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Chromite Compositional Variation in the
Twin Sisters Dunite, Washington State

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Harry Evan Trebing

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John T. Wilband
Major professor

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CHROMITE COMPOSITIONAL VARIATION IN THE TWIN SISTERS DUNITE, WASHINGTON STATE

By

Harry Evan Trebing

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ABSTRACT

CHROMITE COMPOSITIONAL VARIATION IN THE TWIN SISTERS DUNITE, WASHINGTON STATE

By

Harry Evan Trebing

The Twin Sisters dunite, located in Washington State, is the lower part of an ophiolite sequence which contains podiform chromite. Chromite pods are an important source of high grade chromium ores and refractory grade chromite ores. Chromite pods associated with the dunite are internally homogeneous; however, the chemical composition varies between pods. This compositional variation makes mining difficult and expensive.

Compositional data from 31 pods were examined. Results show that divalent cation variations can be attributed to subsolidus reequilibration between adjacent crystals within a pod. Trivalent cation variations in chromite can be attributed to fractional crystallization processes, suggesting that chromite pod formation is a product of spreading center injection mechanics and constrictive flow.

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INTRODUCTION

Chromite ores exist in both layered intrusives and ophiolite sequences. Chromite in layered intrusives, traditionally attributed to fractional crystallization, has recently been suggested to be concentrated by double diffusion convection in magma chambers (Irvine et al, 1984). Podiform chromites from ophiolites, however, have an obscure origin. This origin is poorly understood because of complex injection mechanics associated with ophiolites (Lago et al, 1982), considerable metamorphism usually associated with ophiolitic sequences, and the apparently random compositional variation between chromite pods of the same deposit. Because these podiform deposits are a principal source of high content chromium ores (Cr_2O_3>45%) important in metallurgy, and an important source of refractory grade (Al_2O_3>20%) chromite ores (Thayer, 1969), a study addressing the problem of compositional variation is economically important.

Podiform chromite deposits, or Alpine type chromite deposits, are known from many dunite and harzburgite bodies in which they occur. The dunite host rock in which the chromite occurs is considered a residual product of partial melting of the upper mantle at oceanic or marginal basin ridges (Hutchinson, 1983; Nicolas and Prinzhofer, 1983). The creation of thick, relatively pure (more than 90% olivine) dunitic piles may be the result of crystal settling processes or, as is more likely, it is the result of density controlled separation of liquids of dunitic composition from the magma (Ridgen et al, 1984). Dunites occur near the stratigraphic bottom of the ophiolite sequence (fig.1). The complete ophiolite sequence can rarely be demonstrated in the field, but the sequential order and rock assemblage are common to all ophiolite sequences. It is therefore possible to conclude that there are processes common to all podiform chromite deposits that may result in chromite compositional variations (Hutchison, 1983).

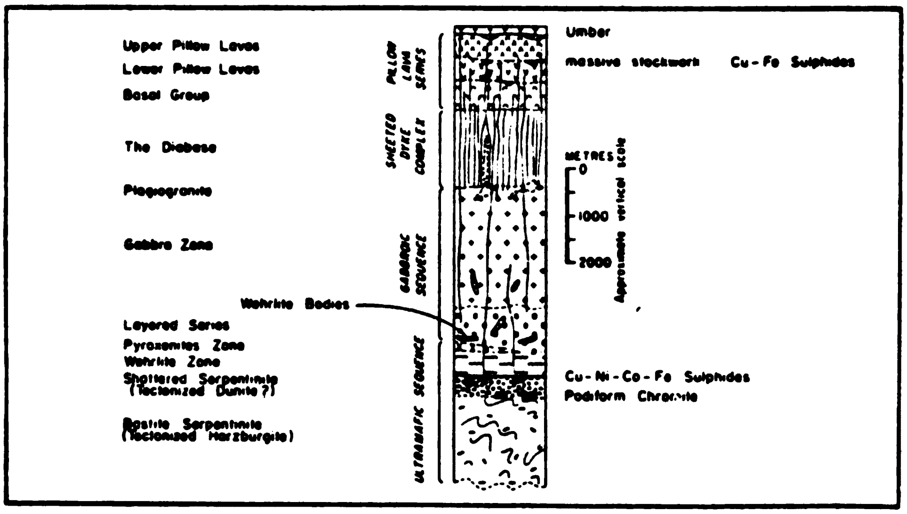

Figure 1. Idealized ophiolite sequence.

The typical features of podiform chromites have been summarized by Thayer (1964). The ore bodies are fundamentally tabular, pencil shaped or irregular, in which chromite crystals are characteristically anhedral in pod structures but euhedral to subhedral in grains disseminated in the host rock. Chromite pods less than a few meters in length are commonly referred to as lenses. Chromite grains in the pods and host rock commonly show the effects of granulation, which may create a sense of banding through the rock (Nicolas and Prinzhofer, 1983). The chromite crystals in pod structures commonly exhibit welded grain boundaries, making the pod a highly durable, unique, single entity within the host rock (Thayer, 1969).

Flow layering, foliation, and lineation, present in all chromite deposits and peridotite host rocks to varying degrees, have been used by Cassard et al (1981) to develop a classification scheme based on pod orientation relative to these structural features. Chromite pods are classified as concordant when they are aligned with the foliation or lineation. Pods are subconcordant when they are only partially aligned, and they are discordant when they show no alignment. These structural features are parallel to each other in most chromite deposits and peridotite host rocks, and normally pass through major rock units, including the chromite pods. It is possible for the foliation and lineation to cross the layering on a local scale. Most podiform chromites are concordant to subconcordant but occasionally, some are discordant (Cassard, 1981). Those chromite pods, whether concordant, subconcordant, or discordant, which exhibit internal flow structures are always consistent with the flow structures of the surrounding host rock, except where disturbed by post-magmatic faulting (Ceuleneer et al, 1985). Relict structures in the form of crystal cumulates are sometimes preserved in podiform chromites but most features are due to extensive flowage during emplacement under magmatic conditions and to recrystallization during metamorphism and emplacement of the ophiolite (Ragan, 1967; Hutchinson, 1983).

An earlier model of chromite pod formation involved crystal settling in a basic magma chamber, associated with the lower crust of oceanic ridge systems. This crystal settling process results in ultrabasic cumulates (Thayer, 1961; Thayer, 1969; Thayer, 1970; Auge, 1982; Brown, 1982; Auge et al, 1982; Christiansen, 1982; Lago et al, 1982). However, recent work on Thayer's speculation (1969) has suggested the possibilty that the chromite pods were emplaced in the dunite - harzburgite host during periods of intense flowage in the solid state at near solidus temperatures (Nicolas et al, 1980; Cassard et al, 1981; Ceuleneer et al, 1985).

Economically important stratiform chromites occur in stable craton interiors and are Precambrian in age. Conversely, all podiform chromites occur along island arcs and mobile mountain belts in ophiolite sequences within Paleozoic or younger rocks. This lead Hutchinson (1983) to conclude that there are two possible sources for the chromite in the pods. These are first, considering the age discrepancy, the chromite pod source may be a function of continental denudation and recycling (e.g. crustal heritage). Second, the source of the chromite may be incongruent partial melting of the primative pyrolitic mantle (e.g. mantle heritage).

This study will focus on possible mechanisms for the compositional variation of the chromite found in the Twin Sisters dunite. It will use 31 samples of the dunite (fig.2), where samples X-9, X-10, X-11, X-29, X-30, X-31 were collected by the author and the remainder were supplied by G. Spansky. The Twin Sisters dunite has been the subject of several petrologic studies (Gaudette, 1963; Ragan, 1963; Christensen, 1971; Onyeagocha, 1973) all of which concluded that the dunite is fairly typical of the dunites associated with ophiolite complexes. That is, the dunite is homogeneous in composition, has flow layering and foliation, and its attendant chromite pods are internally homogeneous and have a randomly variable composition between pods. Because the intrusion has the classical attributes of the podiform chromite deposits, it lends itself well to an investigation designed to evaluate the variation in chromite composition.

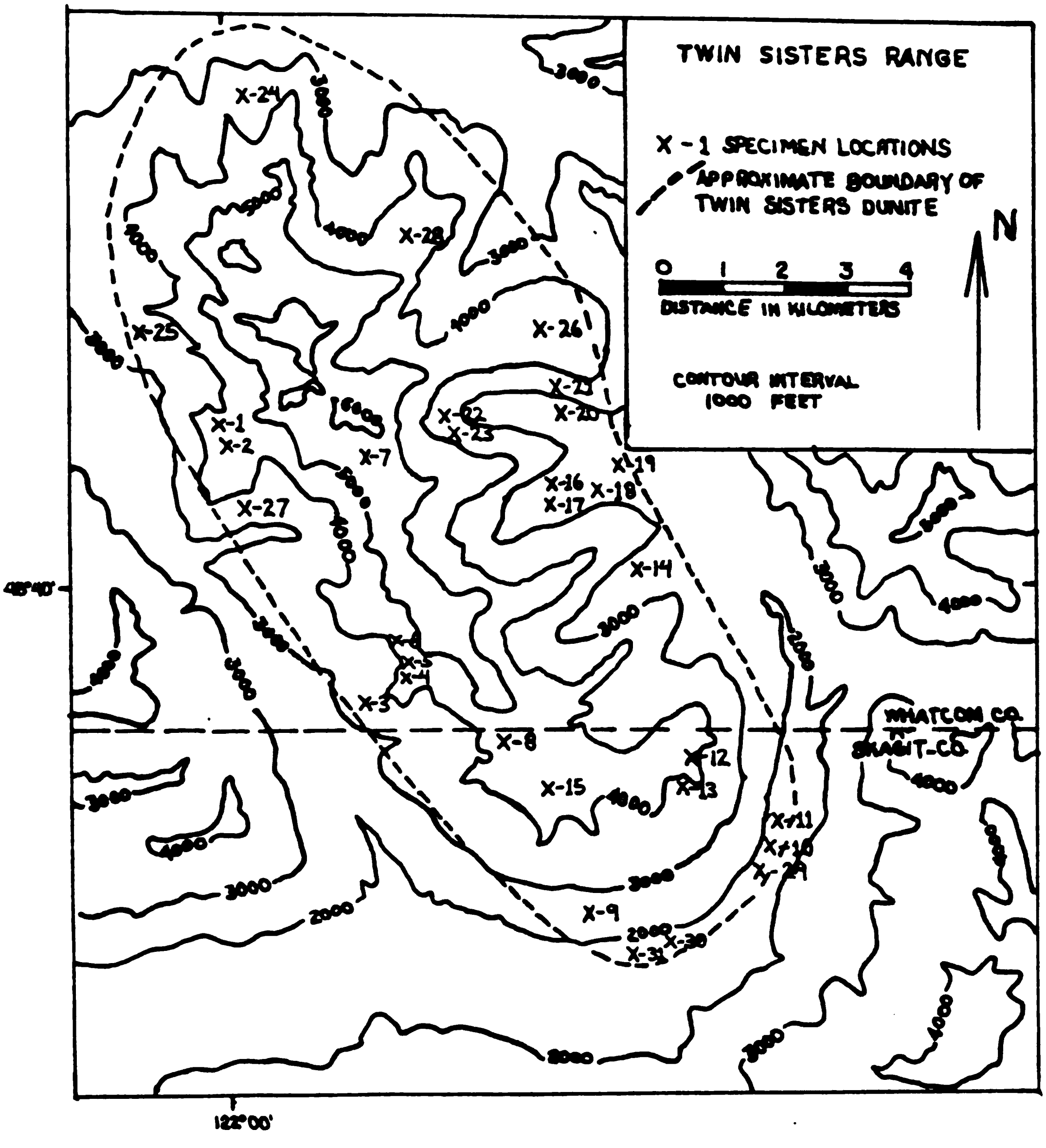

Figure 2. Map of sample localities within the Twin Sisters dunite.

REGIONAL GEOLOGY

The Twin Sisters dunite is located in Whatcom county, Washington State, four miles southwest of Mt. Baker, 18 miles south of the Canadian border, and 24 miles east of Bellingham. They are part of the western edge of the Cascade Mountain Range of northwestern Washington. The dunite body extends in a north - northwest direction for approximately 10 miles and averages 3.5 miles in width. The exposure contains approximately 4000 feet of vertical relief. Above the 5500 foot elevation mark, the dunite is partially covered by snow, which is present most of the year. Between the 5500 foot and the 4000 foot elevation, the dunite is well exposed while below that, the dunite is partially covered with glacial material. Geophysical work by Thompson (1963) and Christensen (1971) has shown that the dunite has shallow roots relative to the present erosional surface, suggesting most of the dunite is exposed.

The oldest rock unit in the area of Twin Sisters Mountain is the Early Devonian Yellow Aster Complex (Misch,1966) which is found as blocks, to the northeast and southwest, directly adjacent to the dunite.

The unit contains the fragmented record of a complex and long history of igneous and metamorphic events.

Cascade regional metamorphism of the post basement rock can be separated into three major subdivisions, based on post - metamorphic major faults. These are: (a) the Shuksan Metamorphic Suite, (b) the Skagit Metamorphic Suite, and (c) the Eastern Metamorphic Belt. Of these, only the Shuksan Metamorphic suite is observed in the region surrounding the dunite (Misch,1966).

The Shuksan Metamorphic Suite, which also forms the Shuksan Thrust Plate, is located west of the metamorphic core of Northern Cascades (fig.3). The suite is bordered by faults on both its east and west margins; these being the Straight Creek fault and the Shuksan Thrust fault, respectively (Misch, 1966). This suite is composed of the metabasaltic Shuksan Greenschist and, beneath that, the Darrington Phyllite. This unit is exposed directly west and south of the Twin Sisters dunite, as well as some distance farther east of it. Misch (1966) estimated the age of Shuksan Metamorphism to be late Permian, or early Triassic.

The Church Mountain Thrust Plate, located below the Shuksan Thrust Plate, is composed of Upper Paleozoic graywackes, slates, phyllites, limestones and volcanics (Misch, 1966). These strata are referred to as the

Chilliwack Group and form most of the immediate country rock to the east of the Twin Sisters dunite.

The Swauk-Chuckanut Formation rests unconformably upon both the Shuksan Thrust Plate and the Church Mountain Thrust Plate. This formation consists principally of arkosic sandstones, conglomerates, shales, and the Mt. Baker volcanics. The Swauk-Chuckanut Formation appears to be early Tertiary in age (Misch, 1966).

Ragan (1961) first reported the mantle origin of the Twin Sisters dunite and its solid state mode of emplacement. Misch (1966) later showed that the high angle fault, which Ragan (1967) postulated to have been the passageway for the dunite's emplacement to be part of the Shuksan Thrust fault. Ragan (1967) further demonstrated Tertiary emplacement by showing the dunite to be intrusive to the Church Mountain and Shuksan Thrust Plates and the Chuckanut Formation. Misch however, believes this post-Chuckanut motion was only a minor reactivation following Cretaceous emplacement of the dunite (Misch, referred to in Onyeagocha, 1973).

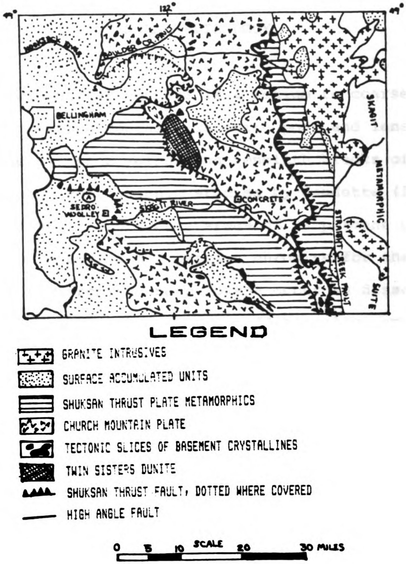

Figure 3. Geological map in the vicinity of the Twin Sisters dunite. (after Misch, 1966)

GENERAL PETROLOGY

The Twin Sisters dunite is a medium to coarse grained rock which contains chromite pods and lenses, olivine and pyroxene veins, and xenolith blocks of dunite and pyroxene. Petrographic studies by Gaudette (1963) and Ragan (1963) report an average of 93 percent olivine, 5 percent pyroxene, and 2 percent chromite for the fresh dunite. Both chromite and pyroxene occur as disseminated crystals throughout the dunite. Additionally, pyroxene crystals can be found within chromite pods although their occurrence is very rare (Onyeagocha, 1973), and none were observed in this study. Mineral alteration does occur and is confined to a few fractures and portions of the margin of the dunite.

Texture

Ragan (1967) determined that four textures exist within the dunite body. These are: 1. Primary magmatic textures, which are demonstrated by chromite pod structures with cumulus textures (Thayer, 1969), subhedral to euhedral disseminated chromite, and a medium to coarse grained fabric of anhedral olivine crystals apparently lacking any physical orientation; 2. Early solid state flow textures, which are demonstrated by numerous thin layers of pyroxene generally trending parallel to the main axis of the dunite, and a preferred crystallographic orientation present in recrystallized olivine; 3. Transitional textures, which are demonstrated by the partial recrystallization of fine grained olivine and pyroxene zones which surrround, and embay larger nonrecrystallized olivine and pyroxene; 4. Cataclastic textures, which are demonstrated by zones of finely granulated olivine with abundant kink banding and bent enstatite crystals, leading to mylonitization.

Olivine

Petrofabric studies by Christensen (1971), indicate that recrystallized olivine has a strongly preferred crystallographic orientation throughout the dunite, while olivine which has not undergone recrystallization is lacking this feature. This preferred orientation is independent of the host structure (i.e. dunite, chromite pods, veins, and xenolith blocks). The olivine crystallographic b axes generally trend east-northeast with a horizontal lineation while the orientation of the other two axes vary in a complex pattern. Although olivine crystal orientation would have significant impact on oxygen diffusion throughout the dunite during solid state flow (Reddy et al, 1980), and could therefore potentially affect chromite pod composition (Hill et al,1974), no regional patterns in chromite pod composition have been observed.

Chromite

Chromite crystals within pod structures are typically anhedral and medium - grained. Additionally, chromite crystals near pod margins may display granulated edges. This frequently results in a smeared appearance to portions of the pod margins in the field. This granulation process is present in a significant minority of chromite pods throughout the Twin Sisters dunite (Ragan, 1963).

Pod structures contain up to 20% olivine and trace amounts of pyroxene. Some pods are cross-cut by pyroxene veins and some of these veins have undergone metamorphic changes resulting in an olivine - tremolite +/- diopside assemblage (Onyeagocha, 1973).

Veins

Veins are present throughout the entire body of the Twin Sisters dunite, and show no preferential orientation. All of the veins are narrow (generally about 10 centimeters wide or less), and contain up to 90% pyroxene, with lesser amounts of olivine and trace amounts of chromite (Ragan, 1963). The dunite has been subjected to two episodes of vein formation. The oldest veins have been folded and cross cut by a younger set of apparently undeformed veins (Onyeagocha, 1973).

Onyeagocha (1973) demonstrated that approximately one-third of the veins displayed zoning from the dunite host at the margins to enstatite, with enstatite plus chromium rich diopside in the center. Additionally, the boundaries of crystals in the veins are marked by a mortar of crushed and recrystallized olivine, enstatite, and diopside. Pyroxene crystals in veins, like those in the main dunite, are kinked, bent, and exsolved. Exsolution in these vein pyroxenes is more pronounced than in the main dunite, and Onyeaghocha (1973) attributes this to the coexistence of two pyroxenes in the veins. Onyeagocha (1973) determined that the exsolved phase in enstatite is diopside and that in diopside, the exsolved phase is enstatite.

Onyeagocha (1973) believes that the absence of chilled borders, combined with their zoned mineralogy and small width would indicate a non-magmatic origin for these veins. Onyeagocha further suggests that the sequence of events in vein formation are first, the segregation of olivine, enstatite, and diopside into a coarse sutured mosaic; second, deformation of the mosaic into a mortar by the crushing of interstitial crystals; third, recrystallization of the mortar; and fourth, exsolution of pyroxene. This sequence is a questionable interpretation in view of the fact that the veins contain considerable amounts of pyroxene and the surrounding dunite shows no sign of pyroxene depletion (Ragan, 1963). It is more probable that the veins are the last magmatic products created from the residual magmatic liquid, and injected into a cooling dunite body.

Alteration

Serpentinization occurs along portions of the dunite's margin, at some places reaching a thickness of one-third of a mile (Christensen, 1971). Additionally, internal fractures within the dunite are also serpentinized. However Christensen (1971) states this process is common, while Onyeagocha (1973) states that alteration along fractures is uncommon and occurs only on a localized scale.

The principal alteration in the original chromite pods is the breakdown of chromite plus olivine and enstatite to ferritchromit (an iron rich chromite; Beeson and Jackson, 1969) and chlorite. Onyeagocha (1973) emphasized that this alteration occurs on a very local scale. Also, the alteration occurs only in the podiform chromite while the disseminated chromite in the adjacent dunite remained unaltered (Onyeagocha, 1973). No alteration products were observed in this study.

STRUCTURE

The Twin Sisters dunite has undergone considerable folding, faulting and fracturing. However, the structure of the dunite, while prominent, has no discernible connection to the compositional variation of the chromite pods.

Isoclinal folds in the dunite are heavily accentuated by weathering in some areas (Onyeagocha, 1973). Locally, small open folds are superimposed on the well defined isoclinal folds (Ragan, 1967). Additionally, some of the chromite pods have been deformed into similiar folds with steep axial planes. In these cases, the dunite surrounding the chromite pods displays a prominent fracture cleavage parallel to these axial planes (Onyeagocha, 1973).

Bennet (1940) noted the presence of two joint orientations in the Twin Sisters dunite. One set trends north-northwest, parallel to the long axis of the dunite, and dips steeply to the southwest. The second set trends northeast and dips moderately to the northwest. However, some joints with other orientations are also present in the dunite.

Misch (1966) reported the presence of discontinous, small scale faulting throughout the dunite body. Several minor reverse faults were observed at the south-southeast margin of the dunite during this study. All of the fault planes trended parallel to the long axis of the dunite and dipped between 75 and 84 degrees to the southwest. All of the faults showed a displacement of 3 feet or less, measured against the offset in chromite pods or pyroxene veins.

ECONOMIC GEOLOGY

Chromite pods are the principal form of chromite occurrence in the Twin Sisters dunite and they contain an estimated 626,000 metric tons of chromite ore (Scott Paper Company, personal communication) at an average 52% of chromium oxide (Cr_2O_3). The pods occur irregularly thoughout the host dunite, and range in size from a few centimeters in cross section and less than a meter in length, to more than a third of a meter in cross section and up to 40 meters in length. Economic extraction of these pods is difficult due to their random occurrence, lack of continuity, compositional variation, and the mountainous terrain. Less than half of the large pods have ever been worked (Onyeagocha, 1973), and no chromite mines are operating in the area at present.

Olivine is mined at the south-southwest margin of the intrusion by a local paint company. Operations are conducted on an irregular basis and usually do not exceed two months of activity per year. Quantities of olivine extracted are quite small and rarely exceed a few truckloads full (Scott Paper Company, personal communication, 1984).

ANALYTICAL PROCEDURES

Sampling

Thirty one samples from the Twin Sisters dunite chromite pods were used in this study. One sample was used from each of the major chromite deposits (twenty nine in total), along with two samples (labeled X-30 and 31, respectively) from smaller pods (lenses) on the south-southeast margin of the dunite. All samples were taken from the approximate midpoint of the exposed pod.

Mineral separates

All samples of the Twin Sisters dunite were trimmed to remove any altered material to insure accurate analyses of fresh rock. The samples were then ground to between 80 and 200 mesh sizes. Acetone, in an ultrasonic bath, was used to rinse the grains clean of any contamination from the grinding phase. Mineral separates were then obtained from the samples using a Frantz Isodynamic Separator. The Separator settings used were as follows: a forward ramp of 15 degrees, a side ramp angle of 7 degrees, and a magnet setting of 0.35 amps. Usually, three passes through the separator were sufficient to obtain 99% purity in the olivine grains. However, the chromite fraction rarely went above 70%

purity. This necessitated the use of hand picking methods to obtain a chromite fraction clean enough for analyses.

Major element analyses

Major element analyses of olivine and chromite and minor element analyses of chromite were made using the Applied Research Laboratories, three channel, computer driven electron microprobe at the University of Chicago. All samples analysed were mounted either as polished sections, or as polished metallurgical mounts. All samples were carbon coated. The microprobe was operated at an accelerating potential of 15 kilovolts and a sample current of 0.08 microamps. Grains of chromite and olivine were checked to insure the accuracy of Onyeagocha's work on the homogeneous nature of the crystals. After it was confirmed that no zoning was present, four grains of each mineral per sample were analysed and the results averaged to minimize counting variations. The beam current was continually monitored for stability to minimize drift. Counting times for a full analyses were one minute thirty seconds for olivine and two minutes forty seconds for chromite grains. The results are corrected for atomic number, characteristic fluorescence, x-ray absorbtion, background, drift, and dead time. Reference standards from Cambridge and the U.S.G.S. were used.

Trace element analyses

Selected trace element analyses of olivine were made using the computer driven Rigaku x-ray fluorescence spectrometer at Michigan State University. Mineral separates of olivine were powdered and pelletized for analyses. Samples were not diluted with any bonding agent. Reference standards from the U.S.G.S. were used, including DTS-1, a U.S.G.S. standard from the Twin Sisters dunite. The results are corrected for drift, background, x-ray absorbtion, and atomic number.

MINERAL CHEMISTRY

Olivine

Chemical analysis (Onyeagocha, 1973; Ragan, 1963) of the olivine in the Twin Sisters dunite show that the olivine contains from 4 to 10 percent fayalite, while olivine from chromite pods contains from 3 to 9 percent fayalite (table 1). Although these compositions are typical of podiform associated olivines in Alpine settings (Thayer, 1970), they differ slightly from the peridotites of southwest Oregon, also in the Cascade region, where olivine compositions are very close to Fo90 (Medaris, 1972).

Onyeagocha (1973) reported that within each unit (dunite, pods, and veins) olivine is homogeneous within grains and between grains. Full analyses step scans done by the author confirm the homogeneity of the olivine grains. No regional variations were observed in this study, nor did Gaudette (1963) or Onyeagocha (1973) report any variations. Microprobe examination showed coarse-grained and recrystallized olivine within pod structures had no difference in composition. Medaris (1972) and Onyeagocha (1973) also found no difference in composition between primary and recrystallized olivine.

This study notes some differences in the trace element abundances in olivines (table 2) associated with chromite pods compared with the data reported by Onyeagocha (1973). The data presented here have been checked for reproducibilty using double blank tests and is considered more accurate. The most notable differences in the data are the higher concentrations of NiO (0.7% compared to 0.4%), and the presence of both Al_2O_3 and Cr_2O_3 in some of the samples. The present data compare favorably with the U.S.G.S. standard for the Twin Sisters dunite, DTS-1.

Ionic proportions of olivine are recalculated on the basis of four oxygen atoms (table 3). Si ranges from 0.993 to 1.005 and X^{+2} from 1.990 to 2.013, the values being very close to the stoichiometric 1.000 and 2.000 respectively. It should be noted here that the ionic proportions in olivine superficially appear to be worse than the corresponding values in chromite. This is due to the fact that ferric/ ferrous ratios in the chromite are determined by balancing the crystal stoichiometrically so the results add to the required 24 cations with 32 oxygen atoms. No such recalculations are necessary with olivine and their results represent values taken directly from the microprobe.

TABLE 1. Olivine data

I.D.	CaO	MnO	FeO	NiO	SiO_2	MgO	TOTAL	Fo
X-1	0.01	0.08	6.65	-	40.98	51.48	99.20	93.25
X-2	0.03	0.08	7.27	0.76	41.01	50.90	100.05	92.58
X-3	0.02	0.11	7.81	-	41.03	50.72	99.69	92.05
X-4	0.02	0.12	8.62	0.69	41.18	49.71	100.34	91.13
X-5	0.03	0.14	8.07	0.65	41.21	49.85	99.95	91.67
X-6	0.01	0.09	7.06	0.67	40.93	51.40	100.17	92.85
X-7	0.04	0.11	8.08	-	41.39	50.16	99.78	91.71
X-8	0.07	0.11	7.21	1.01	41.20	50.82	100.42	92.63
X-9	0.02	0.05	5.02	-	41.49	52.58	99.16	94.92
X-10	0.03	0.11	7.82	-	40.77	50.86	99.59	92.06
X-11	0.03	0.10	6.45	0.79	41.05	51.87	100.29	93.47
X-12	0.05	0.14	7.78	0.01	41.39	50.03	99.40	91.97
X-13	0.17	0.14	8.64	0.68	41.09	49.64	100.36	91.10
X-14	0.01	0.08	5.45	0.95	42.03	51.63	100.15	94.41
X-15	0.01	0.07	5.53	-	41.68	52.14	99.43	94.39
X-16	0.02	0.12	7.90	0.65	41.44	49.85	99.98	91.83
X-17	0.02	0.10	7.31	0.74	41.18	50.87	100.22	92.54
X-18	0.01	0.09	6.10	0.77	41.26	51.73	99.96	93.79
X-19	0.02	0.11	7.83	0.73	41.15	50.13	99.97	91.94
X-20	0.02	0.08	3.88	-	41.16	53.61	98.75	96.10
X-21	0.01	0.04	3.58	-	41.57	53.95	99.15	96.42
X-22	0.01	0.12	7.82	-	41.06	50.53	99.54	92.02
X-23	0.02	0.00	2.38	0.74	41.03	55.40	99.57	97.64
X-24	0.03	0.11	7.94	-	40.59	50.60	99.27	91.91
X-25	0.03	0.09	6.91	-	41.76	50.65	99.44	92.89
X-26	0.02	0.12	7.43	-	41.11	50.46	99.14	92.38
X-27	0.02	0.14	7.18	-	41.48	50.64	99.46	92.64
X-28	0.02	0.07	6.07	0.90	41.67	51.42	100.15	93.79
X-29	0.01	0.09	4.48	1.01	41.96	52.51	100.06	95.43
X-30	0.04	0.06	3.42	1.08	41.95	53.41	99.95	96.53
X-31	0.00	0.10	8.03	-	41.18	50.44	99.75	91.80
MAXIMUM	0.17	0.14	8.64	1.08	42.03	55.40	100.42	97.64
MINIMUM	0.00	0.00	2.38	0.01	40.59	49.64	98.75	91.10
AVERAGE	0.03	0.10	6.64	0.75	41.29	51.29	99.75	93.22
ST.DEV.	0.03	0.03	1.66	0.24	0.35	1.37	0.44	1.73

TABLE 2. Selected trace element data

I.D.	ZnO	Cu_2O	Cr_2O_3	MnO	CoO	Al_2O_3
X-2	0.0036	0.0032	0.410	0.130	0.023	0.040
X-4	0.0052	0.0006	0.005	0.160	0.029	0.000
X-5	0.0051	0.0008	0.059	0.150	0.031	0.060
X-6	0.0045	0.0008	0.146	0.130	0.027	0.250
X-8	0.0057	0.0013	0.007	0.130	0.032	0.000
X-11	0.0004	0.0007	0.128	0.114	0.017	0.000
X-12	0.0037	0.0009	0.128	0.130	0.027	0.000
X-13	0.0024	0.0007	0.008	0.150	0.034	0.130
X-14	0.0000	0.0010	0.380	0.090	0.004	0.120
X-16	0.0085	0.0007	0.154	0.143	0.030	0.387
X-17	0.0169	0.0006	0.063	0.135	0.032	0.000
X-18	0.0053	0.0003	0.008	0.127	0.029	0.000
X-19	0.0082	0.0006	0.006	0.139	0.034	0.000
X-23	0.0025	0.0008	0.915	0.020	0.000	0.970
X-28	0.0000	0.0006	0.209	0.100	0.013	0.130
X-29	0.0000	0.0008	0.139	0.080	0.005	0.170
X-30	0.0000	0.0013	0.151	0.050	0.000	0.780
MAXIMUM	0.0169	0.0032	0.915	0.160	0.034	0.970
MINIMUM	0.0000	0.0003	0.005	0.020	0.000	0.000
AVERAGE	0.0042	0.0009	0.172	0.116	0.022	0.179
ST.DEV.	0.0043	0.0006	0.227	0.038	0.012	0.285

TABLE 3. Olivine ionic proportions

I.D.	Ca	Mn	Fe	Ni	Si	Mg	R^{+2}	TOTAL
X-1	0.0002	0.0017	0.1349	-	0.9949	1.8631	1.9999	2.9948
X-2	0.0009	0.0017	0.1479	0.0086	0.9975	1.8459	2.0050	3.0025
X-3	0.0005	0.0023	0.1586	-	0.9969	1.8374	1.9988	2.9957
X-4	0.0005	0.0025	0.1758	0.0060	1.0042	1.8069	1.9917	2.9959
X-5	0.0007	0.0028	0.1647	0.0066	1.0058	1.8135	1.9883	2.9941
X-6	0.0004	0.0019	0.1433	0.0078	0.9935	1.8597	2.0131	3.0066
X-7	0.0011	0.0023	0.1642	-	1.0052	1.8161	1.9837	2.9889
X-8	0.0017	0.0022	0.1463	0.0119	0.9998	1.8382	2.0003	3.0001
X-9	0.0004	0.0010	0.1010	-	0.9989	1.8870	1.9894	2.9883
X-10	0.0007	0.0023	0.1592	-	0.9923	1.8457	2.0079	3.0002
X-11	0.0007	0.0020	0.1306	0.0089	0.9933	1.8711	2.0133	3.0066
X-12	0.0012	0.0028	0.1584	0.0083	1.0073	1.8150	1.9857	2.9930
X-13	0.0044	0.0030	0.1762	0.0081	1.0019	1.8044	1.9961	2.9980
X-14	0.0003	0.0016	0.1097	0.0099	1.0120	1.8539	1.9754	2.9874
X-15	0.0002	0.0014	0.1112	-	1.0031	1.8708	1.9836	2.9867
X-16	0.0004	0.0026	0.1609	0.0086	1.0090	1.8095	1.9820	2.9910
X-17	0.0005	0.0021	0.1484	0.0081	0.9998	1.8413	2.0004	3.0002
X-18	0.0003	0.0019	0.1235	0.0098	0.9989	1.8667	2.0022	3.0011
X-19	0.0004	0.0022	0.1597	0.0086	1.0034	1.8224	1.9933	2.9967
X-20	0.0004	0.0015	0.0780	-	0.9901	1.9225	2.0024	2.9925
X-21	0.0003	0.0009	0.0716	-	0.9946	1.9243	1.9971	2.9917
X-22	0.0003	0.0025	0.1590	-	0.9988	1.8324	1.9942	2.9930
X-23	0.0005	0.0002	0.0477	0.0091	0.9825	1.9777	2.0352	3.0177
X-24	0.0006	0.0022	0.1623	-	0.9915	1.8427	2.0078	2.9993
X-25	0.0006	0.0018	0.1399	-	1.0105	1.8271	1.9694	2.9799
X-26	0.0005	0.0024	0.1513	-	1.0015	1.8328	1.9870	2.9885
X-27	0.0005	0.0028	0.1455	-	1.0056	1.8302	1.9790	2.9846
X-28	0.0004	0.0015	0.1226	0.0101	1.0067	1.8519	1.9865	2.9932
X-29	0.0004	0.0018	0.0900	0.0114	1.0081	1.8803	1.9839	2.9920
X-30	0.0009	0.0011	0.0680	0.0145	1.0042	1.9064	1.9909	2.9951
X-31	0.0005	0.0021	0.1631	-	1.0002	1.8262	1.9919	2.9921
MAXIMUM	0.0044	0.0030	0.1762	0.0145	1.0120	1.9777	2.0352	3.0177
MINIMUM	0.0002	0.0002	0.0477	0.0060	0.9825	1.8044	1.9694	2.9799
AVERAGE	0.0007	0.0020	0.1346	0.0092	1.0004	1.8524	1.9947	2.9951
ST.DEV.	0.0008	0.0006	0.0342	0.0020	0.0067	0.0393	0.0130	0.0074

Chromite

The chromite of the Twin Sisters dunite is typical of Alpine Complex deposits described by Thayer (1969). It is a high chromium, low aluminum (except for sample X-13, which is an anomalous high aluminum chromite, fig.4) content spinel where Cr_2O_3 varies between 41% and 58% and Al_2O_3 varies from 10% to 26% (table 4).

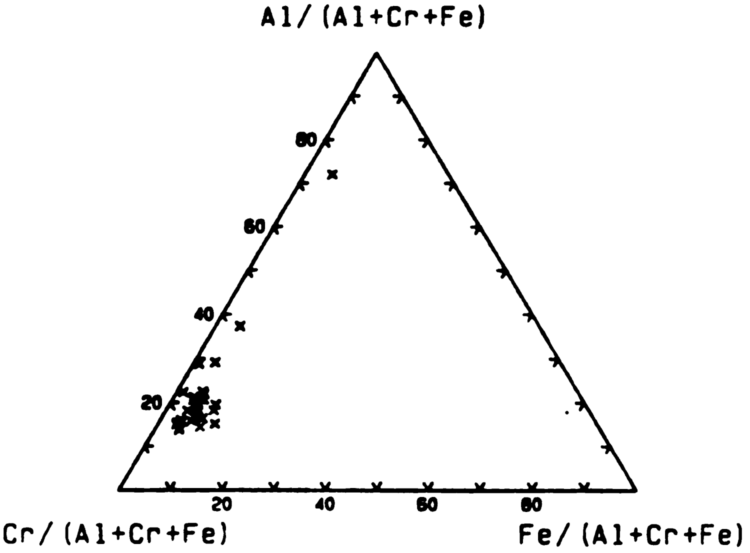

Figure 4. Trivalent cation distribution in chromite.

Microprobe stepscans reveal that chromite grains are homogeneous in composition and show no variation between grains of the same sample. This is supported by Onyeagocha (1973), who additionally notes that inhomogeneity in chromite composition occurs only in samples where chlorite is present. This variation is restricted to the margins of chromite crystals and has been attributed to incipient alteration of chromite to ferritchromit. No example of this alteration was observed in this study. Previous work by Onyeagocha (1973) has shown two distinct but parallel trends for chromite in the dunite and veins and for chromite in pods and lenses. These trends differ in the Mg/(Mg+Fe) ratio, which is higher for podiform chromite than for chromite from the main dunite. No samples of the disseminated chromite from the main dunite were analysed in this study.

A correlation between increasing Cr/(Cr+Al+Fe^{+3}), and decreasing Mg/(Mg+Fe), has been demonstrated in podiform chromites by Irvine (1967), Himmelberg and Coleman (1968), and Loney et al (1971). However, figure 5 shows that while this same general relationship is maintained in the Twin Sisters dunite, the correlation of

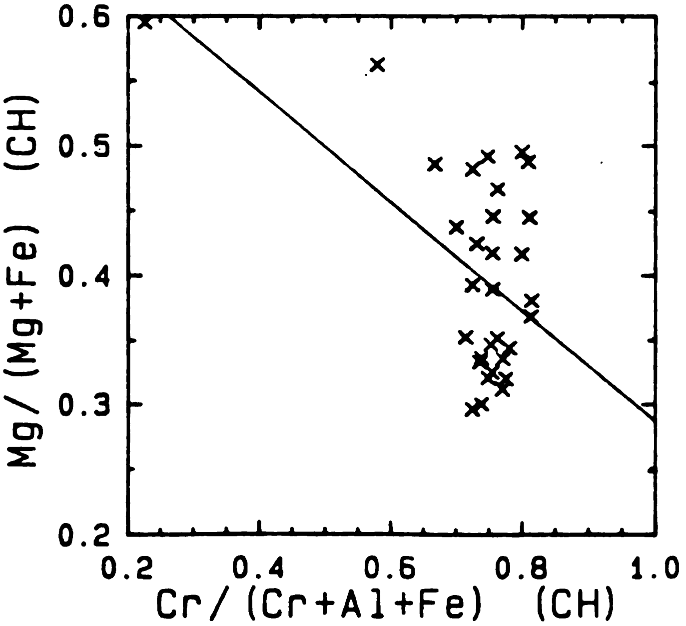

Figure 5. Mg fraction vs Cr fraction in chromite.

$Cr/(Cr+Al+Fe^{+3})$ and $Mg/(Mg+Fe)$ is poor (R=-0.51). This is most likely due to subsolidus reequilibration of the chromite divalent cations with surrounding silicates, and is discussed in detail in later section of this work.

Thayer (1969, 1970) noted that the reciprocity between Cr_2O_3 and Al_2O_3 in podiform chromites is both striking and prominent. This is also true for the chromite pods of this study which give a correlation of R=-0.89 for Al_2O_3 vs Cr_2O_3. He has also remarked that a major decrease in total Fe with increasing Cr_2O_3 content is indicated in stratiform chromites, in contrast with relatively constant total Fe in podiform chromites. Chromites in the Twin Sisters dunite, both podiform and disseminated, show a slight increase in total Fe with an increase in the chromium content. Previous workers have thought this to be indicative of reequilibration between the chromite crystals and the coexisting olivines crystals (Irvine, 1967; Himmelberg and Coleman, 1968; Thayer, 1969; Loney et al, 1971; Onyeagocha, 1973; Cassard et al, 1981; Kanevsky, 1984).

Ramp (1961) described high aluminum chromites in the Josephine peridotite massif, in southwest Oregon. At Woodcock Mountain, he reports both high chromium and low chromium, high aluminum chromites ranging from 62.4% Cr_2O_3 and 11.7% Fe^{TOT} to 16.8% Cr_2O_3 with 9.78% Fe^{TOT} respectively. Thayer (1969) suggested local variations of this magnitude are caused by mixing of peridotite mush that carried fragments of chromite from widely separated primary layers during reemplacement. Variations of this magnitude were not found in the Twin Sisters dunite either on a local or broader scale. In fact, the closeness in composition of chromites from all over the body, in addition to to essentially constant composition of olivine and pyroxene (Onyeagocha, 1973), would support Ragan's (1967) interpretation that the Twin Sisters dunite was emplaced in the solid state.

$Fe^{+2/+3}$ determinations in chromite are recalculated from total Fe assuming perfect spinel stoichiometry since deviations from the formula $R_1^{+2}R_2^{+3}O_4$ are negligible (Irvine, 1965). Ionic proportions are then calculated on the basis of 32 oxygen atoms (table 5). On this basis, a perfect chromite analysis has $X + Y + Z = 24$ where X = the sum of all divalent cations, Y = the sum of all trivalent cations, and Z = the sum of all quadrivalent cations. In addition, $X = 8 + Z$, and $Y = 16 - 2Z$. It should be noted that since the ferric- ferrous ratio is determined in this manner, the chromite analysis is always perfect, i.e. a sum total of 24 cations.

Table 4. Chromite Data

I.D.	TiO_2	V_2O_3	Cr_2O_3	MnO	FeO	NiO	Al_2O_3	MgO	Fe_2O_3	TOTAL
X-1	0.15	0.07	57.43	0.10	16.03	0.06	11.48	11.44	2.85	99.59
X-2	0.14	0.12	52.40	0.13	16.01	0.07	14.83	11.81	4.37	99.87
X-3	0.22	0.17	54.02	0.12	17.00	0.08	11.69	10.82	5.77	99.89
X-4	0.23	0.14	51.04	0.21	20.51	0.08	12.81	8.63	6.54	100.19
X-5	0.29	0.12	50.64	0.19	18.48	0.10	13.83	10.02	6.36	100.03
X-6	0.16	0.09	57.82	0.12	17.59	0.07	10.58	10.24	2.64	99.30
X-7	0.24	0.13	54.55	0.21	19.64	0.08	10.19	8.89	6.05	99.96
X-8	0.22	0.09	54.59	0.20	18.90	0.08	11.76	9.51	4.40	99.76
X-9	0.13	0.07	58.36	0.15	17.15	0.06	9.75	10.52	3.52	99.71
X-10	0.16	0.14	52.28	0.21	20.14	0.12	10.68	8.63	7.80	100.14
X-11	0.22	0.08	54.21	0.12	16.11	0.06	12.90	11.53	4.62	99.84
X-12	0.10	0.16	51.39	0.14	17.21	0.08	15.95	11.11	3.56	99.70
X-13	0.11	0.11	15.65	0.09	12.09	0.38	49.77	17.78	3.75	99.72
X-14	0.22	0.10	41.41	0.14	12.06	0.14	26.65	15.51	3.46	99.69
X-15	0.21	0.10	47.64	0.09	14.30	0.07	20.78	13.52	2.92	99.63
X-16	0.05	0.20	51.82	0.19	19.31	0.05	14.57	9.61	3.96	99.76
X-17	0.12	0.25	52.97	0.18	18.75	0.07	14.44	9.92	2.92	99.62
X-18	0.06	0.17	55.47	0.17	18.61	0.05	11.17	9.73	4.36	99.78
X-19	0.04	0.22	52.63	0.20	19.73	0.04	14.11	9.29	3.52	99.78
X-20	0.08	0.15	58.01	0.07	13.36	0.12	11.30	13.11	3.17	99.35
X-21	0.08	0.12	58.59	0.06	13.59	0.11	11.15	12.93	2.63	99.27
X-22	0.09	0.11	54.00	0.10	13.77	0.06	15.35	13.33	2.82	99.65
X-23	0.03	0.18	52.30	0.10	14.13	0.10	15.77	13.15	4.04	99.80
X-24	0.08	0.16	54.59	0.19	19.60	0.06	12.81	9.21	2.95	99.64
X-25	0.10	0.10	58.67	0.14	14.97	0.07	10.29	11.99	3.33	99.66
X-26	0.06	0.16	53.24	0.12	19.51	0.02	12.96	9.37	4.32	99.76
X-27	0.06	0.13	54.22	0.22	18.36	0.09	12.06	9.93	4.77	99.84
X-28	0.10	0.11	49.55	0.14	15.91	0.10	20.35	12.37	0.82	99.45
X-29	0.21	0.10	54.35	0.09	15.19	0.11	13.82	12.21	3.66	99.74
X-30	0.07	0.12	54.66	0.06	14.65	0.05	15.99	12.82	0.95	99.39
X-31	0.06	0.24	51.98	0.16	19.20	0.07	14.54	9.68	3.83	99.76
MAXIMUM	0.29	0.25	58.67	0.22	20.51	0.38	49.77	17.78	7.80	100.19
MINIMUM	0.03	0.07	15.65	0.06	12.06	0.02	9.75	8.63	0.82	99.27
AVERAGE	0.13	0.14	52.27	0.14	16.83	0.09	14.98	11.25	3.89	99.72
ST.DEV.	0.07	0.05	7.64	0.05	2.51	0.06	7.37	2.11	1.49	0.22

Table 5. Chromite Ionic Proportions

I.D.	Ti	V	Cr	Mn	Fe
X-1	0.0285	0.0138	11.8677	0.0221	3.5406
X-2	0.0260	0.0243	10.6283	0.0285	3.4697
X-3	0.0425	0.0361	11.1856	0.0260	3.7787
X-4	0.0455	0.0298	10.6524	0.0474	4.5907
X-5	0.0574	0.0251	10.4379	0.0428	4.1047
X-6	0.0317	0.0185	12.1241	0.0261	3.9439
X-7	0.0478	0.0274	11.5161	0.0470	4.4490
X-8	0.0437	0.0197	11.4083	0.0448	4.2350
X-9	0.0265	0.0153	12.2178	0.0332	3.8310
X-10	0.0311	0.0299	11.0223	0.0465	4.5307
X-11	0.0419	0.0162	11.1116	0.0270	3.5488
X-12	0.0183	0.0327	10.4359	0.0313	3.7206
X-13	0.0182	0.0182	2.6759	0.0172	2.2097
X-14	0.0401	0.0197	7.8239	0.0273	2.4642
X-15	0.0391	0.0199	9.3363	0.0178	3.0160
X-16	0.0102	0.0423	10.6897	0.0413	4.2277
X-17	0.0243	0.0527	10.9189	0.0404	4.1182
X-18	0.0115	0.0365	11.6008	0.0379	4.1302
X-19	0.0079	0.0462	10.8982	0.0453	4.3307
X-20	0.0146	0.0305	11.8867	0.0143	2.9159
X-21	0.0160	0.0256	12.0336	0.0134	2.9748
X-22	0.0179	0.0230	10.8323	0.0213	2.9454
X-23	0.0053	0.0366	10.4766	0.0219	2.9990
X-24	0.0149	0.0341	11.3853	0.0425	4.3440
X-25	0.0197	0.0212	12.1358	0.0317	3.3000
X-26	0.0115	0.0338	11.0799	0.0256	4.3107
X-27	0.0127	0.0281	11.2768	0.0484	4.0568
X-28	0.0196	0.0221	9.8050	0.0301	3.3567
X-29	0.0396	0.0212	11.0525	0.0205	3.3214
X-30	0.0138	0.0239	10.9889	0.0125	3.1332
X-31	0.0124	0.0500	10.7181	0.0342	4.2040
MAXIMUM	0.0574	0.0527	12.2178	0.0484	4.5907
MINIMUM	0.0053	0.0138	2.6759	0.0125	2.2097
AVERAGE	0.0255	0.0282	10.7169	0.0312	3.6807
ST.DEV	0.0140	0.0101	1.7339	0.0112	0.6333

Table 5 (cont'd.)

I.D.	Ni	Al	Mg	Fe	TOTAL
X-1	0.0135	3.5356	4.4561	0.5232	24.0010
X-2	0.0134	4.4838	4.5184	0.8089	24.0013
X-3	0.0171	3.6093	4.2237	1.0820	24.0009
X-4	0.0168	3.9860	3.3956	1.2376	24.0016
X-5	0.0212	4.2484	3.8927	1.1711	24.0013
X-6	0.0156	3.3069	4.0493	0.4850	24.0011
X-7	0.0163	3.2056	3.5384	1.1534	24.0010
X-8	0.0179	3.6651	3.7489	0.8176	24.0009
X-9	0.0128	3.0442	4.1526	0.6676	24.0010
X-10	0.0247	3.3581	3.4326	1.5252	24.0011
X-11	0.0131	3.9404	4.4577	0.8448	24.0015
X-12	0.0157	4.8288	4.2552	0.6629	24.0014
X-13	0.0663	12.6810	5.7292	0.5857	24.0014
X-14	0.0269	7.5052	5.5257	0.5682	24.0012
X-15	0.0142	6.0703	4.9955	0.4924	24.0014
X-16	0.0103	4.4807	3.7357	0.7637	24.0016
X-17	0.0143	4.4359	3.8550	0.5415	24.0012
X-18	0.0102	3.4835	3.8364	0.8540	24.0010
X-19	0.0084	4.3540	3.6265	0.6839	24.0011
X-20	0.0246	3.4518	5.0643	0.5988	24.0015
X-21	0.0238	3.4133	5.0083	0.4926	24.0014
X-22	0.0122	4.5912	5.0422	0.5155	24.0010
X-23	0.0204	4.7097	4.9669	0.7645	24.0009
X-24	0.0132	3.9819	3.6202	0.5657	24.0018
X-25	0.0156	3.1713	4.6759	0.6300	24.0012
X-26	0.0047	4.0209	3.6746	0.8398	24.0015
X-27	0.0186	3.7406	3.8929	0.9265	24.0014
X-28	0.0201	6.0034	4.6160	0.1281	24.0011
X-29	0.0223	4.1895	4.6804	0.6542	24.0016
X-30	0.0108	4.7928	4.8608	0.1645	24.0012
X-31	0.0145	4.4702	3.7641	0.7340	24.0016
MAXIMUM	0.0663	12.6810	5.7292	1.5252	24.0018
MINIMUM	0.0047	3.0442	3.3956	0.1281	24.0009
AVERAGE	0.0177	4.4761	4.2997	0.7253	24.0013
ST.DEV	0.0104	1.7961	0.6354	0.2932	0.0002

MAGMATIC AND REEQUILIBRATION CONDITIONS

The original magmatic conditions of temperature and partial oxygen pressure are difficult to estimate in non-volcanic igneous systems. To date, no reliable geothermometer for such systems exist. Oxygen geobarometers do exist and are based on determinations of rare earth element concentrations (Moller and Muecke, 1984; Drake, 1975; Philpotts, 1970; Philpotts and Schnetzler, 1968). This method is possible due to the lack of chemical reequilibration of the REEs during cooling (Green et al, 1969). This method could not be applied to the Twin Sisters dunite however, because of the very low concentrations of REEs present. These concentrations, on average 4 ppb as reported by the U.S.G.S., are insufficient to make any determinations about the variablity of the partial pressure of oxygen within the dunite, and are below the limits of detection with the methods presently used at Michigan State University.

The reequilibration temperature and corresponding partial pressure of oxygen value has been calculated for all olivine - chromite pairs and are reported in table 6. In addition, attempts were made to place constraints on both the rate of cooling and the depth of formation of the Twin Sisters dunite although both efforts yielded unsatisfactory values, and are discussed later.

The reequilibration temperatures are calculated from the olivine - chromite geothermometer of Jackson (1969) with modifications to the equations from Roeder et al (1979), Engi and Evans (1980), Roeder et al (1980), Jamieson and Roeder (1984).

$$T(K)=\frac{\alpha 3480 + \beta 1018 - \gamma 1720 + 2400}{\alpha 2.23 + \beta 2.56 - \gamma 3.08 - 1.47 + \mathrm{Ln}(K)} \; ; \; K=\left[\frac{Mg}{Fe}\right]_{OL}\left[\frac{Fe}{Mg}\right]_{CH}$$

$$\text{Spinel fractions: } \alpha=\frac{Cr}{Cr+Al+Fe} \; ; \; \beta=\frac{Al}{Cr+Al+Fe} \; ; \; \gamma=\frac{Fe}{Cr+Al+Fe}$$

Work by Jamieson and Roeder (1984) has clearly demonstrated that the geothermometer records the lowest temperature at which chemical equilibration stops; which is the reequilibration temperature in non - volcanic rocks. For the Twin Sisters dunite, these temperatures define a region that is completely subsolidus, ranging from a high of 844 degrees centigrade to a low of 579 degrees with an average value of 707 degrees. It should also be mentioned that the olivine - pyroxene geothermometer of Hervig and Smith (1982) gives values very close to that of the modified Jackson (1969) geothermometer for the pyroxene analyses reported by Onyeaghoca (1973).

The reequilibration values for the partial pressure of oxygen were calculated from the spinel composition model proposed by Y. Poltavets (1976, 1983) (table 6).

$$\mathrm{Log}(PO_2)=\frac{32730}{T(K)} + 13.12 - 4\log(x) - 2\log\frac{2+x}{3} + \log\frac{4-x}{3}$$

Where x = the end member percentage of spinel.

For the purposes of the calculations, the end - member percentages in the spinels were calculated according to rules detailed by Poltavets (1983). Those cations not discussed by Poltavets were handled according to the observations of Schuiling and Feenstra (1980), and the methods of Stormer (1983). The temperature estimates according to the modified Jackson geothermometer were used in the determination of the oxygen partial pressure values. While the temperature estimates from the equations of Poltavets were in excellent agreement with the examples given by Spenser and Lindsey (1980), discrepancies arose when the Poltavets temperature estimates were compared to the modified Jackson estimates. The remainder of Poltavets equations for the determination of oxygen partial pressures are applicable to systems like the Twin Sisters dunite and produce geologically reasonable estimates when compared to values in the literature for similar systems (Hill 1980, Snethlage and Klemm 1978).

Unsuccessful attempts were made to determine both the rate of cooling (geospeedometry) and the depth of formation. Considerable work has been done on determining the cooling rates of ultramafic rocks by Ozawa (1984), Lasaga (1983), Onorato et al (1978), Taylor et al (1977). All of this work to date has been dependent on zoning of Fe^{+2} and Mg in coexisting olivine and spinel crystals. Because the olivine and chromite crystals of the Twin Sisters dunite exhibit no zoning, (this study; Onyeagocha 1973) it is not possible to estimate the cooling rates in the dunite. Work has also been done on methods determining the depth of formation of mafic and ultra- mafic rocks by Stroh (1976). The calculations for the Twin Sisters dunite yield negative pressures, which are of course, unreasonable.

Partitioning values (Kds) are calculated according to the general format:

$$Kd = \frac{\text{Olivine concentration}}{\text{Chromite concentration}}$$

using oxide weight percent values for all coexisting olivine-chromite pairs. The K value used in the reequilibration computations is determined from the equation:

$$K_{\text{VALUE}} = \left(\frac{X_{Mg}}{X_{Fe}}\right)_{\text{OLIVINE}} \left(\frac{X_{Fe}}{X_{Mg}}\right)_{\text{CHROMITE}}$$

These calculations are made using ionic proportions. The K value is dependent on the composition of the spinel crystal, specifically the value Al/(Al+Cr+Fe), (Marakushev, 1981; Jameison et al, 1984) in samples reflecting original magmatic composition, although this is not the case for samples from the Twin Sisters dunite, and is discussed in detail in a later section.

Table 6. Calculated Data

I.D.	T.K	log.pO2	Ni.kd	Mn.kd	Cr.kd	K.kd	Al.Kd
X-1	751.57	-17.19	-	0.84	-	0.0921	-
X-2	754.34	-16.97	10.83	0.63	0.0078	0.1054	0.0270
X-3	756.76	-16.78	-	0.96	-	0.0979	-
X-4	683.50	-19.14	8.63	0.56	0.0001	0.0729	0.0000
X-5	715.00	-18.09	6.54	0.70	0.0012	0.0878	0.0043
X-6	727.79	-17.97	9.56	0.78	0.0025	0.0799	0.0236
X-7	703.16	-18.49	-	0.54	-	0.0729	-
X-8	692.89	-19.00	12.61	0.54	0.0001	0.0714	0.0000
X-9	673.07	-19.77	-	0.34	-	0.0585	-
X-10	675.53	-19.29	-	0.54	-	0.0659	-
X-11	730.39	-17.72	13.17	0.80	0.0024	0.0891	0.0000
X-12	736.62	-17.59	0.09	0.94	0.0025	0.1005	0.0000
X-13	745.79	-17.34	1.79	1.53	0.0005	0.2561	0.0026
X-14	735.04	-17.69	6.81	0.56	0.0092	0.1359	0.0045
X-15	706.53	-18.67	-	0.81	-	0.1002	-
X-16	693.87	-18.98	12.93	0.66	0.0030	0.0788	0.0266
X-17	690.54	-19.20	10.50	0.55	0.0012	0.0760	0.0000
X-18	670.19	-19.79	15.50	0.56	0.0001	0.0617	0.0000
X-19	684.81	-19.33	18.19	0.52	0.0001	0.0736	0.0000
X-20	699.87	-18.85	-	1.17	-	0.0710	-
X-21	680.50	-19.58	-	0.70	-	0.6310	-
X-22	844.05	-14.54	-	1.21	-	0.1497	-
X-23	579.18	-23.53	7.38	0.03	0.0175	0.0401	0.0615
X-24	695.29	-19.02	-	0.56	-	0.0737	-
X-25	799.53	-15.71	-	0.62	-	0.1093	-
X-26	682.78	-19.34	-	1.03	-	0.0706	-
X-27	703.85	-18.56	-	0.64	-	0.0766	-
X-28	695.67	-19.21	9.04	0.51	0.0042	0.0918	0.0064
X-29	675.46	-19.69	9.19	0.94	0.0026	0.0686	0.0123
X-30	635.57	-21.42	21.67	0.97	0.0276	0.0560	0.0488
X-31	698.04	-18.85	-	0.66	-	0.0803	-
MAXIMUM	844.05	-14.54	21.67	1.53	0.0276	0.6310	0.0615
MINIMUM	579.18	-23.53	0.09	0.03	0.0001	0.0401	0.0000
AVERAGE	707.01	-18.62	10.26	0.72	0.0049	0.1063	0.0128
ST.DEV	47.47	1.61	5.34	0.28	0.0074	0.1046	0.0187

THEORIES OF CHROMITE COMPOSITIONAL VARIATION

Most investigators attribute the variation in chromite composition between pods to one of three theories. These are: 1) Subsolidus reequilibration of chromite with adjacent silicates (Henderson, 1975; Oen et al, 1979; Henderson et al, 1981); 2) Reactions of cumulus chromite with intercumulus liquids (Onyeagocha, 1973; Ridley, 1977; Hamlyn et al, 1979; Henderson et al, 1981); 3) Primary magmatic variations which include: A) fractional crystallization processes, B) localized variations in the parental magma due to constrictive flow and convection associated with ophiolites, and C) fluctuations in magmatic conditions, i.e. pressure, temperature and oxygen fugacity (Ulmer, 1969; Hill et al, 1974; Hamlyn et al, 1979; Lago et al, 1982; Sack, 1982; LeBlanc et al, 1983). Primary magmatic variations would also account for the recent theory of pod emplacement in the solid state because the pods crystallize over a wide area and are brought together only when injected into the plastic dunite (Thayer 1969; Cassard et al 1980; Ceuleneer and Nicolas 1985).

It is important to note that each of these theories manifests itself differently (fig. 6), because each one operates in a different region of the phase diagram; i.e. primary magmatic variations occur totally above the liquidus, requilibration with intercumulus liquids occurs in the region of crystals plus liquid, and subsolidus reequilibration occurs totally below the solidus. However, all three have the potential of causing significant variations in the composition of the chromite. It should be noted that it is possible for these processes to operate either in concert or individually within the chromite deposit.

The first two theories imply a passive in situ change of an initially homogeneous chromite, due to reequilibration with adjacent crystals or liquid. Reequilibration, whether it occurs with adjacent silicate crystals or with an intercumulus liquid, would produce the following results: A) high correlation between partitioning values (Kds) and reequilibration conditions, B) a high correlation between inter-mineral elemental ratios and C) a high correlation between intra-mineral elemental ratios and the reequilibration conditions. The first two theories differ, however, in the following way. Subsolidus reequilibration will show all crystals to be very similiar in composition and will show 'normal' concentrations of trivalent cations in the olivine crystals; i.e. trivalent cations will appear as trace elements. Reequilibration with intercumulus liquids will show petrographic evidence of the presence of an intercumulus liquid phase, higher than predicted concentrations of incompatible elements in the olivine crystals, and compositional variations in the olivine.

The third case depicts the dynamic creation of chemically unique zones in the magma chamber from which chromites of differing compositions crystallize. High correlations would be expected between inter and intra-mineral elemental ratios and the magmatic conditions. It would also yield satisfactory multiple linear regession models of chromite compositions as a function of fractional crystallization. It should be noted that while in theory it is possible to model olivine compositions using multiple linear regression, in practice it is not possible due to the overwhelming dominance of Fe and Mg in the olivine structure.

DISCUSSION

Examination of major and minor element data for both the chromite in the pod structures and the attendant olivine has shown that, in many respects, the chromite deposits are typical of podiform chromite deposits worldwide. Olivine major element composition is remarkably consistent over individual grains as well as over the entire 16 kilometer length of the body. Minor element data is slightly less consistent, most notably with regards to values of chromium and aluminum but shows no discernable zoning pattern over the area of the dunite body. Major element determinations for the chromite shows a variation in the ratios Al/Cr and Mg/Fe between pods, however within both pods and individual grains, there is no variation (This study; Onyeagocha, 1973). Minor element data for the chromite also shows marked variablity between pods but in no case do any of the minors ever comprise more than one percent of crystal composition. As with the olivine, no pattern for the variation could be detected over the dunite's area.

Subsolidus reequilibration between adjacent crystals

Subsolidus reequilibration produced a distinct, discernable effect on the compositions of coexisting chromite and olivine crystals. Reequilibration affected the partitioning of both the major and minor divalent cations (X^{+2}) between chromite and olivine as well as their bulk concentrations. Additionally, reequilibration also affected the intermineral partitioning of the trivalent cations (Y^{+3}) and their concentrations in olivine. Significantly, trivalent concentrations and intramineral ratios in chromite do not appear to be affected by subsolidus reequilibration.

<u>Major divalent cation concentrations.</u> Figure 6 demonstrates the strong positive correlation (R=0.88) between the reequilibration temperature and the partitioning coefficient for the Mg/Fe^{+2} ratio between chromite and olivine (K value). This is a complex relationship in which the relative proportions of Fe^{+2} to Mg in one mineral phase are dependent on both the relative proportions of Fe^{+2} to Mg in the other mineral phase and the reequilibration temperature. Figures 7,8, and 9 show that Fe^{+2} and Mg concentrations cannot be adequately described solely as functions of reequilibration temperature or intermineral X^{+2} concentrations. These three figures all demonstrate

increased scatter and lower correlation coefficients (R=0.34, R=-0.51, R=0.70 respectively) when compared against the graph of reequilibration vs K value (figure 6).

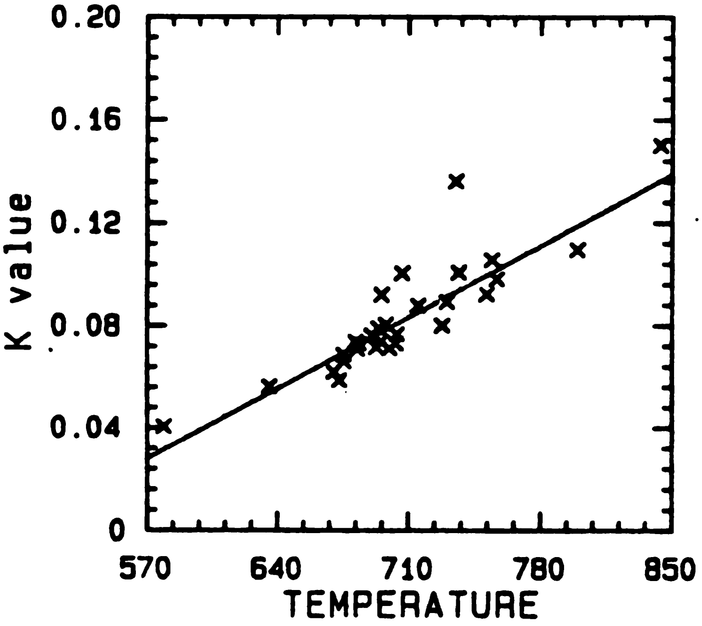

Figure 6. K value vs reequilibration temperature.

It is important to note that research by Marakushev (1981) and Jamieson et al (1984) indicate that in samples of original magmatic composition, the K partitioning value is a direct function of the composition of the trivalents in the spinel phase. Figure 10 shows clearly that this is not the case for the chromite pods of the Twin Sisters dunite. The correlation between the Al^{+3} fraction and the K partitioning value is poor (R=0.51) with considerable scatter present in the plot of the data points. Both the lower correlation value and the high

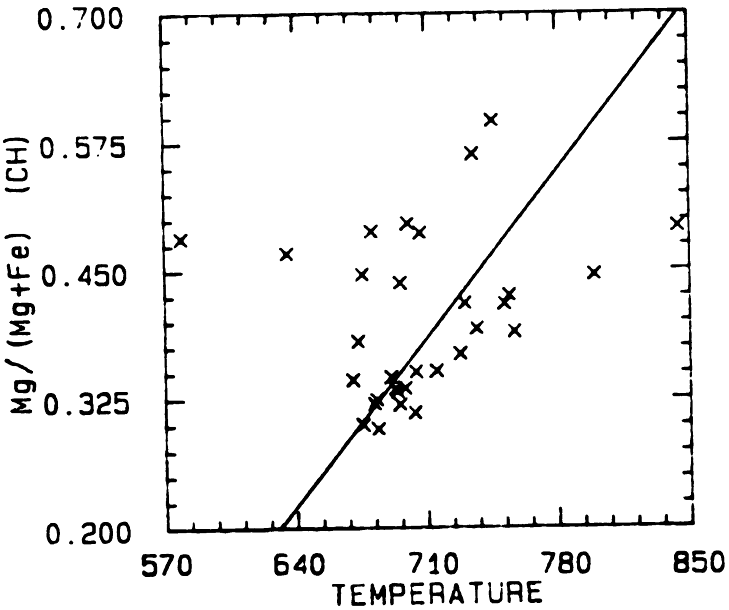

Figure 7. Mg/(Mg+Fe) vs reequilibration temperature for chromite.

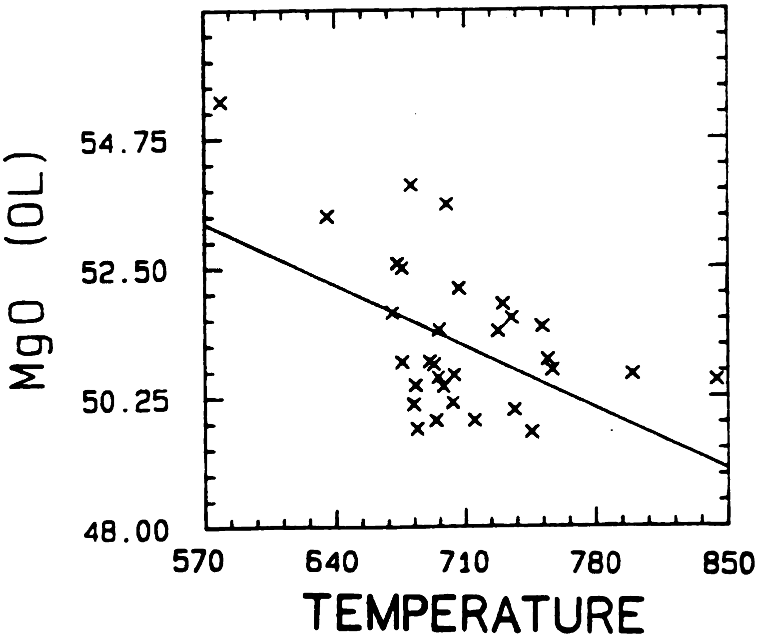

Figure 8. MgO vs reequilibration temperature for olivine.

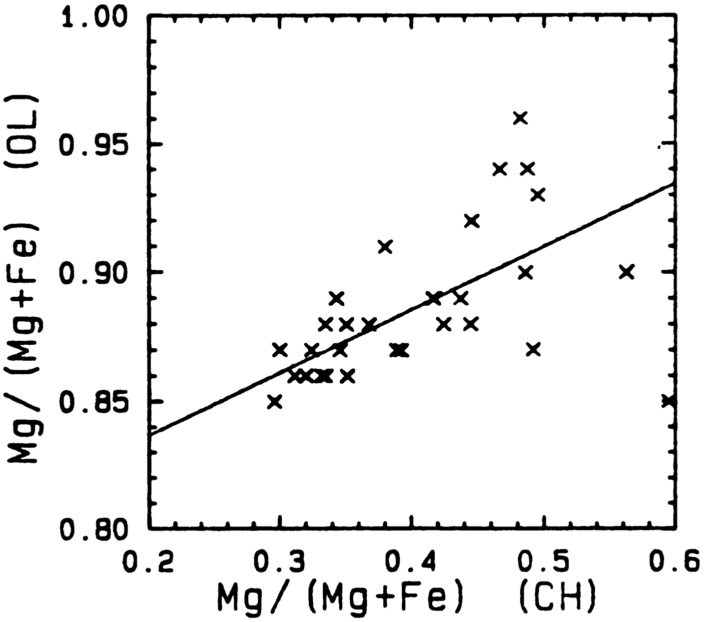

Figure 9. Mg fraction for olivine vs Mg fraction for chromite.

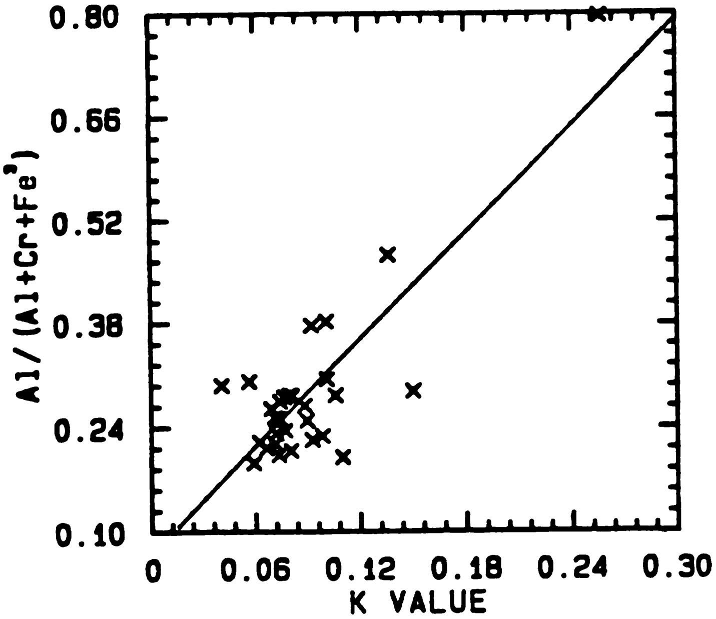

Figure 10. K partitioning value vs chromite Al fraction.

degree of scatter in figure 10 are indicative of a subsolidus reequilibration imprint on original magmatic processes.

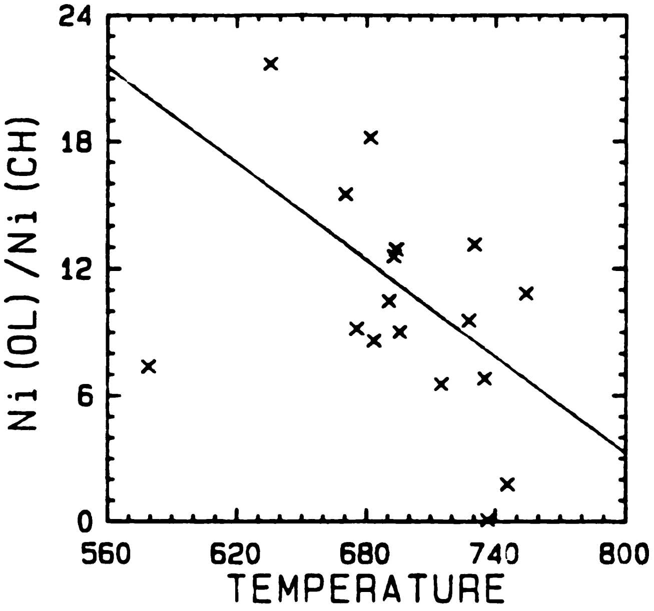

Figure 11. Ni Kd vs reequilibration temperature.

Minor divalent cation concentrations. The partitioning of nickel and manganese between chromite and olivine are also affected, to varying degrees, by the reequilibration temperature for the same reason as magnesium and iron; an abundance of suitable structural sites in both mineral phases. Figure 11 shows a negative trend between the nickel Kd and the reequilibration temperature (R=-0.74), which is to be expected in view of chromite's high crystallization temperature compared to olivine, and nickel's high compatibility (Cox et al, 1979). Note that nickel does not tend to follow magnesium patterns (R=0.47, fig.12), as indicated by

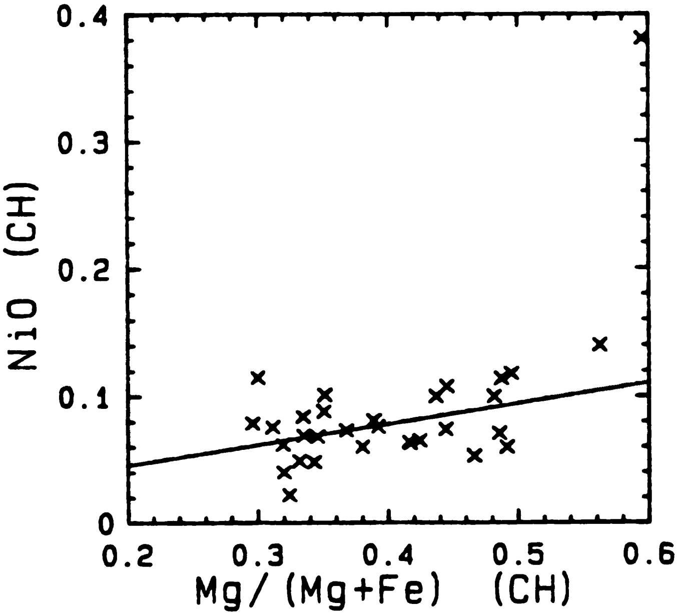

Figure 12. NiO vs Mg/(Mg+Fe) for chromite.

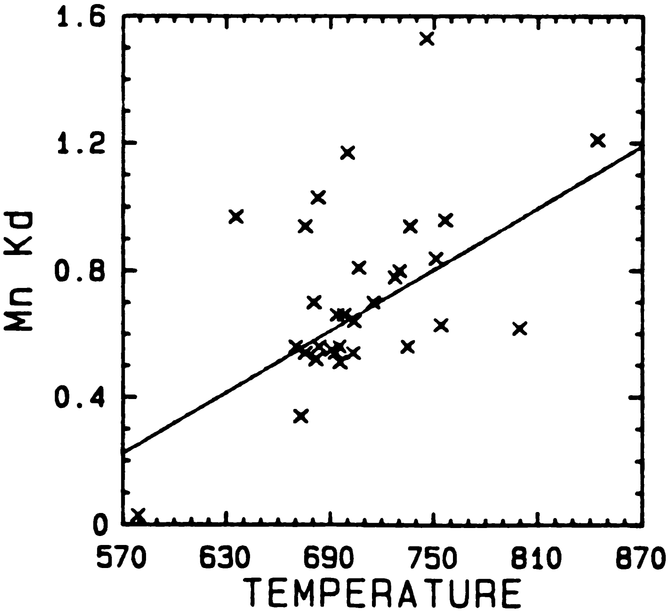

Figure 13. Mn partitioning vs
reequilibration temperature.

Onyeagocha (1973). Rather, nickel concentrations and partitioning appear to be a function of reequilibration temperature (fig.11). Figure 13 shows a slightly lower positive correlation (R=0.69) between the manganese Kd and the reequilibration temperature. MnO is partitioned towards olivine, away from chromite with increasing reequilibration temperature. This observation supports the data of Best (1982), and can be attributed to the large ionic radius of manganese and temperature effects on the olivine crystal structure. Note that figure 13 shows definite scatter in the data points, suggesting that MnO only partially reequilibrated. Although the correlations of figures 11 and 13 (R=-0.74 and 0.69, respectively) are not extremely high, they are regarded as significant in view of the dunite's complex history and the low concentrations of nickel and manganese present.

Trivalent cation concentrations. Reequilibration also affected the trivalent (Y^{+3}) elements in the system. Crystal structure permits only trace concentrations of these cations in olivine, compared to the substantial quantities present in chromite. The two sets of analyses (Y^{+3} for chromite and Y^{+3} for olivine) differ by several orders of magnitude and were obtained using two different machines, each using a different standard (see Analytical Procedures, this study). Consequently, intramineral comparisons of Y^{+3} concentrations are subject to less error and scattering than intermineral comparisons since intramineral comparisons represent internally consistent measurements.

Figure 14 shows a negative correlation (R=-0.72) for the Al partitioning coefficient vs reequilibration temperature, which is significant in view of the preceding discussion. This is consistent with the trend of chromite crystallization (Ulmer, 1969) where the aluminum fraction in chromite increases with temperature. The partitioning coefficient of chromium shows a poor correlation (R=0.52) to the reequilibration temperature (fig.15) with considerable scatter. This is due to the larger ionic radius of chromium, which makes chromium more difficult to incorporate in the olivine crystal lattice than aluminum. This point is illustrated in figure 16, which shows a distinct trend and high correlation (R=0.86) between the Al/Cr ratio of olivine and the reequilibration temperature. Figure 16 indicates that the distribution of Y^{+3} cations in olivine is a function of reequilibration, and that with increasing temperature, aluminum is easier to fit into the olivine structure than chromium. Note that this figure is fundamentally different from figure 14. Whereas figure 14 indicates the actual partitioning of aluminum between chromite and olivine, figure 16 indicates that aluminum,

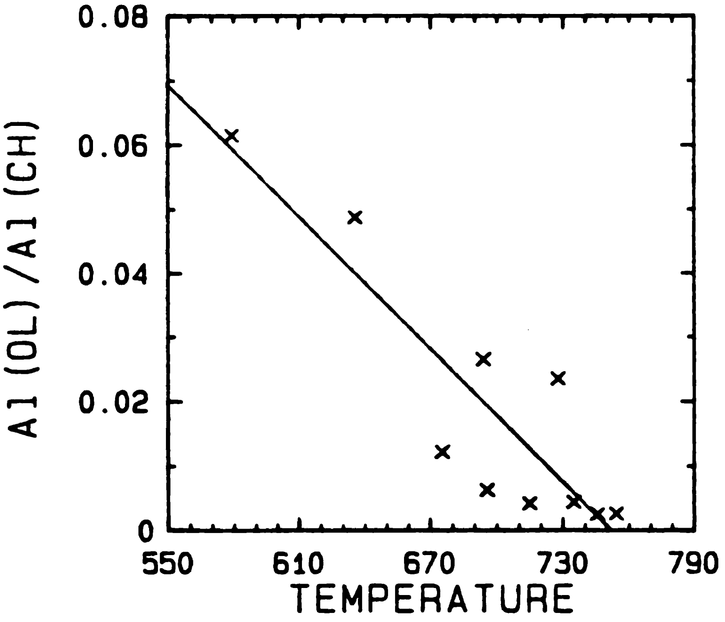

Figure 14. Al partitioning vs reequilibration temperature.

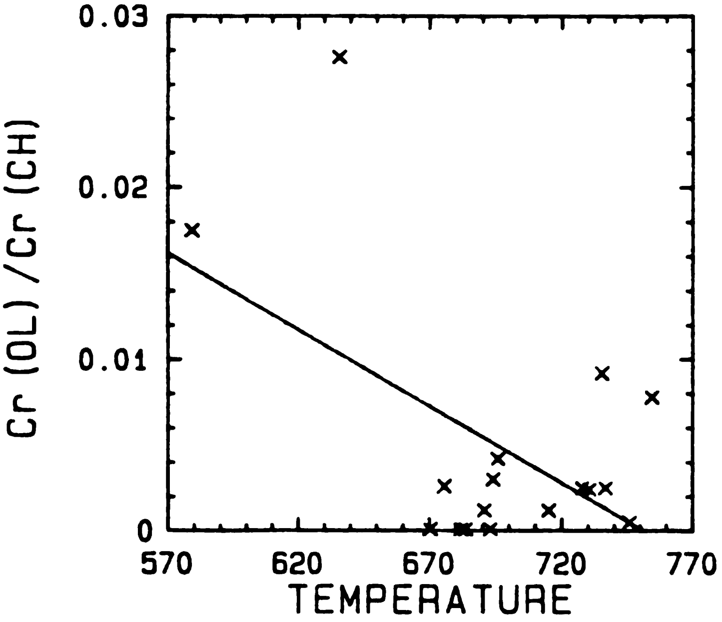

Figure 15. Cr partioning vs reequilibration temperature.

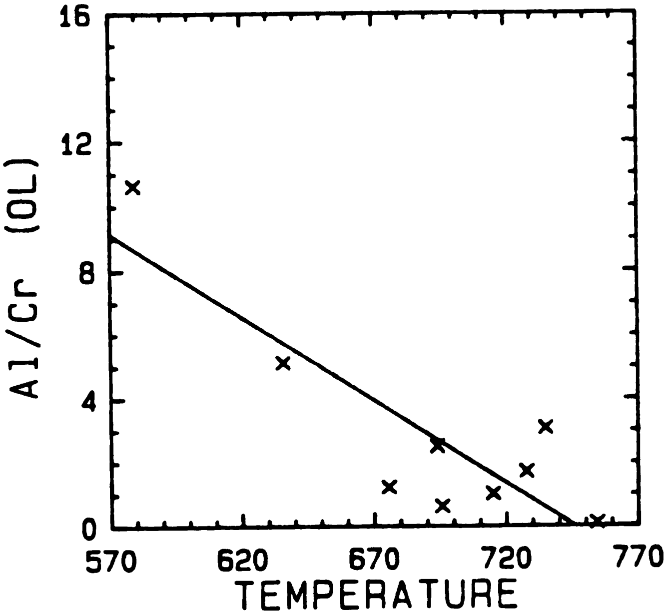

Figure 16. Al/Cr vs reequilibration temperature for olivine.

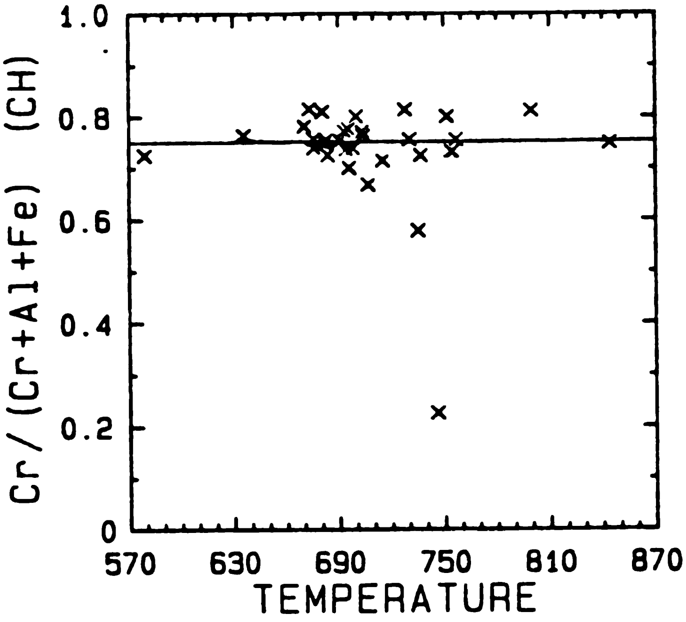

Figure 17. Chromium fraction vs reequilibration temperature for chromite.

by virtue of a smaller ionic radius, will be incorporated into olivine faster than will chromium with increasing temperature.

Reequilibration did not have a significant effect on the trivalent compositions in chromite. The chromium fraction in chromite (fig. 17) demonstrates virtually no correlation ($R=0.008$) with the reequilibration temperature. Chromium content in olivine (fig.18) correlates badly with chromium content in chromite ($R=0.08$). Finally, the Al/Cr ratio (fig. 19) for chromite, which is the heart of the chromite compositional variation problem, has a poor correlation to the reequilibration temperature ($R=0.025$). Collectively, figures 17,18,19 indicate that subsolidus reequilibration did not have a major impact on the compositions of the Y^{+3} cations in chromite. This conclusion is reasonable in view of the lack of suitable structural sites for Y^{+3} cations in olivine, and the absence of a fluid phase during reequilibration (discussed in the next section) to aid in Y^{+3} cation migration.

It is suggested that subsolidus reequilibration offers a satisfactory explanation of the compositional variation of the divalent cations in both mineral phases, and their patitioning coefficients. Additionally, this method also satisfactorily explains the trivalent cation

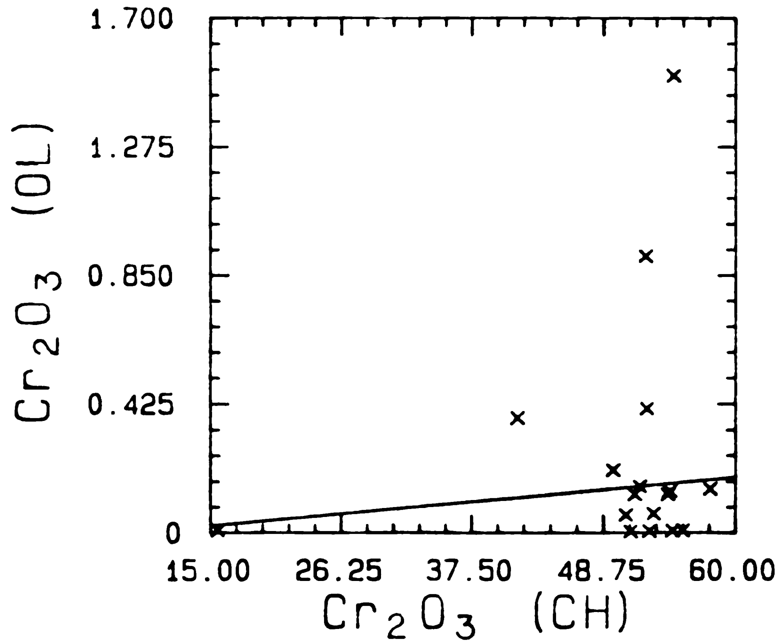

Figure 18. Chromium content in olivine vs chromium content in chromite.

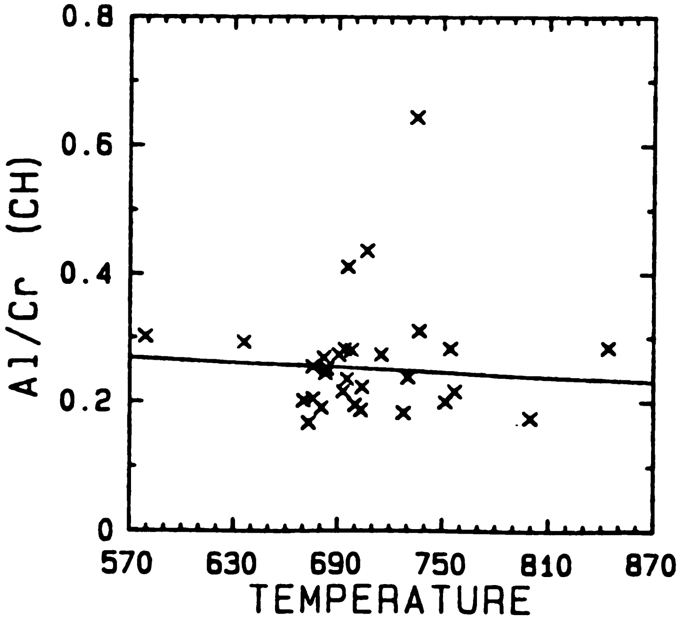

Figure 19. Al/Cr vs reequilibration temperature for chromite.

partitioning coefficients and their concentrations in olivine. However, subsolidus reequilibration cannot account for the trivalent compositions in chromite, most notably the variation in grade of the chromite ore.

Reequilibration with intercumulus liquids

Reequilibration with intercumulus liquids is more difficult to test because the exact composition and/ or presence of such a liquid cannot be determined. Petrographic examinations (Gaudette, 1963; Ragan, 1964; Onyeagocha, 1973; This study) have indicated an absence of mineralogical variation, crystal zoning or alteration around crystal rims. The lack of these features have traditionally been interpreted as an absence of intercumulus liquids in the thick dunite sections, although it must be noted that it could also be interpreted as the presence of trapped intercumulus liquid of dunitic composition. As stated in an earlier section, this would require the existence of olivine crystals with differing compositions from adjacent olivine crystals and anomalous concentrations of trivalent and other incompatible cations compared to cumulus olivine.

In examination of this method as a potential cause of chromite compositional variation, it is important to note that the concentrations of the trivalent cations in the coexisting olivines are low, especially in the case of aluminum (table 3). In no case do the trivalent cation concentrations rise above 1.0% and in several instances concentrations are so low that they are undetectable. In addition, no other incompatible cations were found in the olivine, either in this study or others (Oyeagocha, 1973; Christensen, 1971; Ragan, 1964; Gaudette, 1963). These are not the concentrations one would expect from crystals formed of a trapped intercumulus liquid. Finally, as stated earlier, the olivine in the dunite is very homogeneous, especially on the crystal scale. No olivine crystals of substantially or even moderately different composition were observed in this study or previous studies.

While it is possible to demonstrate that a reequilibration event did occur, it is not possible to generate any support for the idea that the event occurred as a function of intercumulus liquids. In fact, in view of the reequilibration temperatures, there is no reason to suggest the reequilibration event, or any portion of it, occurred anywhere other than within the subsolidus region.

Magmatic variations

Compositional variations due to initial magmatic variations are difficult to demonstrate in view of the extent to which reequilibration has occurred between adjacent chromite and olivine crystals. However, because reequilibration had little effect on the relative concentrations of trivalent cations present in chromite, as already demonstrated, it is possible to examine possible magmatic trends in the distribution of the trivalent cations in chromite.

Conventional multiple linear regression tests were used to model possible fractional crystallization sequences which might account for the variability of the Al/Cr ratio present between different chromite pods. The basic format used was:

Parent = Daughter + End Members

Where parent is the original, high aluminum chromite, daughter is the low aluminum chromite and the end members are pure spinel ($MgAl_2O_4$), magnetite (Fe_3O_4), magnesiochromite ($MgCr_2O_4$), chromite ($FeCr_2O_4$), magnesite ($MgFe_2O_4$). The regression tests were forced through the origin.

The results of the modeling demonstrated that fractional crystallization processes can account for the observed variability in the trivalent cation ratio between chromite pods. The best fit to the model is found using spinel and chromite. These are the most geologically reasonable end - members to be fractionating out to produce low aluminum chromite from high aluminum chromite. All coefficients are geologically reasonable, with spinel fractions varying from 13% to 40% and chromite fractions varying from 3% to 15%. In addition, residuals show variations from 3% to 10%, although most regressions showed residuals below 6%. This method does not point to a specific crystallization sequence, but similar results are true of all high aluminum to low aluminum chromite regressions. These results can be interpreted as a broad crystallization sequence of high aluminum, low chromium spinel to low aluminum, high chromium chromite. This sequence, developed from the best fit regression equation corresponds to the crystallization sequence of Ulmer (1969) and Irvine (1974) of high temperature, high aluminum, low chromium spinels going to lower temperature, low aluminum, high chromium chromite.

Interestingly, the divalent cations do not present a problem for the regressions despite the fact that their distributions and concentrations are a direct function of reequilibration. This suggests that reequilibration resulted in relatively small variations in the divalent cation concentrations. Additionally, this view is further supported by a comparison of Onyeagocha's (1973) data for olivine compositions associated with the main dunite and olivine compositions associated with chromite pods (This Study; Onyeagocha, 1973). From this comparison, it is possible to estimate that reequilibration resulted in less than 4 weight percent variation in either Mg or Fe concentrations.

The fact that the regression equations do not indicate a unique crystallization sequence needs to be addressed. In the regression equation, considerable latitude is given in choosing a parent and daughter before the results become unreasonable. That is, many combinations of high Al chromites and high Cr chromites can be used successfully. This suggests that many of the pods had overlapping crystallization trends but were chemically isolated from each other due to constrictive flow. This has the effect of dividing the parental magma into many smaller individual parental magmas, each undergoing fractional crystallization, each chemically similar to the others but not in chemical contact with the others (Lago et al, 1982).

Proposed model for the origin of chromite compositional variation

The proposed model for the chromite compositional variation is a modified version of a model presented by Dickey (1975), and Lago et al (1982), based on Thayer's (1969) suggestion.

Initially, molten or partially molten material rises from the asthenosphere and possibly the lower lithosphere, at oceanic or marginal basin ridges. As the material rises, the decrease in pressure causes an increase in the degree of melting and the volume of liquid formed. At depths of 15-25 km, the liquid begins to undergo density controlled separation (Ridgen et al, 1984), forming magma bodies capable of generating significant volumes of basaltic magma, and forming a residual peridotite crystal mush. The basaltic liquids continue to rise, with some of these magma bodies forming steeply dipping feeder dikes, pockets of fractionating magma, and pillow lavas (Dickey, 1975).

Dickey (1975) and Lago et al (1982) both state that the zone of magma separation from the forming peridotite crystal mush is a dynamic region that is subject to considerable turbulence during periods of active magmatism. Processes and conditions are subject to sudden and sometimes frequent changes (Lago et al, 1982). Renewals of active magmatism can change precipitation to melting, while the cessation of magmatism can trigger crystal precipitation. Pockets of magma within the peridotite crystal mush are subject to constrictive flow dynamics due to the surrounding mush. Additionally, the mush has the effect of chemically isolating a magma body from other magma bodies present in the mush (Lago et al, 1982). This results in magma bodies of similar composition, undergoing similar processes but effectively isolated from one another (Lago et al, 1982).

Cumulus concentrations of chromite form in magma pockets within the residual peridotite crystal mush. Chromite is formed as a precipitation product from the silicate liquids. It is subject to the fractionation processes of the magma body within which the chromite is forming. Dickey (1975) argued that these magma pockets are long and narrow because they form along plate margins and consequently, the resulting chromite cumulates are long and tabular.

As the chromite pods begin to cool, it begins to sink into the crystal mush. Settling rates are dependent on a number of factors, including pod dimensions, pod density relative to the crystal mush, temperature gradients throughout the crystal mush, and the exact nature of the medium surrounding the pod (Dickey, 1975). Dickey (1975) demonstrated that over a cooling period of one million years, a typical chromite pod could sink more than 600 meters into solidified dunite - harzburgite rock which began cooling near the solidus. Substantially greater distances could be expected from pods sinking in a crystal mush, which would effectively mix the chromite pods together, giving an apparent random distribution.

Emplacement of the peridotite body into the continental crust occurs at near solidus temperatures accompanied by intense flowage in the solid state (Ragan, 1967; Nicolas et al, 1980; Cassard et al, 1981; Ceuleneer et al, 1985). This permits reorientation of the chromite pod structures in a manner predicted by the classification scheme of Cassard et al (1981). Additionally, during this period, extensive reequilibration of the divalent cations occurs between the chromite crystals and the surrounding olivine crystals because of the abundance of suitable structural sites in both minerals. Conversely, trivalent cations retain their original magmatic signature because of a lack of suitable structural sites for trivalent cations in olivine crystals. Therefore, after the dunite is emplaced, the chomite pods will be a hybrid displaying both magmatic trends and reequilibration trends.

CONCLUSIONS

The composition of chromite and olivine associated with the pods are extremely uniform within grains and between grains of the same pod. Olivine has a small variation in composition between pods which can be attributed to the reequilibration processes with adjacent crystals. Compositional variation of the divalent cations in chromite can also be attributed to reequilibration processes with adjacent crystals. This is reasonable in view of the crystal structure requirements of both chromite and olivine for divalent cations.

The compositional variation of the trivalent cations in the chromite show a correlation between their Kds and the reequilibration temperature. This is not sufficient to account for the major variations which the trivalent cations exhibit in the chromite. This is also in agreement with the crystal structure requirements of olivine, which would not allow large concentrations of trivalents to enter the structure. Consequently the olivine could not act as a sink for trivalent cations in the chromite structure. The compositional variation of the trivalent cations in chromite can be satisfactorly explained by fractional crystallization processes operating in a constrictive flow regime within the parental magma.

The proposed model for the compositional variation of chromite describes hybrid pods where the trivalent cation concentrations are the function of original magmatic fractional crystallization processes, and the divalent cation concentrations are the function of reequilibration conditions during emplacement of the dunite host body. Additionally, the apparently random distribution of the pods within the dunite host can be accounted for by the sinking of dense pods into the surrounding crystal mush during initial formation. Pod distribution then, becomes a function of the conditions present in the crystal mush, including temperature gradients, percent crystals present, distribution of pockets of magma within the crystal mush, constrictive flow dynamics, and the frequency and intensity of active magmatism associated with the ridge system.

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