"serpentine" fraction of the Dun Mountain sample (Fig. 1, line 3), the presence of lizardite and a small quantity of chrysotile is indicated. The position of the (204) reflections is also diagnostic in differentiating lizardite and chrysotile, but often these reflections are not visible in the diffractometer tracings. It may be possible to detect significant amounts of antigorite without separation of an olivine fraction, but none of our samples contained antigorite in association with olivine.

The Dun Mountain assemblage of olivine, brucite, lizardite, and minor clinochrysotile is a typical one; in fact, for each of the ten samples in which brucite and "serpentine" were found associated with primary olivine, lizardite was noted as the dominant serpentine-group mineral. In most cases, minor clinochrysotile was also observed.

3) *Chemical Composition.* Two analytical methods were employed. Microprobe analyses were used to determine $Fe/Mg+Fe$ ratios for olivines, brucites, and serpentine-group minerals, and to establish the identity of accessory minerals. Chemical analysis of an acetic acid leach of the "serpentine"-brucite density fraction yielded brucite/"serpentine" molecular ratios and $Fe/Mg+Fe$ ratios for brucites. The molar $Fe/Mg+Fe$ ratios thus represent the molecular percentage of fayalite in olivine, $Fe(OH)_2$ in brucite, and "Fe-serpentine" ($Fe_3Si_2O_5(OH)_4$) in the particular serpentine-group mineral.

An A.R.L. electron probe microanalyzer was used to make simultaneous determinations of Mg, Fe, and Si on individual grains of olivine, lizardite, and brucite in polished rock sections (Table 1). Pure Mg-brucite, olivine ($Fa_{11.5}$), hypersthene, and an analysed lizardite and clinochrysotile (U. S. Geological Survey, Menlo Park, Calif., unpublished analyses) were used for standardization. Analysis of olivines with the microprobe has already been shown to be simple, precise, and accurate (Smith and Stenstrom, 1965; Keil and Fredriksson, 1964). Microprobe analysis of serpentine-group minerals is more difficult because their fibrous habit makes a good surface polish more difficult to obtain, because electrical and thermal conductivities for fine-grained crystalline aggregates are lower than for the single crystals, and because intergrowths of brucite interfere. Although analyzed lizardite and clinochrysotile sam-

Degrees 2 θ
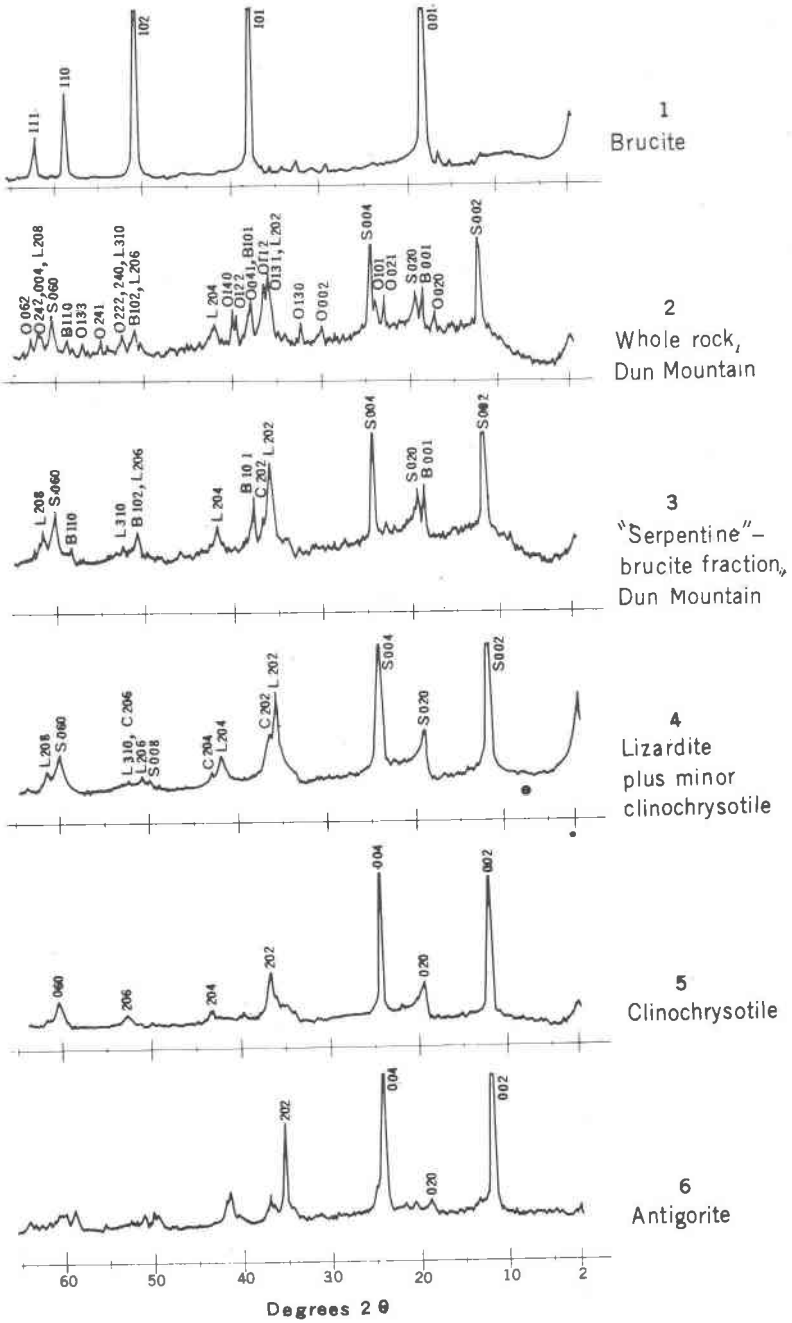
ples were used as standards, an olivine reference was used as an intermediary during routine work. Provided that mass absorption corrections are made, forsterite olivine serves as a reliable standard for the analysis of serpentine-group minerals. Analysis of brucite is possible only if a ratio method is used, for even under the gentlest excitation conditions brucite loses water during electron probe analysis. The percentage of the $Fe(OH)_2$ molecule was determined from the Fe/Mg ratio which remains constant and is independent of the extent of volatilization. Small amounts of lizardite in the analyzed volume of brucite can be accurately accounted for by using the ratio of Si-counts in "brucite" to Si-counts in pure lizardite. Since the brucite is not homogeneous, it is not possible to subtract brucite from a lizardite analysis, and only those lizardite analyses which give the correct maximum Si-counts were considered.

The olivines were found to be very uniform in composition within one rock; all fell within the range already described for olivines from Alpine ultramafic bodies (Green, 1964). The serpentine-group minerals cannot be regarded as virtually iron-free. Typically the lizardites contain about 4 mol per cent "Fe-serpentine". Conventional chemical analysis of purified, non-brucite bearing lizardite and clinochrysotile from New Idria (U. S. Geological Survey, Menlo Park, Calif., unpublished analyses) also indicate an "Fe-serpentine" component of about 4 mol per cent. Within any one rock there is a limited range in composition (Table 1). The probe data also suggest that there may exist a positive correlation between per cent fayalite in the olivine and per cent "Fe-serpentine" in the lizardite.

Whereas lizardites possess lower Fe/Mg+Fe ratios than the parent olivine, the coexisting brucite is richer in iron. In contrast to olivine and lizardite, the Fe/Mg+Fe ratio of different grains of brucite varies widely within any one rock sample, but the range of ratios for each of the five samples is similar. The mol per cent of $Fe(OH)_2$ in brucite varies from 10 to 20 per cent and averages around 15 per cent. Concerning ac-

Fɪɢ. 1. Diffraction tracings of: 1) Pure brucite from Luning, Nevada, 2) Whole rock fraction from Dun Mountain, 3) "Serpentine"-brucite fraction from Dun Mountain, 4) Lizardite plus minor clinochrysotile from New Idria, California, 5) Clinochrysotile from New Idria, California, 6) Antigorite from Milford Sound, New Zealand. Symbols as follows: B-brucite, C-clinochrysotile, L-lizardite, O-olivine, S-undifferentiated serpentine-group minerals.

TABLE I. MINERALOGY AND CHEMICAL COMPOSITION DATA FOR FIVE SELECTED ALPINE ULTRAMAFIC SAMPLES

Sample	Rock Type	Total Rock Density	Volume Per Cent Serpentinized	Serpentine Group Mineral(s)	Density of Brucite+ "Serpentine" Fraction	Olivine- Mol Per Cent Fayalite	Electron Microprobe Data			Acetic Acid Leachate Data		
							Lizardite- Mol Per Cent "Fe-Serp."	Brucite Mol Per Cent Fe(OH)$_2$	Acces- sory Min- erals	Mol Ratio Brucite/ "Serpen- tine"	Weight Ratio Brucite/ "Serpen- tine"	Brucite- Mol Per Cent Fe(OH)$_2$
Dun Mountain	Dunite	2.76	58	L+ minor Cl	2.40–2.53	8.5	Average—3.0 Range 2.9–3.2 (5 grains)	Average—16 Range 10.5–19.0 (10 grains)	C M A	0.50	0.113	15
Hat Island	Serpentinite	2.48	98	L+very minor Cl	2.47–2.60	6	Estimated—2.6 (mostly contami- nated with magne- tite)	Average—16.5 Range 5.9–24.7 (11 grains)	C M A	0.61	0.139	12.5
New Idria 8-NI-63	Serpentinite	2.38	100	L+Cl	2.45–2.58	—	Average—4.3 Range 4.1–4.8 (8 grains)	Average—15 Range 11.4–17.7 (13 grains)	M A H	0.90	0.206	10.5
Twin Sisters	Dunite	2.77	56	L	2.45–2.58	9	Average—5.8 Range 5.1–6.6 (5 grains)	Average—14 Range 11.4–16.0 (8 grains)	C M	0.49	0.112	13
Burro Mountain	Dunite (minor pyroxene)	2.78	54	L	2.51–2.60	7.5	Average—3.5 Range 3.3–3.7 (5 grains)	Average—13 Range 10.5–18.2 (14 grains)	C M	0.39	0.088	19

L=Lizardite.   Cl=Clinochrysotile.   C=Chromite.   M=Magnetite.   A=Awaruite (FeNi$_3$).   H=Heazlewoodite (Ni$_3$S$_2$).

Electron microprobe analyses—experimental conditions: 15kV exciting potential, 0.05 microamps sample current, integration time 20 seconds, probe spot ca. 0.5 microns, estimated area analyzed 3 to 4 microns diameter. Brucite located with headphones coupled to Si detector. Corrections made for background and mass absorption using tables prepared by Adler.

Sample locations.

Dun Mountain, Sample taken from SW flank of mountain, Nelson 1 mile series (S 20/700205), South Island, New Zealand, 41° 20′ S. Lat., 173°22′ E. Long. Partially serpentinized dunite from surface outcrop.

Hat Island, Sample taken from eastern shoreline, NW ¼, Sec. 15, R. 2 E., T. 35 N., Willamette meridian, Anacortes 15-minute quad., Skagit County, Wash., 48°31′ N. Lat., 122°32′ W. Long. Completely serpentinized dunite from glaciated surface outcrop.

New Idria (8-NI-63), Sample taken from Atlas Corp. open pit asbestos mine, NW ¼, Sec. 32, R. 13 E., T. 18 S., Mt. Diablo meridian, New Idria 15-minute quad., Fresno County, Calif., 36°18′ N. Lat., 120°18′ W. Long. Taken from massive serpentinite tectonic boulder in sheared serpentinite approximately 50 feet below surface.

Twin Sisters, Sample taken from west side of dunite mass, Sec. 25, R. 6 E., T. 37 N., Willamette meridian, Hamilton 7 ½-minute quad. Whatcom County, Wash., 48°40′ N., Lat., 121°57′ W. Long. Partially serpentinized dunite from surface outcrop.

Burro Mountain, Sample taken from stream bottom of Los Burros Creek, NE ¼, Sec. 12, R. 6 E., T. 24 S., Mt. Diablo meridian, Burro Mountain 7 ½-minute quad., Monterey County, Calif., 35°52′ N. Lat., 121°16′ W. Long. Surface outcrop of partially serpentinized dunite.

cessory minerals, awaruite ($FeNi_3$) was detected in three of the rocks (Table 1), magnetite in all five, chromite in all save the New Idria specimen, and heazlewoodite (Ni_3S_2) in the New Idria specimen only.

Brucite/"serpentine" ratios for the five selected samples were determined by leaching an approximately 500 mg portion of the sample with a solution composed of one part glacial acetic acid and four parts distilled water. The samples were weighed before and after leaching for 3 hours at room temperature on a Fisher oscillator. Diffraction diagrams of the "serpentine" residue after leaching showed no brucite. The leachate (approximately 50 ml), considered to represent the dissolved brucite, was analyzed for magnesium and total iron. Portions of both the New Idria "serpentine"-brucite fraction from which the magnetite had not been removed, and a "blank" of non-brucite-bearing clinochrysotile were also run to see whether significant amounts of magnesium and iron were being leached from clinochrysotile and minor residual magnetite. The results indicated that perhaps 5 per cent of the soluble magnesium and a lower, but variable, percentage of soluble iron were contributed to the leachate by clinochrysotile. No difference in iron content was detected between the leachates from the magnetite-bearing and non-magnetite-bearing New Idria brucite-"serpentine" fractions.

The acid leaching results are also shown in Table 1. Although the amounts of $Fe(OH)_2$ in the brucites agree moderately well with those obtained by microprobe analysis, the results are considered to support the probe analyses only in a general way because of the variations in soluble magnesium and iron contributed to the leachate from serpentine-group minerals. The average molar $Fe(OH)_2$ content for the five samples is 14 per cent as compared with the 15 per cent figure determined with the electron probe. The molar brucite/"serpentine" ratios for the Twin Sisters, Dun Mountain, Hat Island, and Burro Mountain samples range between 0.4 and 0.6, whereas for the New Idria sample the ratio is 0.9. There is some evidence of reworking and reprecipitation of both brucite and "serpentine" for the New Idria sample in that: (1) the brucite crystals are about an order of magnitude larger than the brucite crystals occurring in the other samples, and (2) the brucite-bearing sample was found adjacent to a band of splintery, non-brucite-bearing clinochrysotile.

DISCUSSION

Serpentinization—Temperature Control. Experimental information concerning the pressure-temperature conditions for the univariant reaction:

$$\text{forsterite} + H_2O \rightleftarrows \text{clinochrysotile} + \text{brucite} \tag{I}$$

is given by Bowen and Tuttle (1949) and Yoder (1952). In neither of these studies was the curve fixed reversibly. Clinochrysotile and brucite are more stable than forsterite and water at least to 365° C. at 15,000 psi water vapor pressure according to Bowen and Tuttle, and to 430° C. at 15,000 psi according to Yoder. Olsen's (1963) calculated curve passes through 390° C. at 15,000 psi, with an uncertainty between $\pm 60°$ and $\pm 100°$ C.

Olivines in Alpine-type ultramafics contain approximately 10 mol per cent fayalite (Olsen, 1963; Green, 1964). Bowen and Tuttle's (1949) estimate of an 80° C. lowering of olivine stability as a result of this amount of solid solution cannot be accepted since oxygen partial pressure was not controlled, and magnesioferrite ($MgFe_2O_4$), rather than magnetite, was produced. Olsen (1963), assuming that clinochrysotile and brucite are iron-free phases, calculated a 20°–30° C. reduction in temperature for the reaction:

$$\text{olivine (Fa}_{10}) + H_2O + O_2 \rightleftarrows \text{clinochrysotile} + \text{brucite} + \text{magnetite} \qquad \text{(II)}$$

as compared to (I). Combining this result with the experimental data, it seems likely that the stability limit of olivine of $Fo_{90}Fa_{10}$ composition is around 400° C. in the presence of 15,000 psi water vapor pressure.

The stability limit of pure Mg-clinochrysotile, as given by the reaction:

$$\text{clinochrysotile} \rightleftarrows \text{forsterite} + \text{talc} + H_2O \qquad \text{(III)}$$

was shown by Bowen and Tuttle (1949) to be no higher than 505° C. at 15,000 psi. If Olsen's calculations on the influence of fayalite solid solution are again accepted, the equilibrium temperature for the reaction:

$$\text{clinochrysotile} + \text{magnetite} \rightleftarrows \text{olivine (Fa}_{10}) + \text{talc} + H_2O + O_2 \qquad \text{(IV)}$$
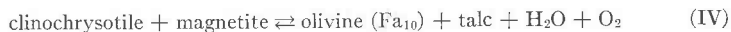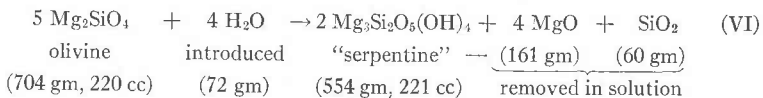
is no higher than 485° C. at 15,000 psi. The widespread occurrence of brucite in Alpine serpentinites implies that pressure-temperature conditions during serpentinization are commonly those characterizing reaction (II) rather than reaction (IV). The temperature difference between the two reactions may be assumed provisionally to be about 80° C., but it should be remembered that neither reaction considers the stability of lizardite or antigorite rather than clinochrysotile, or the influence of iron substitution in brucite and the serpentine-group minerals. Furthermore, talc is a relatively uncommon phase in serpentinized Alpine ultramafic rocks; olivine and pyroxene generally alter directly to serpentine minerals. Therefore, the upper stability limit for "serpentine" can be described by a metastable reaction of the type:

$$\text{"serpentine"} \rightleftarrows \text{olivine} + \text{enstatite} + H_2O \qquad \text{(V)}$$
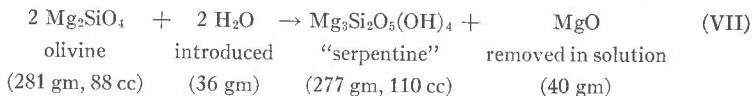
The invariant for reaction (V) lies at a higher temperature than for (III), since we know from Bowen and Tuttle (1949) that forsterite plus talc is more stable than enstatite plus water in the 500° C.—one kilobar water vapor pressure region.

Recognizing the widespread occurrence of awaruite, a nickel-iron alloy of restricted composition (approximately Ni_3Fe), as a product of serpentinization, Olsen (1963) suggested that serpentinization may frequently have taken place in the region near 400° C. and 24,000 psi water vapor pressure, since lower temperatures of hydration would be expected to yield awaruite compositions lower in nickel content. Within the New Idria, California serpentinite mass, Coleman (1961) has described calc-silicate mantles between jadeite pods and the surrounding serpentinite. In these mantles the hydrogrossular composition and the presence of thomsonite suggest crystallization temperatures ranging from 240° C.— 360° C. The jadeite pods presumably originated from the desilication of keratophyres which were tectonically engulfed in the serpentinite (Coleman, 1961). Loss of SiO_2 and addition of CaO to the mantle surrounding the pods favors the idea that alteration and crystallization were contemporaneous with serpentinization. Within the New Idria mass brucite generally accompanies serpentine-group minerals.
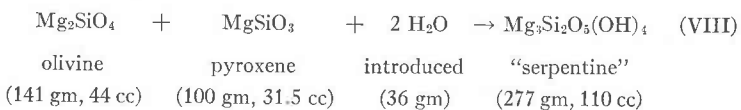
Serpentinization—Volume Changes and Transfer of Material. According to the concept of serpentinization at constant volume (Turner and Verhoogen, 1960, p. 319), large amounts of both magnesia *and silica* must be removed in solution from the ultramafic mass.

$$5\ Mg_2SiO_4\ +\ 4\ H_2O\ \rightarrow 2\ Mg_3Si_2O_5(OH)_4 +\ 4\ MgO\ +\ SiO_2 \quad (VI)$$

olivine   introduced   "serpentine" — (161 gm)   (60 gm)

(704 gm, 220 cc)   (72 gm)   (554 gm, 221 cc)   removed in solution
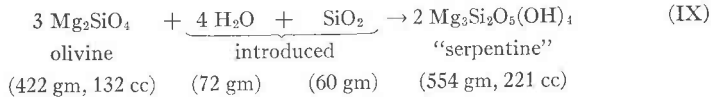
Removal of magnesia alone will not suffice; serpentinization of pure dunites with attendant leaching of all excess magnesia will result in a volume increase of 25 per cent.

$$2\ Mg_2SiO_4\ +\ 2\ H_2O\ \rightarrow Mg_3Si_2O_5(OH)_4 +\ MgO \quad (VII)$$

olivine   introduced   "serpentine"   removed in solution

(281 gm, 88 cc)   (36 gm)   (277 gm, 110 cc)   (40 gm)

The addition of silica, either as pyroxene within the serpentinizing mass (equation VIII), or from aqueous solutions derived from country rocks (equation IX), calls for larger volume increases of 46 per cent and 67 per cent respectively:

$$Mg_2SiO_4\ +\ MgSiO_3\ +\ 2\ H_2O\ \rightarrow Mg_3Si_2O_5(OH)_4 \quad (VIII)$$

olivine   pyroxene   introduced   "serpentine"

(141 gm, 44 cc)   (100 gm, 31.5 cc)   (36 gm)   (277 gm, 110 cc)

$$3\ Mg_2SiO_4\ \ +\ \underbrace{4\ H_2O\ +\ \ SiO_2}\ \rightarrow 2\ Mg_3Si_2O_5(OH)_4 \qquad \text{(IX)}$$

olivine   introduced   "serpentine"

(422 gm, 132 cc)   (72 gm)   (60 gm)   (554 gm, 221 cc)

The widespread leaching of magnesia and silica from a hypothetical ultramafic mass undergoing serpentinization at constant volume should result in notable metasomatic effects in the adjacent wall rocks. Evidence for such metasomatic effects has seldom been encountered in the field (Turner and Verhoogen, 1960, p. 319; Coleman, 1965), but it may be obscured by faulting along the contacts. The leaching of silica, however, from a serpentinizing ultramafic mass is particularly implausible on thermodynamic grounds because it would call for a chemical potential gradient for silica away from the ultramafic mass, which is strongly undersaturated with respect to quartz, and towards the country rocks, commonly made up of graywackes, shales, and cherts, which contain free quartz.
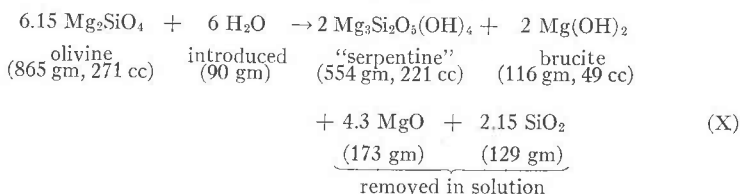
Preservation of olivine grain boundaries in mesh-structure serpentines and the presence of bastite-type pseudomorphs after enstatite is often cited as evidence for "serpentine" replacement at constant volume. This evidence is ambiguous. Interconnecting "serpentine" veins and the innumerable fine veinlets of "serpentine" cutting through parent olivine grains which show optical continuity are, in the manner of septarian concretions, plausible evidence for expansion. Busé and Watson (1960), while describing the alteration of an ultramafic belt near Bryn Mawr, Penna., noted a volume increase due to a "spreading apart" of olivine grains along fractures during serpentinization. Raleigh (1963), studying partially serpentinized enstatite and olivine grains in the ultramafic body on Cypress Island, Puget Sound area, Washington, noted that offsets in exsolution clinopyroxene lamellae and in extinction bands in olivine grains are caused by zones of "serpentine." According to Raleigh, "The offsets in every case are in the sense which would be produced by expansion in the serpentine band normal to its boundaries." Measurements from a number of grains indicated that volume expansions ranging from 20 to 58 per cent were required to produce the observed offsets (Raleigh, 1963, p. 64).

The geologic setting of serpentinized ultramafic bodies supports in a general way the concept of a large volume increase during serpentinization. Faulted contacts, slickensided and highly sheared border zones, and the lack of contact metamorphism suggest an upward diapiric movement in response to tectonic forces along paths of least resistance.
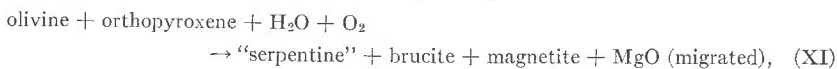
Surface extrusions of serpentinites in California (Dickinson, 1963) and the occurrence of these serpentinites on topographic highs indicates upward and outward movements suggestive of volume increases. Inflow

of water from surrounding sediments with concomitant serpentinization and an increase in volume and decrease in density should enhance such movement and may result in the inclusion of numerous fragments of country rock as observed by Ducloz and Vuagnat (1962) in Cuba, and Coleman (1961, 1963) in New Idria, California, and New Zealand.

Lastly, the formation of significant amounts of brucite during serpentinization is a powerful argument against the hypothesis of constant volume alteration, because it would necessitate the removal of enormous quantities of silica from the ultramafic mass. Such a removal for pure dunite requires that 35 weight per cent of the original silica in the olivine be removed in solution from the ultramafic mass:
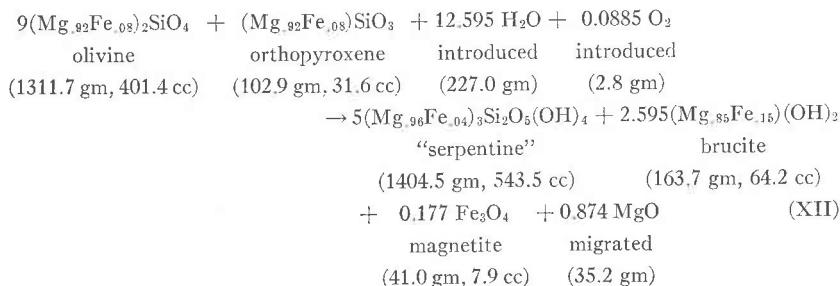
$$6.15 \ Mg_2SiO_4 \ + \ 6 \ H_2O \ \rightarrow 2 \ Mg_3Si_2O_5(OH)_4 + \ 2 \ Mg(OH)_2$$

$$\underset{(865 \ gm, \ 271 \ cc)}{\text{olivine}} \quad \underset{(90 \ gm)}{\text{introduced}} \quad \underset{(554 \ gm, \ 221 \ cc)}{\text{``serpentine''}} \quad \underset{(116 \ gm, \ 49 \ cc)}{\text{brucite}}$$

$$+ \ 4.3 \ MgO \ + \ 2.15 \ SiO_2 \qquad (X)$$

$$\underbrace{(173 \ gm) \qquad (129 \ gm)}_{\text{removed in solution}}$$

If serpentinization is expressed by the general reaction:

olivine + orthopyroxene + H_2O + O_2

$$\rightarrow \text{``serpentine''} + \text{brucite} + \text{magnetite} + MgO \ \text{(migrated)}, \quad (XI)$$

we may calculate a range of volume increases depending upon the initial ratio of orthopyroxene to olivine and upon the migration of variable, but small, quantities of magnesia away from the considered rock volume. Calculations were made for molar orthopyroxene/olivine ratios of from 0 to 1/1 and for migrations of 0, 5, 10, 15, and 20 per cent of the original magnesia. Calculations performed according to reaction (XI) do not account for any silica that may be added to or removed from the ultramafic mass. Several other assumptions should also be mentioned. Except in magnetite, iron was assumed present entirely as ferrous iron and was distributed according to the analytical results described earlier: olivine—$Fo_{92}Fa_8$, orthopyroxene—$En_{92}Fs_8$, "serpentine"—$(Mg_{.96}Fe_{.04})_3Si_2O_5$ $(OH)_4$, brucite—$(Mg_{.85}Fe_{.15})(OH)_2$. Although no orthopyroxenes were analyzed, Green (1964) has shown that $Mg/Mg+Fe+Mn$ ratios for coexisting olivines and enstatites within the Lizard Alpine peridotite body are practically equal. Among the coexisting olivines and pyroxenes listed by Ramberg and Devore (1951) are two pairs from Alpine ultramafics; in these also, the $Mg/Mg+Fe$ ratios are nearly identical. Assumed densities were: olivine ($Fo_{92}Fa_8$)—3.26 (Deer, *et al*. 1962, v. 1, p. 22), orthopyroxene ($En_{92}Fs_8$)—3.26 (Deer, *et al*., 1963, v. 2, p. 28), lizardite and clinochrysotile—2.55 (Deer, *et al*., 1962, v. 3, p. 170). Brucite of composition $(Mg_{.85}Fe_{.15})(OH)_2$ was also assumed to have a

density of 2.55 because we were not able to effect any specific gravity separation of brucite from serpentine-group minerals. Lastly, possible differences in porosity between the initial dunite or peridotite and the final serpentinite were neglected.[1]

A sample calculation with an initial olivine-orthopyroxene ratio of 9/1 and a migration of 5 mol per cent of the original magnesia, is shown in reaction (XII), below:

$$9(Mg_{.92}Fe_{.08})_2SiO_4 \; + \; (Mg_{.92}Fe_{.08})SiO_3 \; + 12.595\, H_2O + \; 0.0885\, O_2$$

olivine	orthopyroxene	introduced	introduced
(1311.7 gm, 401.4 cc)	(102.9 gm, 31.6 cc)	(227.0 gm)	(2.8 gm)

$$\rightarrow 5(Mg_{.96}Fe_{.04})_3Si_2O_5(OH)_4 + 2.595(Mg_{.85}Fe_{.15})(OH)_2$$

"serpentine"   brucite

(1404.5 gm, 543.5 cc)   (163.7 gm, 64.2 cc)

$$+ \;\; 0.177\, Fe_3O_4 \;\; + 0.874\, MgO \qquad\qquad\text{(XII)}$$

magnetite   migrated

(41.0 gm, 7.9 cc)   (35.2 gm)

Reaction (XII) was balanced as follows:

(1) Moles of "serpentine" produced were calculated from total amount of Si present in olivine and orthopyroxene, (2) The moles of Mg originally present in the primary silicates, less the molar sum of Mg migrated and present in "serpentine," represents moles of brucite produced, (3) Moles of magnetite produced represents one-third of the moles of Fe originally present, less moles of Fe present in "serpentine" and brucite, (4) Moles of water and oxygen required were obtained by balancing first for hydrogen, then for oxygen.

The volume increase of 182.6 cc is a 42.1 per cent increase over the original peridotite volume. The molar ratio of brucite to "serpentine" is 0.52, the volume and weight ratio is 0.12, and the weight of migrated Mg (as Mg^{++}) is slightly more than one per cent of the rock mass.

Calculation results are graphically depicted in Fig. 2. The vertical coordinate represents the percentage volume increase; the lower horizontal coordinate shows molar ratios of brucite/"serpentine", and the upper horizontal coordinate shows volume or weight ratios.[2] Each dashed line represents the serpentinization reaction from a constant olivine/orthopyroxene ratio but with various molar amounts (0–20 per cent) of magnesia migration. Each solid line represents reaction from various original ratios of olivine/orthopyroxene but with a fixed amount of migrating magnesia.

Assuming no significant addition of silica from country rocks, a knowl-

[1] Although we have no measured values as guide lines, the ability of "serpentine" cores to sorb several excess per cent of water during shelf storage (Hess and Otalora, 1964, p. 165) suggests that serpentinites may be more porous than primary dunite or peridotites.

[2] Volume and weight ratios are identical because the density of the iron-bearing brucite is considered to be identical with lizardite and clinochrysotile.

edge of the brucite/"serpentine" ratio and of the olivine/orthopyroxene ratio of the original ultramafic is sufficient to determine the percentage of volume increase and the amount of magnesia migration. Examples from four samples, described earlier, from Dun Mountain, Burro Mountain, Hat Island, and Twin Sisters, are shown on Figure 2 by solid circles. The Dun Mountain and Twin Sisters samples are partially serpen-
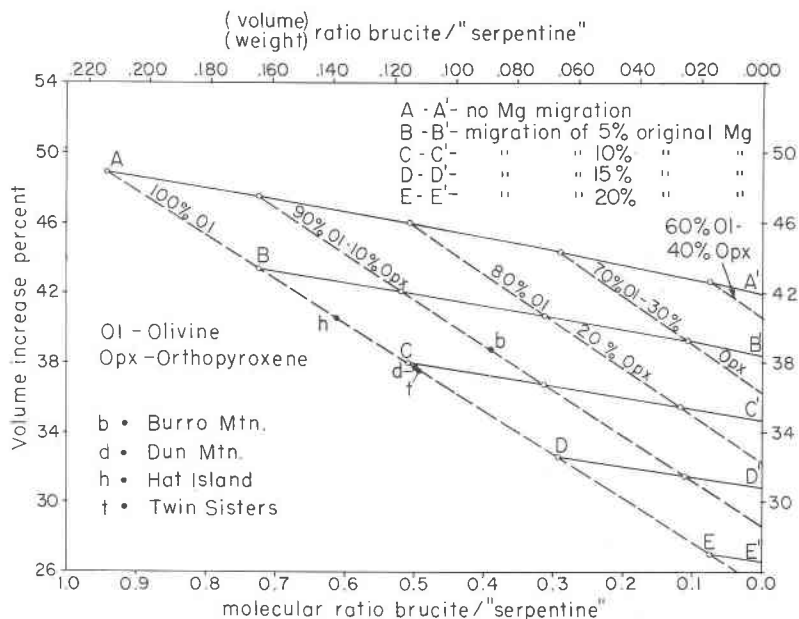

Fig. 2. Volume increase during serpentinization, assuming no addition of silica from surrounding country rocks. Volume increase plotted as a function of original mineralogic composition and resultant brucite/"serpentine" ratios. Molecular amount of migrated magnesium also derived from original mineralogic composition and resultant brucite/"serpentine" ratios. Dun Mountain, Hat Island, Twin Sisters, and Burro Mountain samples shown by solid circles.

tinized dunites, the Hat Island sample is an almost totally serpentinized dunite, and the Burro Mountain sample is a partially serpentinized peridotite with a molar olivine/orthopyroxene ratio of approximately 9/1. Brucite/"serpentine" ratios from these samples are shown in Table 1. Calculated volume increases, applicable only to the serpentinized portions of the rock samples, range from 37–41 per cent and the magnesia migrations from 7–10 per cent. If the molar olivine/orthopyroxene ratio of the Twin Sisters and Dun Mountain samples is 9/1 instead of being pure olivine as shown, the percentage of volume increase would be 41

per cent instead of 37 per cent, and the amount of magnesia migration would be only 5 per cent instead of 10 per cent.

Several chemical mechanisms may account for the 7–10 per cent migration of magnesia, but the observed lack of magnesia metasomatism in the country rocks associated with serpentinites indicates, that a large-scale removal of magnesia from the ultramafic mass is probably not realistic. Incremental serpentinization may indicate that small increments of magnesia have dribbled away into adjacent wall rocks during the ascent of the ultramafic mass. Fixation with available CO_2 as magnesite is sporadic, but may be of local importance. At least part of the magnesite that has apparently migrated may actually be incorporated in brucites with a higher Mg content than the $(Mg_{.85}Fe_{.15})(OH)_2$ composition used in our calculations. Juxtaposed dunite and peridotite layers with imbalances of silica and magnesia are probably important in fixing migrating magnesia. As shown on Figure 2, serpentinization of a primary mass containing forty or more molecular per cent (28 weight per cent) of pyroxene will not form brucite but will instead free excess silica. Movement of magnesia from dunite layers into more silica-rich peridotite layers would allow the serpentine-group minerals to form in the veins so commonly observed within serpentinite bodies.

The weight per cent of brucite will, under the most favorable conditions, appear so modest that one may be tempted to neglect its importance in determining volume relationships. For instance, the weight per cent of brucite in the partially serpentinized Dun Mtn. sample is only 5 per cent, yet the observed brucite/"serpentine" ratio enables us to calculate a volume increase of 37 per cent for the serpentinized portion of the sample. This figure for volume increase cannot be lowered significantly unless it is supposed that massive amounts of silica have been removed from the sample; a supposition which, as mentioned earlier, lacks field verification and is thermodynamically implausible.

Other factors may modify somewhat the calculated estimates of volume increase. First, the Mg/Fe ratios in the primary silicates may be somewhat different than the 92/8 figure used for our calculations. For example, in the Glen Urquhart, Scotland serpentinite (Francis, 1956) optical data indicate an olivine of 96 per cent forsterite and an orthopyroxene of 94 per cent enstatite. Although we do not have a good idea of the fluctuations of iron content in associated serpentine-group minerals and brucites, differences in calculated volume increases would be negligible. Secondly, orthopyroxene is commonly more resistant to serpentinization than is olivine (Bowen and Tuttle, 1949, p. 457). Preferential preservation of orthopyroxene in partially serpentinized rocks would probably result in too low an estimate of the original olivine/

orthopyroxene ratio, and from Fig. 2, somewhat too high a figure for the percentage of volume increase. Thirdly, a significant increase in porosity during serpentinization would mean that the calculated volume increase is somewhat too low.

Lastly, there remains the possibility of important contributions of silica to the ultramafic mass from surrounding sediments. Addition of silica, rather than migration of magnesia, indicates that calculated volume increases are *low* by a considerable margin. For example, the calculated volume increases shown in Fig. 2 for serpentinization of the Dun Mountain and Twin Sisters samples (assuming migration of 10 mol per cent of the original magnesia) are 37 per cent but if serpentinization is calculated on the basis of addition of silica, the resultant volume increase is 52 per cent.

Enormous volumes of water would probably be required for even small additions of silica to the ultramafic mass. Depending on depth and temperature of the ultramafic mass at the time of serpentinization, the volume of water required for the conversion of the primary silicates to "serpentine"-brucite is 50 to 80 per cent of the total volume of the original rock. The introduction of reasonable amounts of silica into the ultramafic rock mass by solution transport would require this estimate for water volume to be increased by at least an order of magnitude and probably much more. For example, at 400° C. and 1500 bars the volume of water required for complete serpentinization of the Dun Mountain sample is 75 per cent of the original volume of the sample, assuming migration of 10 mol per cent of the original magnesia away from the sample. If, on the other hand, it is assumed that additional silica, derived from quartz-saturated water in the country rocks, is responsible for the observed MgO/SiO_2 ratio in the serpentine-brucite fraction, then the total volume of water required to provide this additional silica is *140 times* the volume of the original sample (quartz solubility data from Kennedy (1950)).

One can speculate on the feasibility of rapid rates of diffusion for silica as a means of drastically reducing these water volume requirements. To be effective, the chemical potential gradient for silica must lead to a rate of diffusion markedly more rapid than the flow of water. This is an untested mechanism to account for the movement of silica between country rocks and the interior portions of large ultramafic masses, but it may be important in accounting for local migrations of magnesia and silica within the ultramafic mass. Chemical analyses of a sufficiently large number of samples from an ultramafic mass will average out local migrations of magnesia and silica and show, for the bulk rock, whether the MgO/SiO_2 ratio has changed during serpentinization. Constant bulk

MgO/SiO_2 ratios during serpentinization were noted by Shteĭnberg (1960) in his study of the serpentinized dunites of the Urals.

Regardless of the applicability of the speculation in the several preceding paragraphs, the initial volume of water ultimately incorporated as (OH) groups within the crystalline brucite and serpentine-group minerals must have been nearly as large as the combined volume of the primary anhydrous silicates; a fact which of itself makes implausible the concept of serpentinization as an autometasomatic process. Furthermore, the large volume increases required for complete serpentinization suggest that this process does not occur *in situ* or as the result of one enormous injection of water, because of the problem of accommodating such a volume increase within the surrounding country rocks. We prefer the concept that pervasive serpentinization is a gradual, possibly continuous, possibly intermittent, process that feeds on water derived from adjacent country rocks and that accompanies the rise of the ultramafic mass during tectonism. Volume increases resulting from serpentinization serve as an impetus to the continued diapiric ascent of the mass. This concept of serpentinization is harmonious with structural and geometrical features typical of Alpine ultramafics; namely, their ellipsoidal, fault-bounded configurations, the numerous inclusions of country rock near the margins and especially the distal ends of the ellipsoidal mass, and the occurrence of the masses along topographic highs, even where the density of the ultramafic mass is considerably greater than the surrounding rocks.

Brucite Stability and Carbonate Formation. Shteĭnberg (1960) has noted the lack of brucite in aphanitic serpentinites which occur as small veins along diagonal fractures in the serpentinized, brucite-bearing dunites of the Urals. Lack of brucite may be due to variations in compositional type, or to local, but intensive, removal of magnesia and/or introduction of silica. Thus, brucite is probably not stable along the sheared borders of ultramafic masses, or in the immediate vicinity of fresh fractures opened in brucite-bearing serpentinites, or in weathering zones where CO_2 may be present or low pH values could develop. The dark, brucite-bearing core of serpentinized dunite from Hat Island, described earlier, is surrounded by a greenish weathering rim of identical serpentine-group minerals but devoid of brucite.

Brucite formed during pervasive serpentinization must be regarded as a prime candidate for reaction with available CO_2-bearing solutions at depth to form the magnesite commonly associated with ultramafic rocks. In a hydrous surface or near surface environment brucite is converted to hydromagnesite $[Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O]$ if the partial pressure

of CO_2 is at least 10^{-6} atm. (Hostetler, 1960). Probably even smaller P_{CO_2} values are required for conversion of brucite to artinite [$Mg_2(CO_3)$ $(OH)_2 \cdot 3H_2O$] or pyroaurite [$Mg_6Fe_2(CO_3)(OH)_{16} \cdot 4H_2O$] and coalingite [$Mg_{10}Fe_2CO_3(OH)_{24} \cdot 2H_2O$]. Within the New Idria, California, serpentinite mass, recent open-pit mining for short fibre asbestos has afforded the authors an opportunity to relate paragenetically brucite with these magnesium carbonate minerals. In those pits extending below the water table (30–60 feet) brucite is a common constituent of both the sheared short fibre ore and of the larger, massive, unsheared serpentinite blocks contained within the sheared material. The amount of brucite may approach a 1/1 molar ratio with the serpentine-group minerals. At the surface and above the water table as exposed in these open pits, white "cottonballs" of hydromagnesite (1–5 mm in diam.) and occasional radiating artinite needles are ubiquitous in the sheared serpentinite to the near exclusion of brucite. Commonly the surfaces of residual blocks of massive serpentinite exposed in the same zone are coated with reddish-brown coalingite and pyroaurite (Mumpton, *et al.*, 1965) which apparently result from the oxidation of iron-bearing brucite *in situ*. However, the unweathered interiors of these blocks do contain brucite. Thus, where air and/or CO_2-bearing groundwater have easy access to brucite-bearing serpentinite, the brucite is readily converted to magnesium carbonates, whereas within those massive serpentinite blocks impervious to groundwater percolation, brucite is preserved.

Future Problems

The logical sequel to a general and pragmatic paper such as this is a study in depth of a particular ultramafic body where assumptions and conclusions can be tested against critical field observations. Particular attention should be paid to zones of partial serpentinization between fresh, primary silicates and fully serpentinized areas. Detailed investigation and comparison of MgO/SiO_2, Fe/SiO_2, and Fe/Mg ratios in zones of partial serpentinization and in adjacent unserpentinized zones should indicate the extent of magnesia and silica migration, the extent to which silica has been added from country rocks, and reliable estimates of volume increase during serpentinization. Possible relationships between the various serpentine-group minerals and association with primary silicates or with successive generations of "serpentine" should be explored. Our data suggest that lizardite-brucite is the initial result of serpentinization of olivine. Knowledge of the variation in serpentine-group minerals of NiO and CoO content and of oxygen and hydrogen isotopic ratios should prove useful in tracing initial and successive generations of serpentinization.

Summary

The apparently widespread occurrence of brucite in serpentinized Alpine ultramafics (up to 10 weight per cent), as related to the experimental work of Bowen and Tuttle (1949) indicates that the temperatures of serpentinization are probably some 100° C. lower than generally accepted, because the presence of brucite lowers the maximum value (500° C.) given for the reaction:

$$\text{olivine} + H_2O + \text{silica} \rightarrow \text{``serpentine''}$$

Moreoever, the occurrence of brucite as a product of pervasive serpentinization demands a large volume increase during serpentinization unless it can be shown that truly massive quantities of both silica and magnesia have been removed from the ultramafic mass. Field observations yield no evidence in support of such massive migrations. Depending on the original ratio of pyroxene to olivine, our calculations show that volume increases of 35–40 per cent are common during serpentinization. The tectonic implications of such expansions are immediately apparent. The complete serpentinization of a large Alpine ultramafic body *in situ* by water derived from adjacent country rocks is unrealistic because of the difficulty in accommodating a great increase in volume within the surrounding country rocks. We assume that serpentinization of the large Alpine ultramafic belts is accomplished by moderate additions of water during the tectonic ascent of these bodies through the earth's crust. The widespread serpentinization of these Alpine ultramafics combined with their nearly universal occurrence in and along structural discontinuities suggests that much, or all, of the expansion is accommodated during tectonism. Further careful field and laboratory work is necessary before the process of serpentinization can be related to the origin of the ultramafics.

References

ALLAKHVERDIEV, SH. I. (1958) Carbonates from the weathered crust of ultrabasic rocks of Azerbaidzhan. *Izvest. Akad. Nauk, Azerbaidzhan S.S.R., Ser. Geol.-Geograf. Nauk.* **3,** 79–87.

ALLEN, C. C., J. C. GILL AND J. S. KOSKI (1957) The Jeffrey Mine of Canadian Johns-Manville Company, Limited. *In, The Geology of Canadian Industrial Mineral Deposits, Sixth Commonwealth Min. Metall. Cong., Vancouver, B. C.* 27–36.

BENSON, W. N. (1913–1918) The geology and petrology of the Great Serpentine Belt of New South Wales. *Proc. Linn. Soc. N.S.W.* **38**, 490–517, 569–596, 662–724; **40**, 121–171, 540–624; **42**, 223–283, 693–700; **43**, 320–393, 593–599.

—— (1926) The tectonic conditions accompanying the intrusion of basic and ultrabasic igneous rocks. *U.S. Nat. Acad. Sci.* **1**,

BOWEN, N. L. AND O. F. TUTTLE (1949) The system MgO-SiO$_2$-H$_2$O. *Geol. Soc. Am. Bull.* **60**, 439–460.

BUSÉ, M. L. AND E. H. WATSON (1960) Alteration of ultrabasic rocks near Bryn Mawr, Pennsylvania. *Pa. Acad. Sci. Proc.* **34**, 117–123

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. Spe. Paper* **73**, 130.

—— (1965) New Zealand serpentinites and associated metasomatic rocks. *Geol. Bull. New Zealand Survey* (in press).

DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1962) *Rock-forming Minerals, v. 1, Ortho- and Ring-silicates.* John Wiley and Sons, Inc., New York.

—— (1962) *Rock-forming Minerals, v. 3, Sheet Silicates.* John Wiley and Sons, Inc., New York.

—— (1962) *Rock-forming Minerals, v. 5, Non-silicates.* John Wiley and Sons, Inc., New York.

—— (1963) *Rock-forming Minerals, v 2, Chain Silicates.* John Wiley and Sons, Inc., New York.

DICKINSON, W. R. (1963) Brecciated serpentine extrusion on Table Mountain in central California Coast Ranges. *Geol. Soc. Am. Spec. Paper.* **73**, p. 34.

DUCLOZ, C. AND M. VUAGNAT (1962) A propos de l'âge des serpentinites de Cuba. *Archives des Sciences, Genève, Vol. 15*, **2**, 309–332.

ECKHARDT, F. J. (1956) Röntgenographische Untersuchungen am Schweizerit. *Neues Jahrb. Mineral. Monatsh.*, 32–43.

FACKLER, W. C. (1945) The occurrence of nemalite in Alaska. *Am. Mineral.* **30**, 640–641.

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

FENOGLIO, M. (1930) Sulla presenza della nesquehonite nella serpentina di Viv in Val di Lanzo. *Accad. Naz. dei Lincei, Rend.* **11**, 310–316.

—— (1933) Sulla lansfordite della miniere di Cogne in Val d'Aosta. *Period Mineral.* **4**, 443–462.

FERRARI, A., G. SCANINI AND L. CAVALCA (1950) La brucite di Carro ed i minerali che l'accompagnano. *Period. Mineral.* **19**, 41–49.

FRANCIS, G. H. (1956) The serpentinite mass in Glen Urquhart, Invernesshire, Scotland. *Am. Jour. Sci.*, **254**, 201–226.

GREEN, D. H. (1964) 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 Leopoldsgrün (Münchberger Gneismasse). Ein Betrag zur Geochemie ultrabasischer Gesteine. *Geochim. Cosmochim. Acta.* **21**, 165–181.

HESS, H. H. 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. Sciences-NRC Publ.* **1188**, 152–168.

HOCHSTETTER, F. VON (1859) Lecture on the geology of the Province of Nelson. *New Zealand Govt. Gazette (Prov. Nelson)*, **7**, (20), 90–102.

HOSTETLER, P. B. (1960) Low temperature relations in the system: MgO-SiO_2-CO_2-H_2O. Ph.D. diss., Harvard Univ., Cambridge, Mass.

KEIL, K. AND K. FREDRICKSSON (1964) The iron, magnesium, and calcium distribution in coexisting olivines and rhombic pyroxenes of chondrites. *Jour. Geophys. Res.*, **69**, 3487–3515.

KENNEDY, G C. (1950) A portion of the system silica-water. *Econ. Geol.* **45**, 629–653.

MEIXNER, H. (1938) Kraubather Lagerstättenstudien. *Zentralblatt Mineral.*, Abt. A, 5–19.

——— (1956) Seltene Magnesiumminerale aus dem Serpentingebiet von Kraubath, Obersteiermark. *Der Karinthin*, **33**, 166–171.

MUMPTON, F. A., H. W. JAFFE AND C. S. THOMPSON (1965) Coalingite, a new mineral from the New Idria serpentinite, Fresno and San Benito Counties, California. *Am. Mineral.* **50**, 1893–1913.

OLSEN, E. (1963) Equilibrium calculations in the system Mg, Fe, Si, O, H, and Ni. *Am. Jour. Sci.* **261**, 943–956.

RALEIGH, C. B. (1963) Fabrics of naturally and experimentally deformed olivine. Ph.D. diss. California Univ., Los Angeles, Calif.

RAMBERG, H. AND G. DEVORE (1951) The distribution of Fe^{++} and Mg^{++} in coexisting olivines and pyroxenes. *Jour. Geol.* **59**, 193–210.

SAKAMOTO, C. (1959) Studies on serpentine containing brucite. *Kogyo Kagaku Zasshi.* **62**, 1485–1488.

SERDYUCHENKO, D. P. (1949) Hydromagnesite. *Doklady Akad. Nauk S.S.S.R.* **68**, 581–584.

SHTEĬNBERG, D. S. (1960) New data concerning the serpentinization of dunites and peridotites of the Urals. *Inter. Geol. Cong., XXI sess. Dokl. Sovet. Geol. Petrograf. Prov. Izverzh. Metamorfi. Gornye Porody, Izdalel'stvo Akad. Nauk S.S.S.R., Moskva*, 250–260.

SMITH, J. V. AND R. C. STENSTROM (1965) Chemical analysis of olivines by electron microprobe. *Mineral. Mag., Tilley vol.* 436–459.

THAYER, T. P. (1960) Some critical differences between Alpine-type and stratiform peridotite-gabbro complexes. *Inter. Geol. Cong., XXI Sess., Copenhagen, Rept. Pt.* **13**, 247–259.

TURNER, F. AND J. VERHOOGEN (1960) *Igneous and Metamorphic Petrology*, 2nd ed. McGraw-Hill Book Co., New York.

VAN BILJON, W. J. (1960) Chemical reactions in the thermal breakdown of the serpentine minerals. *Neues Jahrb. Mineral., Abha.* **94**, 1223–1240.

YODER, H. S., JR (1952) The MgO-Al_2O_3-SiO_2-H_2O system and the related metamorphic facies. *Am. Jour. Sci., Bowen vol.* 569–627.