A high-pressure experimental study on the effects of Cr^{3+} on the stability, phase relations and compositions of ilmenite in the Fe-Mg-Ti-Cr-Si-O system

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Introduction

Cr, Mg-rich ilmenites (picro-ilmenites) occur nearly exclusively in ultramafic kimberlites, lamproites and associated ultramafic rocks such as MARID-type (mica-amphibole – rutile – ilmenite - diopside) and IRPS-type (ilmenite – rutile – phlogopite - sulfide) xenoliths in kimberlites. Their occurrence is inferred to be related either to the crystallization of ultramafic, alkaline liquids such as kimberlites or lamproites (Moore, 1987; Griffin et al. 1997) or produced through reaction of a Ti-Fe-rich alkaline ultramafic liquid/fluid with common lherzolite/harzburgite mantle rocks. Picro-ilmenites occurrences and diagnostic chemistries are an important tool in prospecting of potentially diamondiferous kimberlite and lamproite pipes.

Ilmenite, $FeTiO_3$, forms a solid solution with geikielite $MgTiO_3$ that provides the basis for geothermometers based on the Fe^{2+}-Mg exchange between pyroxene and ilmenite and olivine and ilmenite. Solid solution of hematite Fe_2O_3 is utilized as a potential monitor of mantle fO_2 conditions (Haggerty and Tomkins, 1983). Therefore, it is proposed that ilmenite megacrysts with high hematite component could be indicative for a reduced 'survival potential' of diamonds. There is a rough correlation between the 'oxidation state' of megacrystic ilmenite and the diamond grade of a particular diamondiferous pipe (Gurney and Zweistra, 1995). At low pressure, the join $MgTiO_3$ - Fe_2O_3 is characterized by a large miscibility gap, only compositions close to endmembers are stable. Intermediate compositions are represented by the paragenesis Fe_2TiO_5 (pseudobrookite) - Mg_2TiO_4-$MgFe_2O_4$ (spinel) solid solution. A classical application of ilmenite mineral chemistry is the 2-oxide (ilmenite-hematite and magnetite-ulvoespinel) thermometry-oxybarometry. A number of experimental studies have been performed to measure the partitioning of Fe^{2+} and Mg between ilmenite and the Fe-Mg silicate mantle phases olivine, pyroxene and garnet to calibrate potential geothermometers. Only limited information is available for the Mg-Fe-Ti-O system containing trivalent cation other then Fe^{3+}; high pressure data are extremely rare. However, to extract crucial petrologic information from compositional variations observed in picro-ilmenite megacrysts originating from kimberlites and associated rocks, it is essential to include Cr (and Al) in such studies. Therefore, we are conducting a high-pressure experimental study to determine some of the fundamental parameters that control occurrence and composition of oxide accessory phases in ultramafic, but Ti and Cr-rich system.

The system Fe-Mg-Ti-Cr-(Al)-Si-O provides a useful simplification for phase equilibrium studies applied to the Earth mantle. The experimental study reported here is conducted in peridotite like, Ti-rich systems to specifically evaluate the behavior of Cr^{3+} in oxide – silicate mantle-like systems. The prime target is to investigate the phase relations and composition of the oxide phase, in particular ilmenite, as a function of pressure, temperature and bulk composition.

Starting material, experimental and analytical procedures

Starting materials are prepared from pure synthetic oxides fired at 1000°C (SiO_2, TiO_2, Fe_2O_3, MgO, Cr_2O_3, and Al_2O_3). Moderate amounts of H_2O (ca. 5 wt. %) is added to the starting material in the form of $Mg(OH)_2$ to enhance crystallization and equilibration. Homogenized, fine-grained powder aliquots of the starting materials are loaded into 2.6mm (piston cylinder) or 1.4mm (multi anvil) graphite capsules sealed into 3mm (piston cylinder) or 1.6mm (multi-anvil) Pt capsules to oppose relatively reducing conditions consistent with graphite/diamond stability and to minimize Fe-loss resulting from alloying with Pt.

Experiments at 2.5 and 3.5 GPa are conducted in end-loaded piston cylinders with 14 mm bore employing NaCl-Pyrex-MgO assemblies; experiments at 5.0 and 7.0 GPa (only partly included in this abstract) are performed in a Walker-type 6/8 multi-anvil apparatus employing 18mm edge length MgO octahedra and gasket fins and 11mm truncations on 32mm WC anvils. Temperatures range from 1000 to 1400°C and are measured with B-type Pt-Rh thermocouples. Quenching is achieved by turning off the power supply to the graphite furnaces, resulting in a temperature drop to less than 200°C within less than 10 seconds.

Several series of experiments were/are conducted using different starting compositions primarily in the Fe-Mg-Ti-Cr-Si-O system with additional runs in the Fe- and Si-free systems and in the Al-bearing system employing variable Mg/Fe, Cr/Al ratios, and silica activities.
Recovered charges are embedded in epoxy resin and ground to expose longitudinal cross sections. All runs are analyzed with a GEOL JXA-8200 electron microprobe employing 15 kV acceleration voltage and 20 nA sample current.

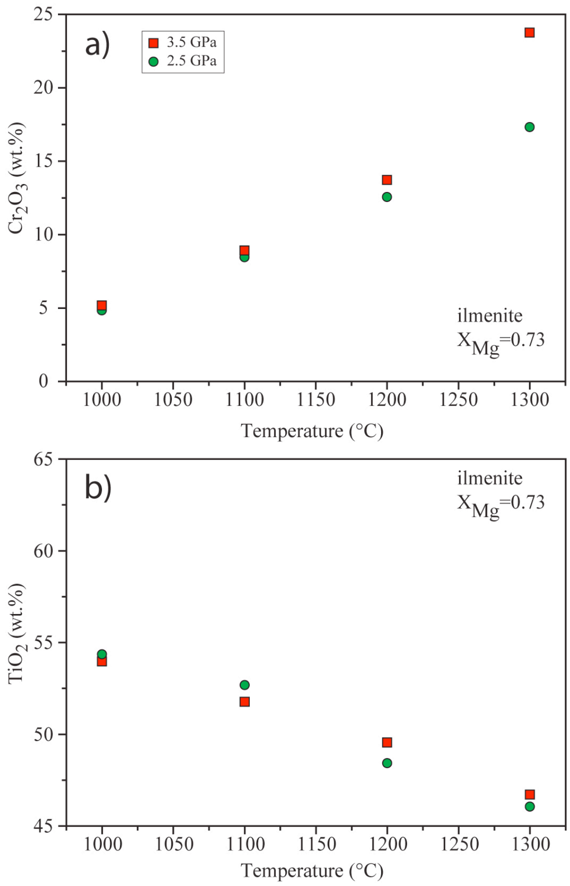


Fig. 1 Compositional variations of ilmenite (in wt.%) as a function of temperature and pressure for a system with x_{Mg} = 0.73. a) Cr_2O_3; b) TiO_2.

Results

Phase Assemblages: Ilmenite is stable together with olivine + orthopyroxene (opx) + spinel at bulk X_{Mg} (=molar MgO/(MgO+FeO) of less than 0.8, rutile + olivine + opx + spinel are coexisting phases at a bulk X_{Mg} of 0.85. Compositions with lower SiO_2 contents and low X_{Mg} values are characterized by the presence of three oxides: ilmenite + rutile + spinel coexisting with olivine and opx. Compositions with high X_{Mg} (0.85) and lower SiO_2 contents result in the disappearance of opx and rutile; present phases are olivine + spinel + ilmenite. In the iron-free system (X_{Mg} = 1.0) phase parageneses are similar to runs with high Mg# (0.85) and high SiO_2 contents: olivine + opx + spinel + rutile. For composition with lower amount of SiO_2 only olivine is present as a silicate phase and three oxides are observed: spinel + rutile + ilmenite (geikielite). In Si-free experiments ilmenite is only stabilized at pressure exceeding 3.5 GPa. Additional phases are spinel and periclase with high iron contents (ferripericlase).

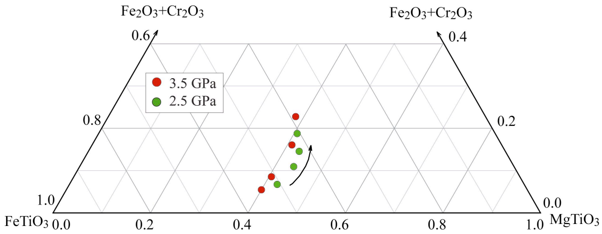


Fig. 2 Ilmenite compositions (cation units) expressed as endmember components as a function of pressure. Arrow indicates increasing temperature.

Phase compositions: *Ilmenites* exhibit Cr contents that increase with increasing temperature and pressure reaching up to 25 wt% Cr_2O_3 in experiments with X_{Mg}=0.73 (Al-free system); such high values are not commonly observed in natural picro-ilmenite samples from kimberlites and other mantle xenoliths (Fig 1a). The incorporation of Cr is counter balanced by decreasing TiO_2 contents (Fig. 1b). At X_{Mg}=0.85, ilmenites are enriched in Ti and contain considerably lower Cr concentrations. In Al-bearing systems, ilmenites exhibit increasing Al concentrations with increasing pressure and temperature but values do not exceed 3 wt% Al_2O_3. In general, increasing temperature leads to an enrichment of trivalent cations. This feature is well illustrated in ternary diagrams displaying recalculated endmember compositions for ilmenites (Fig 2); increasing pressure results in decreasing $MgTiO_3$ component. Compositions of ilmenites coexisting with spinels at an X_{Mg} of 0.73 are displayed in Fig. 3, a ternary wt.% diagram combining divalent (FeO+MgO), trivalent (Fe_2O_3+Cr_2O_3 (+Al_2O_3)) and tetravalent (TiO_2) oxides respectively. Ilmenite compositions at 2 and 3.5 GPa fall between $FeTiO_3$ and $MgTiO_3$ and shift toward Cr-rich compositions with increasing temperature and toward Mg-rich compositions in systems with an X_{Mg} of 0.85.

Spinels are present in all experimental run charges. The general characteristic is decreasing Cr and increasing Ti contents with increasing temperature; their compositions lie close to the join Fe_2O_3-Mg_2TiO_4 and move towards Mg-rich endmembers with increasing X_{Mg} of the system. Spinels coexisting with rutile contain higher Cr contents, but the general behavior is similar. *Rutiles* contain high Cr_2O_3 (6-10%) and low Fe_2O_3 (<1%) concentrations.

Silicates are represented by high Mg# orthopyroxene and olivine, rarely garnet is present in Al-bearing systems. The occurrence of enstatitic orthopyroxene is bulk composition dependant; it occasionally forms intergrowths with ilmenite.

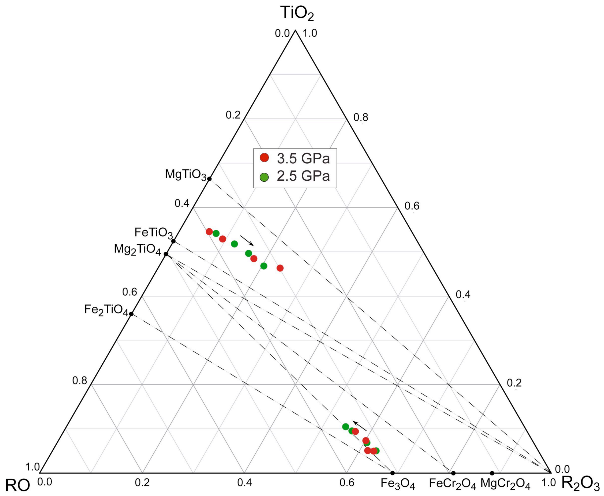
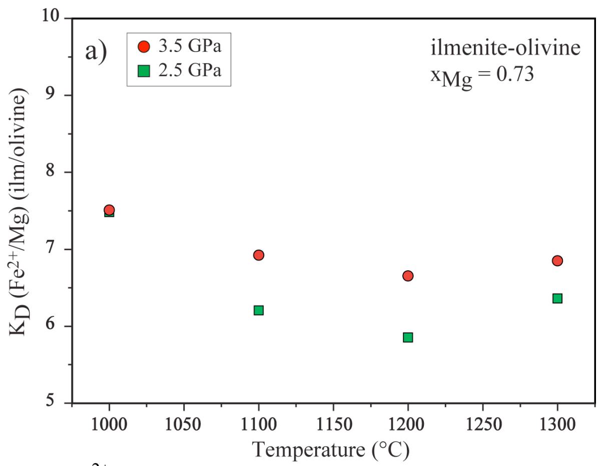


Fig. 3 Ilmenite – spinel compositions in wt.% in a ternary oxide diagram; x_{Mg} = 0.73. Arrows indicate increasing temperatures.

Ilmenite – silicate Fe^{2+} - Mg partitioning: We observe a rather complex dependence of the Fe^{2+}-Mg distribution coefficients (K_D = $(Fe^{2+}/Mg)_{ilmenite}$ / $(Fe^{2+}/Mg)_{silicate}$) between ilmenite and coexisting olivine and opx on pressure and temperature, indicating that the incorporation of Cr into ilmenite (and coexisting spinel) considerably complicates the popular ilmenite-olivine and ilmenite-opx Fe^{2+}-Mg geothermometers. Partitioning of Fe^{2+}/Mg correlates positively with pressure and negatively with temperature (Fig. 4) between 1000 and 1200°C. However, between 1200 and 1300°C (X_{Mg} = 0.73) we observe an inversion of the temperature dependence most probably related to strongly increasing Cr-contents in the ilmenite in this temperature interval resulting in strong non-ideality of the Fe^{2+}-Mg incorporation into ilmenite.



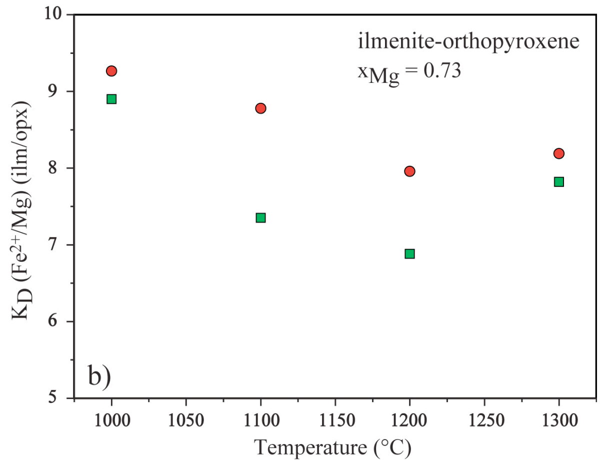


Fig 4 Fe^{2+}-Mg distribution coefficients as a function of temperature between ilmenite and a) olivine and b) orthopyroxene for x_{Mg} = 0.73 at 2.5 and 3.5 GPa.

Conclusions and Outlook

Ilmenites (and spinel) exhibit complex but systematic compositional changes as functions of bulk composition, temperature and pressure in mantle-like systems when Cr^{3+} is added as a component. The data set obtained at 2.5 and 3.5 GPa is complemented by higher pressure experiments at 5.0 and 7.0 GPa to investigate the compositional variations of ilmenites coexisting with other oxides (spinel and/or rutile) and silicates (olivine, opx, ±garnet) at conditions consistent with the formation of kimberlite and the stability of diamond.
Additionally, we currently focus our efforts on the quantitative effects of Cr^{3+} on ilmenite solid solutions by conducting thermodynamic analyses of the experimental results in order to provide activity-composition relations as a function of temperature and pressure (and fO_2) to compute stabilities and compositions of Fe-Mg-Ti-Al-Cr oxides under conditions relevant for kimberlite genesis, differentiation and ascent. Ultimately, we aim to provide a comprehensive data set enabling ilmenite compositions to be utilized as probes for mantle conditions (and compositions?) and to evaluate and identify the obvious link between picro-ilmenite occurrence and diamondiferous kimberlites and lamproites.

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