| Πρακτικά 3ου Συνέδριου Μάϊος 1986 | | | |
|---|---|---|---|
| Δελτ. Ελλ. Γεωλ. Εταιρ.<br>Bull. Geol. Soc. Greece | Τομ.<br>XX/2<br>Vol. | σελ.<br>247-257<br>pag. | Αθήνα<br>1988<br>Athens |

# THE CHEMICAL COMPOSITION OF CHROMITE FROM THE SKOYMTSA - XEROLIVADO CHROMITE DEPOSITS, VOURINOS OPHIOLITIC COMPLEX, GREECE, AS A PETROGENETIC INDICATOR.

A.A. ALEVIZOS

Abstract: The mineral composition, texture, and field relation of chromite ores and their serpentinized dunite host at the Skoumtsa-Xerolivado, Mines, Vourinos Complex, Greece, are similar to those of podiform chromite ores hosted by alpinetype peridotites of ophiolites.

An electron microprobe study in those deposits shows that the chromite has average composition of $[(Mg_{.62}Fe^{2+}_{.38})(Cr_{.75}Al_{.19}Fe^{3+}_{.06})_2O_4]$.

Chemical characteristics, such as the high chromium content ( >46 wt.% $Cr_2O_3$ and Cr/Fe wt. ratio > 2), total iron content < 20 wt.%, constancy of the $Fe^{2+}$/Mg atomic ratio, low $Fe_2O_3$ (<8 wt.%), and $TiO_2$ < 0.3 wt.% are in accord with those of chromite from podiform deposits in alpine peridotites.

A few chromite grains are strongly zoned with "ferrit-chromit" margins richer in Cr/(Cr+Al) and poorer in $Mg/(Mg+Fe^{2+})$ (atomic).

Differences in $Mg/(Mg+Fe^{2+})$ ratios (atomic) between disseminated and segregated chromite grains arise from subsolidus re-equilibration after they have crystallized and do not reflect magmatic temperature differences as based on olivinespinel subsolidus relationships (Irvine 1965).

The olivine-spinel geothermometer (Evans and Frost, 1975) based on Mg-$Fe^{+2}$ exchange between the two minerals, shows an average temperature of cessation of the Mg-$Fe^{2+}$ equilibration of 800°C which reflects the subsolidus stage.

Summary: An electron microprobe study in the Skoumtsa-Xerolivado chromite deposits, Vourinos Complex, Greece shows that the chromite has a chemistry similar to that of podiform chromite ores which occur in alpine-type peridotites of ophiolitic origin. Chromite grains are unzoned and chemical hanogeneous and only a few show "ferrit-chromit" margins richer in Cr/(Cr+Al) and poorer in $Mg/(Mg+Fe^{2+})$ (atomic).

Differences in $Mg/(Mg+Fe^{2+})$ ratios (atomic) between disseminated and segregated chromite grains are explained by olivine-spinel subsolidus re-equilibrations (Irvine, 1965) and the olivine-spinel geothermometer (Evans and Frost, 1975), shows an average temperature of cessation of the Mg-$Fe^{2+}$ equilibration of 800°C.

## General Geology and Location of the Deposits

Ultramafic igneous rocks, which are the characteristic rocks of chromite deposits, occur widely in Greece. The Vourinos Complex is located in the Vourinos Mountains approximately 500 Km northwest of Athens, between the cities of Grevena and Kozani in northern Greece. It trends generally northwesterly, parallel to regional tectonic strike and dips southwesterly forming part of the western Balkan ultramafic belt (Moores, 1969).

The ophiolitic rocks of the Vourinos Complex were emplaced over lower Jurassic limestone and terrigenous deposits, now metamorphosed to marble, phyllite and near the contact, ampibolite (Moores, 1969). The ophiolitic sequence includes the following units from bottom to top shown in Figure 1:

Tectonite Zone or Ultramafic Zone composed of harzburgite, dunite, pyroxenite, serpentinite and chromite ore bodies.

Cumulate Rocks including two zones: the Lower Cumulate Zone and Upper Cumulate Zone composed of ultramafic rocks at the base grading to mafic or intermediate rocks at the top.

Noncumulate Plutonic Rocks ranging from ultramafic to mafic.

Diabase Zone composed dominantly of sheeted dikes and massive diabase.

The location of the study is at Skoumtsa-Xerolivado mining area which occupies a part of the Tectonic Zone (Ultramafic Zone), (rectangular area A of Fig.1). The major igneous types of this portion of the complex are harzburgite and dunite with accompanying deposits of chrome spinel. Most chromite deposits are confined to the dunite bodies, and give this area a significant importance for underground mining.

A topographic map of the area with the associated chromite bodies namely 1-13, along with the two major fault zones $F_1$ and $F_2$ is given in Figure 2. These two almost vertical fault zones separate the area into three sections: the North, Central and South Section. All faults shown underground (ug) have been projected at mining level 716 (corresponding to the elevation). The chromite bodies of Central Section are projected at mining level 915 and of South Section at level 716. Four chromite bodies were studied, namely, Bodies 2, 3, 5 and 6 in the South Section of Figure 2. Samples were collected underground in a section which is defined by the rectangular area C of Figure 2, and along the drifts following the ore bodies. Polished thin sections of these samples were studied microscopically to determine mineral textures and mineral identities prior to electron microprobe analysis.

## Petrography

The dunite body which hos the chromite bodies of this study shows varying degrees of serpentinization and nowhere free of serpentine minerals. Degrees of serpentinization range from completely serpentinized matrices to partly serpentinized matrices with olivine relicts present. The serpentinized dunite is generally lacking in pyroxenes. The proportion of chromite to silicates within the dunite body ranges from a few percent in the disseminated ore to nearly 100 percent in the massive chromitite ore. Hand specimens of chromite ores show textures, namely, disseminated, schlieren or banded, and massive.

The disseminated texture consists of a wide percentage range of chromite as relatively uniform, fine-grained single crystals evenly scattered in host silicates.

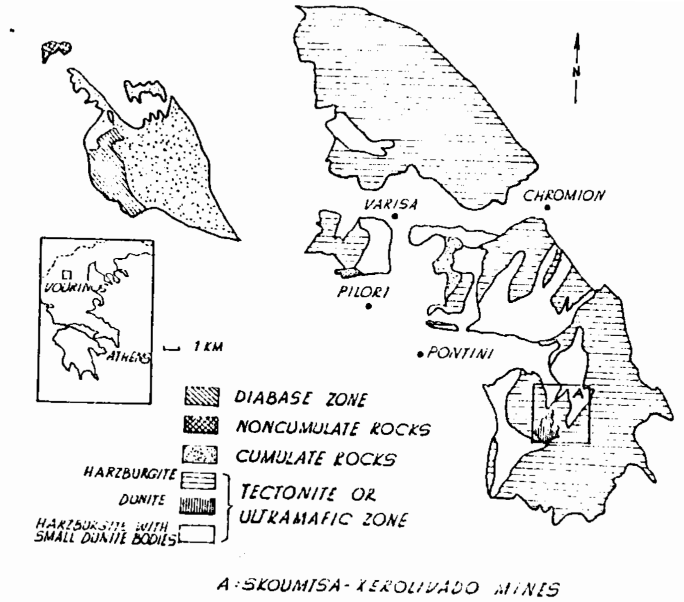

Figure 1. Geologic map of the Vourinos Ophiolitic Complex, Greece.

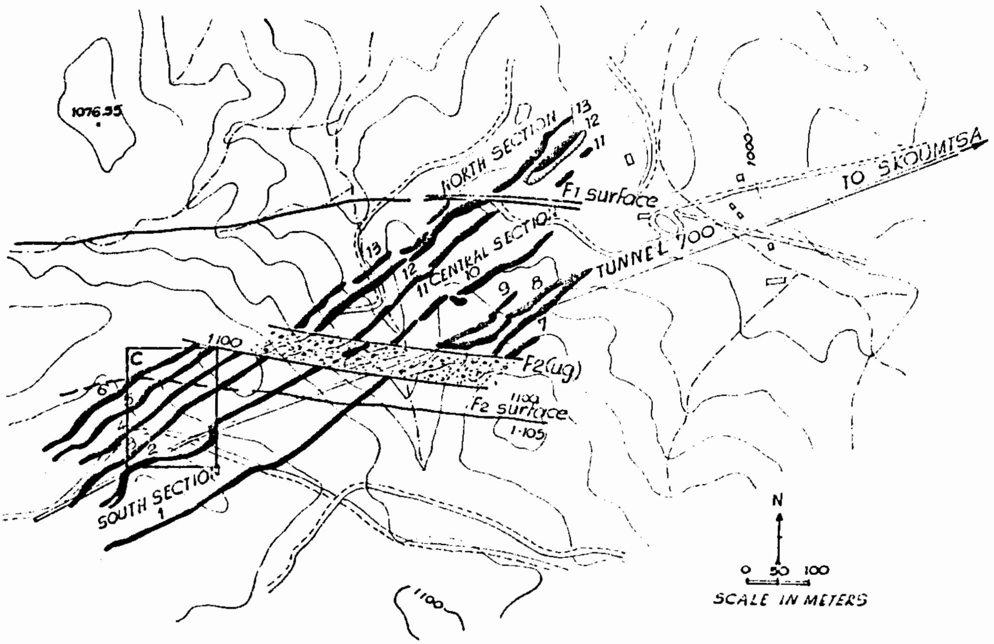

Figure 2. Topographic map showing the chromite deposits of the Skoumtsa-Xerolivado mining area along with major fault zones.

Chromite ores with alternate chromite-rich and silicate-rich rhythmic bands are dominant in all the bodies and is the schlieren or banded texture type typical of the Vourinos Complex. Massive ore is composed of more than 80 percent chromite as relatively coarse granular aggregates of chromite with a small volume of silicates in the interstices. The silicate is usually serpentine, but in places chlorite is also present.

## Mineral Chemistry

All electron microprobe analyses were obtained with a JEOL 733 Superprobe initially at the Institute of Geology and Mineral Exploration (IGME)-Athens, and mostly at the Department of Metallurgy and Materials Science, Lehigh University. Operating conditions were: accelerating voltage 15 Kv, sample current 5 nA (IGME), and 10 and 20 nA (Lehigh Un.), takeoff angle 40°. The data were corrected for matrix and interelement effects by the method of Bence and Albee (1969).

Analyses of disseminated and segregated chromite grains from Bodies 2, 3, 5 and 6 were carried out. Compositional data of disseminated and segregated grains appear in Table 1. Many disseminated grains were analysed from center to rim, and most of them revealed no major changes in Mg, Al, Cr or Fe concentrations from core to edge. Only a few chromite grains are strongly zoned with "ferrit-chromit" rims which are higher in Cr/(Cr+Al)(atomic) and lower in $Mg/(Mg+Fe^{+2})$(atomic). The geochemical distribution of the elements Mg, Al, Cr and Fe has been studied with the electron microprobe by taking X-ray scans of these grains for each element as shown in Figure 3 (enrichment is shown by relatively higher concentration in white dots).

The plotting and comparison of analyses of disseminated and segregated chromite grains is done on the picrochromite-chromite-hercynite-spinel face of the Johnston's spinel compositional prism. In practice the comparison is established simply by plotting Cr/(Cr+Al) against $Mg/(Mg+Fe^{+2})$ (cationic fractions ) as shown in Figure 4-B. In this figure the disseminated chromites (dots) show a consistent $Fe^{2+}$ enrichment and Mg depletion compared with the segregated chromites. However, there is no sharp boundary separating the disseminated and segregated chromites. No significant Cr-Al variations in either the disseminated or the segregated chromites is shown and all analyses plot above 0.76 Cr/(Cr+Al) ratio. The calculated cationic fraction of $Fe^{3+}$ is below 0.05 in all bodies. These analyses generally plot in the overlapping fields of chromites from stratiform and podiform-alpine complexes after Irvine and Findlay (1972) as shown in Figure 4 A, B. However, all of them plot in the alpine-podiform field and only in part plot in the stratiform field.

The following chemical parameters are used to establish the resemblance of the chromites of this study to other podiform deposits which develop in alpine-type peridodites of ophiolites throughout the world and are from Thayer (1964, 1969, 1970, 1973), Irvine (1967), Dickey and Yoder (1972), Dickey (1975), Malpas and Strong (1975), Craig and Vaughan (1981):

1. They are high-chromium chromites (> 46 wt% $Cr_2O_3$ and Cr/Fe > 2/1). Most podiform deposits are of the high-chromium type. The high-chromium chromites of the Eastern Hemisphere, except for the Great Dyke, Rhodesia (stratiform) are mostly in podiform deposits.
2. A more magnesian character, with total iron content lower than that of stratiform chromites. The total iron content is below 20 percent.
3. Constancy of the $Fe^{2+}/Mg$ atomic ratio in chromites from each deposit, relative to stratiform complexes.
4. Low $Fe_2O_3$ content in wt% (below 8 percent).
5. Low $TiO_2$ content ranging from 0.00 to 0.84 wt% but in most analyses below 0.3 percent and lack of significant correlation between Ti and other major elements.

## Table 1

### Electron microprobe analyses of disseminated "D" and segregated "S" chromite grains

| | "D" | "S" | "D" | "S" |
|---|---|---|---|---|
| Weight Percent: | | | Mol Percent: | |
| $Al_2O_3$ | 10.42 | 11.06 | 10.21 | 10.44 |
| $Cr_2O_3$ | 58.09 | 60.19 | 38.17 | 38.12 |
| $Fe_2O_3$ | 5.45 | 4.37 | 3.41 | 2.63 |
| MgO | 10.90 | 13.99 | 27.01 | 33.42 |
| FeO* | 19.57 | 15.09 | | |
| FeO | 14.77 | 11.16 | 20.52 | 14.95 |
| NiO | 0.13 | 0.11 | 0.17 | 0.14 |
| MnO | 0.36 | 0.00 | 0.51 | 0.00 |
| $TiO_2$ | 0.00 | 0.24 | 0.00 | 0.29 |
| Total | 99.58 | 100.67 | 100.00 | 100.00 |
| Cr/Fe | 2.60 | 3.51 | | |
| $Cr/(Cr+Al+Fe^{+3})$ | 0.76 | 0.76 | | |
| $Al/(Cr+Al+Fe^{+3})$ | 0.20 | 0.21 | | |
| $Mg/(Mg+Fe^{+2})$ | 0.55 | 0.67 | | |
| Cr/(Cr+Al) | 0.79 | 0.79 | | |
| Number of Cations on the basis of 32(0): | | | | |
| Al | 3.26 | 3.34 | | |
| Cr | 12.20 | 12.20 | | |
| Mg | 4.32 | 5.34 | | |
| Fe | 4.37 | 3.23 | | |
| Ni | 0.03 | 0.24 | | |
| Mn | 0.08 | 0.00 | | |
| Ti | 0.00 | 0.05 | | |

* Total Fe

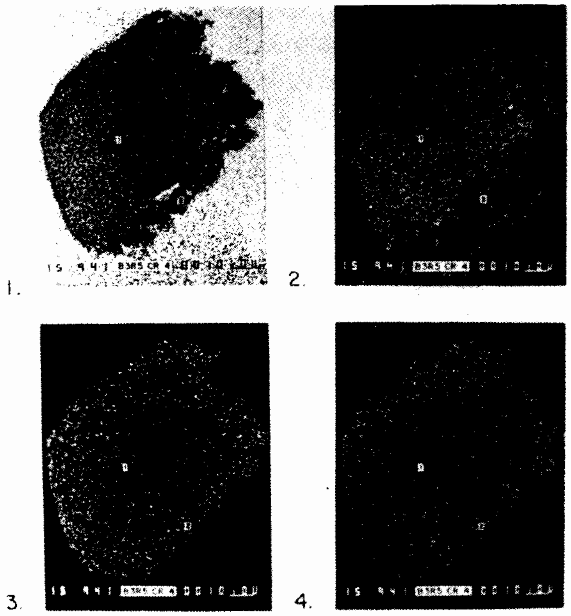

Figure 3. X-ray scanning photographs for distribution of Magnesium (1), Aluminum (2), Chromium (3), and Iron (4) from a disseminated chromite grain, magnification 400X.

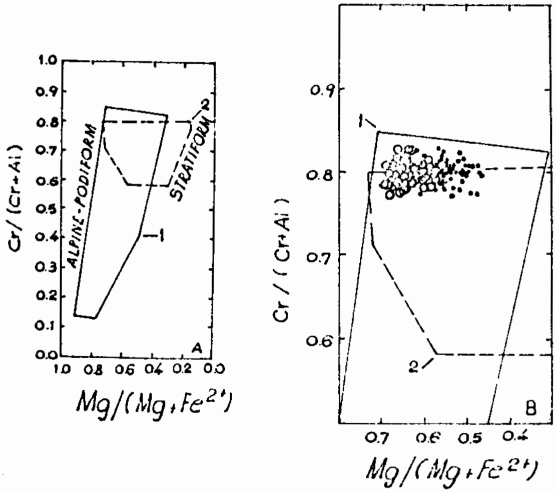

Figure 4. Plot B for the disseminated (dots) and segregated (circles) chromites of this study compared with plot A with fields of alpine-podiform (1) and stratiform (2) complexes after Irvine and Findlay (1972).

Moreover in Figure 5 showing the variation of total weight percent Fe against $Cr_2O_3$ weight percent, chromites from Vourinos generally plot in the overlapping fields of chromites from stratiform and podiform-alpine complexes after Thayer (1970), but, again, most of them plot in the podiform-alpine field and only a few of them plot in the stratiform field. In the $Cr$-$Al$-$Fe^{3+}$+$Ti$ triangular plot of Figure 6 after Bird and Clark (1976) chromites from Vourinos plot clearly in the alpine-podiform field. The average molecular composition for the chromites is given by the formula

$$(Mg_{.62}, Fe^{+2}_{.38})(Cr_{.75}, Al_{.19}, Fe^{3+}_{.06})_2O_4.$$

The olivine relicts that were analyzed with the electron microprobe are all highly magnesian and unzoned and their forsterite content ranges from 90.9 to 98.1 percent. An olivine analysis appears with the following weight percent composition: $SiO_2$ 41.00, $Al_2O_3$ 0.04, $Cr_2O_3$ 0.07, MgO 53.42, FeO 5.69, NiO 0.37, CaO 0.01, MnO 0.06 and $TiO_2$ 0.02 (total 100.68 and Fo 95.90).

Chlorites which occur along chromite grain boundaries were also analyzed. They are rich in MgO, they have a high Mg/Fe ratio and are chromian. Such a chlorite analysis has the following weight percent composition: $SiO_2$ 34.55, $Al_2O_3$ 9.51, $Cr_2O_3$ 6.22, MgO 33.39, FeO 0.91, NiO 0.21, CaO 0.00, MnO 0.04 , $TiO_2$ 0.13 (total 84.96).

## Olivine-Spinel Geothermometry

Geothermometry based on the $Mg$-$Fe^{2+}$ exchange between coexisting chromian spinels and olivines, was applied to chromite deposits of this study. The partitioning of Mg and $Fe^{2+}$ between coexisting $(Mg, Fe^{2+})(Al, Cr, Fe^{3+})_2O_4$ (spinel) and $(Mg, Fe^{2+})_2SiO_4$ (olivine) was first suggested as a potential geothermometer by Irvine (1965) and later developed by many others. Mineral grains were analysed in pairs of adjacent olivine-chromite grains which occur very close together (50-100 μm) to avoid the possibility of disequilibrium. Olivine-chromite grains in direct contact could not be found because of serpentinization. Very low values of $Fe^{3+}/(Cr+Al+Fe^{3+})$, less than 0.05 for chromites from Vourinos, justify the use of this geothermometer. The results of this application are shown in the calibration diagrams by Evans and Frost (1975) drawn separately for olivine-disseminated chromite pairs and olivine-segregated chromite pairs and given as Figure 7 and Figure 8, respectively. These show that the temperature of cessation of equilibration of $Mg$-$Fe^{2+}$ exchange between olivine and spinel ranged between 750° and 850°C and reflects the subsolidus stage. The spread of equilibration temperatures for segregated chromites is greater than that for disseminated chromites. However, linear isotherms can be drawn in Figures 7 and 8 with a mean value of 800°C. The 1,000°C isotherm is drawn proportional to $1/T$, after Ahmed (1984). However, the original crystallization temperatures cannot be determined.

## Discussion - Conclusions

Textures of chromite ores of this study, which are described above, are usually regarded as magmatic (Thayer, 1964, 1969; Greenbaum, 1977). Schlieren or banded texture, in some cases is considered to be tectonic in origin (Dickey, 1975) and explained by shearing or granulations (Thayer, 1969; Greenbaum, 1977) or mechanical flow.

Compositional data for the disseminated and segregated chromites shows similar Cr and Al contents and differences only in $Mg/(Mg+Fe^{2+})$ ratio , supporting the view that both formed from the same magmatic liquid. Differences

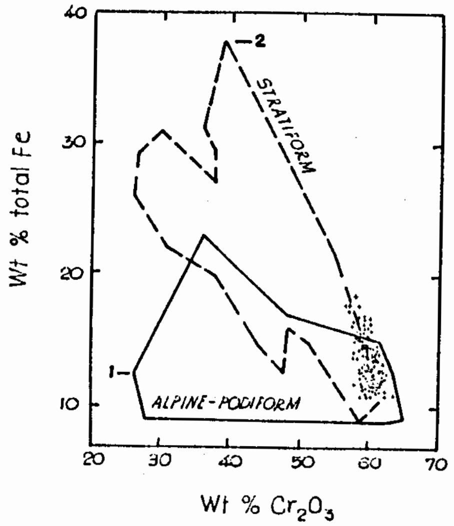

Figure 5. Plot of disseminated and segregated chromites (crosses) on total iron vs. $Cr_2O_3$ weight percent diagram, after Thayer, 1970.

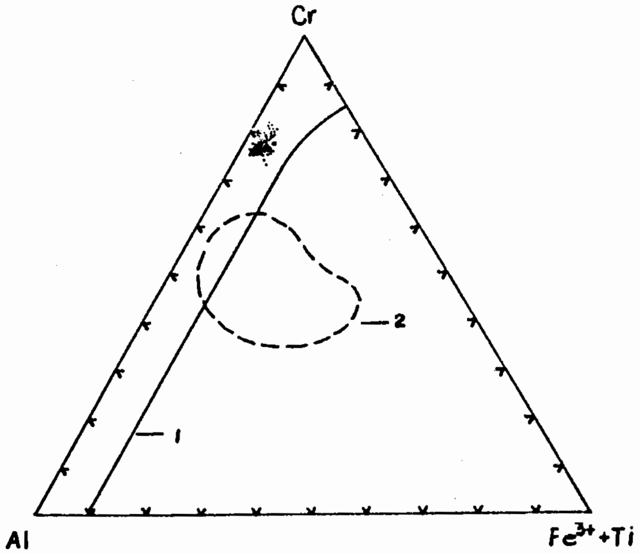

Figure 6. Plot of disseminated and segregated chromites (dots) on Cr-Al-$Fe^{3+}$+Ti triangular plot with fields of chromites from alpine-podiform (1) and stratiform (2) complexes, after Bird and Clark (1976), and Dickey (1975).

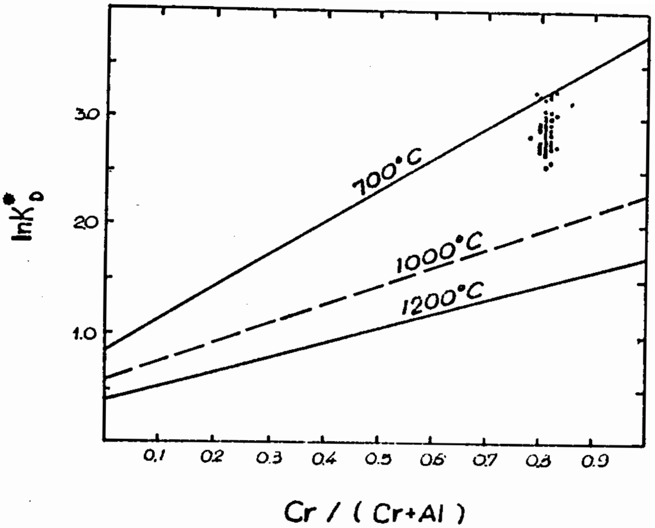

Figure 7. Plot of Cr/(Cr+Al) in chromite against lnk$_D^*$ of Mg-Fe$^{2+}$ exchange between olivines and disseminated chromites, normalized to the chromite ferrite ratio of 0.05, and isotherms after Evans and Frost (1975).

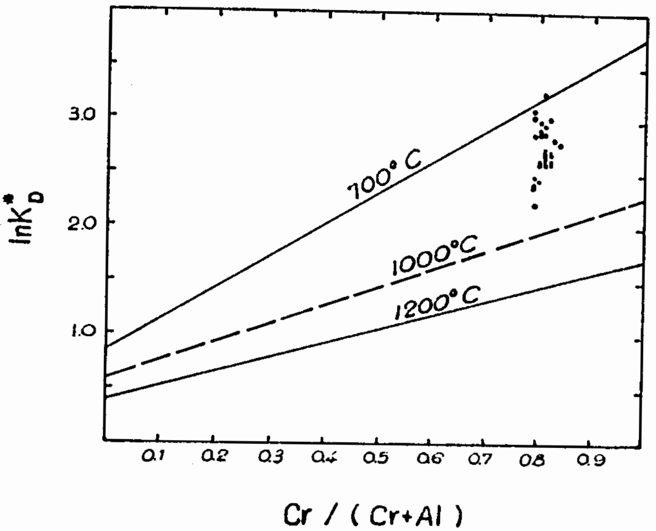

Figure 8. Plot of Cr/(Cr+Al) in chromite against lnk$_D$ of Mg-Fe$^{2+}$ exchange between olivines and segregated chromites, normalized to the chromite ferrite ratio of 0.05, and isotherms after Evans and Frost (1975).

in $Mg/(Mg+Fe^{2+})$ ratio (higher in the segregated chromite and lower in the disseminated chromite) may be explained by the subsolidus reequilibration model proposed by Irvine (1965). It appears that the $Mg-Fe^{2+}$ variations between relatively coarse-grained chromite of segregations and relatively fine-grained disseminated chromite reflect changes that occured just after the fractional crystallization of the magma and continued down to the subsolidus stage. Subsolidus reequilibration is suggested by temperatures obtained from olivine spinel geothermometry (Figures 7 and 8 after Evans and Frost, 1975). Thus, $Mg-Fe^{2+}$ differences between segregated ore-forming and disseminated chromites do not reflect magmatic temperature differences.

"Ferrit-chromit" zoning of chromite grains is not intense, and, in the few cases that it was found as outer margins of grains lower in $Mg/(Mg+Fe^{2+})$ and higher in $Cr/(Cr+Al)$ is probably genetically related to the formation of chlorites (5.07-6.22 wt% $Cr_2O_3$) by hydrothermal alteration of the host dunite. Chromite appears to be the only mineral which could have contributed the Al, Cr, and Mg necessary for the formation of the chlorites.

Chemical parameters, such as high chromium content (>46wt% $Cr_2O_3$ and $Cr/Fe > 2/1$), total iron content below 20 percent, constancy of $Fe^{2+}/Mg$ atomic ratio, low $Fe_2O_3$ (< 8wt%) and $TiO_2 < 0.3$ wt% strongly support their alpine-podiform type character. On conventional $Cr/(Cr+Al)$ vs. $Mg/(Mg+Fe^{2+})$ and wt% total Fe vs. wt% $Cr_2O_3$ diagrams, chromites of this study generally plot in the overlapping field of alpine-podiform and stratiform complexes but mainly in the alpine-podiform field. However, the $Cr-Al-Fe^{3+}+Ti$ plot shows clearly their relationship with alpine-podiform types.

Acknowledgements: This paper is based on a M.S thesis by A.A. Alevizos (1985) submitted to Lehigh University in partial fulfillment of the requirements for the Master of Science in Geological Sciences.

Financial aid in support of this project was provided by grants from the Chevron Oil Company and the Department of Geological Sciences, Lehigh University. I thank the "Institute of Geology and Mineral Exploration" (IGME), Athens for the many courtesies extended, as well as, for the access to the electron microprobe and the Skoumtsa-Xerolivado Mines for access to the chromite deposits and to the mine maps. Many thanks go to Mr. J. Kerner of the Department of Metallurgy and Materials Science, Lehigh University, for his assistance in operating the microprobe.

## References

Ahmed, Z. (1984): Stratigraphic and Textural Variations in the Chromite Composition of the Ophiolitic Sakhakot-Qila Complex, Pakistan.-Econ. Geol. 79, 1334-1359.

Alevizos, A.A (1985): The chemical composition of chromite from Skoumtsa-Xerolivado Mines of the Vourinos Ophiolitic Complex, Greece, as a petrogenetic indicator.-Unpubl. M.S. thesis, Lehigh Univ.

Bence, A.E.& Albee, A.L. (1969): Emperical Correction Factors for the Electron Microanalysis of Silicates and Oxides.-Jour. Geol., 76, 382-403.

Bird, M.L.& Clark, A.L. (1976): Microprobe Study of Olivine Chromitites of the Goodnews Bay Ultramafic Complex, Alaska, and the Occurence of the Platinum.-U.S. Geol. Survey Jour. Research, 4, 717-725.

Craig, J.R.& Vaughan, D.J. (1981): Ore Microscopy and Ore Petrography.-New York: J. Wiley & Sons.

Dickey, J.R., Jr.& Yoder, H.S., Jr.(1972): Partitioning of chromium and aluminum between clinopyroxene and spinel.-Carnegie Inst. Washington Yearbook, 71, 384-392.

Dickey, J.R., Jr. (1975): A hypothesis of origin for podiform chromite deposits-

Geochim.et Cosmochim. Acta, 39, 1061-1075.

Evans, B.W.& Frost, B.R. (1975): Chromian spinel in progressive metamorphism-a preliminary analysis.-Geochim.et Cosmochim. Acta, 39, 959-972.

Greenbaum, D. (1977): The chromitiferrous rocks of the Troodos ophiolite complex, Cyprus.-Econ. Geol., 72, 1175-1194.

Irvine, T.N. (1965): Chromian spinel as a petrogenetic indicator, Part 1, Theory.-Canadian Jour. Earth Sci., 2, 648-672

Irvine, T.N. (1967): Chromian spinel as a petrogenetic indicator, Part 2, Petrologic Applications.-Canadian Jour. Earth Sci., 4, 71-103.

Irvine, T.N.& Findlay, T.C. (1972): Alpine type peridotite with particular reference to the Bay of Islands Igneous Complex.-Pub. Earth Phys. Br., Dept. Ener. Min. Resour. (Canada), 42, 97-140.

Malpas, J.& Strong, D.F. (1975): A comparison of chrome spinels in ophiolites and mantle diapirs of Newfoundland.-Geochim.et Cosmochim. Acta, 39, 1045-1060.

Thayer, T.P. (1964): Principal features and origin of podiform chromite deposits and some observations on the Guleman-Soridag district, Turkey-Econ. Geol., 59, 1497-1524.

Thayer, T.P. (1969): Gravity differentiation and magmatic reemplacement of podiform chromite deposits.-Econ. Geol. Mon. 4, 132-146.

Thayer, T.P. (1970): Chromite segregations as petrogenetic indicators.-Geol. Soc. South Africa, Spec. Pub. 1, 380-390.

Thayer, T.P. (1973): Chromium- U.S. Geol. Survey, Prof. Paper 820, 111-121.