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THE APPLICATION OF REFLECTIVITY MEASUREMENTS TO THE STUDY OF CHROMIFEROUS SPINELS

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Abstract

Although the compositions of chromiferous spinels are known to vary widely in igneous rocks, in individual tholeiitic intrusions the variations tend to follow regular paths between chromite and chromian titanomagnetite. This permits a useful correlation to be established between optical reflectivity and composition. Absolute values of reflectivity are dominated by the relative levels of Al and Fe^{3+}, with changes in the $Mg/(Mg+Fe^{2+})$ ratio exerting a lesser influence. Optical measurements are used to confirm microprobe data, which suggest that spinel compositions in the layered Insizwa intrusion (South Africa) vary according to the identity of the host silicate phase. It is shown that systematic compositional changes with stratigraphic height in the Elephant's Head cumulus complex (South Africa), which are indicated by microprobe analyses of a small sample of grains, are clearly demonstrated by optical measurements on a much larger sample.

Keywords: chromiferous spinels, reflectivity, titanomagnetite, Insizwa, Elephant's Head, tholeiitic stratiform complex, South Africa.

Sommaire

Quoique la composition des spinelles chromifères varie fortement dans les roches ignées, cette variation, dans toute intrusion tholéiitique, montre une évolution régulière de chromite à titanomagnétite chromifère. On peut établir une corrélation utile entre réflectivité et composition. Les valeurs absolues de la réflectivité dépendent surtout des teneurs en Al et Fe^{3+}, et ensuite du rapport $Mg/(Mg + Fe^{2+})$. Les mesures optiques confirment les données de la microsonde, selon lesquelles c'est la phase silicatée encaissante qui gouverne la composition des spinelles du complexe stratiforme d'Insizwa (Afrique du Sud). L'évolution systématique de la composition du spinelle avec le niveau stratigraphique dans le massif à cumulats Elephant's Head (Afrique du Sud), révélée par la microsonde sur un petit nombre de cristaux, est nettement mise en évidence par mesures optiques sur un échantillon beaucoup plus volumineux.

(Traduit par la Rédaction)

Mots-clés: spinelles chromifères, réflectivité, titanomagnétite, Insizwa, Elephant's Head, complexe stratiforme tholéiitique, Afrique du Sud.

Introduction

The application of electron-microprobe techniques has, within recent years, led to increasingly better documentation of variations of composition within the spinel-group minerals of layered intrusions and basaltic rocks. Not only are zonal variations more fully understood (Haggerty 1975, El Goresy 1976), but substantial variations from grain to grain are now well established within the spinel populations of individual intrusions or lava series (Evans & Moore 1968, Henderson 1975, Beeson 1976, Ridley 1977, Eales & Snowden 1979). The study of large samples of grains in polished thin sections is not, however, always expedient by microprobe methods, where examination of the associated minerals may be hindered by the limited optical facilities of the instrument, under conditions in which the aluminum or carbon coating of the specimens obscures fine intergrowths or other details.

The present paper shows that useful data can be gathered by reflectivity measurements, either as an adjunct to earlier microprobe studies or in pilot studies designed to render subsequent microprobe work more effective. Although the complete data provided by microprobe analysis will not be forthcoming from optical work, the technique is highly effective for indicating trends of variation and polymodal distributions of composition within populations of grains, and for selecting specific grains lying at the limits of variation trends.

The present paper is based on 181 microprobe analyses of spinels from three separate intrusions. Of these grains, 82 were selected to cover as broad a range of composition as possible, and reflectivity measurements performed on them for purposes of calibration. Microprobe analyses were run on a C.S.I. Mark V instrument, operated at an accelerating potential of 20 kV with a specimen current of 30 nA. Count rates were processed by computer for dead-time losses, and corrections were applied according to the procedure of Bence & Albee (1968), using the α factors of Albee & Ray

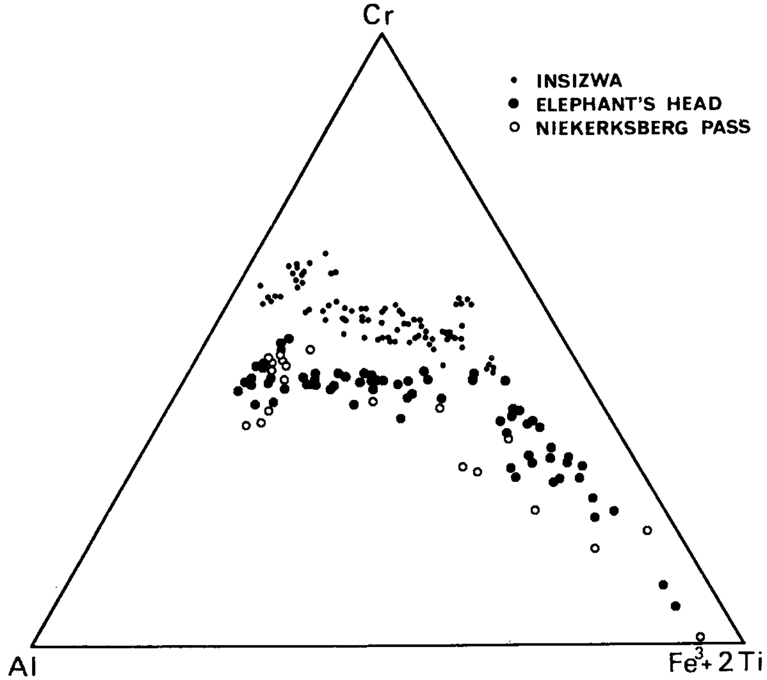

FIG. 1. Compositional variations (cation percentages) exhibited by spinel populations in three tholeiitic Karroo Central Province intrusions, South Africa.

(1970). The distribution of total Fe between Fe^{2+} and Fe^{3+} is made by assuming spinel stoichiometry, with Ti assigned to ulvöspinel Fe_2TiO_4. Optical measurements were carried out on a Zeiss MPM–01 microphotometer, employing a photomultiplier as sensor and a continuous interference filter as monochromator; each determination was performed twice at azimuths 90° apart. All samples were prepared as polished thin sections by lead lapping with diamond abrasive and brief finishing with 0.05 μm γ-alumina on "Pellon" cloth laps.

The Correlation of Chemical and Optical Reflectivity Data

The complexity of a system with major variables Cr, Al, Fe^{3+}, Fe^{2+}, Mg and Ti would seem to offer little prospect of deriving an effective correlation between chemical and optical parameters. Within individual intrusions, however, compositional variations between aluminian chromite and chromian magnetite are not random, but follow definable paths as illustrated in Figure 1. Consequently, a simple plot of Al cations against optical reflectivity produces a useful working curve for individual samples, but data points become somewhat scattered if data from different samples or different intrusions are combined; although it is the trivalent cations that are dominant in controlling optical reflectivity, the $Mg/(Mg + Fe^{2+})$ ratio also exerts an influence. Within the intrusions studied thus far, a correlation exists between the Al content and the $Mg/(Mg + Fe^{2+})$ ratio of the spinels (Fig. 2) but it is imperfect. A more effective correlation can be achieved by segregating the data within a "high-Mg series" (filled circles in Fig. 2) and a "low-Mg series" (open circles). The dividing line between the series so defined is shown by the solid line in Figure 2. A breakdown of the data on this basis permits effective working curves to be derived by the plotting of cations (Al + Cr/2) *per* formula unit, against optical reflectivity, for each of the high- and low-Mg series. Such a working curve for the low-Mg series is shown in Figure 3, in which a correlation coefficient of –0.982 is achieved between compositional and optical parameters. The working curve for the high-Mg series is similar but more curved, and is displaced towards lower absolute reflectivity values.

A total of 82 data points drawn from three separate intrusions has been used to construct curves showing changes of optical reflectivity with composition, within part of the Cr–Al–

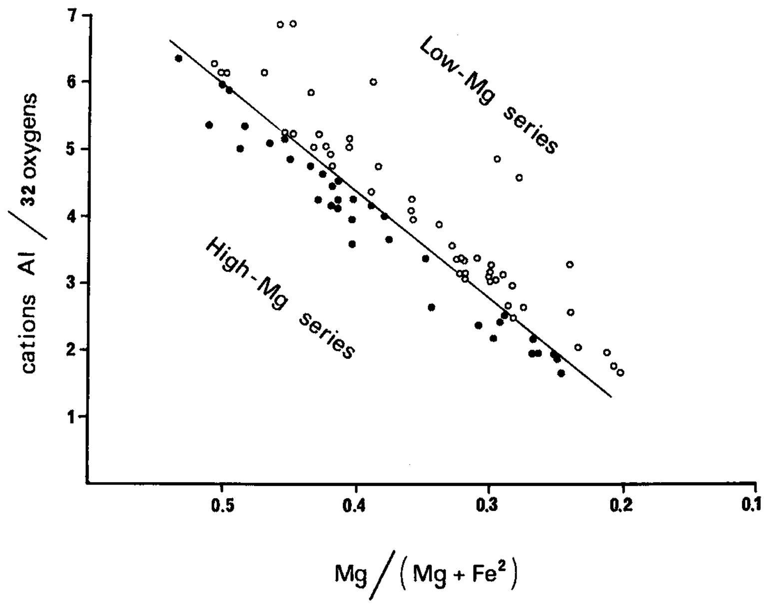

FIG. 2. Plot of Al cations (*per* 32 oxygens) against Mg/(Mg + Fe^{2+}) ratio for 82 spinel grains from three intrusions depicted in Figure 1. Data points are segregated into "high–Mg series" (filled circles) and "low-Mg series" (open circles).

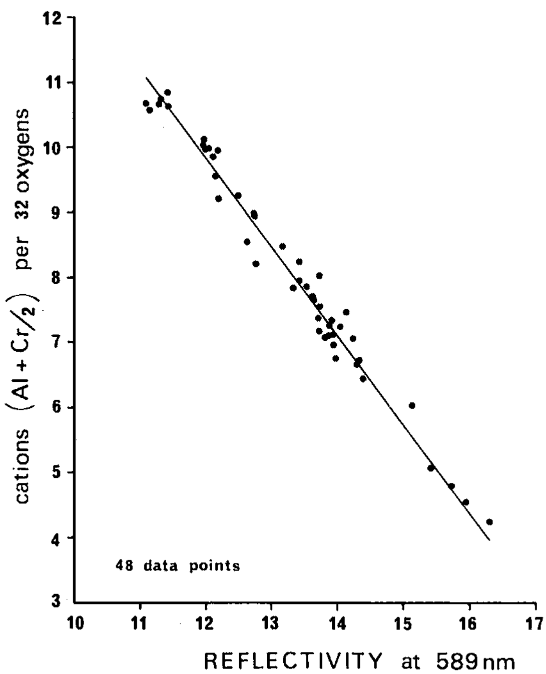

FIG. 3. Plot of reflectivity (at wavelength 589 nm) against cations (Al + Cr/2) *per* formula unit of 32 oxygens for 48 spinel grains of low-Mg series. Calculated regression line shows reflectivity = 19.2 – 0.729 (Al + Cr/2). Correlation coefficient is –0.982.

(Fe^{3+} + 2Ti) triangle, as shown in Figure 4. The small differences between the high-Mg and low-Mg series are clearly shown. These curves are useful in studying specific populations of spinels in which compositional variations follow consistent paths. However, the interpretation of optical data must, in general, be subject to some ambiguity arising out of nonsystematic variations in Al, Cr and the Mg/(Mg + Fe^{2+}) ratio, as well as fluctuations in the levels of Ti.

PRACTICAL APPLICATIONS OF REFLECTIVITY MEASUREMENTS

A study of the chromiferous spinels of two Karroo cumulus complexes, within which the spinel populations show contrasting styles of compositional variation, provides an illustration of the quantitative use of reflectivity data.

The Insizwa complex

Eroded remnants of this layered complex in Transkei cover approximately 1000 km^2 and attain a thickness exceeding 900 m. Peridotitic and picritic rocks are well developed along the base (Scholtz 1936, Bruynzeel 1957). These rocks consist dominantly of cumulus olivine with intercumulus ortho- and clinopyroxene, plagioclase and subordinate phlogopite. Chromiferous spinels constitute 1–2% of these cumu-

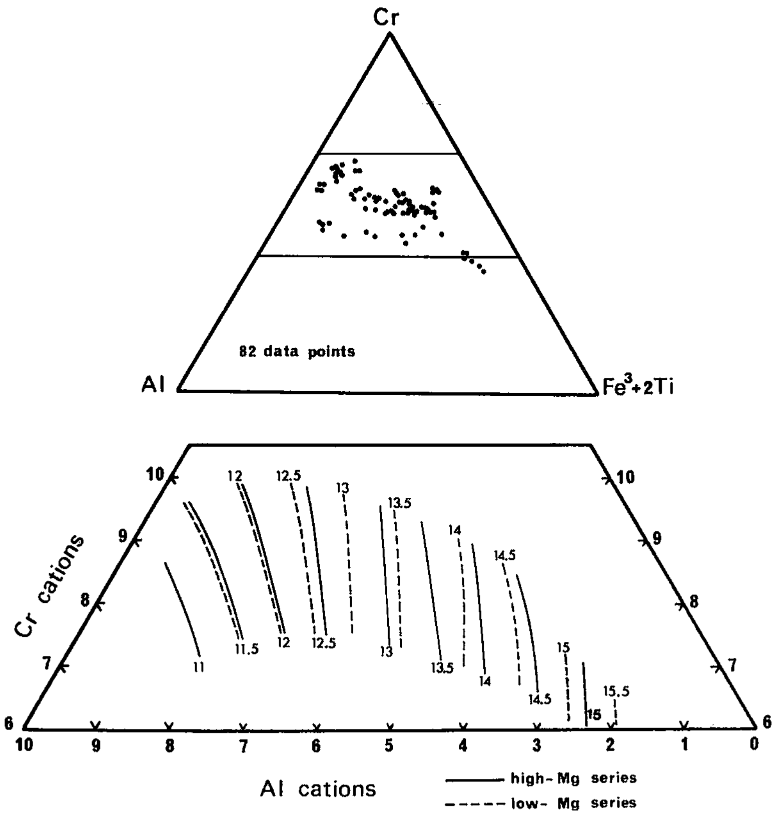

FIG. 4. Variations of reflectivity (589 nm) for high-Mg series (solid lines) and low-Mg series (broken lines) within a portion of Al–Cr–(Fe^{3+} + 2Ti) spinel triangle. Spread of 82 data points is shown in upper triangle.

lates; they are present as octahedra and roundish grains less than 0.2 mm in diameter. The immediate host phases within which the spinels occur are olivine, pyroxene, plagioclase and mica.

Electron-microprobe data reveal consistent compositional differences among the fractions of the spinel population enclosed by different host phases. The data are summarized in Figure 5, which shows that chromiferous spinels encapsulated within pyroxenes have consistently higher levels of Al and higher Mg/(Mg + Fe^{2+}) ratios than those within olivine hosts. Spinels enclosed by plagioclase feldspar tend to overlap the compositional ranges exhibited by grains within either olivine or pyroxene. Furthermore, the absolute levels of Al and the Mg/(Mg + Fe^{2+}) ratio are highest in the stratigraphically lowest cumulate sample (INS–1 at 143 m) and lowest in the highest sample (INS–1 at 43 m, near the top of the picritic zone).

The data provided by the microprobe analyses are unequivocal, but somewhat inadequate on a statistical basis. In order to test the conclusions on a larger sample, we made precise reflectivity measurements, the results of which are given in Figure 6. Here the frequency distribution of reflectivity values measured on 394 separate spinel grains clearly reveals the following: (1) In spinel grains encapsulated by olivine, both the range and mean are shifted to higher values than is the case where pyroxene is the host phase. (2) Spinel grains entrapped within plagioclase feldspar either exhibit a wider range of compositions than those entrapped within olivine (sample INS–1, 100 m) or show their arithmetic mean reflectivity to be intermediate between the values for grains entrapped within olivine and pyroxene, respectively. (3) Spinels of the basal picrites (sample INS–1, 143 m) have distinctly lower absolute-reflectivity values (higher Al and Mg values) than those

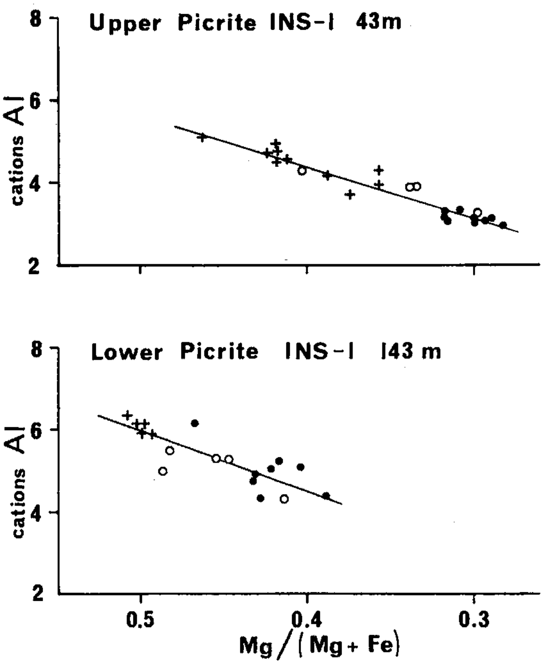

FIG. 5. Plot of cations Al *per* 32 oxygens against Mg/(Mg + Fe^{2+}) ratio of spinels from two horizons of picrites intersected by drillhole INS–1, Insizwa intrusion. Crosses: spinels enclosed by pyroxenes; filled circles: spinels enclosed by olivine; open circles: spinels enclosed by feldspars.

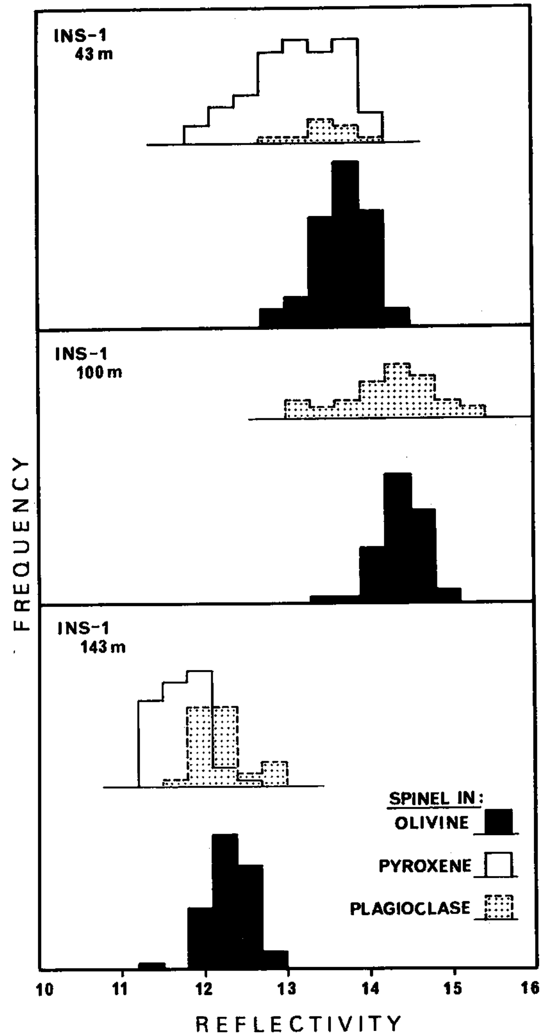

FIG. 6. Frequency distribution of measured reflectivities (589 nm) of 394 spinel grains from three horizons of picrites, Insizwa intrusion, demonstrating consistently lower reflectivity (and thus higher Al) in spinels hosted by pyroxene grains. Chromite grains within pyroxene are rare in sample INS–1, 100 m; the scanty data are not shown.

from higher horizons. Chromite grains entrapped within pyroxenes are rare in sample INS–1, 100 m and the scanty data are therefore not shown. It is clear, however, that spinel composition is not merely a simple function of stratigraphic height within this layered complex.

The conclusions regarding compositional variations based on the microprobe analysis of a relatively small sample are therefore fully supported by optical measurements on a much larger, statistically more significant sample.

The Elephant's Head intrusion

This intrusion is a relatively small but strongly differentiated body showing significant development of cumulus picrites (Poldervaart 1944, Eales & Snowden 1979). As at Insizwa, chromiferous spinels are mere accessory phases, but their compositional variations here follow quite a different pattern. There is no relationship between spinel composition and the nature of the host phase as there is at Insizwa; compositions at Elephant's Head are related to stratigraphic height within the pile of cumulates. Although there is overlap in successive samples, Al- and Mg-rich chromiferous spinels at the base of the body give way progressively to Fe^{3+}- and Ti-rich chromian titanomagnetites upward through the section. The very wide overall range in composition is shown in Figure 1. The spinels of the chilled margins show strong zoning of

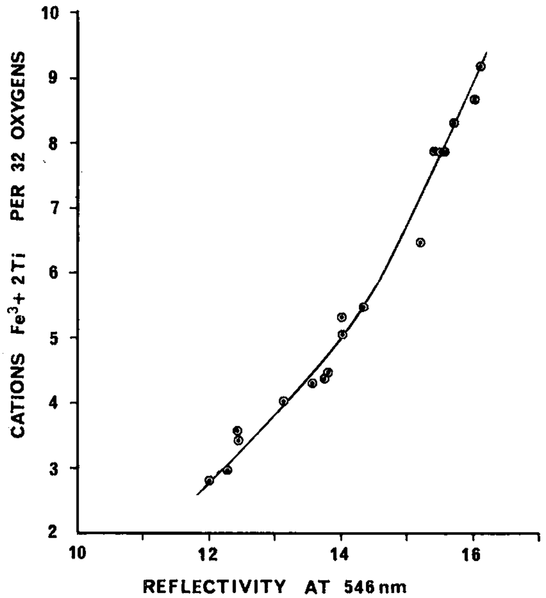

FIG. 7. Calibration curve for cations (Fe^{3+} + 2Ti) *per* formula unit of 32 oxygens *versus* reflectivity at 546 nm, for spinels in Elephant's Head picrites.

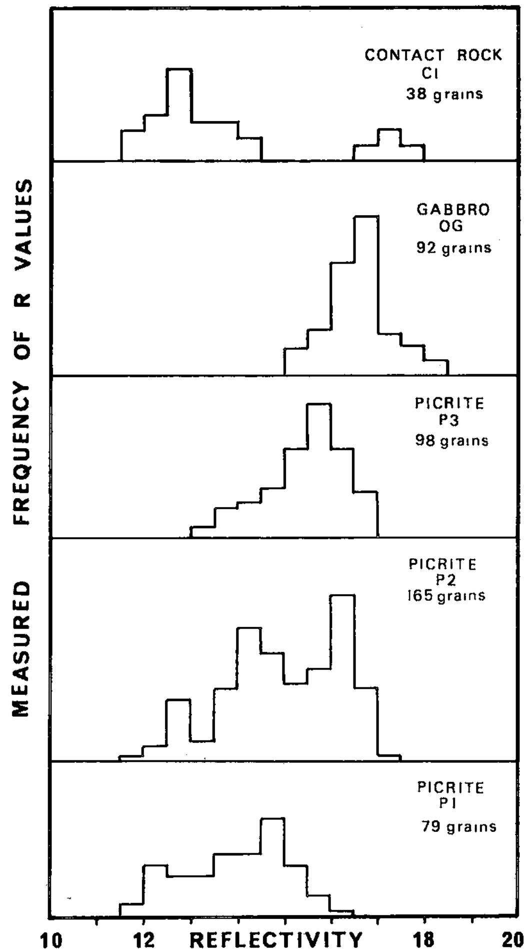

FIG. 8. Frequency distribution of measured reflectivities (546 nm) of 472 spinel grains from chilled margin, olivine gabbro and picrites of Elephant's Head intrusion. The gabbro and picrites are shown in appropriate stratigraphic sequence.

grains, with chromian titanomagnetite around aluminian chromite cores.

A correlation curve relating optical reflectivity to spinel compositions in this body is given in Figure 7. Figure 8 shows the frequency distribution of reflectivity measurements on 472 separate spinel grains from different levels and the chilled margin of the intrusion. This figure illustrates (1) the increase in mean reflectivity (increase in Fe^{3+} + 2Ti) of the spinels from the lowermost picrite (sample P1) towards the overlying olivine gabbro (sample OG), (2) the zonal nature of the spinels in the chilled contact facies (sample C1) and (3) a polymodal distribution of spinel compositions in horizon P2. The petrogenetic implications surrounding the existence of a polymodal distribution of compositions in a mineral population prompted further study of sample P2 by microprobe methods. The results of 26 analyses are summarized in Figure 9, which confirms a compositional hiatus within the population, between 2.5 and 3.5 cations Al *per* formula unit of 32 oxygens.

Discussion and Conclusions

An analysis of the fractionation trends and subsolidus equilibration reactions that have governed the compositional variations exhibited by spinel grains of the Insizwa and Elephant's Head intrusions lies beyond the scope of the present paper. The purpose has been to demonstrate the use of reflectivity measurements as an adjunct to microprobe studies. Despite the wide range of compositions possible within the group, there may be, within individual intrusions, a close adherence to a well-defined variation trend, enabling the plotting of relectivity values against more significant compositional parameters. It has also been shown that reflectivity is governed mainly by the relative proportions of cations Al, Fe^{3+} and Cr (see Fig.

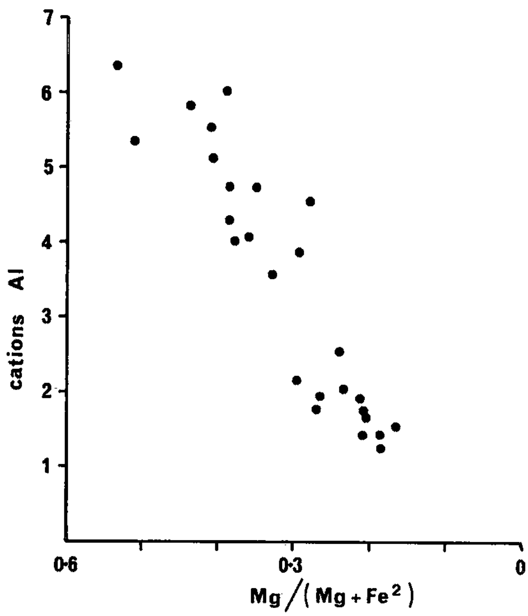

FIG. 9. Al *versus* $Mg/(Mg + Fe^{2+})$ for 26 spinel grains from horizon P2 of Figure 8, showing bimodal distribution of compositions and a hiatus between 2.5 and 3.5 Al cations *per* formula unit.

4), but also to a lesser degree by the $Mg/(Mg + Fe^{2+})$ ratio. Nonsystematic fluctuations in the levels of cations or variations in Ti will produce scattering in the data. The value of reflectometric methods lies in the speed with which large samples of grains may be studied under conditions in which examination is not hindered by the presence of the conductive coating necessary for microprobe analysis. Study of the associated silicates and of fine intergrowths is therefore possible during the course of measurements.

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