SPINELS AND ILMENITES IN HIGH PRESSURE REGIMES: AN EMPIRICAL ANALYSIS

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In an attempt to establish the nature of compositional variations among spinels and ilmenites in high pressure regimes a detailed analysis of mafic and ultramafic suites has yielded the following results:

(1) The distribution of spinel compositions are summarized in Fig. 1 and the following characteristic trends emerge: (a) an early enrichment of Cr and a later enrichment in Al is the typical kimberlite trend; (b) an early enrichment of Mg and a later enrichment of Fe^{2+} is the stratiform magmatic ore deposit trend; and (c) an early enrichment of Al and a later enrichment in Cr is exemplified by xenolith suites, and this is termed the peridotite trend. A preferred directional sweep towards the Fe-ternary is exhibited by all suites with the exception of kimberlitic spinels which continue to show relatively high MgO contents with increasingly higher concentrations of Fe^{3+} + Ti. In contrast, xenolith and peridotite suites are confined to the spinel prism base with little or no enrichment in either Fe^{3+} or Ti. The three basalt trends are for: (a) subaerially extruded tholeiitic suites; (b) island-arc volcanism; and (c) mid-oceanic ridge basalts. The latter trend is comparable to the trends exhibited by spinels in xenoliths and in peridotites and these basalts include the range from picrites with low Cr/Cr + Al, to olivine tholeiitic basalts with intermediate R^{3+} ratios, and to alkali olivine basalts with high Cr/Cr + Al ratios. Early enrichment trends are considered to be pressure and temperature dependent. Progressively later trends are a reflection of initial bulk rock chemistry, relative paragenetic relationships of co-precipitating Mg, Al and Fe-bearing silicates, and the degree of interstitial liquid interaction.

(2) The P-T lherzolite petrogenetic grid is broadly confirmed for spinel distributions in which the partitioning of Cr and Al among silicates and oxides results in: (a) a spinel absent field for high pressure garnet lherzolites (Cr is present in clinopyroxene + garnet); (b) a chromite, but Al-depleted, field in the region of low pressure plagioclase lherzolite stability (Al is present in plagioclase); and (c) a variable range in Cr/Cr + Al ratios for spinels which are stabilized between these two extremes in spinel lherzolites. This trend suggests that Cr/Cr + Al ratios should decrease with increasing pressure; however, the unresolved anomaly in this otherwise coherent pattern is that spinel inclusions in diamonds have an extremely high $FeCr_2O_4$ component which is supported, in part, by the overall trends displayed by kimberlitic spinels. A major and significant new result is that the Fe/Mg relationships of spinels are key to the spinel P-T grid and to the variations in Cr and Al. In a test of lunar intrusive rocks (gabbro, anorthosite, troctolite and dunite) the Fe/Mg variations of spinels fall along a smooth curve with the gabbro having the highest Fe value and the dunite the highest Mg content; the anorthosite and the troctolite occupy an intermediate range which is interpreted to be P-T dependent. The terrestrial test confirms this overall interpretation but is complicated by the fact that fractional crystallization and partial melting in particular, disrupt the inherent signature of the spinel.

(3) The distribution of ilmenite compositions for a variety of rock types is illustrated in Fig. 2 and from these the most significant component in the context of pressure regimes is the behavior of Mg as determined from diamond inclusion studies, from kimberlite studies, from autholith studies,

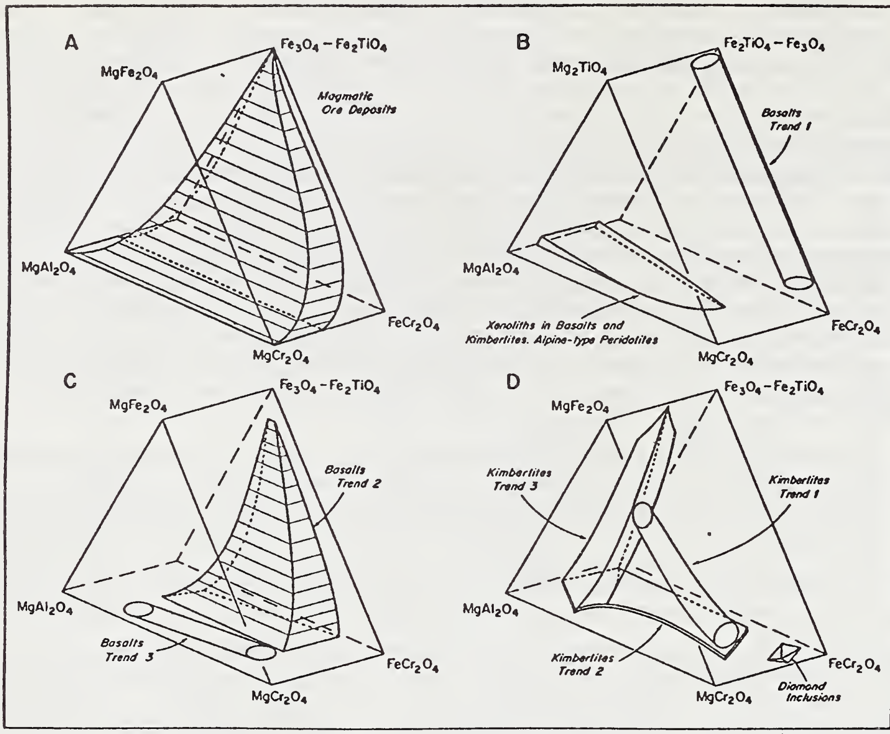
and from basaltic phenocrystal studies. The results of these data show: (a) phenocrystal ilmenites in kimberlites are commonly reversely zoned, with higher MgO contents at the margins and lower concentrations in the cores, a trend which is also observed in basaltic suites; (b) the MgO contents of ilmenites intergrown with diamonds are moderately high, in common with the encasements on autolith nucleii, the compositions of groundmass ilmenites, and the compositions of ilmenites in symplectic pyroxene intergrowths; (c) ilmenites included in diamonds have extremely low MgO contents and these are similar in composition to ilmenites in autolith nucleii. This suggests that an increase in pressure should lead to a decrease in the geikielite component, but this relationship is also clearly dependent on olivine precipitation. Early crystallization of olivine and magnesian chromites results in low MgO content ilmenites and this is reflected in all basic suites. The implied pressure dependency, however, is substantiated by volume changes associated with the reaction Fo + Ilm → Fa + Geik which is positive, and is indicative therefore of $Mg_{olivine} > Mg_{ilmenite}$ at high P.

(4) The high concentrations of Cr_2O_3 (1-8 wt%) in kimberlitic ilmenites is a unique property of this mineral in this setting. Low pressure experimental results demonstrate the instability of Cr in the ilmenite structure under high and very low f_{O_2} conditions, and the preferred partitioning of Cr between coexisting ilmenites and spinels is widely recognized with $Cr_{Sp} >> Cr_{Ilm}$. An expected substitution of the form Cr → Fe^{3+} in the system $FeTiO_3$-$MgTiO_3$-Fe_2O_3, which may be possible under mantle conditions, should result in chromian-stabilized members of the ilmenite-geikielite series. Hence, Cr-Mg relationships should correlate in some systematic manner but repeated tests yield a parabolic curve. Parabolic curves also result between Cr and Ti, Al, and Fe^{3+}.

In summary, this empirical analysis has identified three major aspects of spinel and ilmenite mineral chemistry in high pressure regimes: (a) that Al/Cr variations in spinel lherzolites are likely to result in a refinement of the P-T petrogenetic grid; (b) that Fe/Mg ratios are a sensitive and integral component of the P-T spinel grid; and (c) that the MgO contents of ilmenites are unequivocally related to pressure in kimberlitic suites. The outstanding problems which remain are: (a) that lherzolitic suites suggest a decrease in the Cr/Cr + Al ratio with increasing pressure, whereas kimberlites suggest the reverse; and (b) what is the role of Cr in kimberlitic ilmenite? For both, the concommitant effects of Fe/Fe + Mg variations in spinel and in coexisting silicates are considered to play a major role.

◊ — coexist tone chromites but Cr   See Ulmer & White

◊ stability — Cr^{2+} at ~~PmO~~ Cr^{2+}/Cr^{3+} inc. w. P.



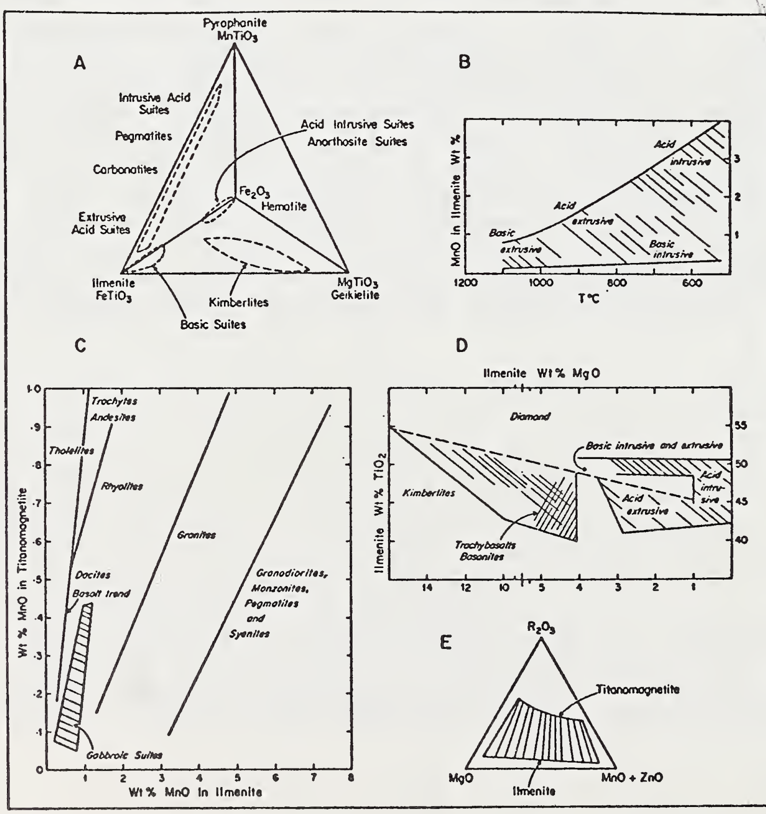
high P
Ti - Fe^{+++} depleted.

base complex

Vac in $\overline{IV}$ site

Fe-Mg binary

Ilm
Mn - CO3



Fe
Base
K
Mg

— doesn't tell much

Cr/Al in $\overline{VIII}$ site

Xenolith
K
Kerd
Cr
Volc
Al