CALCIUM METASOMATISM IN THE JOSEPHINE PERIDOTITE, SOUTHWEST OREGON

by

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A Thesis submitted to the faculty of the
DEPARTMENT OF GEOSCIENCES
In Partial Fulfillment of the Requirements for the degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

1989
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ACKNOWLEDGMENTS

I wish to thank Drs. Christopher J. Eastoe, Eleanour Snow, and Joaquin Ruiz for their valuable assistance in preparing this thesis. Special thanks go to Dr. Eastoe for the use of his facilities.

Thanks also go to Dr. E. J. Dasch of Oregon State University for introducing me to rodingites and pointing me toward the Klamath Mountains.

Special thanks go to my family for their continued support throughout my college career.
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The Josephine peridotite is similar to other ultramafic occurrences in the western United States in terms of chemistry, mineralogy, and alteration. Serpentinization of the peridotite has been accompanied by volume increases of 20 to 30 percent, with constant MgO. Several stages of serpentinization have affected the peridotite, and serpentinization appears to continue at present.

Mafic dikes of variable original composition intrude the peridotite and have been Ca-metasomatized to rodingite. The formation of rodingite resulted in small decreases in volume, at constant Al₂O₃.

Both rocks have lost silica. Mass balance calculations show that more than enough calcium is lost during serpentinization to account for the metasomatic effects common to ultramafic bodies.
CHAPTER 1
INTRODUCTION

Statement of problem

The result of Ca-metasomatism of igneous dikes which intrude ultramafic rocks is a rock termed rodingite, consisting of Ca-rich minerals such as hydrogrossular garnet, diopсидic pyroxene, prehnite, epidote, idocrase, and xonotlite. All occurrences of rodingite are, at first approximation, quite similar in bulk composition and mineral assemblages. At the completion of metasomatism, hydrogrossular and diopside are commonly the only minerals present, and the bulk composition approaches 3CaO-Al$_2$O$_3$-2SiO$_2$-H$_2$O (Coleman, 1967).

Rodingitized rocks are found only in contact with serpentinized ultramafic rocks suggesting that Ca-metasomatism is a direct consequence of the serpentinization of ultramafic rocks. Calcium required for the metasomatism is believed to come from the breakdown of pyroxene during serpentinization. Serpentinization and rodingitization are thus simultaneous and complementary processes. Although
this hypothesis is qualitatively reasonable, the degree to which the two processes are truly complementary has not been quantitatively determined.

The focus of this thesis will be an examination of the volume-composition relations of serpentinization and rodingitization. Volume-composition calculations will provide information on the fluxes of components during alteration and will establish the magnitude of volume changes that occur. Comparison of the amounts of components gained or lost during serpentinization of the peridotite and rodingitization of the dikes will show to what degree the two processes are complementary. The question of whether serpentinization occurs under constant-volume, or constant-component conditions will be answered. Comparison of P-T-X conditions indicated by phase relations in the peridotite and rodingite will show if the two processes can occur under similar P-T-X conditions.

Results of this study on the Josephine ultramafic rocks and rodingites should be applicable to other ophiolites since alpine peridotites and rodingites are so broadly similar wherever they occur.

**Location of Field Area**

The field area for this study is in the western
Jurassic belt (WJB) of the Klamath Mountains (figure 1), northwest of Cave Junction, Josephine County, Oregon (figure 2). The study covers a main 52 square kilometer area southwest of Eight Dollar Mountain, and a roadcut strip along the Illinois River Road, west of Selma. Access to the main area includes the West Side Road, west of Kerby, and Eight Dollar Road, north of Kerby.

These areas were chosen because of the easy access to large exposures of ultramafic rocks of the Josephine ophiolite, the many well-exposed rodingite dikes, and the almost negligible degree of metamorphism of rocks in this part of the WJB.

**Previous Work**

Early geologic investigations in the western Klamath Mountains began with Diller (1902, 1907), Wells and Walker (1953), Cater and Wells (1953). Structural studies of the western Klamath Mountains and the Josephine peridotite were performed by Dott (1966), and Loney and Himmelberg (1976). Ages of rocks in the region were determined by Lanphere et al (1968), Hotz (1971), Dick (1973), Irwin (1973), Harper and Saleeby (1980), and Saleeby et al (1982). Geochemical and petrologic investigations of the Josephine peridotite in or near this study area include Himmelberg and Loney (1973),
Figure 1. Geologic setting of the study area, in the Klamath Mountains. The four major lithotectonic units of the Klamath Mountains province are the Eastern Klamath belt, EKB; the central metamorphic belt, CMB; the western Paleozoic and Triassic belt, WPTB; and the western Jurassic belt, WJB. (After Harper, 1980)
Figure 2. Location of the study area, Josephine County, Oregon. Samples were collected from the main study area, outlined, and from roadcuts along the Illinois River Road. (Geologic map of study area in pocket.)
Dick (1974, 1976, 1977), and Vail (1977). Rodingites in the area were investigated by Coleman (1967). Important ore deposits of the Josephine peridotite include nickel laterites (Hotz, 1964), chromite, (Ramp 1961, 1975), and massive sulfides (Strickler 1986; Kuhns and Baitis, 1987).

**Methods of Investigation**

Rock samples were collected during field mapping in 1982 and 1987. Ultramafic samples were collected throughout the field area, while rodingites were collected from outcrops in Josephine Creek and roadcuts along the Illinois River road. Rocks selected were as fresh as possible.

Whole-rock analyses by XRF were performed by X-ray Assay Laboratories Limited, Ontario, Canada. Major elements, along with Ba, Sr, and Rb were analyzed using fused pellets, with detection limits of 0.01 weight percent for major elements and 10 ppm for the trace elements. Pressed pellets were used for Zr, Y, and Nb analyses, with a detection limit of 3 ppm for Zr and 2 ppm for Y and Nb.

For summation, major elements are calculated as oxides. Total iron is reported as Fe$_{10}$O$_9$, and water as LOI.

X-ray diffraction was used to identify phases present in several ultramafic samples. A Siemens powder diffractometer was employed for the determinations. The
settings were: 30 mA and 40 kV power, 2° 20 per minute scan rate, 2 cm per minute chart speed, scintillation counter at 964 V and graphite monochromatic filter. Diffractograms were compared with standard cards and data from Buttner and Saager (1982) and Hostetler et al. (1966) for phase identification.

Abbreviations of Minerals, and Literature Sources

Throughout this thesis, graphs are used to display analytical data. For reference, the compositions of common minerals associated with ultramafic rocks or rodingites are also plotted. Abbreviations of minerals used in figures and text are listed in table I.

In addition, chemical analyses taken from published sources are used to supplement those from this study. The sources of analyses of ultramafic rocks are listed in table II, and rodingites in table III.
TABLE I.
Abbreviations of minerals used in text and figures.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Abbreviation</th>
<th>Ideal formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>anorthite</td>
<td>an</td>
<td>CaO·Al$_2$O$_3$·3SiO$_2$</td>
</tr>
<tr>
<td>chlorite</td>
<td>chl</td>
<td>≈4MgO·Al$_2$O$_3$·4SiO$_2$·4H$_2$O</td>
</tr>
<tr>
<td>(≈penninite)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diopside</td>
<td>di</td>
<td>CaO·MgO·2SiO$_2$</td>
</tr>
<tr>
<td>epidote</td>
<td>ep</td>
<td>CaO·0.5Fe$_2$O$_3$·Al$_2$O$_3$·2SiO$_2$·0.5H$_2$O</td>
</tr>
<tr>
<td>grossular</td>
<td>gro</td>
<td>3CaO·Al$_2$O$_3$·3SiO$_2$</td>
</tr>
<tr>
<td>hibschite</td>
<td>hib</td>
<td>3CaO·Al$_2$O$_3$·2H$_2$O</td>
</tr>
<tr>
<td>hydrogrossular</td>
<td>hyd</td>
<td>3CaO·Al$_2$O$_3$·2SiO$_2$·2H$_2$O</td>
</tr>
<tr>
<td>idocrase</td>
<td>ido</td>
<td>10CaO·2Al$_2$O$_3$·2(MgO,FeO)·9SiO$_2$·2H$_2$O</td>
</tr>
<tr>
<td>prehnite</td>
<td>pre</td>
<td>2CaO·Al$_2$O$_3$·3SiO$_2$·H$_2$O</td>
</tr>
<tr>
<td>wollastonite</td>
<td>wo</td>
<td>CaO·SiO$_2$</td>
</tr>
<tr>
<td>xonotlite</td>
<td>xon</td>
<td>3CaO·3SiO$_2$·H$_2$O</td>
</tr>
<tr>
<td>zoisite</td>
<td>zo</td>
<td>2CaO·1.5Al$_2$O$_3$·3SiO$_2$·0.5H$_2$O</td>
</tr>
<tr>
<td>(clinozoisite)</td>
<td></td>
<td></td>
</tr>
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</table>
**TABLE II.**

Literature sources for analyses of ultramafic rocks.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample number</th>
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<tbody>
<tr>
<td>Bilgrami and Howie, 1960.</td>
<td>6, 7</td>
</tr>
<tr>
<td>Bonatti, 1968.</td>
<td>5a, 33a</td>
</tr>
<tr>
<td>Bowin et al., 1966.</td>
<td>D2-2, D10-6</td>
</tr>
<tr>
<td>Coleman and Keith, 1971.</td>
<td>21, 23, 25, 27</td>
</tr>
<tr>
<td>Larrabee, 1969.</td>
<td>2, 3</td>
</tr>
<tr>
<td>Loney et al., 1971.</td>
<td>1, 4, 8, 10, 11, 13, 16, 18.</td>
</tr>
<tr>
<td>Miyashiro et al., 1969.</td>
<td>T20, AM3, T37, T5, T6, Am5; pg 123:3, 5, 6, 7.</td>
</tr>
</tbody>
</table>

**TABLE III.**

Literature sources for analyses of rodingites.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhaeusser, 1978.</td>
<td>1, 2, 3, 4, 11, 12, 13.</td>
</tr>
<tr>
<td>Bilgrami and Howie, 1960.</td>
<td>1, 3</td>
</tr>
<tr>
<td>Bloxam, 1954.</td>
<td>A, C</td>
</tr>
<tr>
<td>Larrabee, 1969.</td>
<td>5</td>
</tr>
<tr>
<td>Sivell and Waterhouse, 1986.</td>
<td>1, 2, 3, 4, 5.</td>
</tr>
</tbody>
</table>
CHAPTER 2
GEOLOGY OF FIELD AREA

Regional Geology

The Klamath Mountains Province (figure 1) is divided into four arcuate, north-south trending tectono-stratigraphic belts, each bounded by regional east-dipping thrust faults (Irwin, 1964, 1966, 1981). Structural and lithologic relations suggest that the "eugeosynclinal" belts, which decrease in age to the west, represent progressively accreted ophiolitic and island-arc terranes (Saleeby, et al., 1982; Wright, 1982). Beginning in the early Paleozoic, four major episodes of accretion occurred, the last being the late Jurassic Nevadan orogeny that emplaced the terrane of the western Jurassic belt (WJB).

In Oregon, the Klamath Mountains province ends where the WJB is thrust westward over the Cretaceous eugeosynclinal rocks of the Dothan and Otter point formations, which are equivalent to the Franciscan formation of California (Irwin, 1964).

The Josephine ophiolite forms the basement on which the
WJB was constructed (Harper, 1984). Although thoroughly dismembered, all the stratigraphic units of a classic ophiolite sequence have been described by workers studying the WJB. At the base of the ophiolite is the Josephine peridotite, a typical "Alpine type" ultramafic occurrence. It is predominantly a tectonized harzburgite which represents the residuum of at least one episode of partial melting in the mantle (Dick, 1976, 1977).

The other units of a classic ophiolite sequence, generally not present at any one locality, include cumulate ultramafic rocks and gabbros (Vail, 1977), sheeted dikes (Ramp, 1980; Harper, 1984), plagiogranite (Harper and Saleeby, 1980), and pillow basalts, with associated massive sulfide and exhalative deposits (Harper, 1984; Strickler, 1986; Kuhns and Baitis, 1987).

Overlying the ophiolite are the Galice and Rogue formations. The Galice formation consists mostly of dark gray mudstones and graywackes that have been interpreted by Saleeby and others (1982) to be a submarine-fan complex. The formation contains volcaniclastic sediments derived from the west, as well as sediments derived from older metamorphic rocks to the east. The Galice formation is believed to have formed in a small marginal basin between the old continental margin and a young island arc complex.
The Galice formation was named for exposures near the town of Galice, Oregon by Diller (1907). The thickness of the sediments has been estimated to be about 5 km (Wells et al., 1949). Volcanic rocks are also present in the formation, and these are indistinguishable from those of the Rogue formation (Garcia, 1979).

Various workers have considered the Galice formation and Rogue formation to be different members of the same formation. Diller (1907), and Wells and others (1949) regarded the abundant volcanic rocks in the WJB as the volcanic member of the Galice formation. Saleeby and others (1982) also favored this view.

Wells and Walker (1953) separated the volcanic rocks from the sediments of the Galice formation and named them the Rogue formation after the extensive exposures of the volcanic rocks in the canyons of the lower Rogue River. The separation was prompted by their observation that, in the northern WJB, the contacts of the Galice formation with the Rogue formation are always fault contacts.

The Rogue formation is interpreted by Garcia (1979, 1982) to be the remains of a Jurassic island arc. It is a 3 to 5 km thick pile of predominantly (>95%) fragmental
material, with flows being very minor in abundance. The formation progresses from predominantly coarse fragments of basaltic to andesitic composition in the lower sections to fine-grained basaltic to rhyolitic tuffs and minor basalt flows in the upper sections. Fossils are lacking in the Rogue formation, and amphiboles are too altered for K-Ar dating, but the Oxfordian to Callovian (mid-late Jurassic) age of the formation is constrained by fossils in the the Galice formation (Dott, 1971), which interfingers with the Rogue formation along depositional contacts in the southern WJB (Harper, 1983, 1984).

Both the Rogue and Galice formations have undergone variable metamorphism from slightly altered or lower greenschist facies to amphibolite faces conditions (Wells et al., 1949; Garcia, 1982).

The entire Klamath Mountains province has been intruded by granitic plutons ranging in size from tens of meters to kilometers across. The plutons date from late Jurassic to Cretaceous (Lanphere et al., 1968; Hotz, 1971).

**Geology of the Field Area**

**Ultramafic Rocks**

The major rock unit in the study area is the Josephine peridotite (geologic map, figure 3, in pocket).
Harzburgite and its serpentinized equivalent make up the bulk of the ultramafic mass. The harzburgite is relatively unaltered (10 to 20 percent serpentine) on Eight Dollar Mountain, but elsewhere is typically 50 percent or more serpentinized. Where sheared, the peridotite has been completely replaced by serpentine.

In outcrop, the harzburgite is olive green when fresh, becoming dark green to dark gray or black with increasing serpenatinization. The peridotite weathers to a distinctive reddish brown, becoming brown to grey with progressive alteration. Conspicuous knobs on the weathered surfaces of the ultramafic rocks are the result of the preferential weathering of olivine, leaving the more resistant pyroxene grains protruding to form a very rough texture.

In some locations, a distinctive planar fabric results from the alignment of elongate olivine and orthopyroxene grains, or from minor variations in the relative amounts of olivine and pyroxene.

Several prominent joint sets break the peridotite into large blocks. The most pronounced joints are near vertical and trend roughly ten degrees either side of east-west, and around N20E. A third, less distinct set is sub-horizontal, striking close to N30E. The trends of the joints become erratic as the contacts with the Galice and Rogue formations
are approached.

Mapping of the peridotite is aided by the thin, nutrient-poor soil and resulting sparse vegetation. On aerial photos, the ultramafic rocks stand out in contrast to the other rock units, which are covered by the thick soil and dense vegetation normal in the Pacific northwest. Within the peridotite, the location of dikes and small dioritic stocks is betrayed on photos as small areas of dense vegetation (dark on photos) surrounded by the barren harzburgite (light colored). Where stocks are near small streams, the supply of water, rich soil, and vegetative cover (which provides camouflage) offer excellent conditions for covert agriculturalists to grow Oregon’s leading cash crop.

The contact of the peridotite with the Galice formation is in many places marked by springs and bogs that contain a rare and distinctive plant, Darlingtonia (pitcher plant).

Throughout the ultramafic mass are zones of intense shearing. These zones consist of completely serpentinized peridotite which on photos and in the field are even more barren than the surrounding, less serpentinized harzburgite. A large shear zone extends from Free and Easy pass south to Woodcock Mountain. Many other sheared zones are present, but are too small or too discontinuous to be shown at the
mapped scale.

**Rogue Formation**

In fault contact to the west of the peridotite is the Rogue formation. Exposure of the Rogue volcanics is poor owing to the well developed soil and very thick vegetation. Good exposures were found only in some roadcuts and a few stream bottoms. The structure of the formation was not studied in detail, but near the contact with the peridotite, the rocks have a weak foliation (N 10 to 36 E), parallel to the structural grain of the Klamath Mountains.

Rocks of the Rogue formation range from siliceous tuffs to basalt. A fragmental character is evident in many of the rocks, and the very fine grain size and thin-beded nature of the rocks indicate a tuffaceous origin. Some of the metavolcanic rock samples appear to be fine interlaminations of very siliceous tuffaceous material and cherty material.

Flow rocks are also found in the formation. The composition of the flows ranges from hornblende andesite to basalt. These rocks are very similar to the dikes that intrude the peridotite. Some of the dikes that intrude the peridotite may represent feeder conduits for the volcanic rocks of the Rogue formation.

Just west of the mapped area are abundant red to gray chert beds exposed in roadcuts. Chert cobbles are common in
the drainages of Mikes Creek and Days Gulch.

**Galice Formation**

On the eastern side of the study area the Illinois River floodplain extends almost to the peridotite, and only a narrow strip of the Galice formation is exposed in the southeast corner. The Galice formation is in contact with the peridotite along a west-dipping fault. The sediments are composed of buff weathering fine to coarse grained lithic wackes with interbedded dark gray to black shales. In some cases the sandstones contain small pebbles. Particles in the sandstones include abundant lithic fragments, chert, quartz, feldspar, hornblende, and clay.

The beds have been tectonically contorted, shale layers showing more deformation than the sandstones. Slickensides were noted on many surfaces, especially where the Galice formation is very close to the contact with the peridotite. Attitudes of less contorted beds (N 29 to 34 E) are generally parallel to the structural grain of the Klamath Mountains in the area. The beds dip about 60 degrees to the southeast where relatively undisturbed, but near the peridotite some layers have been overturned to the west. Even in the least disturbed outcrops the rocks are so fractured that it is hard to obtain a piece as large as five centimeters.
Granitic Intrusions

Throughout the area are numerous small granitic stocks with a wide variety of mineralogies. The rocks vary from light colored, fine grained granodiorites to coarse grained hornblende gabbro. Some stocks are so small that their presence is indicated only by pieces of float on slopes or in stream sediments, and the actual size and location of the intrusion cannot be determined with certainty. Weathering has obscured contacts with the peridotite and it is not known if these intrusive rocks have been rodingitized. The stocks are most abundant in the area south of Free and Easy Pass.

Along the eastern edge of the peridotite, straddling Free and Easy Creek, is a unit of igneous rock which is seemingly out of place. Elsewhere, the rocks in contact with the eastern edge of the peridotite are the sediments of the Galice formation. The igneous body is an andesitic rock, slightly altered to a green color on fresh surfaces, and weathering to the same brownish gray as the adjacent graywackes. The orientation of the contact with the peridotite to the west indicates the body is in contact along an east-dipping fault, whereas the Galice formation contacts the peridotite along a west-dipping fault. The andesite is therefore an isolated wedge-shaped unit that
could represent either a volcanic member of the Galice formation or a piece of the Rogue formation.

**Rodingite Occurrences**

The most obvious exposures of rodingites are in road cuts or along bedrock stream bottoms. Rodingite surfaces quickly weather to white, and so are quite prominent against the dark green to black serpentinites in which they are always found. The main field area straddles Josephine Creek, which occupies a zone of intensely sheared and serpentinized peridotite and numerous dikes.

The dikes are a few to tens of meters apart through the entire length of the creek in the map area and are a few centimeters to two meters in thickness. They are tabular and are usually traceable for distances of tens of meters where soil and plants do not obscure them; they pinch and swell and are offset along small faults. The shapes and the continuity of the dikes indicate that they are intrusive features and are not merely tectonic inclusions in the serpentinite (Coleman, 1967, 1980).

Dikes exposed along the Illinois River Road are typically much more fractured and faulted than those of Josephine Creek. Slickensides are common on these dikes and many appear to have been intensely deformed or almost obliterated. Contacts with the serpentine are irregular and
in some cases the serpentine and rodingite appear to have been kneaded into each other. The main mass of the Josephine peridotite pinches out in this area, with the faults separating the ultramafic sheet from the Rogue formation to the west and the Galice formation to the east converging only about one kilometer north.

Dikes in the center of the peridotite along Illinois River Road are nearly vertical and strike north to NNE, and as the contact with the Rogue formation is approached, the orientation of the dikes becomes more horizontal. The rodingites near the fault (IR-9, 87-2-A) are dismembered and are enclosed in extremely sheared serpentine.

Dikes exposed in the main study area display a variety of orientations, including many which strike east-west. In most cases, especially along Josephine Creek, dikes are cut by NNE trending Nevadan faults. This suggests that intrusion of some of the dikes occurred before the development of the regional structural grain during the Nevadan orogeny. Those dikes which parallel the structural grain may have been intruded along Nevadan faults.

Chilled margins are not evident in any of the dikes. Igneous textures appear to be the same throughout a dike, with no obvious fining of grain size at the margins.

In hand-sample, the degree of alteration ranges from
apparently unaltered to completely rodingitized. There is no obvious correlation between the size of the dikes and the degree of alteration. Every dike has at least a thin selvage of rodingite, but many have unaltered cores.

Deformation of the dikes is reflected by similar intense shearing of the surrounding serpentinite, indicating that both rocks were affected by the same period of shearing. That some, if not most, of the rodingitization occurred after the cessation of deformation is indicated by the presence of rodingite on all surfaces of the dikes, including the offsets. In the areas of greatest deformation, the dikes have formed boudins, which are altered on all sides.
Petrography

Peridotite

The ultramafic complex consists largely of harzburgite, although very minor occurrences of dunite and pyroxenite were described by Dick (1976). Studies of thin sections and chemical analyses indicate that the peridotite is similar to other west coast occurrences of alpine peridotites in composition, mineralogy, texture, and alteration (Page, 1967b; Himmelberg and Coleman, 1968; Loney et al., 1971; Coleman and Keith, 1971). Olivine is the dominant mineral, making up 66 to 80 percent of the mode, with orthopyroxene making up 20 to 30 percent. Chromian spinel varies from one-half to two percent, and only a few small grains of clinopyroxene are found in any sample.

Olivine. Olivine textures vary widely from sample to sample and even within a single thin section. Despite later deformation and alteration, evidence of the earliest process to affect the peridotite, partial melting, is discernible.
Textures associated with partial melting (Dick, 1977) are seen in some of the olivine as ameboid shapes, and as deep embayments of olivine into other olivine or pyroxenes (figure 4). This results from partial melting along grain boundaries, which aids diffusion along the grain boundaries.

High temperature plastic deformation, which probably took place at a temperature greater than 1000°C (Loney et al., 1971), has affected the olivines to varying degrees, as evidenced by the development of undulatory extinction and kink bands (George, 1977). This is found in all samples.

High temperature annealing or recrystallization textures (George, 1977; Dick, 1976) are evident in the less serpentinized peridotites. In olivine, recrystallization forms more equant grains, with straightened grain boundaries tending to meet at 120 degree triple junctions. Recrystallization was incomplete in the harzburgite. With serpentinization, former olivine grain boundaries are not always discernible, so recrystallization textures become unrecognizable. Some original grain boundaries can be picked out, however, by a dusting of magnetite grains which form during serpentinization (figure 5).

Later, low temperature deformation has granulated the olivine of the harzburgite along irregular fractures. Grain size has been greatly reduced by the fracturing, but former
Figure 4. Partial melting texture in olivine, peridotite PER 16. Original olivine grains (such as those outlined) display irregular, cuspatc boundaries, with deep embayments. The rock is thoroughly granulated, and serpentine is largely confined to numerous small veins. Field of view is 6.2 mm. Transmitted light, crossed polars.
Figure 5. Magnetite along grain boundaries in serpentinite SP 12. Fractures in former olivine grains, now almost completely replaced by serpentine, are marked by a fine dusting of magnetite. Field of view is 0.35 mm. Plane-polarized reflected light.
grains up to 1 cm can be recognized by simultaneous or sweeping extinction of groups of olivine grains now 0.1 to 2 mm in size. Under the microscope, fine shear zones are distinguished by olivine greatly reduced in size relative to grains nearby. It is along these zones that the earliest and most pervasive serpentinization has taken place. Shearing has rotated the larger and more resistant pyroxene grains, and the surrounding olivines are granulated, forming a mortar texture (figure 6).

In the peridotite thin sections studied, only two euhedral olivine grains were seen. Both are inclusions within large, relatively undisturbed orthopyroxene grains in one of the least serpentinized peridotites, PER 11.

**Orthopyroxene.** Enstatite accounts for 20 to 30 percent of the original mode. Partial melting and deformation have affected the texture and grain size of the enstatite, but not nearly to the degree that it has affected the olivine. Partial melting is evident in the orthopyroxene as deep embayments filled with olivine, interpenetrating pyroxenes, and extremely irregular, or cuspatc grain boundaries (figure 6).

In the Josephine rocks, exsolution lamellae are visible in some orthopyroxene grains. There is no systematic distribution of grains with or without exsolution, and in
Figure 6. Mortar texture olivine and partial melting texture in orthopyroxene, peridotite PER 9. Pyroxenes (large grains) show very irregular, cuspatate boundaries, and the pyroxene grains at bottom of photo interpenetrate (arrows), characteristic features produced by partial melting. The pyroxene grains have rotated during shearing, and are surrounded by granulated (mortar texture) olivine. Field of view is 6.2 mm. Transmitted light, crossed polars.
many cases, adjacent grains have quite different degrees of exsolution. Most exsolution is in the form of narrow linear lamellae parallel to (100), but some pyroxenes contain abundant blebs of exsolved pyroxene. Exsolution commonly is best developed at kinks, where strain energy probably assisted the exsolution (Dick, 1976).

The enstatite grains are 1 to 5 mm. Many of the grains are bent or fractured, with serpentine filling the fractures. Grains in or at the edge of shear zones appear to have been rotated and are surrounded by mortar texture olivine. The grains are rounded to some degree, with ragged or splintery edges, and are commonly surrounded by small pieces of pyroxenes that have apparently broken off the larger grains.

Clinopyroxene. Clinopyroxene is a minor phase in the harzburgite. In all but SP-12, it accounts for less than one percent of the mode; sample SP-12 contains about two percent clinopyroxene.

In all samples, clinopyroxene grains are smaller than the orthopyroxene. The grains are anhedral and are usually irregular in shape. Exsolution lamellae of orthopyroxene are abundant in all clinopyroxene grains. Clinopyroxene is the most resistant of the primary minerals to serpentinization and even in the most altered samples (e.g.
SP-12) small clinopyroxene grains are still visible. In orthopyroxene grains, clinopyroxene exsolution lamellae survive after all orthopyroxene has been replaced with serpentine or talc.

**Spinel.** In the least-serpentinized harzburgites, chromian spinel is a ubiquitous accessory phase. The spinel is anhedral and is reddish brown in plane-polarized light. The spinel is concentrated near pyroxene grains and commonly occurs as small blebs in clinopyroxene. Its association with pyroxenes, and its texture led Dick (1976) to conclude that the spinel formed as the remains of partial melting of pyroxenes.

**Serpentinite**

In alpine peridotites, fresh, unserpentinized ultramafic rocks are virtually non-existent. Harzburgites are generally at least five or ten percent serpentinized (e.g. Page, 1967b; Coleman and Keith, 1971), and the Josephine peridotite averages over 50 percent serpentinized (e.g. Himmelberg and Loney, 1973; this study).

The product of serpentinization of harzburgites is an alteration assemblage of serpentine minerals (chrysotile, lizardite, antigorite), and opaque minerals (magnetite, sulfides, native metals) ± brucite ± talc.

**Serpentine.** Serpentine minerals (chrysotile and
lizardite) are present in all samples from the Josephine peridotite. Chrysotile is largely confined to veins and recrystallized areas, and lizardite forms the primary mesh texture around olivine.

Serpentinization appears to have taken place in several stages. In the least serpentinized rocks, such as PER 9, serpentine is found almost entirely in veinlets up to 0.5 mm thick. Serpentine has not yet begun to form the characteristic mesh texture around olivine grains.

Serpentine veins are commonly offset, and in sample 0-5-2 (from the Illinois River Road near the fault contact with the Rogue formation), at least three generations of veins can be recognized.

In the earliest stages of serpentinization, water easily infiltrates along fractures and partings in olivine and hydration is rapid. The serpentine thus formed, being less dense than olivine, expands, effectively sealing the fractures and greatly reducing the rate of diffusion of H$_2$O to the olivine surfaces and slowing the rate of serpentinization. It is this slower second stage that produces mesh texture lizardite (Dungan, 1977), present in many of the Josephine serpentinites. In most thin sections, the serpentine surrounding olivine is distinctly banded, possibly reflecting slightly different conditions during
serpen tinization or varying rates of growth (Wicks and Whittaker, 1977).

**Opaque Minerals.** The most common opaque phase in serpentinites is magnetite. Iron for the magnetite comes from the serpen tinization of olivine and pyroxene, and from the oxidation of spinel and sulfides. Fresh peridotites contain virtually no opaque minerals, but with serpen tinization, Fe, Ni, Co, Cr, and other metals are released and form the opaque oxide or sulfide assemblage. In the earliest stages of alteration, Fe comes from olivine, the first mineral to be affected. Serpen tinization begins along original grain boundaries and fractures and these are marked by magnetite and sulfide dust. Magnetite grows in size and tends to move out to the edge of the veins as alteration progresses (Wicks and Whittaker, 1977). The latest veins in all samples are relatively free of magnetite.

A yellow sulfide phase, pyrite or pyrrhotite (the grains are too small to identify with certainty), is abundant as tiny disseminated, typically euhedral grains concentrated in serpentine veins. Several of the larger sulfide grains are partially oxidized to magnetite (figure 7).

**Talc.** Minor amounts of talc are found in pyroxene
Figure 7. Pyrite (white in this photo) altering to magnetite (light gray) in serpentine SP 12. Field of view is 0.35 mm. Plane-polarized reflected light.
bastites and in veinlets through partially serpentinized pyroxene grains. Some talc veins continue out of the pyroxenes but change to serpentine as they traverse olivine. The talc is distinguished by its bright interference colors which contrast with the dull gray of the serpentine minerals.

**Brucite.** No brucite was recognized in thin section, nor did chemical analyses or volume-composition relations indicate its presence. However, x-ray diffraction analysis indicated its presence in minor amounts in several serpentinites.

**Chemistry**

**Major Elements**

Analyses of two relatively unserpentinized harzburgites and three serpentinites are reported in table IV, in order of increasing water content (a measure of the degree of serpentinization). Where needed, the number of the analysis is used in graphs to identify the sample.

The major element chemistry of these samples of the Josephine peridotite is similar to that of other ultramafic occurrences (e.g. table II), with the exception of CaO in PER 9 and SP 10. These samples contain 3.99 and 3.41 weight
Table IV. Whole rock and trace element analyses of ultramafic rocks from the Josephine peridotite. Analyses listed in order of increasing water content, a measure of the degree of serpentinization. Total iron reported as Fe₂O₃. Total water reported as LOI.

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PPM

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| MgO/SiO₂ | .81 | 1.04 | .80 | .93 | .95 |

Table IV. Whole rock and trace element analyses of ultramafic rocks from the Josephine peridotite. Analyses listed in order of increasing water content, a measure of the degree of serpentinization. Total iron reported as Fe₂O₃. Total water reported as LOI.
percent CaO, more than the typical harzburgite contains, and far more than any serpentinite analyses found in the literature. Petrographic examination has failed to reveal any Ca-rich phases in these rocks, and neither contains any more clinopyroxene than the other harzburgites.

The oxide sums for both rocks are low. These samples were run through a second XRF scan to check for the presence of other elements not in the original analysis, and nickel was found in "greater than trace/minor quantities" (no value given). The matrix correction program does not account for the presence of nickel, and this may have caused erroneous correction factors for CaO. The problem may extend to MgO and SiO₂, as well, both samples having unusually low MgO/SiO₂ ratios. These two analyses are probably unreliable.

Analyses of Josephine ultramafic rocks are plotted in the diagram MgO-SiO₂-H₂O (figure 8). The graph shows the characteristic trend of a pronounced increase in H₂O with little change in MgO/SiO₂ during serpentinization. The three serpentinites plot closer to H₂O than monomineralic serpentine, in part because lizardite and chrysotile contain H₂O⁺ in excess of the ideal formula (Moody, 1976a) and because the XRF analyses report water as LOI, which includes H₂O⁻.
Figure 8. Analyses of Josephine ultramafic rocks in the diagram MgO-SiO$_2$-H$_2$O. Common phases in ultramafic rocks are plotted for reference. Samples numbers are the same as in table IV.
**Trace Elements**

Typical of ultramafic rocks, the trace element contents of the Josephine rocks are extremely low. The lack of trace element values reported in the literature makes comparisons with other ultramafic bodies impossible. It is difficult to assess the accuracy of the trace element values because most are near or below their detection limits. With only three reliable analyses, the true range of values cannot be gauged.

**Chemical Trends of Serpentinization**

**Major elements**

The greatest compositional change that takes place during serpentinization, besides addition of $H_2O$, is a loss of CaO. Serpentinite minerals contain little or no CaO, whereas an unaltered peridotite may contain several percent, principally in clinopyroxene. Poldervaart (1955) reports an average CaO for peridotites of 3.5 weight percent, and that of dunites 0.75 percent. Faust and Fahey (1962) analyzed 26 serpentinites and found an average CaO content of only 0.08 percent. The Josephine serpentinites contain more CaO than the average owing to the presence of unaltered clinopyroxene.

In figure 9 (includes literature sources), the trend of
decreasing CaO with increasing H₂O, i.e., progressive serpentinitization, does not appear to be as dramatic as was indicated from the analyses of peridotites versus serpentinites just mentioned. However, it is possible that two trends are shown by the graph, one for the serpentinitization of harzburgites, and another for lherzolites. Alpine peridotites are predominantly harzburgites, with lherzolites generally insignificant in abundance. Dick (1976) noted that the few lherzolites found in the Josephine peridotite were not gradational with harzburgites but, rather, were rich in clinopyroxene. This bimodal mineralogy, with peridotites having either virtually no clinopyroxene, or large amounts, would lead to two separate trends on a CaO versus H₂O plot.

In ultramafic rocks, the order of resistance of minerals to alteration has been shown to be: clinopyroxene > orthopyroxene > olivine (Moody, 1976a). This sequence is quite obvious in the samples from the Josephine peridotite; even in the most intensely serpentinized rocks, e.g. SP-10 and SP-12, clinopyroxene is the only mineral that shows little alteration. In rocks that are about 30 percent serpentinized, e.g. Per-16, the clinopyroxene does not appear to be affected, while orthopyroxene has begun to alter. Lherzolites would not lose large amounts of calcium
until serpentinization is almost complete, when clinopyroxene begins to alter. The alteration trend of Iherzolites would, therefore, be displaced to the right of that of harzburgites, and would be much steeper at the high water end of the plot.

From mineralogical considerations (Faust and Fahey, 1962; Page and Coleman, 1967; Phillips and Griffen, 1981), a slight decrease in Al\textsubscript{2}O\textsubscript{3} should be expected as serpentinization of Iherzolites proceeds owing to the breakdown of clinopyroxene and spinel. However, harzburgites show little change in aluminum. The Josephine data show a slight increase in Al, although with only three good data points, the significance of the trend is uncertain. The behavior of Al\textsubscript{2}O\textsubscript{3} shows the same double trend as that for CaO with increasing serpentinization, and is even more pronounced (figure 9). In the case of CaO, the amount of clinopyroxene controls the position and slope of the trends, whereas Al\textsubscript{2}O\textsubscript{3} is controlled by clinopyroxene and spinel. Both minerals are important reservoirs for aluminum, and both are affected only at high degrees of serpentinization.

The double trend also extends to SiO\textsubscript{2}, MgO, and TiO\textsubscript{2}. Titanium is another element concentrated in clinopyroxene and spinel.
Figure 9. Variation of major elements with increasing serpentinization. Solid squares are XRF analyses of Josephine peridotite samples from this study; open circles are analyses from literature sources (table II). Water = LOI for Josephine analyses, $H_2O^+$ for literature analyses.
Figure 9. (continued)
Figure 9. (continued)
Manganese and chromium, which are both accepted into the serpentine and magnetite structure (Faust and Fahey, 1962; Page and Coleman, 1967), vary little with serpentinization.

The MgO/SiO_2 ratio versus H_2O also shows a double trend, with one trend steeper and displaced to the right. Coleman (1971) found that the average MgO/SiO_2 for alpine type harzburgites is 1.02, which is very close to the .99 to 1.0 for monomineralic serpentine, while lherzolites have lower ratios. Since the final products of serpentinization are the same regardless of starting material, the trends of MgO/SiO_2 should converge toward the value for that of monomineralic serpentine as serpentinization approaches completion.

The apparent lack of geochemical gradation between harzburgites and lherzolites may be explained by two factors, both of which may contribute to some degree. First, it may represent a real phenomenon, the result of the homogenization that partial melting processes tend to produce. The process of partial melting usually produces a monotonous harzburgite as a refractory residue. Lherzolites in ophiolites would represent either a portion of the mantle that did not experience as great a degree of partial melting as that which produced harzburgites, or were themselves
concentrated products of a very small degree of partial melting, such as the pyroxenite dikes found in the Josephine peridotite (Dick, 1976). Either process would result in a large difference in the amount of clinopyroxene between lherzolite and harzburgite.

A second (and probably more likely) explanation for the bimodal nature of the data may be that it reflects a bias in the literature toward presenting analyses of "average" dunites, harzburgites, lherzolites, and serpentinites, and in selecting those analyses out of the literature for this study. For this study, rocks identified as harzburgites were selected to the exclusion of dunites and lherzolites, but literature sources seldom identify the parent rocks of the serpentinites analyzed, so serpentinized lherzolites are probably included.

As serpentinization proceeds, the rocks become increasingly oxidized. The analyses in this study did not distinguish divalent from trivalent iron, but analyses from the literature show a clear trend (figure 10) of increasing Fe$_{\text{III}}$/Fe$_0$ as serpentinization progresses (although total iron is constant). This is manifest in the alteration of sulfides and spinel to magnetite, as shown in figure 7.

Oxygen could come from a variety of sources during serpentinization. Oxygen dissolved in fresh or sea water
Figure 10. Trend of increasing oxidation with increasing serpentinization. Analyses from literature sources (table II). $\text{H}_2\text{O} = \text{Fe}_2\text{O}^+$ from analyses.
may represent a potential source, but the water molecule itself is probably a more important donor of oxygen. The decomposition of water produces hydrogen, and its presence would argue for the water molecule being the oxygen source. Hydrogen gas has been reported bubbling from a spring at Burro Mountain, California (Barnes et al., 1972) and from a peridotite in the Philippines (Thayer, 1966). Seawater sulfate is also a potentially significant oxidizer. Reactions of seawater-basalt and seawater-peridotite have produced \( \text{H}_2\text{S} \), indicating the reduction of sulfate (Wolery and Sleep, 1976; Seyfried and Dibble, 1980). The presence of pyrite and other sulfides in the Josephine rocks is further evidence of the involvement of seawater sulfate.

Hydrogen produced by the decomposition of water will react with sulfides to form reduced metals, such as awaruite (Ni-Fe), and native copper, iron, and nickel, which have all been reported from the Josephine peridotite (Ramdohr, 1967; Dick, 1974).

**Trace elements**

Little attention has previously been paid to trace element behavior during serpentinization. One of the major problems with studying element mobility in ultramafic rocks is the extremely low concentration of trace elements.

Plots of the trace elements show some scatter,
indicating either that these elements are mobile to some degree during the serpentinization process, or the inaccuracy inherent in analyzing for elements with such extremely low concentrations prevents reliable comparisons. Analyses of Y and Nb could not be found in the literature so no comparisons could be made to check the validity of the Josephine trace element contents and correlations, as is possible with major components.

The trace element variation with increasing serpentinization is shown in figure 11. Slight decreases in Zr and Y and a small increase in Nb can be seen, if the uncertain values for PER 9 and SP 10 (5 and 10.5 percent H₂O, respectively) are ignored. It is interesting to note that the variations in Zr and Y are virtually identical, even for the suspect rocks. This behavior of the Zr/Y ratios are the most coherent of the element ratios plotted. Element ratios involving Nb show noticeable scatter.

Trace element correlations are presented in figure 12. Compared against TiO₂, the trace elements show fairly coherent behavior. In all comparisons, Nb and Y show opposite trends, and Nb again displays the most scatter.
Figure 11. Trace element variation with increasing serpentinization.
Figure 12. Trace element correlations in the Josephine ultramafic rocks.
Volume-composition Relations

Volume-composition Calculations

In order to understand the gains and losses of components during alteration processes either the volume change or mobility of at least one component must be known or assumed. Conclusions about fluxes of components or volume changes based on direct comparisons of chemical analyses are misleading because they do not take into account changes in density.

The fundamental equation for volume-composition was derived by Gresens (1967) and modified by Grant (1986). The basic equation is $C_i^A = \frac{M^0}{M^A}(C_i^0 + \Delta C_i)$, where $C_i$ is the concentration of a component $i$, $M$ is the mass of the samples, and the superscripts $A$ and $O$ refer to the altered and original (or least altered) rocks, respectively. By plotting analytical data $C_i^A$ against $C_i^0$, the immobile components (for which $\Delta C_i = 0$) will generate a line of slope $M^0/M^A$, termed an "isocon" (Grant, 1986). This line connects those components that have behaved identically during the alteration and are thus immobile relative to each other. The line may be determined by connecting data points with a best-fit line, by assuming constant volume or mass, or by assuming immobility of a component.

The equation of the isocon is $C_i^A = \frac{M^0}{M^A}C_i^0$. If
component \( i \) is constant, the equation becomes
\[
C^o = \left( \frac{C^i}{C_i^0} \right) C^0.
\]
If constant volume is assumed, the equation becomes
\[
C^o = \left( \frac{q^0}{q^o} \right) C^o,
\]
and for constant mass the equation is simply
\[
C^o = C^0.
\]
These relations for several pairs of samples are illustrated in part A of figures 14 through 17.

If it can be established that during alteration some components have been relatively immobile, volume changes can be calculated by using these components. The behavior of other components can then be calculated using the volume factor fixed by the immobile elements.

In the absence of any evidence indicating the actual volume change or flux of a component, volume-composition diagrams (Gresens, 1967; Babcock, 1973) may also be used to establish the possible volume changes. These diagrams (part B of figures 14 through 17) result from the basic equation of Gresens (1967), substituting the notation of Grant (1986) and rearranging so that the volume factor \( f_\nu \) is solved for in terms of the ratio of densities of the altered and parent rock, and their chemical composition:
\[
f_\nu = \frac{A_C}{(A_C + C_i^0)[q^o/(q^o)(C_i^0)]}.
\]
Setting \( A_C = 0 \) for each component yields the theoretical volume change that would have to occur for the alteration to take place with no gain or loss of that component. If two or more component lines cross the isochemical (no relative gain or loss) line at or near the
same point, the volume factor for that point can be taken as the likely volume change for the alteration. That value can then be fed back into the volume-composition equation to determine the net flux for the other components.

Gains and losses of components may be read directly from the diagrams by locating the intersection of the horizontal line representing the value of the volume factor and the line for any component. The chemical change of that component in weight percent is then read off the bottom scale.

**Volume-composition Relations of Serpentinization**

The diverse conditions under which serpentinization occurs has led to some confusion and argument over whether the process is one of constant volume or increasing volume. The solution to this problem requires more than just petrographic observations or theoretical considerations based on molar volumes of the reacting minerals. Use of volume-composition relations (Gresens, 1967) is necessary to determine actual relative fluxes of components involved in an alteration process, and any accompanying volume changes.

Early workers (Turner and Verhoogen, 1960; Thayer, 1966) concluded that serpentinization is a constant-volume process. They argued that volume increases of 25 to 40
percent, as proposed by many studies, would result in linear expansions of 8 to 12 percent and should be easily recognized in petrographic studies. Thayer argued that constant-volume alteration can be shown by the presence of undisturbed original textures, such as intact layers of chromite in serpentinized peridotite. Condie and Madison (1969) found, however, that primary mineral bands did not appear to be disrupted even though composition-volume calculations indicated a volume increase of 16 to 20 percent.

Coleman and Keith (1971) reported that chromite grains in the serpentinized ultramafic mass of Burro Mountain, California, show evidence of expansion in the form of serpentine-filled fractures. Since chromite alters to magnetite, not serpentine, the serpentine must have been introduced into expanded fractures.

Volume increases detectable in thin-section have also been reported by Clark and Greenwood (1972) in a study of serpentinization of dunites at Union Bay, Alaska. They found evidence of disruption of internal features such as offsets of kink bands along transecting serpentine veins, rotation of olivine grains surrounded by serpentine, expanded chromite grains, and radially fractured clinopyroxene grains adjacent to serpentinized olivine
grains.

Thompson (1968) found similar expansion features on a larger scale, that of a 14 inch pod of serpentine surrounded by unserpentinized harzburgite. A radiating system of serpentine veins is centered on the pod, hinting that expansion during serpentinization ruptured the enclosing harzburgite. Thompson also reported petrographic evidence of expansion in the form of olivine poikilitically enclosed in clinopyroxene. The serpentinization of the olivine apparently fractured the pyroxene, and chrysotile now fills the cracks.

Several thin sections of serpentinized peridotite from the Josephine peridotite (PER 16, PER 12) show serpentine veinlets radiating away from large olivine masses which are nearly completely altered. Figure 13 illustrates the radial fracturing of adjacent orthopyroxene grains, which are much less altered than the former olivine mass, now completely replaced by serpentine. Although radial fracturing is a convincing indication of expansion, this petrographic evidence should not necessarily be taken as proof by itself. However, it will be demonstrated by composition-volume calculations that the Josephine peridotite has, in fact, undergone a volume increase during serpentinization.

Some workers (e.g. Hostetler et al., 1966; Page, 1967a;
Figure 13. Petrographic evidence of expansion in serpentinite SP 12. Fractures radiate from large mass of completely serpentinized olivine, at bottom, into matrix. Field of view is 6.2 mm. Plane-polarized transmitted light.
Thompson, 1968) have argued that serpentinization takes place at constant composition. Several lines of evidence support their conclusion. Serpentinization at constant volume requires the removal of large quantities of MgO and/or SiO$_2$. However, this would probably result in large-scale Mg or Si metasomatism in adjacent rocks, which has not been reported. Also, the composition of the serpentinites and the parental peridotites is essentially the same except for the addition of water.

Pairs of ultramafic rocks chosen for the calculations fit the simultaneous requirements that the more altered of the two had more H$_2$O and less CaO, since loss of calcium is a universal feature of serpentinization. With rodingite dikes, the relation of the least-altered and the altered rock is clear in cases where both came from the same dike, but with the peridotites, the intense deformation and faulting make it virtually impossible to trace an altered unit of rock into its unaltered parent. Lacking field evidence, only compositional constraints can be used to select rocks for pairing.

The isocon diagrams (figures 14 through 17) support the argument for constant Mg during serpentinization. The constant Mg isocons are usually shared by ΣFe, as well. If the isocons are correct, components plotting above the lines
are those that have shown gains, while points below the lines indicate components that have suffered losses. All diagrams show the characteristic gain in $H_2O$ and loss of $CaO$.

Interestingly, $MnO$, $CrO_3$, and the trace elements $TiO_2$, $Zr$, $Nb$, and $Y$ usually do not fall on the best fit or constant mass isocons. Given the very low concentrations of these elements, however, it is possible that if their error bars are taken into account, they may actually overlap the isocons. Another possibility is that these elements became mobile during serpentinization. Although $TiO_2$, $Zr$, $Y$, and $Nb$ are generally regarded as immobile in most alteration or metamorphic processes (Floyd and Winchester, 1978; Evans, et al., 1981), several studies (Finlow-Bates and Stumpf, 1981; Lesher et al., 1986) indicate that during intense hydrothermal alteration, some trace elements, including $Y$ and $Nb$, may be very mobile.

When volume changes versus composition changes for the major components are plotted following the method of Gresens (1976) and Babcock (1973), a volume factor of between 1.22 and 1.38 is indicated by the compositional lines for the components falling on the best fit isocons, confirming that serpentinization of the Josephine peridotite involved substantial volume increases.
Figure 14. Volume-composition relations for peridotite PER 14 altering to serpentinite 0-5-2.
Figure 15. Volume-composition relations for peridotite PER 14 altering to serpentinite SP 2.
Figure 16. Volume-composition relations for peridotite 66-R-20 altering to serpentinite 66-R-10 (analyses from Himmelberg and Coleman, 1968).
Figure 17. Volume-composition relations for peridotite 18-BU-66 altering to serpentine 4-BU-66 (analyses from Loney, Himmelberg, and Coleman, 1971).
In order to corroborate the volume-composition relations for serpentinization of the Josephine peridotite, calculations were also performed on data from the Burro Mountain ultramafic mass (Loney, Himmelberg, and Coleman, 1971), and the Red Mountain-Del Puerto ultramafic mass (Himmelberg and Coleman, 1968). For each location, a typical, relatively unserpentinized harzburgite (least altered parent) was selected, along with a typical serpentinite (altered equivalent).

The isocon diagrams for Burro Mountain and Red Mountain-Del Puerto ultramafic rocks are remarkably similar to those for the Josephine peridotite. Unavailable for the Josephine calculations, Fe\textsubscript{2+}O\textsubscript{4} is seen to increase at the expense of FeO. Volume-composition diagrams are also essentially identical to those of this study. By extrapolation, complete serpentinization would result in a volume increase of about 20 percent at Burro Mountain and close to 30 percent at Red Mountain.

**P-T-X Conditions of Serpentinization**

Textural evidence points to the occurrence of all serpentinization after completion of the high-temperature deformation and annealing processes, and probably after most or all of the low temperature deformation (granulation of
olivine) associated with emplacement of the ophiolite on to the continent.

Stability relations in the system MgO-SiO$_2$-H$_2$O±FeO are shown in figure 18 (Johannes, 1968; Moody, 1976b). These data indicate that increasing the iron in the olivine shifts the serpentine/olivine reaction boundary to lower temperatures. For an olivine of composition Fo$_{90}$ (common in alpine peridotites), serpentine + brucite is stable up to 370°C at 2 kbar, and 350°C at 1 kbar. In the absence of brucite, serpentine is stable at higher temperatures (Yoder, 1952).

Brucite is present in trace amounts in some of the Josephine samples. Johannes (1969) established that brucite is stable only when the fluid phase is extremely low in CO$_2$. At 2 kbar the fluid phase must have less than 0.5 mole percent CO$_2$ or brucite reacts to form magnesite.

There is little evidence as to the relative timing of serpentinization and shearing of parts of the peridotite. Sheared rocks are usually completely serpentinized, but it is not clear if shearing took place where it did because altered rocks are of lower strength than fresher peridotites, or if shearing of unaltered peridotite promoted serpentinization by allowing easier infiltration of water. In samples PER 9 and PER 16, several small-scale sheared
Figure 18. Stability relations in the MgO-SiO$_2$-H$_2$O system. Curve 1 for the reaction olivine (Fo$_{90}$) + H$_2$O = serpentine + brucite (Johannes, 1968; Moody, 1976b); curve 2 for the same reaction, using pure forsterite (Kitahara and Kennedy, 1967). Curve 3 for the reaction forsterite + talc + H$_2$O = serpentine (Yoder, 1952).
zones transect the sample and are characterized by granulated olivine of extremely small size. However, the rocks are only slightly altered.

On the other hand, sample 0-5-2 displays evidence of many episodes of disruption of previously formed serpentine. This serpentinite is from an outcrop along the Illinois River Road about 30 meters from the major fault juxtaposing the peridotite with the Rogue volcanics to the west. Whereas the serpentinites showing little disruption of mesh textures are from the interior of the peridotite, rocks from near the edges of the peridotite do show signs of later movement. This suggests that serpentinization began after emplacement of the ophiolite, which deformed the entire ultramafic mass, and that after serpentinization had progressed, later tectonic deformation was limited to the edges of the peridotite.

Parting with the long-held assumption that serpentinization was a single event in the early history of ultramafic bodies, Hostetler and others (1966) argued that serpentinization may take place in increments, some of which may take place during or after emplacement. The possibility of contemporary serpentinization under surface conditions has been confirmed by investigations of Barnes et al. (1967), Barnes and O'Neil (1969), and Barnes et al., (1972).
who observed waters of unusual composition issuing from several incompletely serpentinized ultramafic bodies in California. The waters are of high pH (10-11), extremely low in Mg$^{2+}$, and high in Ca$^{2+}$. Reaction between local meteoric waters and ultramafic rocks is believed to control the composition of these waters because such chemical compositions have not been found in springs in other types of rocks (Barnes et al., 1978). The chemical compositions of the waters are independent of geographic location, and vary negligibly with climate.

The Ca$^{2+}$-OH$^{-}$ waters are unsaturated with respect to forsterite and enstatite and have the ability to dissolve them. The waters are supersaturated with respect to diopside, and this inability to dissolve diopside explains the persistence of clinopyroxene even after olivine and orthopyroxene have been largely replaced by serpentine. The waters are also supersaturated with respect to chrysotile and brucite, and can cause the precipitation of these phases. Both undersaturation and supersaturation of talc has been found.

Carbonates (particularly calcite) are likely to precipitate from Ca$^{2+}$-OH$^{-}$ waters (Barnes et al., 1972). The carbonates form by reaction of the strongly alkaline water with atmospheric CO$_2$. Carbon and oxygen isotopic
compositions of the resulting travertines and carbonate fracture fillings confirm their low temperature origin (O'Neil and Barnes, 1971). Several springs with small travertine aprons were found near Free and Easy pass. This indicates that the Josephine peridotite may be undergoing the same low temperature alteration processes as other west coast ultramafic bodies.

The presence of sulfide phases, in addition to magnetite (and native metals reported in Dick, 1973; Ramdohr, 1967), in the opaque assemblage of the Josephine ultramafic rocks provides constraints on the activities of sulfur, iron, oxygen, and hydrogen. Figure 19a displays some phase relations in the system Fe-S-O at 300°C and 500 bars (Seyfried and Dibble, 1980) in terms of the fugacities of oxygen and sulfur. Ekstrand (1975) studied opaque assemblages in ultramafic rocks from dozens of localities and found that the fugacities of O₉ and S₉ defined by the assemblages fell into fairly restricted ranges for peridotites and serpentinites (figure 19b).

Sulfides seen in the Josephine serpentinites are typically very spongy, which may indicate that these are secondary sulfides that formed during near-surface conditions from oxidation of primary Fe-Ni sulfides (Groves, et al., 1974). Further oxidation (or desulfurization) of
Figure 19. $f_{O_2}$ versus $f_{S_2}$ diagrams.
the secondary sulfides will produce magnetite, with an inherited spongy texture. Much of the magnetite in the Josephine samples is very porous, and may be the result of replacement of spongy secondary sulfides by magnetite. Sulfides with rims of magnetite point to oxidation continuing after the initial formation of secondary sulfides in the serpentine.

That most, if not all, of the sulfur in the sulfides was introduced with the serpentinizing fluids (e.g. seawater sulfate) seems well established by the distribution of the sulfides. In all thin sections studied, the sulfides are concentrated in all but the latest serpentine veins, and are not found in unaltered olivine or pyroxene grains.

Evidence from sulfides points to a significant contribution of seawater in the serpentinizing fluids, yet isotopic studies point to meteoric water. Wenner (1979) explains that although seawater may be involved early in the serpentinization history, at higher temperatures and pressures, lizardite and chrysotile may re-equlibrate at low temperatures in contact with meteoric water. Geographic variation in δD serpentine minerals has been established by studies of west coast serpentinites (Wenner and Taylor, 1974). These results point to meteoric water as the source of water for current low temperature serpentinization.
Magaritz and Taylor (1974) obtained $\delta^{18}O$ and $\delta D$ values for hydrous minerals (amphiboles and antigorite) of higher temperature origin from the Troodos ophiolite that do show signatures of heated seawater. Temperatures of 200 to 400°C are indicated by the isotopic compositions of the amphiboles, whereas lizardite and chrysotile at Troodos could not have formed at temperatures higher than 200°C, with 100°C being the most probable temperature. The isotopic data require a very high water/rock ratio ($W/R \approx 100$) if any kind of hydrothermal water was involved in the formation of lizardite and chrysotile.

A multistage history of serpentinization is indicated for the Josephine peridotite. In the early stages, serpentinization involved seawater, as suggested by sulfides, and occurred at higher temperatures than the later-formed serpentine. The significant volume increases demonstrated by volume-composition calculations are most characteristic of higher temperature serpentinization, in which rates of hydration and precipitation are fast relative to dissolution, and relative to the rate of fluid flow (Nesbitt and Bricker, 1978).

Serpentinization continued without interruption for a long period of time, as demonstrated by the well-developed, intact mesh texture lizardite surrounding olivine in rocks
from the interior of the peridotite. Near the perimeter of the peridotite, however, tectonic movements occurred several times, disrupting previously formed serpentine. Cross-cutting veins and recrystallization of mesh textures are characteristic of the rocks from near fault contacts.

Isotopic studies of west coast ultramafic masses, including the Josephine peridotite (O'Neil and Barnes, 1971; Wenner and Taylor, 1974; Wenner, 1979), show that the later serpentine formed at low temperatures, and the presence of Ca$^{2+}$(OH)$^-$ type waters and travertine aprons in several springs in the study area demonstrates that serpentinization is continuing presently, under surface conditions and with meteoric water.
CHAPTER 4

RODINGITES

Petrography

Rodingites contain a large variety of calc-silicate minerals. Extreme alteration produces rocks that are so fine grained that identification of the secondary minerals is difficult without the aid of x-ray diffraction or an electron microprobe.

The original Josephine dike rocks are holocrystalline, fine to medium grained gabbros and diorites, and are generally hypidiomorphic granular or subophitic. Primary minerals are plagioclase, and hornblende, with abundant accessory sphene and minor zircon and apatite.

Hornblende is euhedral, and is pleochroic brown to green-brown. Many of the dike rocks are porphyritic, with hornblende phenocrysts commonly up to 5 mm. Some of the larger hornblendes are faintly zoned, and the cores contain abundant tiny inclusions, primarily sphene. As alteration of the rocks progresses, chlorite and diopside begin to replace hornblende.

Plagioclase is most commonly in the form of tiny
interlocking laths, producing a felty texture. Even in the least altered dikes no plagioclase has survived metasomatism, but except where rodingitization is complete, original textures may still be seen in the secondary minerals. Some rocks have flow structures, with strong alignment of (former) plagioclase laths in the matrix and swirled laths around hornblende phenocrysts.

Rodingites from the Illinois River road outcrops are brecciated and their original textures have been obscured by cataclastic textures. Rocks from Josephine Creek display no cataclastic features.

Many of the dikes have cores that appear unaltered in hand sample, but even the least altered rocks have been metasomatized to some degree, as revealed under the microscope. The earliest stages of alteration produce clinozoisite, idocrase, and prehnite from plagioclase. Hornblende is replaced by epidote and chlorite.

Progressive metasomatism results in the replacement of early clinozoisite and prehnite by more idocrase. Hydrogrossular may appear early, but is difficult to distinguish from idocrase owing to their almost identical compositions and structures (Ito and Arem, 1970).

The final assemblage consists largely of hydrogrossular garnet and diopsidic pyroxene. Much of the diopside is
pseudomorphous after hornblende, and is colorless. The cloudy, brown color of hydrogarnet is distinctive. The garnet is invariably anhedral and is commonly so fine-grained that individual grains cannot be resolved. Late veins are present in some rocks, and are filled with xonotlite and prehnite.

Sphene is a ubiquitous accessory phase in dike rocks, and survives the metasomatism. In the more altered rocks, leucoxene is present with sphene, and is extremely abundant in altered hornblende.

In reflected light, small amounts of magnetite and pyrite can be identified. The tiny pyrite grains are found in veins, and are more abundant near the serpentine contact. Magnetite is distributed more evenly throughout the rocks as small particles or dust.

**Chemistry**

Analyses of ten dike rocks are presented in table V. The rocks are listed in order of increasing calcium, which is used as a measure of the degree of rodingitization. In general, the major element compositions of the Josephine rodingites are quite similar to those of rodingites from other locations (e.g. table III).

Triangle diagrams (figures 20 and 21) are used to
Table V. Whole rock and trace element analyses of Josephine rodingite samples. Total iron reported as Fe₂O₃. Total water reported as LOI.
illustrate the compositions of the Josephine rodingites in relation to minerals commonly associated with rodingites. Figure 20 illustrates the compositions in the CaO-SiO$_2$-Al$_2$O$_3$ system. Progression away from unaltered average igneous rock compositions toward more Ca-rich compositions along a constant Al$_2$O$_3$ line is conspicuous. The final compositions approach the typical final assemblage of hydrogrossular and diopside (Coleman, 1967).

Figure 21 displays the compositions in an ACF diagram. A general trend of increasingly calcium-rich compositions is shown, but the progression is not as orderly as in the previous diagram owing to the much larger initial variations in MgO and $\Sigma$Fe than those of SiO$_2$ and Al$_2$O$_3$ in rodingites. A composition fitting that of a mixture of hydrogrossular and diopside is approached.

**Major Elements**

The most striking characteristics of rodingites are their low SiO$_2$ and enrichment of CaO. These are the reflection of the ubiquitous presence of hydrogrossular garnet, the dominant mineral in rodingites. Aluminum and magnesium are the most variable elements, Al$_2$O$_3$ varying by a factor of more than two, and MgO by a factor of five.

One sample, 87-2A, yields values for several major elements that are different from any other rodingite
Figure 20. Analyses of Josephine rodingites in the diagram CaO-SiO$_2$-Al$_2$O$_3$. Compositions of common phases in rodingites are plotted for reference. Symbols represent average compositions of volcanic rocks from island arcs (Jakes and White, 1972): triangle, tholeiitic basalt; square, tholeiitic andesite; circle, calc-alkaline basalt.
Figure 21. Analyses of Josephine rodingites in the diagram CaO-Al$_2$O$_3$-(MgO+FeO). Compositions of common phases in rodingites are plotted for reference. Symbols represent average compositions of volcanic rocks from island arcs (Jakes and White, 1972): triangle, tholeiitic basalt; square, tholeiitic andesite; circle, calc-alkaline basalt.
analysis seen in this study or in the literature. The water content of 0.12 percent and total iron of less than two percent are very low, especially for such an extremely rodingitized rock. Manganese and phosphorus are also anomalously low, and MgO and TiO$_2$ are well below average. Under the microscope, the sample is extremely fine-grained and has been intensely deformed. The rock has a very small percentage of ferromagnesian minerals and is predominantly hydrogrossular, idocrase(?), and prehnite, explaining some of the peculiarity.

**Trace Elements**

The levels of trace elements in samples from the field area are comparable to those of other rodingites, although no analyses in the literature included Nb, and only two reported Y.

As with the major elements, sample 87-2A gave unusual values for Zr and Y. In all graphs, this sample plotted well away from the other rocks. The other trace elements are at levels comparable with those of other rodingites.

**Magmatic Affinities**

Discrimination diagrams are valuable aids in determining the origin of mafic rocks. One of the important assumptions in using discrimination diagrams is that the
elements used are essentially immobile. Although the discrimination diagrams were designed to be used with relatively unaltered rocks, several studies which used the diagrams on metamorphosed rodingites (Evans et al., 1979; Evans et al., 1981) yielded good results.

A simple discrimination diagram uses TiO$_2$ versus Zr to determine basalt parentage (Pearce and Cann, 1973). The Josephine rodingites show considerable scatter in this diagram (figure 22), with data falling in each of the fields for basalts.

Pearce and Cann (1973) proposed that a triangle diagram of Ti/100-Zr-3Y can be used to distinguish basalts. A plot of these elements in Josephine rodingites (figure 23) reveals overlap of the data on to several fields. More points fall in the field for ocean floor basalts than in the other fields, including several of the least altered rocks.

Another method of distinguishing igneous rocks involves Zr/TiO$_2$ and Nb/Y ratios (Winchester and Floyd, 1977). Josephine samples again plotted across several fields (figure 24), but six of the ten samples fall in or on the boundary of the sub-alkaline basalt field.

In the different discrimination diagrams, the Josephine rodingites do not fall neatly into one unequivocal magma type. A significant aspect of the scatter is that the
Figure 22. Discrimination diagram using Ti and Zr (Pearce and Cann, 1973). Ocean floor basalts plot in fields D and B, low-potassium tholeiites in fields A and B, and calc-alkaline basalts in fields C and B.
Figure 23. Discrimination diagram using Ti, Zr, and Y (Pearce and Cann, 1973). "Within plate" basalts i.e. ocean island or continental basalts plot in field D, ocean floor basalts in field B, low-potassium tholeiites in fields A and B, calc-alkaline basalts in fields B and C.
Figure 24. Discrimination diagram using Zr/TiO<sub>2</sub> versus Nb/Y (Winchester and Floyd, 1977). The Zr/TiO<sub>2</sub> ratio acts as a differentiation index and the Nb/Y ratio as an alkalinity index. R = rhyolite; RD-D = rhyodacite-dacite; A = andesite; A-B = andesite and basalt; SUB = sub-alkaline basalt; AB = alkali-basalt; TA = trachyandesite.
relatively unaltered rocks show as much scatter as the most altered ones. This may indicate a variety of rock types in the samples.

It is interesting to compare the diversity of these rocks with some from the central Alps (Evans, et al., 1979; Evans et al., 1981). In those studies, analyses of rodingites were plotted on TiO$_2$ versus Zr, and Ti/100-Zr-3Y diagrams. The former diagram (1979 study) yields an almost perfectly linear array of points centered across the MORB field, and the latter diagram (both studies) displays all data points neatly clustered in the middle of the MORB field. What is interesting about those results is not just that they seem to indicate more coherent trace element behavior, but that all the basalts in the studies have not only been completely rodingitized, but have later been metamorphosed to upper amphibolite to eclogite facies.

Several explanations are possible for the scatter of the Josephine trace elements. First, slight mobility of any element will affect the results of comparisons with other elements, and its use in ratios. However, many studies argue against mobility (e.g. Evans, et al., 1979; Evans, et al., 1981; MacLean and Kranidiotis, 1987)

Another distinct possibility is that the discrimination methods are designed to be used on rocks from mature
settings and so should not be used for Josephine rocks. Pearce and Cann (1973) warn that the diagrams do not work well for immature island arcs, where initial variations in elements can be large within a particular rock type, and evidence indicates that the Josephine ophiolite was the basement of an immature volcanic arc (Garcia, 1979, 1982; Harper, 1980, 1984).

The variability may also indicate the presence of more than one rock type in the dikes. The early stages of back arc spreading are always associated with subduction, and the magmas produced by the two processes are different. If the magma generated by subduction rises through a spreading center, the magmas may interact.

**Chemical Trends of Rodingitization**

**Major Elements**

A common characteristic of rodingites is the pronounced trend of decreasing silica with alteration. Figure 25 illustrates this trend in the samples from the Josephine peridotite. Aluminum shows a slight increase with CaO, a result of high \( \text{Al}_2\text{O}_3 \) as well as CaO in rodingite minerals. A strong trend of increasing water is the result of the increasing amount of hydrogrossular.

With increasing alteration, MgO shows significant
Figure 25. Variation of major elements with increasing rodingitization in Josephine dike rocks. Symbols represent average compositions of volcanic rocks from island arcs (Jakes and White, 1972): triangle, tholeiitic basalt; square, tholeiitic andesite; circle, calc-alkaline basalt.
Figure 25. (continued)
scatter, and no obvious trend of gain or loss of MgO with increasing CaO is seen. The scatter in MgO may reflect differences in the original composition of the dike rocks, which ranged from quartz diorite (low Mg) to gabbro (higher Mg). Near the contact with the surrounding ultramafic rocks, rodingites commonly have serpentine or chlorite veinlets which may penetrate several centimeters into the dike. High MgO could result from the incorporation of a little serpentine into a rodingite sample. This is probably the case for IR-9 and IR-6, which have anomalously high MgO. These samples are from the Illinois River Road and are typically more disrupted than dikes along Josephine Creek, and have obvious serpentine veinlets near the contacts.

No clear trend is discernible in the behavior of TiO₂, ΣFe, MnO, or P₂O₅ with alteration. The scatter in these components may be due in large part to initial variations. This also indicates that if titanium is little affected by the alteration, it can be used as a basis for measuring the relative mobilities of other components.

The alkalis show wholesale depletion at the earliest stages of rodingitization. Sodium and potassium decrease to near their detection limits with only a small gain in CaO.

As with serpentinization, rodingitization is marked by an increase in the oxidation state of iron. Trivalent Fe
may increase with increasing CaO (figure 26a), but the correlation is poor owing to the lack of analyses with lower CaO. That the source of much of the oxygen is from water involved in the alteration is suggested by the relation between water content of the rodingites and the Fe₂O₃/FeO ratios (figure 26b).

**Trace Elements**

To test the different mobilities of components during alteration, various elements were plotted first against CaO (figure 27) to see what effect rodingitization has on trace element behavior.

The trace elements Zr, Y, and Nb show some scatter but no clear gains or losses with increase in CaO. Differences in the scales probably exaggerate the scatter in niobium and smooth out that of Zr, but Zr, Y, and Nb all vary by a factor of about two from lowest to highest values, with the exception of the sample at 36% CaO (87-2A), which has a chemical composition very different from those of the other Josephine samples, and from any literature samples.

The values for Rb, Sr, and Ba have so much scatter that little can be said about their behavior. Most of the Rb and a few Ba analyses are close to or at the detection limit and not much confidence can be given to their accuracy. Those samples with less than the detection limit value of 10
Figure 26. Trend of increasing oxidation with rodingitization.

A. Variation in oxidation state of iron with increase in calcium in dike rocks. An increase in calcium reflects increasing effects of rodingitization. Analyses from literature sources, table III.

B. Variation in oxidation state of iron with water content in dike rocks. Analyses from literature sources, table III.
Figure 27. Variation of trace elements with increasing rodingitization in Josephine dike rocks. Symbols represent average compositions of volcanic rocks from island arcs (Jakes and White, 1972): triangle, tholeiitic basalt; square, tholeiitic andesite; circle, calc-alkaline basalt.
ppm Rb and Ba were plotted as having 10 ppm.

With the dikes originally having such a wide range in composition, some of the apparent decrease in trace elements with increasing CaO may be due to the fact that the more mafic rocks have higher CaO and lower trace element contents to begin with. To avoid this effect, trace elements were also plotted against TiO$_2$ (figure 28), a component that is regarded as being relatively immobile in most alteration processes (Floyd and Winchester, 1978; Evans et al., 1981).

Against TiO$_2$, the trace elements Zr, Y, and Nb exhibit slightly more consistent behavior than when plotted against CaO, but still have noticeable scatter. As with before, Nb appears to have the most scatter among the trace elements.

Interestingly, aluminum has the best correlation with TiO$_2$ of all the components tested. With the exception of JCR 14, all the values for aluminum fall very close to a straight line, decreasing slightly with increasing TiO$_2$. Aluminum is also the only element in sample 87-2A that is in line with other rodingites.

**Volume-composition Relations of Rodingitization**

The problem of establishing a relationship between least-altered and altered pairs is easier to solve with rodingites than with ultramafic rocks. With rodingites it
Figure 28. Correlation of "relatively immobile" elements versus TiO$_2$ in Josephine dike rocks. Symbols represent average compositions of volcanic rocks from island arcs (Jakes and White, 1972): triangle, tholeiitic basalt; circle, calc-alkaline basalt.
is sometimes possible to collect both samples from the same dike, provided the interior of the dike is less altered than the exterior. However, it is frequently difficult to collect pairs from the same dike. Dikes are usually either completely rodingitized, or only a very thin rind of alteration is present. In the latter case, separating the altered portion from the rest of the rock usually proves futile in the field. Rodingites are extremely hard, and are nearly impossible to break without a large sledge hammer. Only one such pair (JCR 11 and JCR 13) was collected from the Josephine dikes.

Figure 29a presents the data from JCR 11 and JCR 13 on an isocon diagram. The best-fit isocon is that of constant aluminum, which is essentially the constant mass isocon. Also falling on or very near the same line are Sr, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, Zr, with Fe and MnO not far away. These rocks represent the best pairing of the samples analyzed in this study, and so the assumption of constant Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in other rodingites seems reasonable.

Significant gains of CaO and water are shown, along with nearly complete loss of alkalis. The trace elements Nb and Y appear to have decreased slightly, a behavior noted in other rodingites (Sivell and Waterhouse, 1986).

Using constant aluminum, figure 29b, yields a volume
Figure 29. Volume-composition relations for JCR 13 altering to JCR 11.
Figure 30. Volume-composition relations for JCR 5 altering to JCR 6.
Figure 31. Volume-composition relations for JCR 5 altering to JCR 19.
Figure 32. Volume-composition relations for JCR 8 altering to JCR 6.
factor of 0.88 for the alteration. A volume factor of 0.9 is calculated holding TiO₂ constant. These calculations indicate that the rodingitization of this dike resulted in a decrease in volume of about 10 percent.

The results of calculations performed on other rock pairs (figures 30 through 32) yielded mixed results. None of these pairs were samples from the same dike, but a few consistent trends are seen in the diagrams. All of the isocon diagrams show losses silica and alkalis. Total iron, TiO₂, and Al₂O₃ were close to the constant mass isocon, but the other components varied considerably among the diagrams. The inconsistent and contradictory results suggest a variety of rock types with large compositional variations, and that none of the rocks in these pairs were related before alteration.

An attempt to compare the calculations from the Josephine rodingites with other occurrences met with disappointing results. Published studies of rodingites focus on the nature of the completely altered rocks, and adequate analyses of least-altered rocks from the same or adjacent outcrops could not be found.

P-T-X Conditions of Rodingitization

A well documented constraint on the conditions of
formation of rodingite is the occurrence of these rocks only in contact with serpentinized ultramafic rocks. It seems reasonable to conclude that rodingitization is driven by the calcium released during serpentinization and that both processes occur simultaneously and, therefore, under the same P-T conditions.

An early phase to form in rodingites is prehnite. The stability relations of this mineral (Liou, 1971) help to limit the possible P-T conditions of formation of prehnite-bearing rodingites. The dehydration reaction: prehnite = anorthite + wollastonite + fluid takes place at 500°C at 3 kbar (figure 33). At 1 kbar, the reaction occurs at 450°C.

The reaction: 5 prehnite = 2 zoisite + 2 grossular + 3 quartz + fluid (figure 33) defines the maximum temperature for formation of prehnite at 403°C at 3 kbar and 393°C at 5 kbar (Liou, 1971). In natural environments, where fluid pressure is usually less than total pressure, the stability limit of prehnite should be lower.

The most characteristic mineral of rodingites is hydrogrossular. Yoder (1950) determined the conditions for the breakdown of hydrogrossular to wollastonite + gehlinite + H₂O (figure 34).

Experiments by Ito and Arem (1970) determined the temperature at which idocrase forms from hydrogrossular plus
Figure 33. Stability relations in the CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O system. Reactions A and B from Liou (1971), C from Newton (1966).
Figure 34. Stability relations of hydrogrossular and idocrase. Curves A and B from Ito and Arem (1970), for CO₂ and sodium-free system. Curve C from Yoder (1950).
Figure 35. Thermal stability limit of hydrogrossular garnet as a function of silica content (Carlson, 1956). The curve marks the lowest temperature of formation of a phase with composition $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ by the hydrothermal breakdown of hydrogarnets (pressure $\approx 1$ kbar).
diopside. This reaction is shown by curve A, figure 34. Also shown is the upper stability limit of idocrase.

Carlson (1956) demonstrated that the stability of hydrogarnets is dependent on the silica content (figure 35). Loss of silica (increase in hydration) lowers the thermal stability limit.

Phase relations in the system CaO-Al₂O₃-SiO₂-H₂O-CO₂ (Bird and Helgeson, 1980, 1981) limit the mole fraction of CO₂ in the fluid involved in rodingitization to less than 0.005 at temperatures lower than 400°C. The presence of CO₂ is incompatible with the observed assemblages, which include clinozoisite, prehnite, and hydrogrossular. Lack of CO₂ in fluids responsible for forming rodingites is consistent with the evidence of a similar lack in serpentinizing fluids.

Although not determined in this study, isotopic compositions of rodingites may shed light on the conditions of their formation. Whereas west coast serpentinites have D/H isotopic compositions that vary latitudinally, suggesting low temperature alteration by meteoric water, the D/H of rodingite minerals (except xonotlite) lack latitudinal variation, suggesting involvement of non-meteoric waters (Wenner, 1979). Xonotlite, always a late rodingite mineral, shows only low temperature, meteoric water signatures.
One explanation given (Wenner, 1979) for the different source waters indicated by the D/H isotopic composition of serpentine versus rodingite is that both involve non-meteoric water (i.e., seawater) during initial formation, at higher temperature and pressure, but lizardite and chrysotile may re-equilibrate at low temperatures in contact with meteoric waters, whereas rodingite minerals resist later exchange.
CHAPTER 5
DISCUSSION

Element Mobility

During alteration both the peridotite and rodingite display major element trends in line with other studies. The lack of trace element analyses from other studies precludes any comparisons between the Josephine rocks and those of other localities.

On the basis of other studies of trace element mobility during alteration (Smith and Smith, 1976; Evans, et al., 1979; Evans et al., 1981; Sivell and Waterhouse, 1986; MacLean and Kranidiotis, 1987) immobility of TiO$_2$ and Zr was expected. Sivell and Waterhouse (1986), in a study of rodingites in New Zealand, found that although Y may increase in the dikes, the other elements remain constant. In isocon diagrams of the Josephine rocks, Y increases slightly in all the pairs except JCR 13-JCR 11, but Zr and Nb are unpredictable. Only TiO$_2$ remains nearly constant.

As discussed earlier, rodingites in the Alps have undergone intense metamorphism with trace elements intact.
This would argue strongly against mobility of the same trace elements in the Josephine rocks. A reasonable argument can be made that the scatter in the trace elements in the Josephine dike rocks must be due to initial variations rather than the effects of element mobility. The rationale for this view is the convincing evidence that immature island arcs and back arc spreading centers generate magmas of variable compositions within a particular rock type (Saunders and Tarney, 1979; Mattey et al., 1981). The variability could result from the melting of different source compositions, or from different degrees of partial melting of the same source.

A further complication is that the early stages of back arc spreading are always associated with subduction, and the different magmas produced by the two processes may interact with each other. Other studies in the Josephine ophiolite (Harper, 1984; Wyld and Wright, 1988) have found that the minor and trace element compositions of mafic rocks (gabbros, pillow basalts, and dikes intruding peridotite) overlap the fields of island arc tholeiites and MORBs.

Mass Balance

One of the central points of the notion that rodingite formation and serpentinization are simultaneous and complementary is the belief that the host peridotite is the
source of calcium for metasomatism. A simple mass balance exercise demonstrates that all the calcium necessary to completely rodingitize an average basalt can be supplied by an average harzburgite undergoing serpentinization.

First, the abundance of rodingite compared to the volume of peridotite must be taken into account. Along the Illinois River Road, for example, sketches of large roadcuts were made during mapping to determine the ratio of areas of dikes versus host peridotite. This area ratio is taken as the volume ratio (in the same way that a two-dimensional thin section is taken to be representative of a three-dimensional rock). For the ten outcrops measured, the average area of dikes is about 1.9 percent of the area of the outcrop. Allowing for the fact that most dikes are not completely rodingitized, and some have only a thin rind of alteration, half the area of dikes, or one percent, is used as the area of rodingite.

Equations provided by Grant (1986) were used to establish the relative gains and losses of components for dike rock JCR 13 altering to rodingite JCR 11, and for peridotite PER 14 altering to serpentine 0-5-2, using constant aluminum for dike rocks and constant magnesium for peridotite (table VI). The change from least-altered JCR 13 to completely altered JCR 11 requires a 66 percent gain over
### TABLE VI.

Gains and losses in a typical ultramafic rock and dike rock.

<table>
<thead>
<tr>
<th></th>
<th>Ultramafic rocks</th>
<th>Dike rocks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PER 14 - 0-5-2</td>
<td>JCR 13 - JCR 11</td>
</tr>
<tr>
<td>Constant MgO</td>
<td></td>
<td>Constant Al₂O₃</td>
</tr>
<tr>
<td>ΔC i/C i₀</td>
<td>ΔM (g/m³)</td>
<td>ΔC i/C i₀</td>
</tr>
<tr>
<td>ΔM (g/m³)</td>
<td></td>
<td>ΔM (g/m³)</td>
</tr>
<tr>
<td>SiO₂</td>
<td>+ 0.12</td>
<td>- 0.17</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>+ 0.89</td>
<td>0</td>
</tr>
<tr>
<td>CaO</td>
<td>- 0.54</td>
<td>+ 0.66</td>
</tr>
<tr>
<td>MgO</td>
<td>0</td>
<td>+ 0.1</td>
</tr>
<tr>
<td>ΣFe</td>
<td>+ 0.01</td>
<td>- 0.12</td>
</tr>
<tr>
<td>TiO₂</td>
<td>+ 2.49</td>
<td>+ 0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>+ 0.35</td>
<td>- 0.92</td>
</tr>
<tr>
<td>MnO</td>
<td>+ 0.34</td>
<td>+ 0.02</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>-</td>
<td>+ 0.02</td>
</tr>
<tr>
<td>H₂O</td>
<td>+ 2.07</td>
<td>+ 0.46</td>
</tr>
</tbody>
</table>

Gains and losses measured in grams per cubic meter of starting material (99 percent peridotite, 1 percent basalt).
the original concentration of CaO. Altering harzburgite PER 14 to serpentine 0-5-2 results in a 54 percent loss of original CaO.

Assuming a density of 3020 kg per cubic meter of peridotite, 0.99 cubic meters of starting peridotite with a CaO concentration of 0.85 weight percent, that in PER 14, will contain 25413 grams of CaO. Of that, 54 percent, or 13723 grams of CaO, is lost during serpentinization.

A volume of 0.01 cubic meters of basaltic rock, representing JCR 13 (2960 kg/m\(^3\), 14.7 percent CaO), contains 4351 grams of CaO. To form rodingite, 66 percent of that amount, or 2871 grams of CaO must be added. Many more times that amount was lost by the harzburgite.

Similar mass balance calculations may also be carried out on idealized starting material to determine the gains and losses of components for peridotite and rodingite to test the reliability of calculations done on the real rocks (which are already altered to some extent). A cubic meter of starting material thus contains 0.99 m\(^3\) of harzburgite with an average content of one percent CaO. The other 0.01 m\(^3\) is basalt containing an average of 10 percent CaO. These calculations assume that half of the CaO in the harzburgite is lost during serpentinization, and that the concentration of CaO increases in the rodingite to 25 percent. The
density for harzburgite is 3.3 g/cm\(^3\), serpentine is given as 2.7, basalt is 2.8, and rodingite, 3.3.

The theoretical harzburgite thus contains 32,670 grams of CaO, of which 16,335 are lost. The starting basalt contains 2800 grams of CaO, while the same volume of rodingite, with its greater density, must contain over 8000 grams of CaO to yield a concentration of 25 percent. A gain of 5450 grams of CaO is required, about one-third that which is available from the (partial) serpentinization of harzburgite. Both mass balance methods predict more than enough calcium is available from the average alpine peridotite to produce the Ca-metasomatic effects common to ultramafic rocks.

A notable aspect of the mass balance exercises is the loss of silica from both the ultramafic rocks and dike rocks. This indicates that large amounts of water must be involved in the alteration processes to carry away components that are in excess of what can be absorbed. High water/rock ratios have been shown by isotopic studies as well (Magaritz and Taylor, 1974; Wenner and Taylor, 1974).

Although rodingites occur only in serpentinized ultramafic rocks, their precursor dike rocks play only an incidental role, and are not necessary for serpentinization to occur. The rate limiting factor of serpentinization has
been shown to be the rate of water influx, rather than temperature or pressure (Nesbitt and Bricker, 1978; Sanford, 1981). Serpentinization depends on a supply of water from external sources circulating through zones of enhanced permeability, rather than on a pervasive fluid. Deformation and faulting that occur during emplacement of an ophiolite provide the major source for fractures that can act as input aquifers. Intrusion of dikes also disrupts the ultramafic rocks, aiding the circulation of water in a peridotite by providing further pathways for fluid flow along the dike-peridotite contact.
CHAPTER 6
CONCLUSIONS

The Josephine Peridotite and Rodingites

In terms of major element chemistry, mineralogy, and alteration, the Josephine peridotite is comparable to other alpine type ultramafic occurrences (Coleman 1966, 1971; Page, 1967; Himmelberg and Coleman, 1968; Thompson, 1968; Coleman and Keith, 1971; Loney et al., 1971; Barnes et al., 1978) Rodingite occurrence, chemistry, and mineralogy also match those of many other studies (Bloxam, 1954; Bilgrami and Howie, 1960; Coleman, 1967; Larrabee, 1969; Anhaeusser, 1978; Leach and Rogers, 1978; Sivell and Waterhouse, 1986).

Chemistry

The analyses of the ultramafic rocks suffered from inaccuracies caused by failing to account for possibly significant amounts of nickel in the matrix corrections. This resulted in anomalously high values for CaO, and low oxide sums for samples PER 9 and SP 10.

The compositions of the Josephine dike rocks are
similar to those of other rodingite occurrences. Although the composition of sample 87-2-A is different from the other rodingites, the difference may be explained by its unusual mineralogy rather than by inaccurate analysis.

**Chemical Trends**

Except for samples PER 9 and SP 10, the chemistry of the Josephine ultramafic rocks fell within the trends displayed by other studies. The most important trend with progressive serpentinization is the loss of CaO.

The alteration of dike rocks results in substantial gains in CaO, and loss of silica. The minor and trace elements display much scatter.

**Trace Element Mobility**

Trace element correlations and mobilities in the ultramafic rocks are difficult to assess owing to the small number of samples analyzed, the problems with inaccurate analyses in two of the samples, and the lack of trace element analyses in the literature with which the Josephine samples can be compared.

A strong argument can be made that the scatter in the trace elements in the Josephine dike rocks reflects initial variations within a rock type, and/or the presence of more
than one rock type, rather than the effects of element mobility.

**Volume-composition Relations**

Serpentinization in the Josephine peridotite resulted in substantial volume increases, on the order of 25 to 30 percent. The alteration occurred with essentially constant magnesium.

Metasomatism of the dike rocks resulted in large gains in CaO, loss of SiO$_2$, with constant Al$_2$O$_3$ (and probably constant TiO$_2$ and Zr). The alteration was accompanied by slight volume decreases of 5 to 10 percent.

**P-T-X Conditions**

Stability relations of common minerals in ultramafic rocks and rodingite confirm that serpentinization and rodingitization occur over similar temperature ranges. Both processes take place under 400°C, and both require extremely low CO$_2$.

Petrographic evidence points to a multi-stage history of the serpentinization process. The substantial volume increase during serpentinization of the peridotite suggests that the early stages of alteration occurred at higher temperature and pressure (Nesbitt and Bricker, 1978), and
with lower water/rock conditions. This is probably the stage at which most rodingitization occurs (Wenner, 1979).

The best evidence for further low temperature formation of serpentine and later rodingite minerals comes from isotopic studies (O'Neil and Barnes, 1971; Wenner and Taylor, 1973, 1974; Magaritz and Taylor, 1974; Wenner, 1979). These studies indicate that serpen tinization can occur at surface conditions, and rodingite formation may occur below 200°C. The deposition of carbonates at seeps in the Josephine peridotite suggests that the body is undergoing serpentinization today.

Mass Balance

One of the central points of the notion that rodingite formation and serpentinization are simultaneous and complementary is the belief that the host peridotite is the source of calcium for metasomatism. Simple mass balance exercises demonstrate that more than enough calcium is available from the average alpine peridotite to produce the Ca-metasomatic effects common to ultramafic rocks.

Role of Rodingite Dikes in Serpentization

Although rodingites occur only in serpentinized ultramafic rocks, their precursor dike rocks play only an
incidental role, and are not necessary for serpentinization to occur. The dikes may, however, aid in the circulation of water in a peridotite by providing channels of increased permeability.
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FIGURE 3.

GEOLOGIC MAP
OF THE JOSEPHINE PERIDOTITE, SW OREGON

MAP BASE FROM U.S. GEOLOGICAL SURVEY: CAVE JUNCTION AND SELMA 15-MINUTE QUADRANGLES

SCALE
3000 feet
3000 meters

EXPLANATION

Bench gravel
Landslide
Rogue Formation Metamorphic rocks
Galice Formation Metasedimentary rocks
Ultramafic rocks Peridotite and serpentinite
Intrusive rocks Diorite and related rocks

GEOLeGIC SYMBOLS

Fault: Arrow shows direction of slip.
Thrust fault: Dashed line where concealed.
Zone of intense shearing:
Strike and dip of joints.
CALCIUM METASOMATISM IN THE JOSEPHINE
PERIDOTITE, SOUTHWEST OREGON

by

Raymond Charles Harris

A Thesis submitted to the faculty of the
DEPARTMENT OF GEOSCIENCES
In Partial Fulfillment of the Requirements for the degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

1989