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CHROMITE: FROM THE FIERY RAIN OF CHONDRULES TO THE KILAUEA IKI LAVA LAKE[1]

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ABSTRACT

Chromite, spinel and magnetite compositions from a wide range of geological environments have been accumulated from published and unpublished sources in order to better characterize the spinel-group mineral as a function of environment of formation. Approximately 17 000 analyses have been included in a spinel database. The factors that control the crystallization of spinel-group minerals from a basaltic melt are discussed, and their composition is compared for rocks from various terrestrial environments, including mid-ocean-ridge basalts, ocean-island basalts, boninites, ophiolites, mantle xenoliths and kimberlites. The variation in composition of the spinel-group minerals from terrestrial sources are then compared to that in chondritic meteorites. The composition of chromite in unequilibrated chondrites is consistent with crystallization from a chondritic melt, whereas its composition in equilibrated chondrites is consistent with metamorphism at temperatures in the range of 600–800°C.

Keywords: chromite, magnetite, spinel, analyses, database, basalt, chondrite.

SOMMAIRE

Des données portant sur la composition chimique de la chromite, du spinelle et de la magnétite provenant d'une très grande diversité de milieux géologiques ont été accumulées de sources dans la littérature ou non publiées, afin de mieux caractériser la composition des minéraux du groupe du spinelle en fonction du milieu de leur croissance. Environ 17 000 compositions se trouvent actuellement dans la banque de données. Les facteurs qui régissent la cristallisation de ces minéraux à partir d'un liquide basaltique sont comparés dans le cas de roches provenant de divers milieux terrestres, y inclus les basaltes de crêtes médio-océaniques, les basaltes d'îles océaniques, les boninites, les ophiolites, les xénolithes du manteau, et les kimberlites. Les variations en composition des minéraux du groupe du spinelle de ces milieux sont ensuite comparées aux variations qui caractérisent ces minéraux dans les météorites chondritiques. La composition de la chromite des chondrites non équilibrées concorde avec sa cristallisation à partir d'un liquide chondritique, tandis que la composition de la chromite des chondrites équilibrées indique un ré-équilibrage métamorphique dans l'intervalle 600–800°C.

(Traduit par la Rédaction)

Mots-clés: chromite, magnétite, spinelle, données chimiques, banque de données, basalte, chondrite.

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[1] Delivered as the Presidential Address, Mineralogical Association of Canada, at Waterloo, Ontario, on May 17th, 1994, at the annual joint meeting of the Mineralogical Association of Canada and the Geological Association of Canada.

INTRODUCTION

I have spent much of the last ten years studying the composition of the spinel-group minerals and the geological conditions under which these minerals formed. This study has enabled me to use these minerals as the "vehicle" to traverse four and a half billion years from the time of chondrule formation, predating the formation of the Earth, to the formation of the 1959 Kilauea Iki lava lake.

Chromite is one of the first minerals to crystallize from basaltic melts, and its stability under a range of geological conditions has made it useful as an indicator of magmatic conditions at the time of initial crystallization. Chromite crystallizes with the spinel structure. Like magnetite and spinel, it can be expressed as a complex solid-solution of the oxides of chromium, aluminum, magnesium, ferrous iron, ferric iron and titanium. The extensive solid-solution among the spinel-group minerals commonly leads to confusion in naming these minerals. I will generally use the term *spinel* to include all the spinel-group minerals, and only rarely will I use the term *spinel* for the $MgAl_2O_4$-rich end member. There have been many attempts to relate the composition of chromite to the composition of the melt from which it crystallized. This paper will focus on the range in composition of chromite, magnetite and spinel found in nature, and on how the chromite that is normally found in rocks on earth compares with that found in chondrites that predate the formation of the earth.

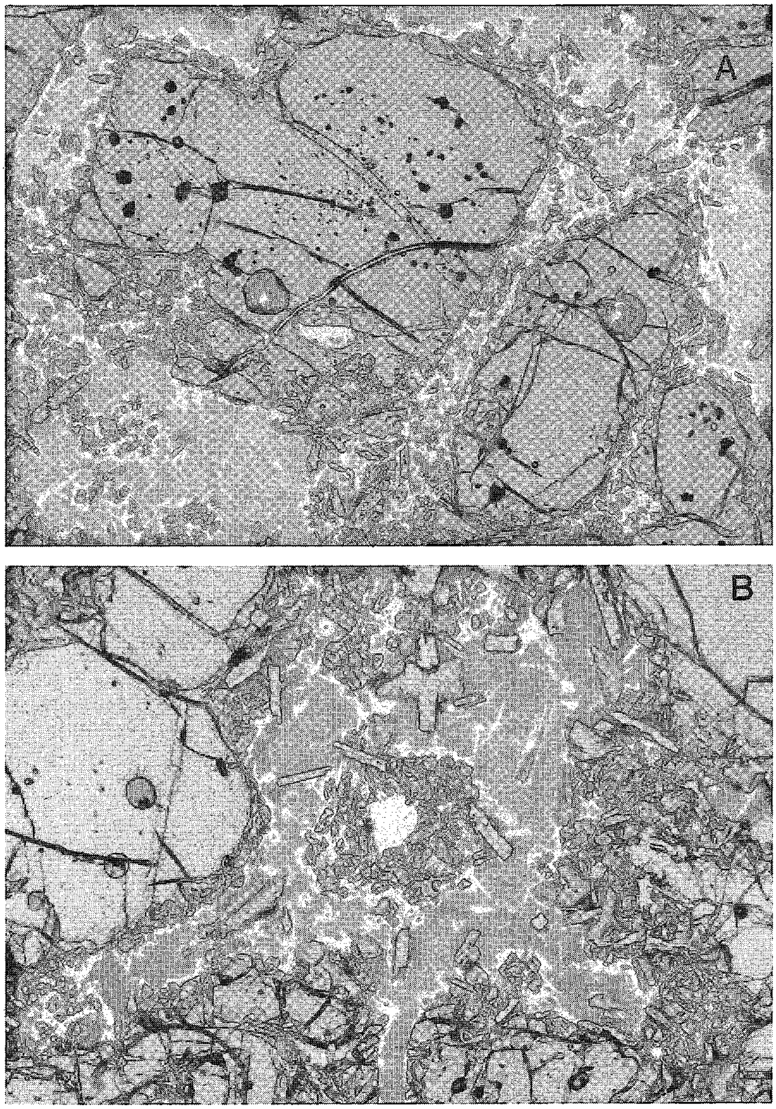

FIG. 1. Photomicrographs in transmitted light of a sample from the Kilauea Iki lava lake (sample KI75–1–141.5) drilled in 1975 (Scowen *et al.* 1991). Width of field: 9 mm. A. Large phenocrysts of olivine containing small opaque crystals of chromite and surrounded by small crystals of clinopyroxene and plagioclase laths in a matrix of glass. B. An opaque crystal of chromite surrounded by a rim of clinopyroxene in a matrix of glass. Large clear phenocrysts of olivine also are surrounded by clinopyroxene.

CHROMITE ON EARTH

The chromite that crystallizes in basaltic rocks is almost always associated with olivine (Fig. 1). The small size of the early crystals and the small amount of chromite relative to other early-crystallizing phases are largely due to the very low solubility (a few hundred ppm) of chromium in most basaltic melts. The solubility in basaltic melts of chromium, and also iron, is very sensitive to the oxygen fugacity (Hill & Roeder 1974, Roeder & Reynolds 1991). The 2+ oxidation state of chromium, like iron, is more soluble (Roeder & Reynolds 1991) than the 3+ state, and thus the very low oxygen fugacity of the basaltic melts on the lunar surface resulted in melts with higher chromium and iron contents. Chromite and olivine not only share the role of early cocrystallizing phases, but both minerals tend to react with the melt at some stage and be replaced by pyroxene (Irvine 1965, 1967). An example of this reaction is shown in Figure 1B, where both olivine and chromite are surrounded by clinopyroxene. As the melt produced by fractional crystallization of basalt becomes higher in iron, both a fayalitic olivine and a spinel phase, magnetite, can return as crystallizing phases. The reaction of early chromite with melt to produce a pyroxene, with a chromium content greater than that of the melt, was elegantly described by Irvine, and shown experimentally by Hill & Roeder (1974). Thus chromite in igneous rocks is more often found associated with forsteritic olivine and calcic plagioclase than with pyroxene.

My interest in chromite and the other spinel-group minerals has been mainly from the perspective of an experimental petrologist trying to duplicate and quantify the relationship between the spinel and the melt from which it crystallized. After completion of an experimental study on the relationship of chromite to basaltic melt (Roeder & Reynolds 1991), I decided to examine the variability of the composition of chromite, magnetite and spinel found in nature by comparing analytical data for chromite, magnetite and spinel from as many different geological environments as possible. Considerable time was spent writing suitable computer software for organizing and graphing these compositional parameters before entering the results of the chemical analyses of spinel, chromite and magnetite into the database. I hope that this database can be used, by myself and others, to explore the potential of spinel-group minerals for a determination of the environment of initial crystallization and later processes that can modify spinel compositions. This ambitious goal has been enunciated by many researchers (*e.g.*, Irvine 1965, 1967, Sigurdsson & Schilling 1976, Groves *et al.* 1977, Eales *et al.* 1980, Kunugiza 1981, Dick & Bullen 1984, Dick 1989), and the present study is one step toward this goal.

At the present time, the results of more than 17 000 analyses of spinel have been included in this database. These analytical data are mainly from the published literature, although some are from unpublished theses and other unpublished sources. All the analytical data were included in the database by myself, so that I could compare and judge their suitability. Only a very few analyses (<1%) were rejected. The survey of the literature is far from complete, mainly because of weariness of the author, but it is estimated that more than two thirds of the published compositions of spinel have been included. There was a specific attempt to survey the many diverse disciplines in geology for data on spinel. The database and the computer software (DOS) to access both the compositional data and the references, and the software to plot various functions, are available on three disks (3.5″) from the author. The list of sources (more than 900) of the analytical data is too long to be included in the reference list at the end of this paper; it is available on disk from the author.

A useful method of comparing spinel compositions is to plot Cr/(Cr + Al) and $Fe^{3+}/(Fe^{3+} + Al + Cr)$ *versus* $Fe^{2+}/(Fe^{2+} + Mg)$. The distribution of spinel compositions shown in Figures 2 and 3 is probably a fair reflection of the variation of spinel found in nature, or at least of those spinels that geologists have chosen to analyze. The spinel structure is sufficiently flexible that solid solution is possible over much of the range in composition shown in these two diagrams. These diagrams do not, however, show the variation of other important substituting elements, such as Ti, V and Zn. It is assumed in this paper that the chemical variation of spinel in the database is mainly a reflection of the chemical environment of the rocks in which spinel is a phase; an attempt is made to suggest some generalizations about how the composition of spinel can be used as a guide to the general geological environment in which it crystallizes.

The large concentration of points at the left and center of Figure 2 and at the bottom left in Figure 3 is due to chromite from igneous rocks. The most magnesian compositions are those usually found in chromite associated with forsteritic olivine in primitive basaltic rocks, mantle peridotite and chromitite. The concentration of compositions at the upper right of Figure 2 is due to magnetite from metamorphic rocks, and those compositions that fall in the lower right of Figure 2 are mainly due to magnetite found in fresh igneous rocks. The paucity of compositions between chromite and igneous magnetite is considered to be due to the hiatus in the crystallization of chromite and magnetite caused by reaction and the crystallization of clinopyroxene. The lack of data points between aluminous spinel [low Cr/(Cr + Al)] and igneous magnetite is due to the limited solid-solution between aluminates and ferrites at the temperatures found in nature (Sack & Ghiorso 1991).

Irvine (1965, 1967) presented, in two classic papers on the spinel minerals, a number of equations by

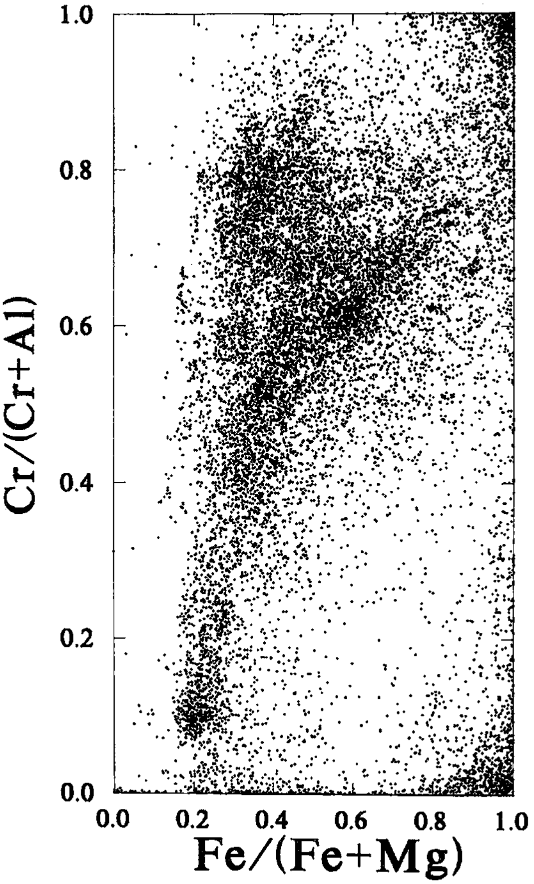

FIG. 2. Cr/(Cr + Al) *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of 16 093 samples of spinel in the database.

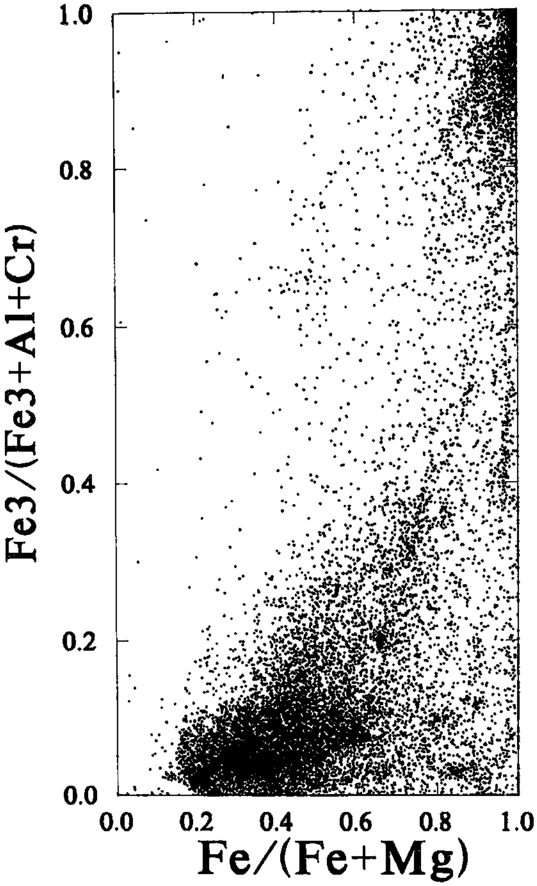

FIG. 3. $Fe^{3+}/(Fe^{3+} + Al + Cr)$ *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of 16 093 samples of spinel in the database.

which the variation in spinel composition can be described. He showed how the composition of spinel in equilibrium with olivine of fixed composition, at constant temperature and constant content of ferric iron, could be described by a line in a diagram of Cr/(Cr + Al) *versus* $Fe^{2+}/(Fe^{2+} + Mg)$. Four such lines are shown in Figure 4. These lines were calculated using the equations and computer program of Sack & Ghiorso (1991), and assuming $Fe^{3+}/(Fe^{3+} + Al + Cr) = 0.05$ for the spinel. The temperature and forsterite content of the coexisting olivine are shown at the top of each line. Irvine described how the composition of coexisting olivine and spinel could be used as a geothermometer. An example is shown by the two left-hand lines on Figure 4. Thus if a small amount of spinel is allowed to equilibrate with a large amount of olivine of composition Fo_{90} as the temperature is lowered from 1300°C to 1000°C, the $Fe^{2+}/(Fe^{2+} + Mg)$ of the spinel changes from that of the 1300°C line to that of the 1000°C line on Figure 4. The left-hand line is essentially parallel to the most magnesian composition of spinel and chromite in the database; the composition of olivine in the mantle is probably the major control on the maximum Mg content of igneous chromite. Thus one might expect that the chromite that crystallizes from the most primitive basalt, that closest to being in equilibrium with the mantle peridotite from which it was derived, will have the lowest $Fe^{2+}/(Fe^{2+} + Mg)$. The composition of chromite depends on the composition of the melt. As the melt changes composition during the crystallization of olivine, plagioclase, pyroxene and chromite, so also will the chromite change composition. As an example, I have shown by three short arrows on Figure 4 the change in chromite that might be expected by the cocrystallization from a basaltic melt of chromite and olivine (OL), chromite and plagioclase (PL), and chromite and pyroxene (PY). I have also shown, by the solid curve with four

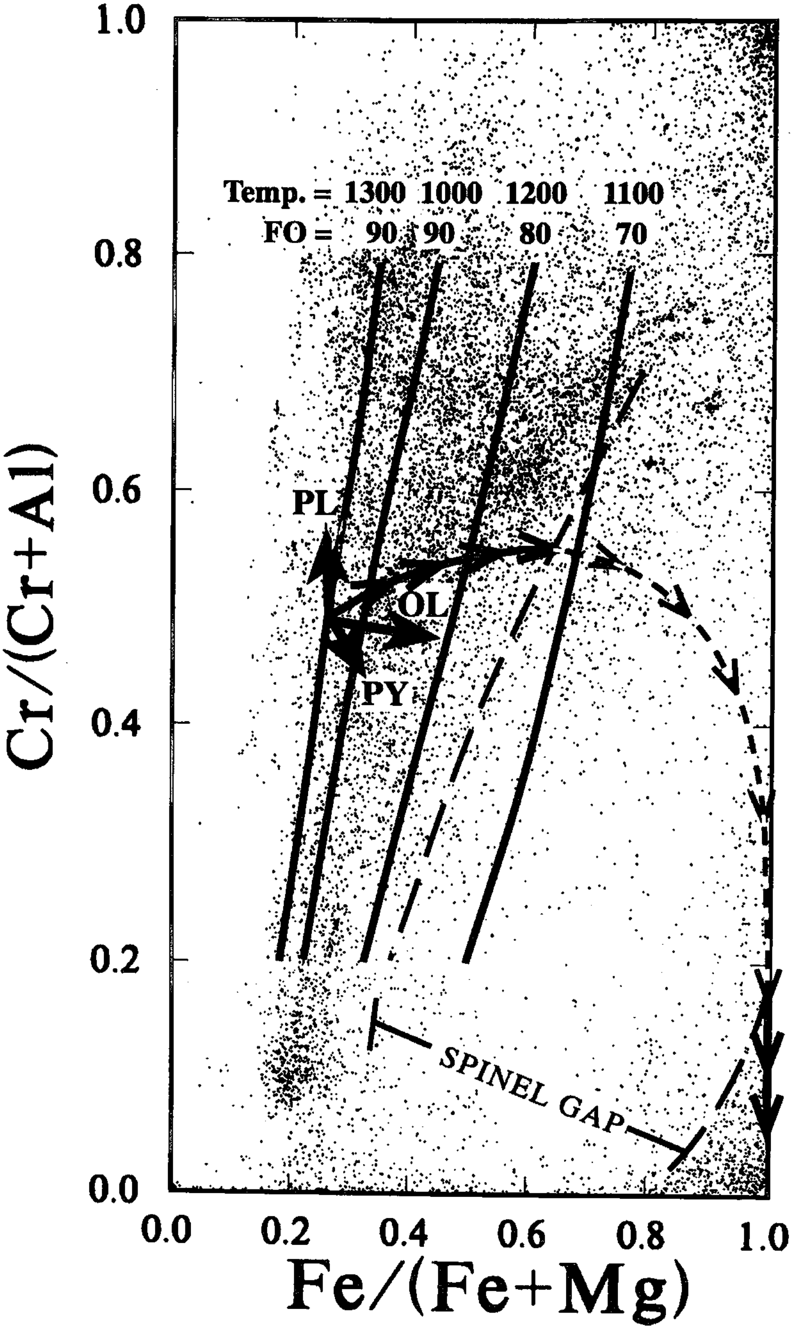

FIG. 4. Cr/(Cr + Al) *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of all spinel samples in the database. The four sloping lines represent the calculated compositions of spinel that would be in equilibrium with the indicated olivine composition (FO: forsterite) at the indicated temperature (Temp. in °C). The calculation was made using the formulation of Sack & Ghiorso (1991) and assumes that the spinel has a $Fe^{3+}/(Fe^{3+} + Al + Cr)$ value of 0.05. See the text for an explanation of the other lines.

arrows, a possible path of chromite crystallization due to the cocrystallization of olivine, plagioclase and chromite. Once pyroxene becomes a dominant phase and thus removes chromium from the melt, the chromite ceases to crystallize, as represented by the dashed curve with arrows. When the melt becomes enriched in elements such as Fe^{2+}, Fe^{3+}, Ti and V, magnetite may start to crystallize, as shown by the end of the solid curved line in the lower right of Figure 4. The igneous magnetite will almost always have a low Cr/(Cr + Al) because the melt at this stage has a very low Cr (<100 ppm) content, but still contains considerable Al (>10 wt.% Al_2O_3). The gap in composition between the crystallization of chromite and magnetite is schematically shown in Figure 4 by the medium-heavy dashed lines labeled "SPINEL GAP". It should be emphasized that a spinel having a composition within this gap can be a stable phase, but is not usually stable in the presence of clinopyroxene and melt. The trend in the composition of chromite and the gap in the composition of the spinels will be very different for each melt and for different conditions of oxygen fugacity (Hill & Roeder 1974) and pressure. Thus the trends shown in Figure 4 are only meant for illustrative purposes.

An example of spinel compositions from three easily identifiable kinds of basalts found in ocean basins is shown in Figures 5 and 6. The chromite from boninites has the highest Cr/(Cr+Al), and the chromite from mid-ocean-ridge basalt (MORB) has the greatest range and the lowest absolute Cr/(Cr + Al). The common wisdom (*e.g.*, Dick 1976, 1977, Fujii 1989) is that the Cr/(Cr + Al) of chromite in primitive basalts is a reflection of the extent of depletion of the mantle peridotite source. The lowest Cr/(Cr + Al) value of spinel in basalt reflects a peridotite source that has not

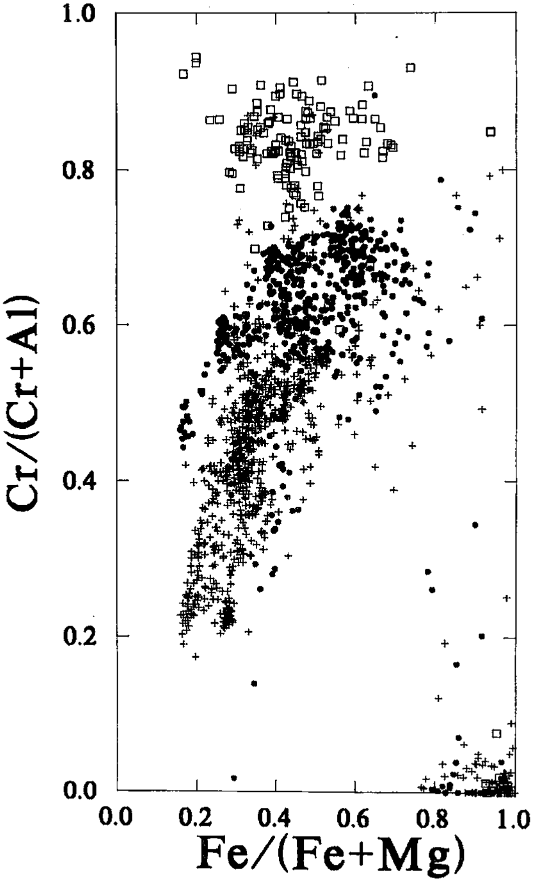

FIG. 5. Cr/(Cr + Al) *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of spinel samples from boninitic basalts (open squares), ocean-island basalts (solid dots) and mid-ocean-ridge basalts (crosses).

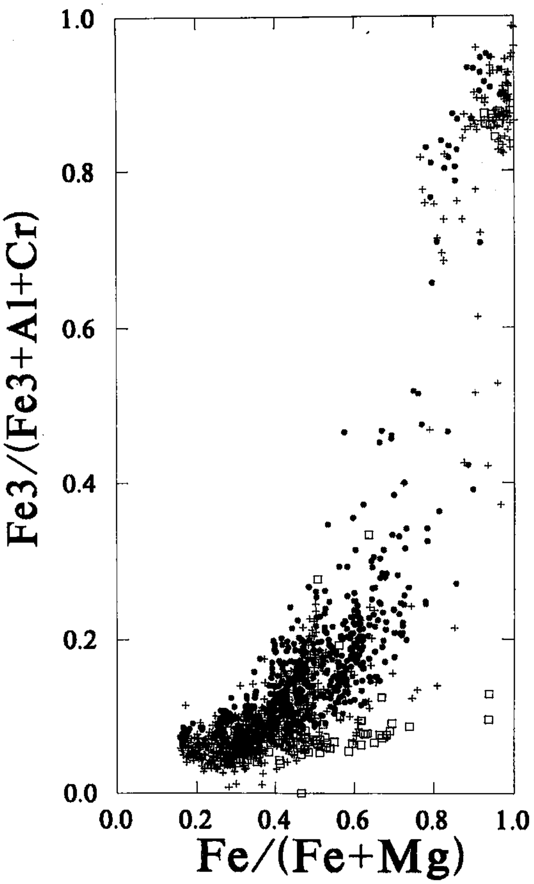

FIG. 6. $Fe^{3+}/(Fe^{3+} + Al + Cr)$ *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of spinel samples from boninitic basalts (open squares), ocean-island basalts (solid dots) and mid-ocean-ridge basalts (crosses).

seen a previous generation of melting, and thus there is considerable Al available in the peridotite, mainly in clinopyroxene, for the melt. The high Cr/(Cr + Al) in chromite from boninites may reflect the large amount of melting in the mantle peridotite that produced the boninitic melt. Note the low Cr/(Cr + Al) in the magnetite, and also note that there are some compositions in the region of the so-called spinel gap. Most examples of spinel from volcanic rocks that fall in this region crystallized during the cooling of the flow, when conditions are far from equilibrium. Thus spinel that has a composition within the so-called spinel gap can be a stable phase, but not stable at equilibrium in the presence of melt and clinopyroxene. This gap in composition of spinel crystallization is also shown in Figure 6 by the few data points between $Fe^{3+}/(Fe^{3+} + Al + Cr)$ values of 0.3 and 0.8.

The range in composition of spinel in terms of Cr – Al – Fe^{3+} is shown in Figures 7 and 8. There are few examples of spinel between Al and Fe^{3+} at low

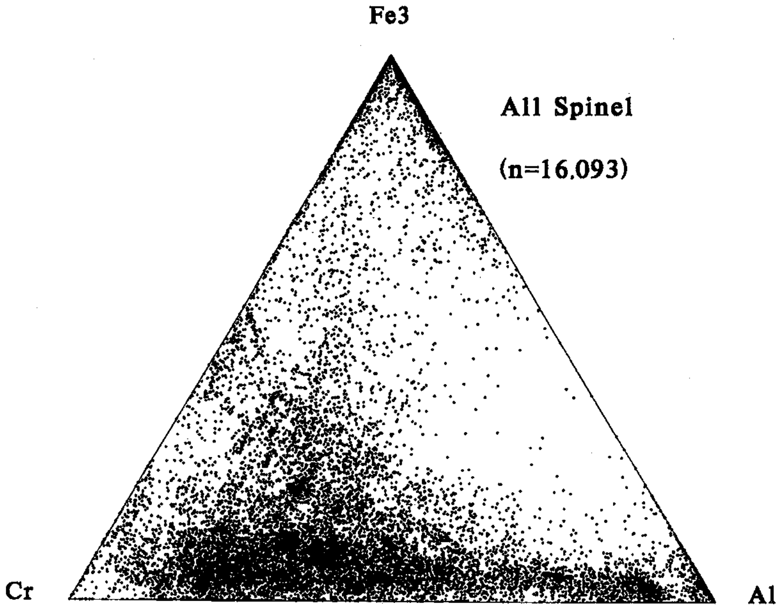

FIG. 7. Cr – Al – Fe^{3+} plot of all spinel samples in the database.

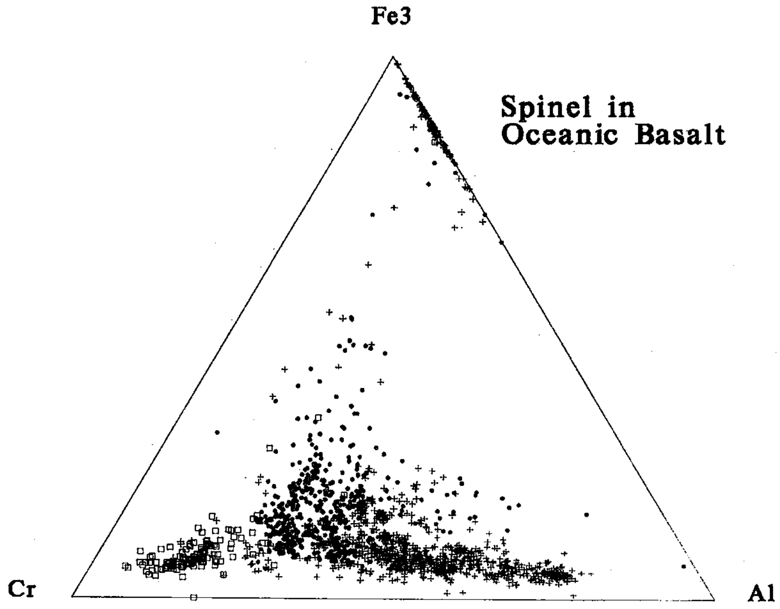

FIG. 8. Cr – Al – Fe^{3+} plot of spinel samples from boninitic basalts (open squares), ocean-island basalts (solid dots) and mid-ocean-ridge basalts (crosses).

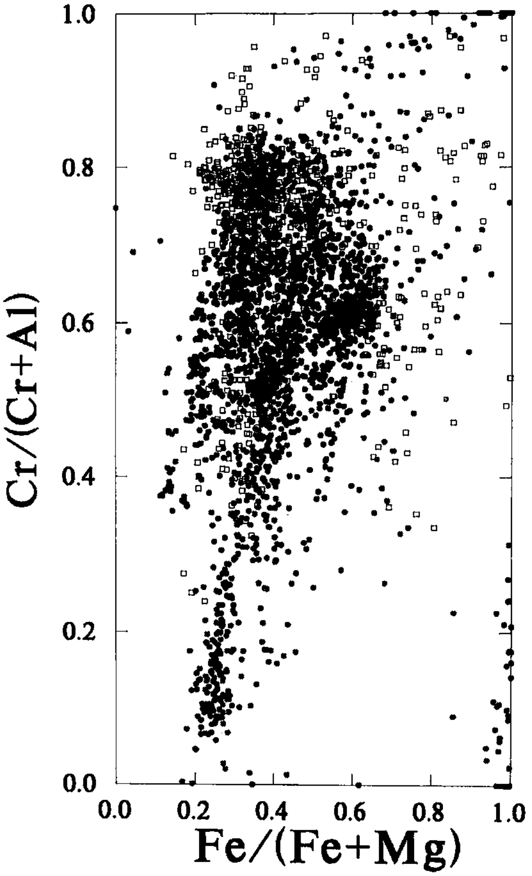

FIG. 9. Cr/(Cr + Al) *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of spinel samples from ophiolites (solid dots) and chromitites (open squares).

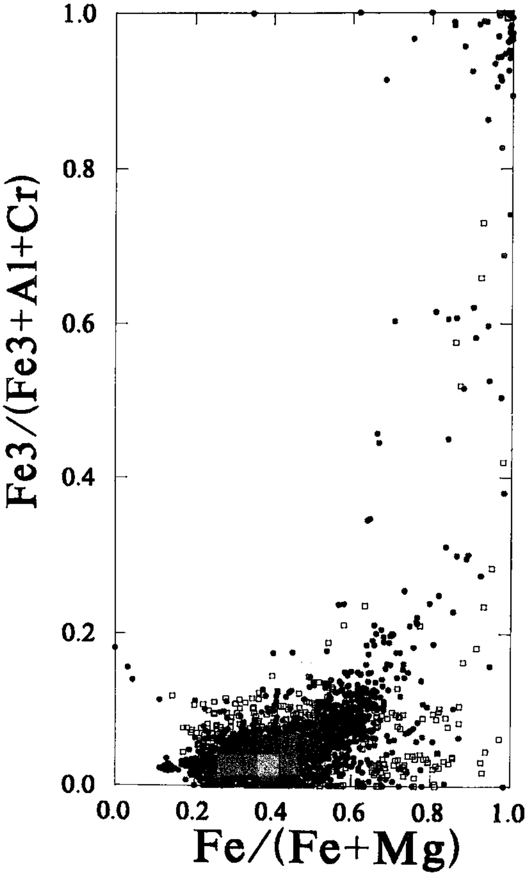

FIG. 10. $Fe^{3+}/(Fe^{3+} + Al + Cr)$ *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of spinel samples from ophiolites (solid dots) and chromitites (open squares).

values of Cr because of limited solid-solution between aluminates and ferrites (Mattioli & Wood 1988, Nell & Wood 1989, Sack & Ghiorso 1991) even at temperatures of the basaltic melt (Fig. 8). The few data points shown in this range on Figure 7 are mainly due to spinel that is rich in Ti. The solid solution between aluminates and ferrites becomes quite limited under metamorphic conditions, and the spinel compositions along the Cr–Fe^{3+} join in Figure 7 are mainly from metamorphosed igneous rocks. One result of metamorphic reactions that involve chromite is the formation of a rim of "ferritchromit" (Onyeagocha 1974, Bliss & MacLean 1975). Such "ferritchromit" has a low-Al composition close to the Cr–Fe^{3+} join; it is commonly found as a rim on chromite, with a sharply defined boundary between the chromite core and the rim. The difference in the Al content of magnetite from fresh igneous basalt and that from metamorphosed igneous rocks is shown by the difference in the concentration of points at the Fe^{3+} apex of Figures 7 and 8. Examples of magnetite from unaltered oceanic basalts (Fig. 8) all fall near the Fe^{3+}–Al join at the Fe^{3+} apex, whereas the large number of magnetite compositions in Figure 7 that are near the Fe^{3+}–Cr join at the Fe^{3+} apex are from igneous rocks that have been altered or metamorphosed to the greenschist or amphibolite facies.

Spinel compositions from some plutonic rocks are shown in Figures 9 and 10. The spinel present in the ophiolite samples (filled circles) is mainly from the mantle section and lower crust section of ophiolites. The chromite in chromitites (squares) commonly has a high Cr/(Cr + Al) value and a low $Fe^{2+}/(Fe^{2+} + Mg)$ value. The chromite that occurs as disseminated grains in low concentration commonly increases in $Fe^{2+}/(Fe^{2+} + Mg)$ during slow cooling, by equilibration with coexisting silicates, such as olivine, and thus does not reflect a magmatic composition (Roeder &

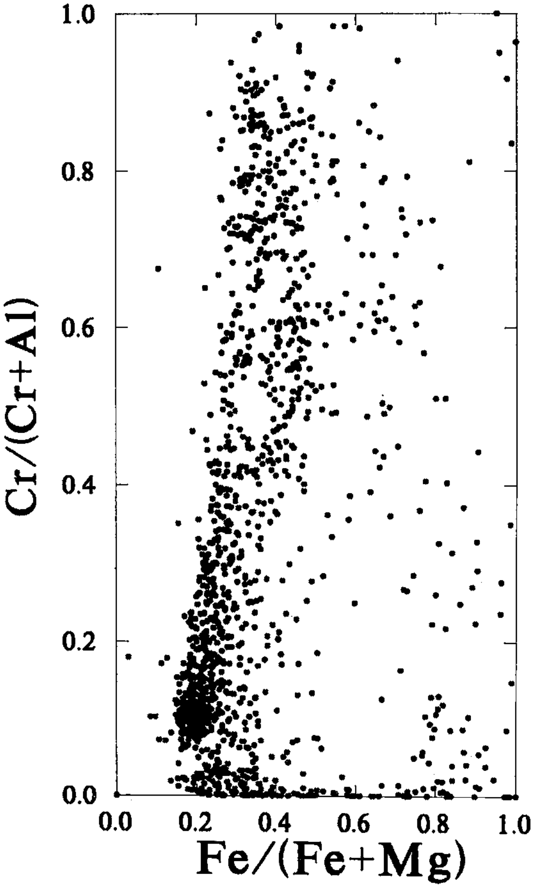

FIG. 11. Cr/(Cr + Al) *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of spinel samples from xenoliths found in alkali basalts and kimberlites.

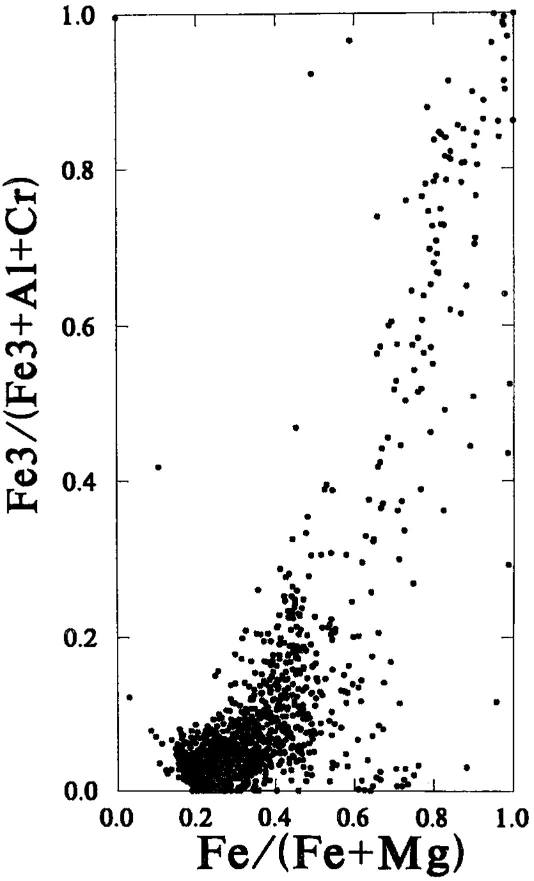

FIG. 12. $Fe^{3+}/(Fe^{3+} + Al + Cr)$ *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of spinel samples from xenoliths found in alkali basalts and kimberlites.

Campbell 1985) . Most massive chromitite has chromite with a low $Fe^{2+}/(Fe^{2+} + Mg)$ value, which may be close to that produced at magmatic temperatures. This inference can be made because of the large amount of chromite relative to the amount of silicate; thus there is little chance for subsolidus equilibration of $Fe^{2+}/(Fe^{2+} + Mg)$ in chromite. The best information concerning the composition of spinel found in mantle peridotite is that from ophiolites and from mantle xenoliths brought to the surface of the earth by kimberlites and by alkali basalt volcanism (Figs. 11, 12). Generally, lherzolite contains spinel with the lowest Cr/(Cr + Al) value, and harzburgite and dunite contain chromite with the highest Cr/(Cr + Al) value. The major concentration of spinel and chromite in Figure 11 is parallel to the left-hand line of constant olivine composition shown in Figure 4, and is a reflection of how forsteritic olivine controls the $Fe^{2+}/(Fe^{2+} + Mg)$ value of dispersed grains of spinel in mantle peridotite. The high concentration of spinel data points of very low Cr/(Cr + Al) found in lherzolite (Fig. 11) is considered to reflect samples that equilibrated at a temperature well below the peridotite solidus. Under these conditions, the solubility of Al in pyroxene is limited, and there is probably more spinel, and more aluminous spinel, than would be present in the same sample at the temperature of the peridotite solidus in equilibrium with basaltic melt. The range in $Fe^{3+}/(Fe^{3+} + Al + Cr)$ values of the spinel in the xenoliths (Fig. 12) is, surprisingly, quite similar to the range for that in oceanic basalts (Fig. 6).

Many of the xenoliths whose spinel is plotted in Figures 11 and 12 were transported to the surface by kimberlitic melts. The composition of spinel found in kimberlite, other than that found in xenocrysts, is shown in Figures 13 and 14. It commonly is impossible to distinguish spinel that crystallized from a kimberlitic melt from xenocrysts that resulted from the

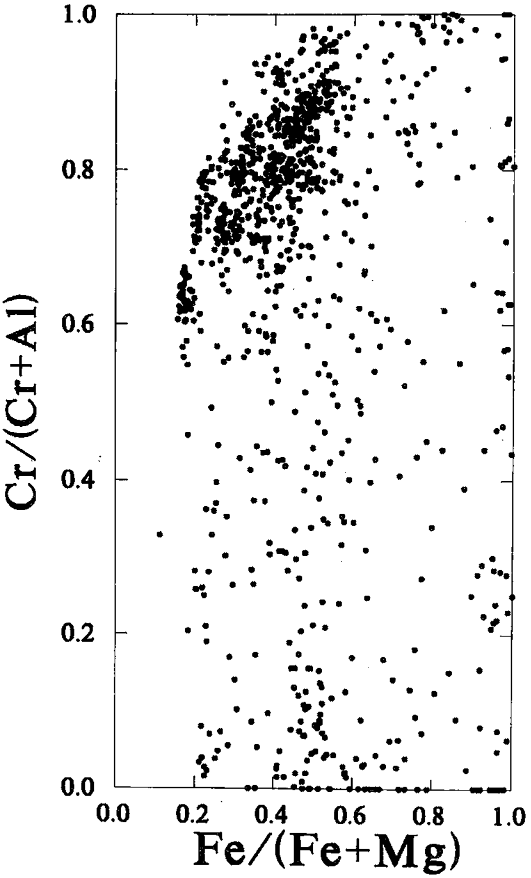

FIG. 13. Cr/(Cr + Al) *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of spinel samples from kimberlites.

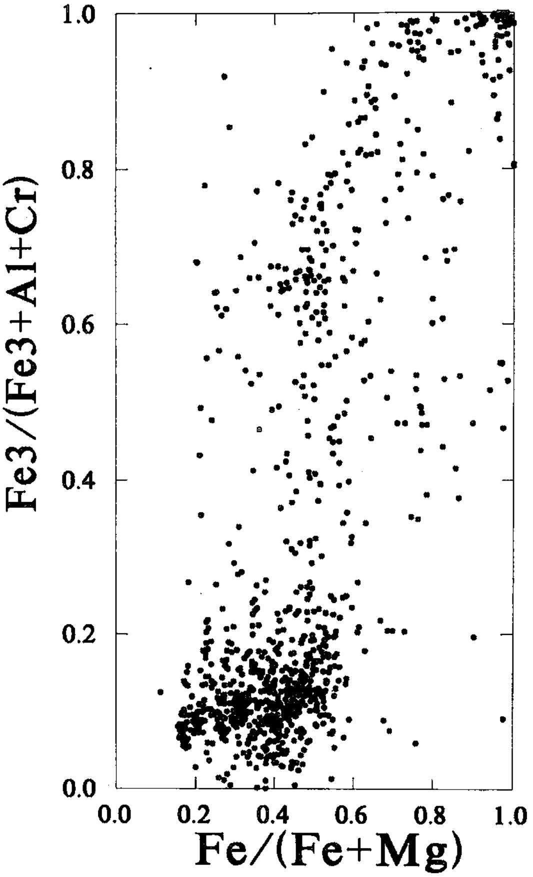

FIG. 14. $Fe^{3+}/(Fe^{3+} + Al + Cr)$ *versus* $Fe^{2+}/(Fe^{2+} + Mg)$ plot of spinel samples from kimberlites.

breakup of xenoliths in the melt. Thus Figures 13 and 14 contain a range of samples from xenocrysts to chromite that crystallized from the kimberlitic melt. The large concentration of chromite compositions in the ranges $0.6 < Cr/(Cr + Al) < 1.0$ (Fig. 13) and $0 < Fe^{3+}/(Fe^{3+} + Al + Cr) < 0.2$ (Fig. 14) at a value of $Fe^{2+}/(Fe^{2+} + Mg)$ between 0.2 and 0.6 probably pertains mainly to xenocrystic chromite. The change in composition of chromite (Pasteris 1980, Mitchell 1986, Hall 1991) crystallizing from kimberlitic melts is very different from the change in composition of chromite crystallizing in basaltic melts. Chromite in basaltic melts usually increases in $Fe^{2+}/(Fe^{2+} + Mg)$ (Fig. 4) during crystallization of the melt, and shows a gradual increase in $Fe^{3+}/(Fe^{3+} + Al + Cr)$ with increasing $Fe^{2+}/(Fe^{2+} + Mg)$. The major change in the chromite crystallizing from a kimberlititc melt is a decrease in Cr/(Cr + Al) and an increase in $Fe^{3+}/(Fe^{3+} + Al + Cr)$ at an almost constant value of $Fe^{2+}/(Fe^{2+} + Mg)$. This is probably due to a major oxidation event during the late stages of crystallization of the kimberlitic melt. Thus much of the ferrous iron is converted to ferric iron while the Mg content of the melt remained relatively high. This oxidation is most likely due to the large evolution of gas during the late stage of kimberlitic intrusion near the Earth's surface (Mitchell 1986). Thus some of the late-stage spinel from kimberlites changes toward magnesioferrite, which is located at the upper-left corner of Figure 14, and magnetite, which is located at the upper-right corner. An important component of spinel in kimberlite is titanium. Figure 15 shows Fe^{2+}, Fe^{3+} and Ti of kimberlitic and oceanic-basalt spinel. The line between ulvöspinel and magnetite has been shown for reference. Most of the spinel compositions above this line (Fig. 15A) are strongly oxidized and thus contain a magnesioferrite component.

The igneous evolution of chromite and magnetite in

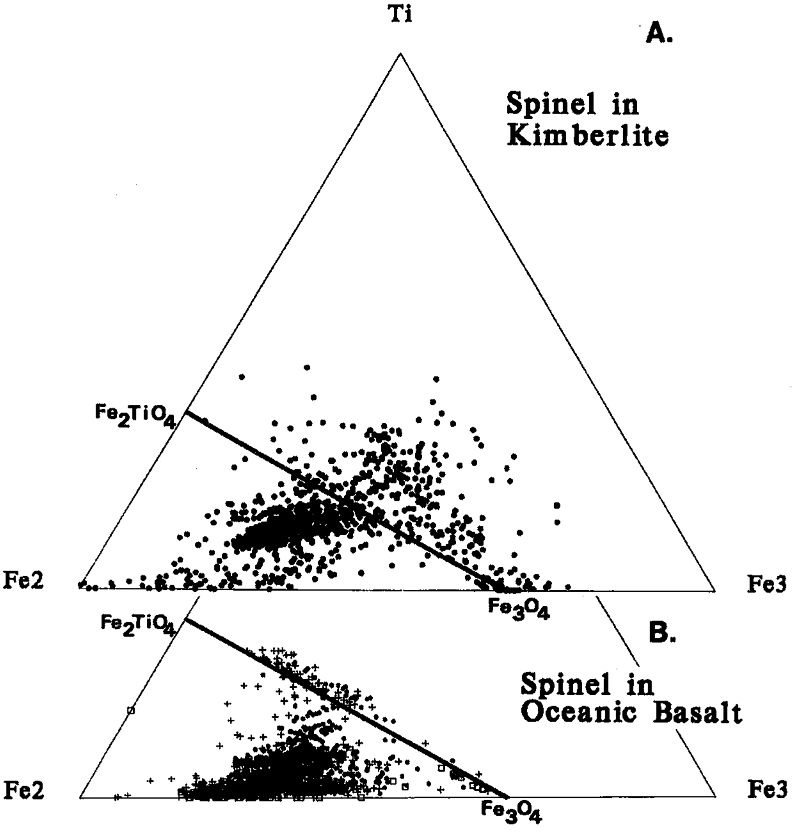

FIG. 15. Fe^{2+} – Fe^{3+} – Ti plot of spinel samples from kimberlites (A) and from oceanic basalts (B), that include boninitic basalts (open squares), ocean-island basalts (solid dots) and mid-ocean-ridge basalts (crosses).

terrestrial samples is in a broad sense fairly well understood; many investigators have used the composition of chromite in igneous and metamorphic rocks in order to reconstruct the igneous history. Chromite is in many cases the only igneous mineral that seems to have survived serpentinization and other metamorphic reactions; however, this may be more apparent than real. Thus in metamorphosed samples, the core of chromite that is surrounded by "ferritchromit" commonly is interpreted as having a composition that may be essentially unchanged in Cr/(Cr + Al) from that when it crystallized from a melt. However, I believe that the Cr/(Cr + Al) value of chromite may change in response to metamorphism and formation of the ferrian chromite rim. It is known that the $Fe^{2+}/(Fe^{2+} + Mg)$ of disseminated chromite re-equilibrates quite readily with surrounding silicates, as shown in the discussion of Figure 4. It has also been shown (Scowen *et al.* 1991) that the chromite trapped within olivine in the Kileaua Iki lava lake has changed composition in response to the changing composition of the melt outside the olivine as temperature dropped from about 1200°C to below 1100°C over a period of about twenty years. I have been slow to realize that although chromite is usually thought of as an igneous mineral, the composition of chromite has often had adequate opportunity to change its composition since initial crystallization from a melt. This may be good news for metamorphic petrologists, but bad news for igneous petrologists.

CHROMITE IN CHONDRITES

When I started preparing for this Presidential Address, I decided to use my experience with the composition of chromite, magnetite and spinel to examine these minerals in an environment completely new to me and to most mineralogists and igneous petrologists, that of chondrules in chondritic meteorites. Chondrites are stony meteorites that represent the only material

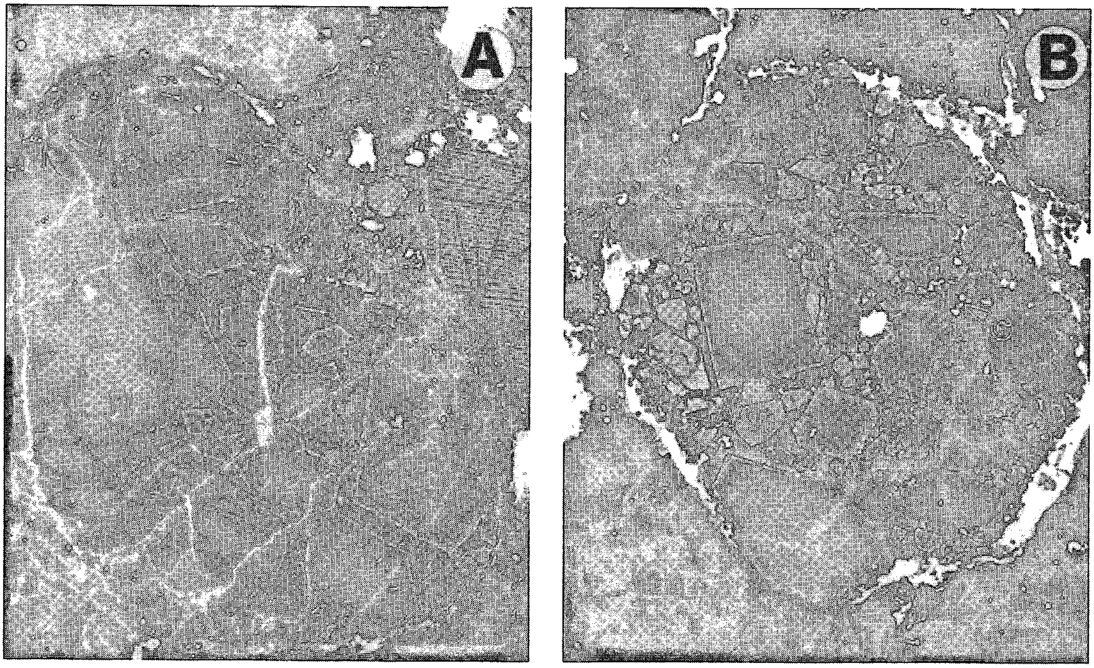

FIG. 16. Type-II porphyritic olivine chondrules in the Semarkona unequilibrated chondrite; back-scattered electron images. A. Chondrule C11, with zoned phenocrysts of olivine set in a mesostasis of glass and fine crystallites. B. Chondrule 51, with zoned phenocrysts of olivine, a small crystal of chromite ("C") and a small crystal of augite ("A") in mesostasis. Scale bar: 200 μm. The photos are reprinted from Jones (1991) with permission (see Acknowledgements).

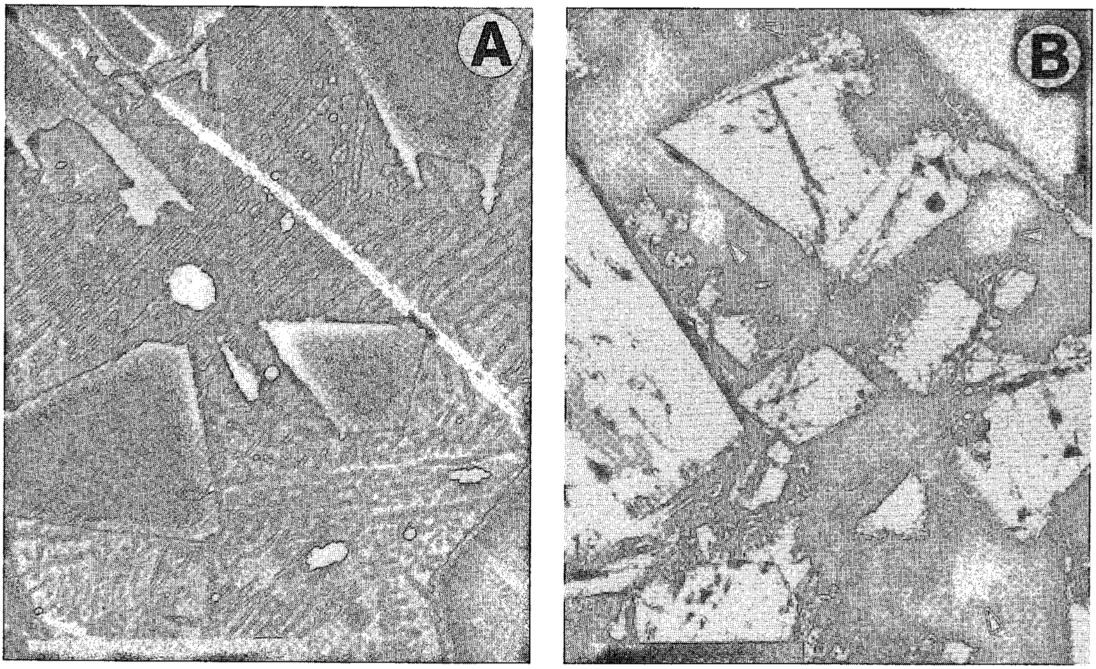

FIG. 17. Type-II porphyritic olivine chondrules in the Semarkona unequilibrated chondrite. A. Back-scattered electron image showing mesostasis texture between olivine phenocrysts in chondrule C11. B. Transmitted-light photomicrograph that shows olivine phenocrysts in a mesostasis containing small crystals of chromite (arrows). Scale bar: 100 μm. The photos are reprinted from Jones (1991) with permission (see Acknowledgements).

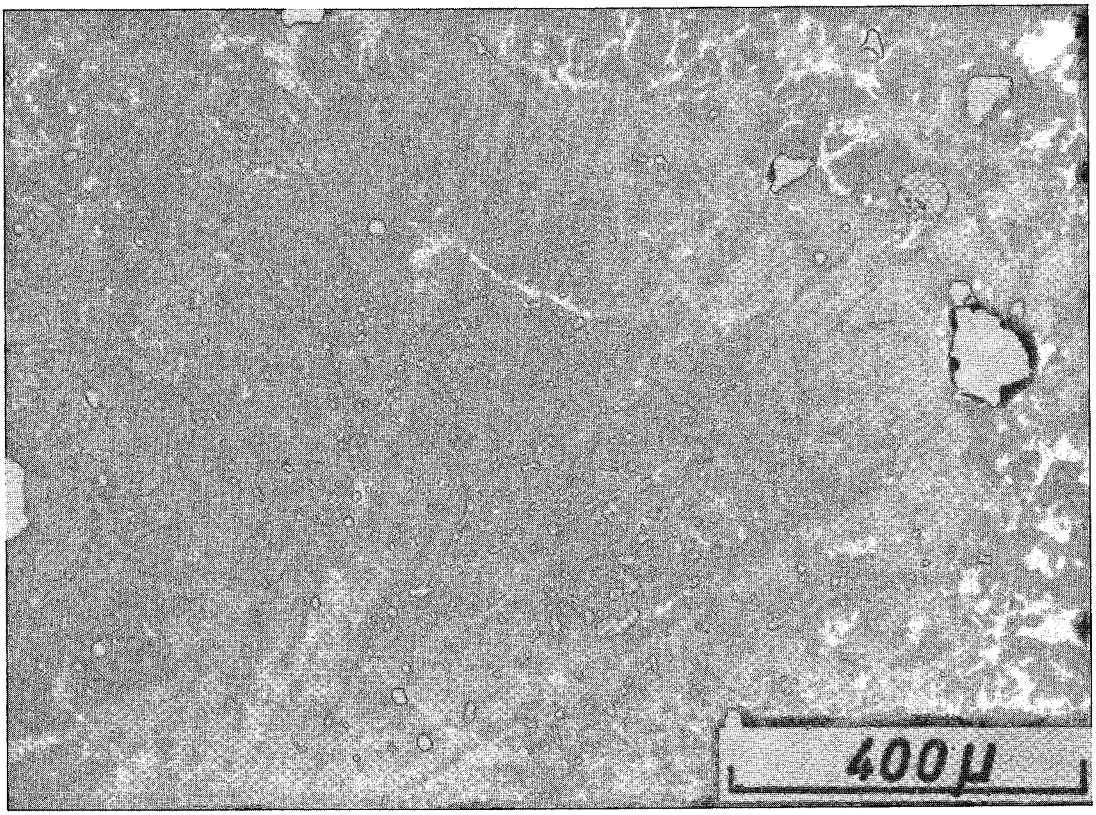

FIG. 18. A metamorphosed chondrule from the Bachmut chondrite. Reflected-light photomicrogragh showing radiating crystals of albite with small crystals of chromite between the albite crystals, set in a fine-grained matrix. The photo is reprinted from Ramdohr (1973) with permission (see Acknowledgements).

available to help us understand the preplanetary history of the solar system. I would like to describe how the chemistry of chromite and spinel in these rocks bears on the processes involved. I will draw freely from the many excellent studies on chondrites, particularly studies by Van Schmus *et al.* (1967), Snetsinger *et al.* (1967), Bunch *et al.* (1967), Ramdohr (1967, 1973), Dodd (1981), Wlotzka (1987), Jones (1990), Wasson (1993) and Krot *et al.* (1993). Chondrites generally contain fragmental material and chondrules, which are round bodies (Figs. 16, 17) of millimeter and submillimeter size that were once molten and were heated rapidly and cooled rapidly. The chondrules plus the fragmental matrix probably accumulated on asteroid-size bodies in a thick blanket that cooled slowly enough that many chondrites show signs of varying degrees of metamorphism and equilibration of the more volatile elements, such as Na, Fe and Cr, within chondrite samples. Chondrites contain a range of materials of different volatility that may also provide evidence for the sequence of condensation of the early solar nebula, from a gas phase to dust particles. The first, and highest-temperature, condensates of the nebula are rich in Ca, Al, Ti and Mg, and are represented by Fe- and Cr-free minerals such as corundum, spinel, anorthite, melilite and hibonite, which are found in CAI (calcium – aluminum – inclusion) fragments both in melted or partially melted chondrules. The elements Fe, Cr, Na, K and S are considered (Wasson 1993) to be concentrated in later condensates, whereas the carbonaceous chondrites are richer in the more volatile carbon and water, and represent very late condensates.

The general sequence of events in the formation of chondrites is considered (*e.g.*, Dodd 1981, Wasson 1993) to be as follows: the gaseous solar nebula cooled and condensed to give a sequence of micrometric to millimetric condensates, from Ca- and Al-rich minerals at higher temperatures to lower-temperature condensates enriched in Fe, Cr and S, to even lower-temperature condensates. There were a series of very sudden heating events that melted these dust particles and produced chondrules, which later were incorporated in a regolith on asteroid-size bodies. This regolith material was metamorphosed, and the metamorphism tended to even out compositional variations in olivine, pyroxene, plagioclase and chromite. Many chondrites show evidence of many repetitions of these events.

Figures 16 and 17 show textures and minerals that are familiar to igneous petrologists who study komatiites and the rapid cooling of other basic silicate melts. These unmetamorphosed (unequilibrated) chondrules contain small amounts of chromite that commonly are found as small euhedral crystals in the groundmass. The large phenocrysts of olivine may be strongly zoned, with a forsteritic core and more iron-rich rim (Figs. 16, 17). The oxygen fugacity at the time of melting may have been quite variable because of the local presence of carbon (Connolly *et al.* 1994) that acted as a reducing agent during melting. Textural evidence and the large amount of olivine in some chondrules suggest that many chondrules were only partially melted, and cooled very rapidly. Rare chondrules contain unmelted iron-free minerals such as anorthite and spinel, which may be unmelted remnants of CAI fragments (Bischoff & Keil 1984). There is little doubt that the minerals, and the mineral zoning and textures found in unmetamorphosed chondrules, are explainable by igneous processes (Jones 1990). However, the majority of chondrites are interpreted as having been metamorphosed (equilibrated), so that the igneous textures become ragged looking, but still plainly visible, and the minerals both within and outside the chondrules tend to the same composition. The textures that result from this metamorphism (Fig. 18) are quite different from those found in most metamorphic rocks on Earth in that many of the primary igneous textures are preserved, and there is no tendency for large-scale recrystallization and grain coarsening. This difference in style of metamorphism may be due to the lower pressures and quite different role played by volatiles in the environment of chondrite metamorphism.

The chromite in chondrules has a fairly distinctive composition, as shown in Figure 19. The $Fe^{3+}/(Fe^{3+} + Al + Cr)$ value of the spinel (Fig. 19B) is very low, which is expected for samples that may contain Fe–Ni alloys and troilite. The spinel in CAI fragments in unmetamorphosed carbonaceous chondrites (circles in Fig. 19) is commonly pure $MgAl_2O_4$ (lower-left corner in Fig. 19A), but there is also relatively pure magnetite reported, although none is present in the database. The chromite in unequilibrated ordinary chondrites (crosses in Fig. 19), such as Semarkona (Jones 1990), has high $Cr/(Cr + Al)$ and $Fe^{2+}/(Fe^{2+} + Mg)$ values. The composition of the chromite in equilibrated (metamorphosed) chondrites (filled squares in Fig. 19) is very distinctive in that the $Cr/(Cr + Al)$ and $Fe^{2+}/(Fe^{2+} + Mg)$ values are quite variable, but the points fall along a line (Fudali & Noonan 1975, Krot *et al.* 1993). In any one equilibrated sample, the

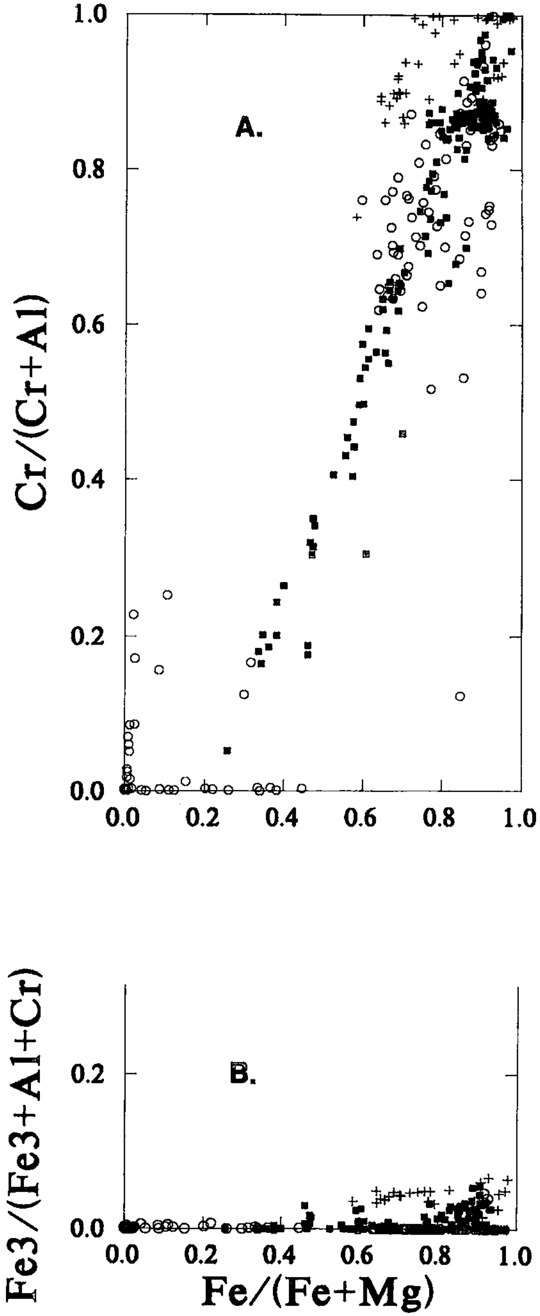

FIG. 19. The composition of spinel in chondritic meteorites. The spinel samples from CAI fragments in unequilibrated carbonaceous chondrites are shown by open circles, the chromite samples from unequilibrated ordinary chondrites are shown by crosses, and the samples of chromite and spinel from equilibrated ordinary chondrites are shown by filled squares. A. $Cr/(Cr + Al)$ *versus* $Fe^{2+}/(Fe^{2+} + Mg)$. B. $Fe^{3+}/(Fe^{3+} + Al + Cr)$ *versus* $Fe^{2+}/(Fe^{2+} + Mg)$.

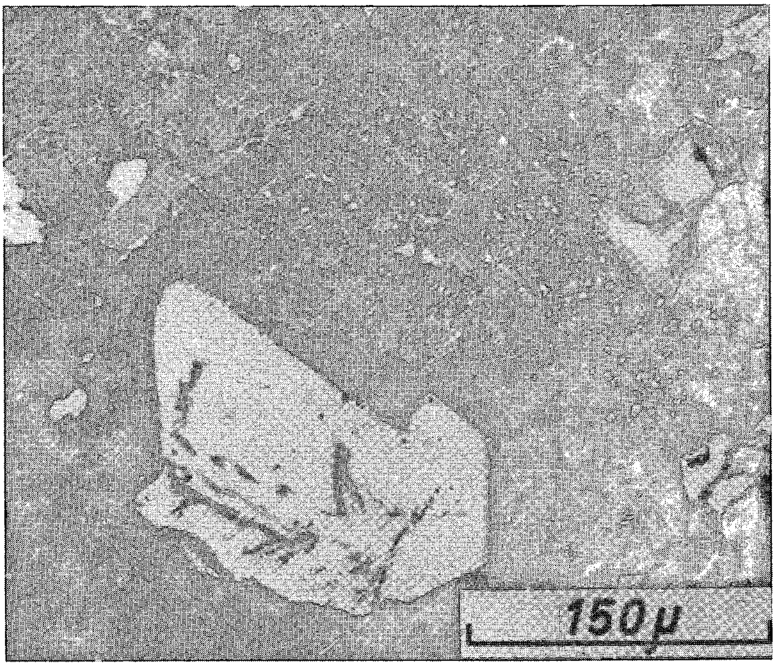

FIG. 20. Skeletal crystal of chromite in chondrule from equilibrated Cavour meteorite, as seen in reflected light. The photo is reprinted from Ramdohr (1973) with permission (see Acknowledgements).

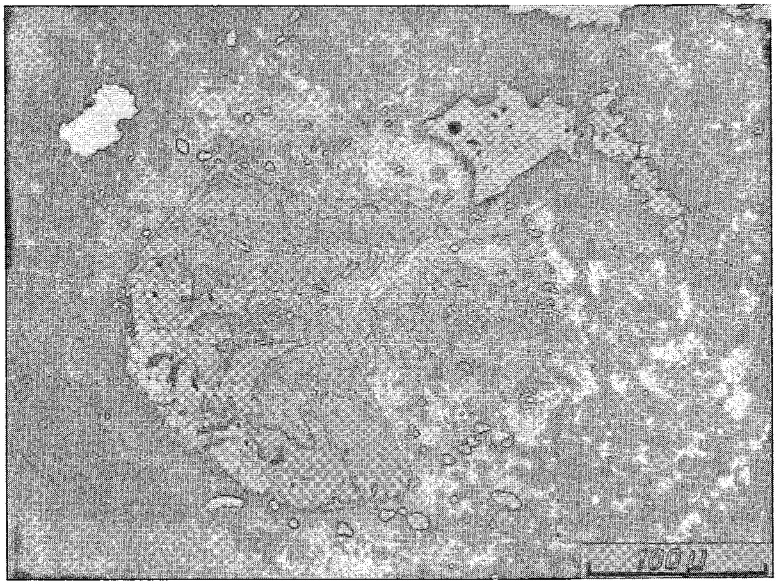

FIG. 21. Skeletal crystal of chromite in a feldspar matrix in a chondrule from the equilibrated Salisbury chondrite, as seen in reflected light. The photo is reprinted from Ramdohr (1973) with permission (see Acknowledgements).

olivine has a relatively constant composition, usually close to Fo$_{70-80}$. The temperature of equilibration for the coexisting chromite and olivine is in the range of 600–800°C, according to the equations of Sack & Ghiorso (1991); this is the reason for the linear variation shown in Figure 19. This is also proof that spinel can and does equilibrate or re-equilibrate at metamorphic temperatures, as suggested earlier in this paper for terrestrial examples. One of the puzzling aspects of the chromite in equilibrated chondrules is the large proportion and size of chromite crystals in a few rare chondrules (Ramdohr 1967, Krot *et al.* 1993). Some of these are skeletal crystals (Figs. 20, 21) that look as though they crystallized from a melt, but the low solubility of Cr in melts (Roeder & Reynolds 1991), even at the low oxygen fugacities expected for chondrule melting, make it unlikely that the amount of chromite found in these equilibrated chondrules (Figs. 20, 21) could have crystallized from the chondrule melt. One explanation proposed to explain the large amount of chromite in some equilibrated chondrules is that the dust particles that were melted to produce these chondrules contained a large crystal of chromite. However, to my knowledge, no example of unequilibrated chondrule has been found with a high concentration of chromite. Another puzzling aspect of chromite in some equilibrated chondrules is the close association with sodic plagioclase and the intimate intergrowth of albite and chromite reported in some samples (Ramdohr 1967, 1973). Wlotzka (1987) and Ireland & Wlotzka (1992) suggested that albite and chromite in equilibrated chondrites may be formed by metamorphism of CAI containing anorthite and spinel. The intergrowth of chromite and sodic plagioclase, which is only found in equilibrated chondrites, was interpreted by Ramdohr and by Brearley *et al.* (1991) as possibly being due to exsolution of chromite and albite from some unknown precursor mineral. The most likely precursor mineral was considered by Ramdohr and Brearley *et al.* (1991) to be a kosmochlor-type mineral [$Na(Cr,Al)Si_2O_6$]. However, no such precursor mineral has been found in either unequilibrated or equilibrated samples. The association of sodic plagioclase and chromite, and the idea of Cr and Fe being mobile elements during metamorphism, are not familiar concepts to those of us who study terrestrial samples. However, the mobility of elements like Na, Fe and Cr may have been considerably enhanced by the low oxygen fugacities prevalent at the time of chondrite metamorphism. These mobile elements acting on anorthite in CAI fragments may have replaced anorthite ($CaAl_2Si_2O_8$) with albite ($NaAlSi_3O_8$), and the excess alumina reacted with Cr and Fe to form chromite.

The small amount of chromite and the associated minerals in unmetamorphosed chondrules is consistent with an origin of crystallization from a basic melt. The large amount of chromite in some metamorphosed chondrules and the associated sodic plagioclase are not considered consistent with growth from a basic melt. I do not believe that the intergrowths of chromite and sodic plagioclase represent exsolution from some unknown precursor mineral; instead, they represent replacement of anorthite by sodic plagioclase and crystallization of chromite by diffusion into the anorthite of Cr, Fe and Mg during the so-called metamorphic event on some protoplanet or asteroid. Thus I interpret the chromite–albite intergrowths as a result of a metasomatic process. The large skeletal crystals of chromite (Figs. 20, 21) that look as though they crystallized from a melt, and that are found in rare chondrules (Ramdohr 1973) in equilibrated chondrites, may have originally crystallized as spinel ($MgAl_2O_4$), but were converted to chromite during metamorphism.

Our knowledge of terrestrial igneous processes involving chromite prepared me quite well to understand the pure igneous crystallization of chromite from basic melts in most unmetamorphosed chondrules. However, our knowledge of terrestrial metamorphic processes, where Cr seems to be fairly immobile, did not prepare me at all for the strange kind of metamorphism envisioned for a regolith on some asteroid where Na, Cr, Fe and Mg seem to be mobile, yet textures remained largely intact during metamorphism.

CONCLUSIONS

One of the most satisfying aspects of accumulating the many analytical data on chromite, spinel and magnetite in my database was being able to examine the tremendous diversity of geological processes from the fairly narrow platform of a very minor mineral, spinel. Although my platform was narrow, it was a platform which for me felt fairly secure, and I felt I could see far. There is a sense of satisfaction at being able to traverse four and half billion years from chromite in a chondrule that lay in a regolith on some strange body to a chromite in olivine from the 1959 Kilauea Iki lava lake (Scowen *et al.* 1991). The chemical rules are the same, but the geological processes were so different.

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