

THE USE OF CHROME SPINELS IN PETROGRAPHIC STUDIES OF ULTRAMAFIC INTRUSIONS¹

I. D. MACGREGOR AND CHARLES H. SMITH

Geological Survey, Ottawa, Canada

ABSTRACT

Data are presented showing the approximate correlation of the chemical composition of chrome spinels with unit cell dimension, index of refraction and colour. It is pointed out that use of such data, although not precise, will provide petrographers with an improved method of recognizing cryptic zoning in ultramafic intrusions, and form a basis for interpreting their cooling history.

INTRODUCTION

Petrographers commonly ignore the large chemical variation which may exist among the accessory chrome spinel minerals in ultramafic intrusions. This is due to their normally low concentration in ultramafic rocks (generally about 1 per cent), the slow and tedious task of producing pure concentrates and the difficulty of chemical analysis. The magnesium-iron ratios of the coexisting silicate minerals are readily determined by *x*-ray or optical methods, but similar techniques have not been commonly used for the spinel group.

This paper outlines a rapid method for studying accessory chrome spinels and for determining their general chemical variation within an ultramafic intrusion. Data are presented showing the approximate correlation of the chemical composition of chrome spinels from the Mount Albert ultramafic pluton with certain physical properties—unit cell dimension, index of refraction, and colour. These properties, while not providing a precise measure of chemical composition, are of value in outlining the major chemical trends in certain ultramafic intrusions.

PREVIOUS WORK

Chrome spinels have the basic formula $R^{2+}O \cdot R_2^{3+}O_3$ where $R^{2+} = \text{Mg, Fe, Mn, Ni}$ and $R^{3+} = \text{Cr, Al, Fe, Mn}$. Ideally the ratio $RO:R_2O_3 = 1$, although it may vary due to solid solution with $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ which have spinel-like structures (Rait, 1946). Bragg (1915) and Nishikawa (1915) analyzed the structure of spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$). The basic structure consists of layers of oxygen atoms approximately in cubic close

¹Canadian Contribution to the International Upper Mantle Project No. 4. Published with permission of the Director, Geological Survey of Canada.

packing, with tetrahedral and octahedral positions between the large oxygen anions. R^{2+} cations occupy tetrahedral sites and R^{3+} cations occupy octahedral sites. There are 8 tetrahedral and 16 octahedral positions in the spinel unit cell. Substitution among the R^{2+} and among the R^{3+} ions, which have differing ionic radii, changes the dimension of the unit cell, the refractive index and the colour. Thus the above parameters reflect the chemical composition of the chrome spinel itself.

The chrome spinels may be expressed in terms of the theoretical and members:

Spinel	MgO.Al ₂ O ₃	Hercynite	FeO.Al ₂ O ₃
Picrochromite	MgO.Cr ₂ O ₃	Chromite	FeO.Cr ₂ O ₃
Magnesioferrite	MgO.Fe ₂ O ₃	Magnetite	FeO.Fe ₂ O ₃

Studies of synthetic spinels between certain of these end members (Rait, 1946; Warshaw & Keith, 1954; Fischer & Hoffman, 1956; Turnock, 1959); indicate that complete solid solution probably exists throughout the spinel composition range. In a single ultramafic intrusion of the Mount Albert type described here, the limits of solid solution actually found are much less than those expressed by the theoretical end members, as can be seen by the analyses given in Fig. 1.

Clark & Ally (1932), from a study of 5 natural chromites, suggested that the cell dimension decreased with increasing Al₂O₃ content. Stevens (1944) pointed to a close relationship between unit cell dimension and Cr₂O₃ content of chromites. DeWet & van Niekerk (1952) found only minor differences in the cell dimensions of 8 analyzed chromites of varying composition from the Bushveld Complex. Their observation that chemical variation may exist among natural chrome spinels with similar unit cell dimensions has been noted also by D. C. Findlay¹ in the Tulameen Intrusion, British Columbia. The cause appears due to cation substitution in tetrahedral positions cancelling the effects of substitution in the octahedral position. In intrusions of the Mount Albert type where a wide variation in unit cell dimensions is found (8.14–8.32 Å) the cancelling effect is of minor importance but in intrusions where the unit cell variation is small, the cancelling effect may invalidate the use of unit cell dimensions as a mapping tool.

PRESENT INVESTIGATION

The data used in this paper were collected during a detailed petrographic study of the Mount Albert ultramafic intrusion. Thirty-nine chrome spinel concentrates were prepared using the Frantz isodynamic

¹Ph.D. thesis, Queen's University, Kingston, in preparation.

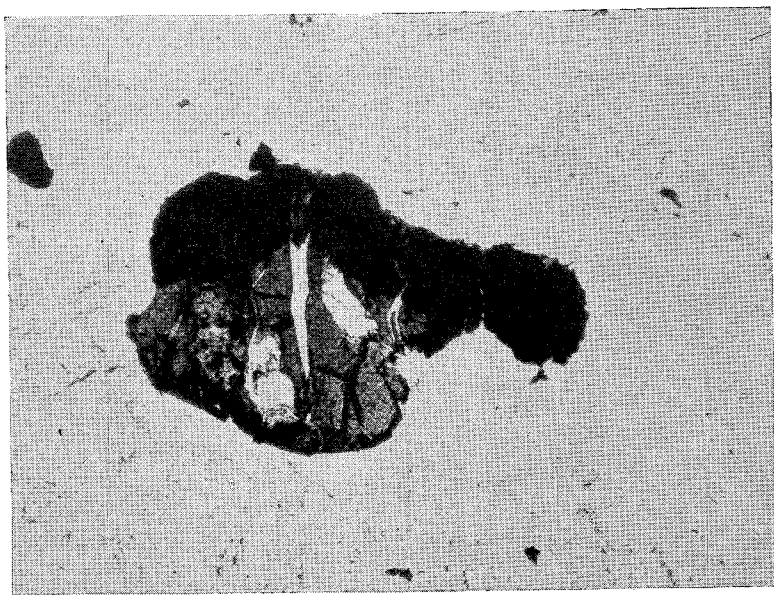
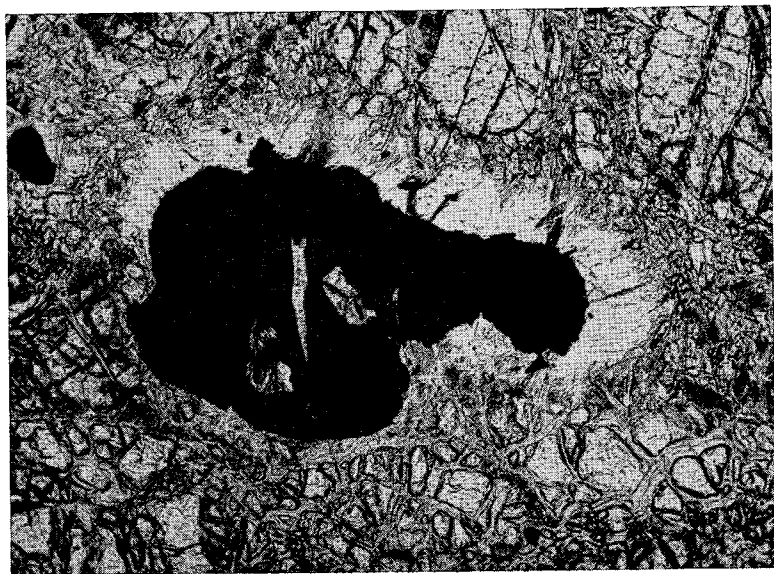


FIG. 1. A typical chromite grain (*a*) normal appearance with plane light, showing chlorite rims (*b*) with increased illumination showing opaque and translucent portions.

separator, heavy liquids and by hand picking. These samples were analyzed by MacGregor using the optical spectrograph at Queen's University. Analytical methods and errors have been discussed by MacGregor (unpublished M.Sc. thesis, Queen's University, 1962). For construction of the determinative curve shown here, the analyses have been recalculated to 100 per cent and the total iron distributed as FeO and Fe_2O_3 on the assumption that the ratio of $\text{RO}:\text{R}_2\text{O}_3 = 1$.

Unit cell dimensions of the chemically analyzed samples were determined by means of a 57.54 mm diameter camera using iron radiation. The accuracy of the dimensions is considered to be $\pm 0.005 \text{ \AA}$. Refractive indices were determined on crushed powders of analyzed concentrates using 0.01 interval oils, to an accuracy of ± 0.005 . The colours of spinels were observed in thin section and compared with a rock-colour chart (1951).

Chrome spinels may show zoning or rims (Fig. 1) composed of another spinel phase. Care was taken to obtain samples representative of the unaltered cores by using the least magnetic portions from the Frantz separator and by leaching the concentrate with concentrated hydrofluoric and sulphuric acid. Powder patterns of the final concentrate showed no doubling of lines due to the presence of two discrete spinel phases, but of course it cannot be assumed that complete separation of the rim material was obtained.

SUMMARY OF DATA

The spectrographic analyses, unit cell dimensions, refractive indices and colours of 39 chrome spinels from the Mount Albert intrusion are summarized in Table 1.

In Fig. 2, the unit cell dimensions are plotted against the content of Al_2O_3 , Cr_2O_3 , $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, MgO and FeO . Assuming a linear relationship between unit cell dimension and composition, the curves of best fit have been calculated and are shown, with their equations. The unit cell dimension increases with increasing Cr_2O_3 , $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and FeO content and decreases with increasing Al_2O_3 and MgO content. The slope for Al_2O_3 ($m = -104.77$) is approximately equal but of opposite sign to that for Cr_2O_3 ($m = 100.00$) and $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ($m = 114.69$). The slopes for FeO ($m = 33.73$) and MgO ($m = -34.35$) are also approximately equal but of opposite sign. The equivalence of the numerical value for the slope of the R^{3+} and the R^{2+} curves reflects the respectively similar structural positions that the R^{3+} and R^{2+} cations occupy in the crystal structure. The different signs of the slopes are a function of the larger ionic radii of Cr^{3+} ($0.63 \text{ \AA}$) and Fe^{3+} ($0.64 \text{ \AA}$) with respect to Al^{3+} ($0.49 \text{ \AA}$),

TABLE 1. SPECTROGRAPHIC ANALYSES OF CHROME SPINELS FROM MT. ALBERT ULTRAMAFIC PLUTON, GASPE, QUEBEC.¹

Cell Edge (Å)	Refractive Index	Colour	Cr ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	MnO	TiO ₂	NiO	V ₂ O ₅	CoO	Total	Sample No.
8.145	1.815	1	35.1	27.1	4.3	16.8	15.9	0.17	0.10	0.22	0.10	0.06	99.9	SDM 95B
8.145	1.835	1	35.9	29.2	3.0	18.4	11.5	0.85	0.72	0.20	0.13	0.06	98.1	SDM 131A
8.150	1.825	1	35.5	31.3	3.0	16.7	12.1	0.72	0.85	0.22	0.12	0.06	98.2	SDM 117
8.150	1.850	1	37.5	29.1	3.3	17.41	12.2	0.16	0.72	0.22	0.11	0.07	100.1	SDM 504
8.150	1.835	1	41.0	31.0	0.0	13.0	14.0	0.22	0.17	0.39	0.19	0.13	100.6	SDM 612
8.145	1.845	1	40.0	29.0	0.0	20.0	10.0	0.12	0.07	0.19	0.08	0.06	99.5	SDM 8
8.155	1.835	1	35.2	29.9	4.7	16.6	11.7	0.71	0.71	0.20	0.10	0.06	99.9	SDM 118
8.155	1.835	2	35.5	32.8	0.0	21.2	10.3	0.13	0.06	0.21	0.20	0.06	100.5	SDM 124
8.160	1.835	1	39.0	23.7	7.5	15.5	13.0	0.21	0.09	0.26	0.19	0.12	99.6	SDM 621
8.160	1.880	1	35.5	29.9	5.1	15.8	13.7	0.15	0.76	0.18	0.13	0.07	99.9	SDM 150
8.170	1.845	1	36.0	29.6	4.7	15.6	13.3	0.13	0.10	0.18	0.11	0.07	103.1	SDM 105
8.170	1.845	2	38.1	25.7	7.6	13.8	14.0	0.18	0.08	0.19	0.15	0.07	99.9	SDM 112
8.170	1.855	2	38.0	29.0	2.2	20.0	10.7	0.16	0.11	0.20	0.15	0.07	100.7	SDM 17
8.200	—	3	40.9	25.5	2.8	20.6	10.0	0.17	0.13	0.15	0.13	0.07	100.4	SDM 528
8.215	1.925	3	41.7	23.6	5.1	18.0	11.8	0.21	0.79	0.12	0.16	0.08	—	SDM 144
8.220	1.945	3	44.1	22.8	3.5	17.9	11.5	0.15	0.08	0.08	0.20	0.07	99.9	SDM 165
8.225	1.970	3	41.5	22.5	1.0	22.9	11.4	0.21	0.05	0.07	0.20	0.07	99.9	SDM 246
8.225	1.950	3	45.0	22.5	2.7	18.3	11.3	0.19	0.08	0.08	0.23	0.07	100.5	SDM 57
8.240	1.955	4	44.2	21.8	4.4	18.0	10.9	0.20	0.10	0.08	0.20	0.07	100.3	SDM 61
8.245	—	3	44.4	18.5	6.9	20.3	9.6	0.16	0.16	0.08	0.16	0.07	100.3	SDM 61
8.255	1.985	5	51.4	18.2	2.2	14.9	13.0	0.16	0.15	0.12	0.09	0.04	99.6	SDM 151
8.260	2.025	5	52.5	15.8	3.9	12.7	14.1	0.15	0.15	0.12	0.20	0.07	100.6	SDM 100
8.260	2.045	3	48.5	16.0	5.5	21.7	8.3	0.20	0.06	0.06	0.19	0.09	100.5	SDM 570
8.265	2.025	4	45.7	16.8	7.0	22.1	8.1	0.25	0.14	0.06	0.21	0.08	99.6	SDM 269
8.270	2.050	4	48.5	15.8	5.4	19.9	9.3	0.25	0.07	0.05	0.23	0.08	100.6	SDM 55
8.275	—	4	48.4	16.3	5.0	20.1	10.1	0.23	0.07	0.05	0.23	0.07	100.2	SDM 41
8.280	2.045	3	52.0	15.7	1.7	20.2	8.9	0.24	0.82	0.45	0.17	0.07	100.2	SDM 628
8.280	2.050	4	47.0	14.9	7.7	20.9	8.5	0.21	0.09	0.06	0.23	0.08	99.7	SDM 186
8.280	2.065	4	49.0	14.6	5.9	22.0	7.9	0.32	0.10	0.05	0.22	0.09	100.2	SDM 126
8.290	—	4	46.5	13.4	8.1	25.4	6.4	0.27	0.11	0.12	0.14	0.08	100.5	SDM 91
8.295	2.110	5	58.4	11.0	3.3	17.9	8.8	0.19	0.13	0.06	0.06	0.05	99.9	SDM 262B
8.300	>2.110	4	50.5	13.3	5.7	24.2	8.2	0.30	0.10	0.05	0.20	0.07	100.8	SDM 270
8.310	>2.110	4	50.0	13.4	6.7	21.6	8.2	0.32	0.13	0.29	0.05	0.09	100.4	SDM 45B
8.315	—	4	48.8	13.4	6.8	20.6	9.8	0.36	0.09	0.05	0.22	0.08	100.2	SDM 44
8.315	>2.110	4	51.0	13.7	5.7	22.4	9.5	0.34	0.13	0.05	0.26	0.08	100.2	SDM 52
8.315	>2.110	4	54.0	11.2	4.5	23.3	6.6	0.28	0.10	0.05	0.12	0.08	100.2	SDM 268
8.320	>2.110	4	53.1	10.6	4.6	28.3	3.4	0.34	0.12	0.05	0.16	0.09	100.8	SDM 25

Analyses by I. D. MacGregor under the direction of G. MacDonald, Miller Research Laboratory, Queen's University. Total iron determined, FeO and Fe₂O₃ calculated. Colours as observed in thin section are as follows: 1—dark yellowish orange; 2—light olive brown; 3—medium red brown; 4—dark red brown to opaque; 5—dusky red.

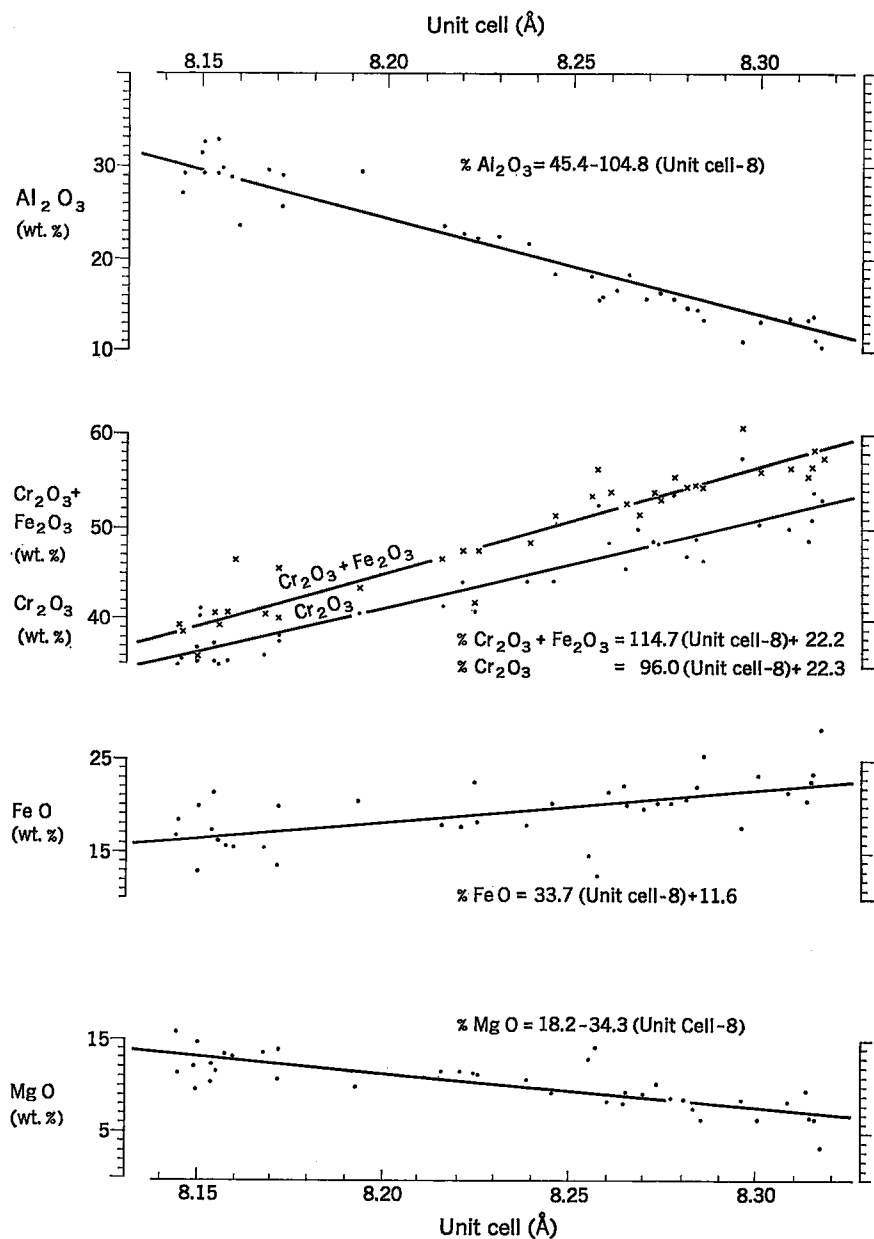


FIG. 2. Determinative curves for Mt. Albert chrome spinel.

and of Fe^{2+} (0.74 Å) to Mg^{2+} (0.66 Å). The superior fit of the $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ curve compared to that for Cr_2O_3 alone is due to the similar ionic radii of Cr^{3+} and Fe^{3+} .

The variation of refractive index with unit cell dimension is shown in Fig. 3. The refractive index increases with increasing cell dimension approximately according to the formula:

$$n = 1.7008d - 12.0332$$

where n represents the index of refraction and d represents the unit cell dimension. Index of refraction measurements may be substituted for unit

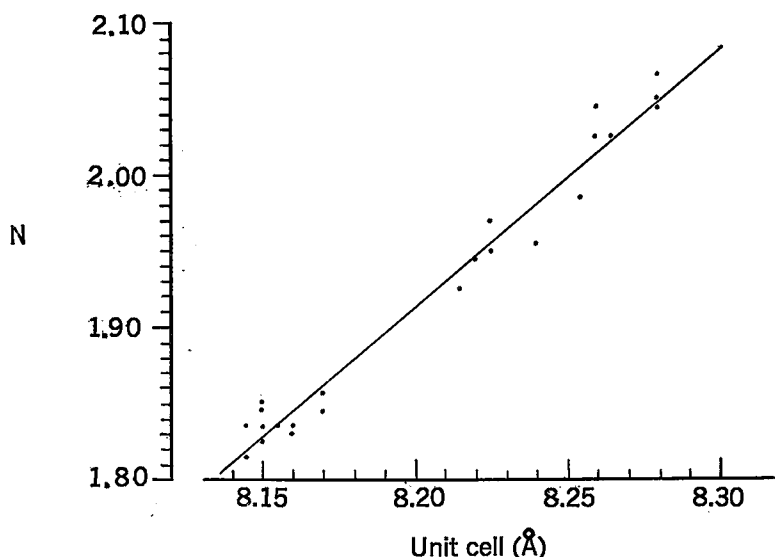


FIG. 3. Correlation of unit cell and index of refraction.

cell determinations to indicate chemical trends among the aluminous chrome spinels. Unfortunately the low-alumina chrome spinels are opaque or have indices above the range of normally available immersion oils (>2.11).

The colours of chrome spinels change with chemical composition and may be used as a qualitative guide. The colours are reported in Table 1 where it may be noted that the redness of the chrome spinels increases with chromium content. Similar relationships are reported by Fisher (1929) and Thayer (1956).

APPLICATION OF DATA

It is evident from the data presented that unit cell determinations may provide a convenient means of mapping chrome spinel variations in igneous intrusions. The Mount Albert data is obtained from a single alpine-type ultramafic intrusion and it remains to be seen whether the data can be applied directly to other geologic environments in which chrome spinels crystallize. The curves are suitable to indicate major chemical trends where unit cell dimensions vary widely. In intrusions where only a small variation in unit cell is found, chemical analyses are required to indicate significant chemical variations.

Compensating substitution and differing temperature-pressure conditions of crystallization may both influence the correlation between unit cell and chemical composition shown here. Compensating substitution occurs when a tendency to decrease the cell dimension due to substitution of Al^{3+} for Cr^{3+} in the octahedral positions is offset by substitution of Fe^{2+} for Mg^{2+} in the tetrahedral positions. Such effect may become important in intrusions of chromite deposits where the overall chemical variation is not large. Data from synthetic mixtures (Warshaw & Keith 1954) show that the unit cell dimension is affected by the temperature of formation of spinel. This factor must be considered when comparing detailed data between intrusions but it is not significant in changing the general chemical trends related to cell sizes shown in Fig. 2.

GEOLOGICAL SIGNIFICANCE

Unit cell measurements have proven useful in outlining cryptic zoning in the Mount Albert ultramafic pluton. The intrusion (Fig. 4) is semi-circular in plan, approximately 6 miles long and 3 miles wide, and composed of serpentized dunite and peridotite. Its bulk composition prior to serpentization was olivine (80–90 per cent), orthopyroxene (10–20 per cent), clinopyroxene (1–2 per cent) and chrome spinel (1 per cent). A form of mineral layering due to layers with alternating proportions of olivine and pyroxene (dunite to peridotite) is present. The layering is considered to have formed during flowage of a crystal mush. This layering is folded and is both parallel and discordant to the margins of the intrusion.

In Fig. 4 it is seen that the intrusion can be zoned on the basis of chrome spinel compositions. Spinels with the larger cell dimension (rich in chromium and iron) occur near the margins of the intrusion. Similar distribution patterns have been found for orthopyroxene (more magnesium pyroxene near the margins) and for olivine (more magnesium olivine near the margins). These distribution patterns can be correlated

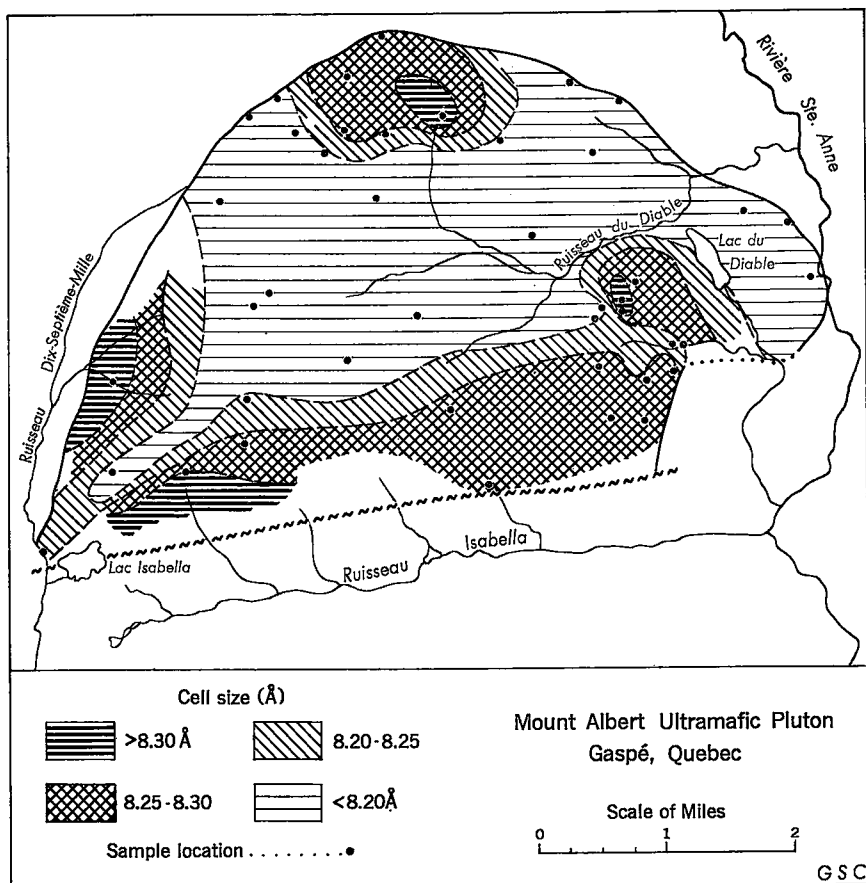


FIG. 4. Variation in unit cell size of chrome spinels in the Mount Albert intrusion.

in a general way with variations in degree of serpentinization in the body, and are believed to be related to the availability of water during crystallization. In areas of high water content and higher partial oxygen pressure, oxidation of Fe^{2+} to Fe^{3+} resulted in the crystallization of more magnesium-rich silicates and more iron (and chromium)-rich spinel. (Smith & MacGregor 1960).

CONCLUSIONS

Chrome spinels are sensitive indicators of compositional variations in a crystallizing magma. In many intrusions they vary widely in chemical composition, more so than the associated silicate minerals, and may indicate cryptic zoning which would not be recognized by other studies. The data and example cited here are given to indicate how chrome

spinel can be used. It is necessary to develop more precise determinative curves for accurate compositional determination, but the curves given here are useful in outlining trends in an intrusion. Increased attention to spinel variations will provide data on the later cooling history of ultramafic intrusions, a means of comparing the petrochemistry of ultramafic intrusions which are otherwise apparently similar in composition, and a clearer understanding of the processes leading to the concentration of chromite ore deposits in ultramafic rocks.

ACKNOWLEDGMENTS

The writers are indebted to the following: Mrs. Joan Climo and Miss Ann Sabina for their determinations of unit cell dimensions in the mineralogical laboratories of the Geological Survey, to Mr. J. G. MacDonald of the Miller Research Laboratory, Queen's University for his assistance with the spectrographic analyses carried out by MacGregor during his graduate studies and Mr. K. Shimizu for calculating the formulae of the determinative curves.

REFERENCES

- Bragg, W. H. (1915): The structure of the spinel groups of minerals, *Phil. Mag.*, **30**, 305-315.
- Clark, G. L., & Alty, A. (1932): X-ray examination of chrome ores: I. Lattice dimensions, II. Theoretical densities, *Am. Mineral.*, **17**, 66-75.
- DeWet, J. F., & Van Niekerk, J. N. (1952): The total analysis, composition and structure of Transvaal chromite, *Jour. Chem. Metal Mining Soc. of S. Africa*, **53**, 10-21.
- Fisher, L. W. (1929): Chromite: Its mineral and chemical composition, *Am. Mineral.*, **14**, 341-357.
- Nishikawa, S. (1915): *Proc. Tokyo Math. Phys. Soc.*, **8**, 199.
- Rait, J. R. (1946): An X-ray investigation into the constitution of chrome ores, *Iron and Steel Inst., Spec. Rept.*, **32**, Third Report on Refractory Minerals, 175-209.
- Anon (1951): *Rock-color chart*, Distributed by Geol. Soc. America.
- Ross, C. S., Foster, M. D., & Myers, A. T. (1954): Origin of dunites and olivine rich inclusions in basaltic rocks, *Am. Mineral.*, **39**, 693-738.
- Smith, C. H., & MacGregor, I. D. (1960): Ultrabasic intrusive conditions illustrated by the Mount Albert ultrabasic pluton, Gaspé, Canada, *Geol. Soc., Am. Bull.*, **71**, p. 1978 (abst.).
- Stevens, R. E. (1944): Composition of some chromites of the western hemisphere, *Am. Mineral.*, **29**, 1-35.
- Thayer, T. P. (1946): Preliminary chemical correlation of chromite with the containing rocks, *Econ. Geol.*, **41**, 202-217.
- Turnock, A. C. (1959): Spinels, *Ann. Rep. Dir. Geophys. Lab., Carnegie Inst. Wash., Year Book* **58**, 134-137.
- Van der Kaaden, G. (1959): On the relationship between the composition of chromites and their tectonic-magmatic position in periodotite bodies of S.W. Turkey, *Bull. Mineral Research Exploration Inst. of Turkey*, Foreign Ed., No. 52, 1-15.
- Warsaw, I., & Keith, M. L. (1954): Solid solution and chromium oxide loss in part of the system $MgO-Al_2O_3 - Cr_2O_3 - SiO_2$, *J. Am. Ceram. Soc.*, **37**, 161-168.

Manuscript received June 26, 1962