THE MINERAL CHEMISTRY OF ILMENITE NODULE ASSOCIATIONS FROM THE MONASTERY DIATREME.

S.E. Haggerty, R.B. Hardie III, and B. M. McMahon (Dept. of Geology, University of Massachusetts, Amherst, Ma. 01003)

A petrographic and electron microprobe study was performed on 163 ilmenite nodules from the heavy mineral concentrate of the Monastery Kimberlite pipe. We have classified these nodules into the following categories: (a) symplectic ilmenite-pyroxene intergrowths (57 nodules); (b) discrete ilmenite nodules (66 samples); and (c) ilmenite nodules encased in a closely adhering kimberlite matrix (40 nodules). This study was undertaken in an attempt to characterize these diverse associations and to evaluate the conditions and setting for ilmenite-pyroxene formation. The following new results have emerged.

(1) Approximately 10% of the ilmenite-pyroxene assemblages contain orthopyroxene and the remainder are clinopyroxene.

(2) The modal proportions of ilmenite to pyroxene vary enormously from a ratio of 1:1 to a ratio of at least 1:10; no preferred modal to compositional populations are apparent and no distinctions are present between Opx and Cpx hosts.

(3) Reactions at Opx-ilmenite interfaces yield olivine + rutile + Ti-phlogopite, whereas interface reactions between Cpx and ilmenite result in perovskite + Fe-phlogopite + Opx.

(4) Two of the pyroxene-ilmenite symplectites examined contain abundant sulfide-bearing tubes which are preferentially located at the terminal contacts of elongated ilmenite laths. The assemblage is pyrrhotite + pentlandite which is partially oxidized to magnetite + geothite.

(5) Ilmenite compositions in Opx assemblages show little variation from those in Cpx assemblages and both form a tight cluster between 9-10 wt% MgO.

(6) Oriented lamellae of magnesian-titanohematites in ilmenites are present in 76% of the symplectic assemblages. This mineral has lower MgO (~7.5 vs 9.0 wt%), lower FeO (~25.0 vs 28.0 wt%) and lower $TiO_2$ (~44.0 vs 49.0 wt%) contents, but higher $Fe_2O_3$ (~21.0 vs 12.0 wt%) and $Al_2O_3$ (0.5-1.0 wt%) concentrations than those of the ilmenite host which forms the main body of the assemblage with pyroxene. An additional 20% of the nodules examined contain an aluminous-Cr spinel, and the remaining 4% are homogeneous.

(7) The discrete nodule suite and nodules encased in kimberlite exhibit similar ranges in compositions and exsolution assemblages to those present in symplectic pyroxene inter growths. The one major exception is that many of the nodules contain trapped ovoid inclusions of calcite + pyrrhotite + pentlandite. Reactions between these inclusions and the ilmenite result in a consistent sequence which is: (a) magnetite at the inclusion contact; (b) an intervening rind which is a strongly zoned titaniferous

magnetite (10-22 wt% $TiO_2$, and 1-4 wt% MgO); and (c) a magnesian-depleted ilmenite which is also higher in $Fe_2O_3$ than the adjacent host ilmenite.

(8) Kimberlite-ilmenite reaction contacts are comparable to those previously reported and these are typically a Mn ilmenite + magnesian titanomagnetite + perovskite, or alternatively rutile + sphene + Fe phlogopite.

(9) Polycrystalline ilmenites with pronounced polygonal-dihedral textures characteristic of intense stress annealing are abundant in the discrete nodule suite and in the pyroxene-ilmenite intergrowths; 67% of the former and 47% of the latter display this feature.

Two aspects of this study have received special attention. The first is a detailed analysis of ilmenite compositional variations among the nodule suites, and the second is related to "exsolution" intergrowths in ilmenite. Our data base consists of 792 electron microprobe analyses. These are summarized in Fig. 1 and the following conclusions may be drawn: (1) The cores of the discrete nodule suite form a tight cluster centered on $Geik_{30}$ $Ilm_{55}$ $Hem_{25}$; (2) Ilmenites in pyroxene intergrowths are lower in $Fe_2O_3$ contents than the discrete nodules and their core population reaches a maximum at $Geik_{35}$ $Ilm_{45}$ $Hem_{20}$; (3) The polycrystalline nodules have even lower $Fe_2O_3$ contents (15 mole % Geik) and $FeTiO_3$ contents are lower ($Ilm_{40}$); (4) Pronounced zoning is present in both the discrete nodules and in ilmenites in pyroxene intergrowths. The former is towards $MgTiO_3$ and the latter towards the join $MgTiO_3$-$FeTiO_3$; (5) Discrete nodules with closely adhering kimberlite have complex reaction mantles that include ilmenites whose compositions trend towards $FeTiO_3$. Associated minerals are magnesian titaniferous magnetites and perovskite.

Our interpretation of these results suggests that there are at least four distinct events which can be identified: The first is the magmatic trend of the discrete nodule suite towards $MgTiO_3$; the second is the ilmenite-pyroxene trend towards $FeTiO_3$-$MgTiO_3$; the third is the kimberlite reaction trend towards $FeTiO_3$; and the fourth is an episode of exsolution in ilmenite. The magmatic nodule trend is a liquid-interaction trend and is most likely the result of a decrease in $P_{total}$ with an accompanying decrease in $f_{O_2}$. The ilmenite-pyroxene trend is a reduction in the $f_{O_2}$ path, and the kimberlite reaction trend marks the onset of nodule incorporation into the kimberlite. A small but marked displacement is apparent between the two compositional populations occupied by the cores of the discrete nodules and the cores of symplectic ilmenites and both have markedly different core-mantle reaction trends. These differences suggest one of two possible origins: (a) the discrete nodules and the symplectites are derived from different source regions with variable crystallization paths; or (b) the discrete nodules formed at high $P_{total}$ followed by the symplectites at lower pressure. It is expected that continued growth of the discrete nodules, towards $MgTiO_3$, would take place but that the pyroxene associated ilmenites would be protected because of their symplectic encasement. The latter origin is the preferred interpretation.

Lamellar intergrowths in ilmenite are of three types: (1) aluminous spinels; (2) magnesian-titanohematites; and (3) magnesian-titanomagnetites. All types are present in the discrete nodule suite but only the first two are observed in the symplectites. These minerals are lamellar in form and all have an exsolution-like appearance oriented along {0001} planes in the host ilmenite. Mg-titanohematite and the Al-spinel are evenly distributed throughout single crystals of ilmenite, whereas the Mg-titanomagnetites are restricted to crystal margins and are frequently distorted. We interpret the Mg-titanohematites as

exsolution sensu stricto, suggest that the Al-spinel may be an exsolution-like process, and have demonstrated experimentally that the magnesian titano-magnetites can result as products of subsolidus reduction in the range T=900-1200C and $f_{O_2}$ $10^{-8}$ to $10^{-14}$ atms. These experiments were performed on a Monastery ilmenite with MgO=7.8 wt% and runs in progress should yield a well defined T-$f_{O_2}$ grid for high MgO oxides.

In summary, we have identified two major ilmenite populations, one for the discrete nodule suite and one for those in pyroxene symplectites which we suggest are most likely derived from the same source region with the latter forming at slightly lower pressures. Although the reaction trends are drastically different, these can be accounted for by allowing progressive growth of the nodules under decreasing pressure and $f_{O_2}$, and by partial insulation of the pyroxene associated ilmenites in symplectic intergrowths. It is our contention, however, that none of the models proposed for pyroxene-ilmenite intergrowths (i.e. garnet decomposition; ilmenite or pyroxene replacement; eutectic crystallization; or exsolution) has adequately addressed (a) the variations in Opx and Cpx; (b) the modal variations of ilmenite and pyroxene; (c) the presence of associated sulfides; (d) the nature of reaction contacts between ilmenite and pyroxene; nor (e) provided an explanation for the abundance of exsolved ilmenite in the primary ilmenite constituent of pyroxene symplectic intergrowths.