THE STABILITY OF ARMALCOLITE AND ILMENITE DURING LUNAR CUMULATE MANTLE OVERTURN. Y. Liang, C. Thacker, Q. Peng, and P. C. Hess (Department of Geological Sciences, Brown University, Providence, RI 02912, email: yan_liang@brown.edu).

Introduction: Ilmenite has played an important role in the petrogenesis of lunar high Ti picritic magmas. According to the lunar cumulate overturn model, a globally distributed ilmenite-rich layer formed just below the anorthositic crust near the very end of crystallization of a lunar magma ocean (LMO) was gravitationally unstable and sank into the lunar mantle where it mixed in various extent with the earlier olivine-rich cumulates such as dunite and harzburgite [1-5]. Partial melting of ilmenite-bearing harzburgite later then produced the high Ti magmas.

One fundamental question that remains is the thermodynamic stability of ilmenite during lunar cumulate mantle overturn. Earlier phase equilibrium studies in simple system MgO-Fe-Ti-O [6-8] demonstrated that armalcolite is more stable than ilmenite at high temperatures and pressures up to 1.4 GPa. Indeed, armalcolite with ilmenite reaction rims was observed in a number of lunar basalts [9], begging the question if armalcolite is stable in the lunar mantle. The stability of armalcolite and ilmenite in dunite and harzburgite has not been examined in the context of lunar cumulate overturn. Here we report near solidus phase relations of armalcolite and ilmenite in a dunite and a harzburgite as a function of temperature (*T*) and pressure (*P*).

Experiments: Experiments determining the stability of armalcolite and ilmenite in LMO cumulates were conducted at 1235-1475°C and 1-2 GPa using a 19.2 mm piston cylinder apparatus and graphite capsule. Two starting compositions were explored: one consists of 89wt% olivine + 11% ilmenite (dunite); and the other consists of 65.6% olivine + 22.1% orthopyroxene (opx) + 12.3% ilmenite (harzburgite). Both starting materials also contain small amount of Al_2O_3 introduced during grinding and mixing in a corundum mortar. Starting olivine and opx (Mg#s = 91) were from a spinel lherzolite xenolith from Kilbourne Hole, NM [10]. Starting natural ilmenite was from Ward's Natural Science (49.5% TiO_2, 45.2% FeO, 0.3% MgO, and 3.5% MnO). Fine powered starting material was first loaded in the graphite capsule and dried in a 200°C vacuum oven for at least 12 hrs. Most of the experiments summarized in Fig. 1 were run at the prescribed *T* and *P* for 48 hrs, except one at 1338°C and 2 GPa for 23 hrs. To minimize the effect of a temperature gradient, each sample was mounted in epoxy and oriented such the polished surface is less than 1 mm from the thermal couple contact. The polished charge was examined first under a petrographic microscope and then a Cameca SX100 electron microprobe. The appearance of melt is taken when quench ilmenite was observed [11].

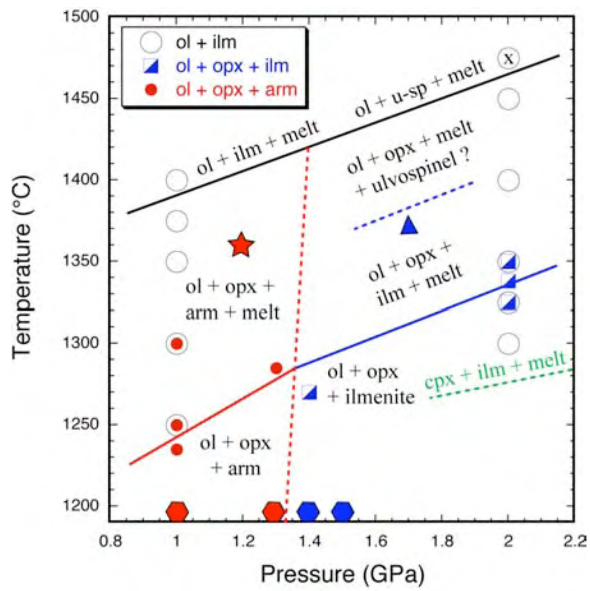

Figure 1. Solidi of an olivine + ilmenite cumulate mixture (upper black line), an olivine + opx + armalcolite mixture (lower red line), and an olivine + opx + ilmenite mixture (lower blue line) between 1 and 2 GPa. Experiments conducted in this study are shown as open circles, filled red circles, and half-filled blue squares. Red star is from phase equilibrium study of [12] that has a phase assemblage of ol + opx + arm + melt. Filled hexagons are from [8] for the system armalcolite-ilmenite-rutile. The red hexagons represent experiments in which armalcolite is stable, while the blue ones represent charges in which ilmenite + rutile are stable. Dotted red line shows schematically the upper pressure boundary for the armalcolite or armalcolite-bearing harzburgite. Filled blue triangle is from [13] for Apollo 14 back glass that has a phase assemblage of ol + opx + ilm + melt. Dashed green line is the solidus for a clinopyroxene (cpx) + ilmenite mixture extrapolated from the high-pressure work of [11].

Results: Figure 1 shows the approximate solidus for the olivine + ilmenite starting composition (solid black line, dT/dP ~ 70/GPa) determined from two sets of experiments (open circles). At 1400°C and 1 GPa, the melting product consists of olivine (Mg# = 88.6) + ilmenite + melt, whereas at 1475°C and 2 GPa, the melting product consists of olivine + ulvöspinel + melt. Ilmenite in the subsolidus cumulate assemblage is stable at least up to 1450°C and 2 GPa. The ulvöspinel has 35.9% TiO_2, 33.0% FeO, 23.5% MgO, 6.6% Al_2O_3, 0.4% Cr_2O_3, and 0.8% MnO.

At pressures less than 1.4 GPa, ilmenite is found to be unstable in our starting harzburgite mixture (filled red circles in Fig. 1). Instead, it transformed into armalcolite (70.2% TiO_2, 11.7% FeO, 11.4% MgO, 4.2% Al_2O_3, 0.9% Cr_2O_3, and 0.2% MnO at 1285°C and 1.3 GPa) through the reaction (Fig. 2):

ilmenite + opx → olivine + armalcolite.

The relatively low-pressure stability field for the armalcolite-bearing harzburgite is in good agreement with previous studies in simple MgO-Fe-Ti-O [6,8] and more complicated systems [7,12]. Figure 1 shows the solidus for the olivine + opx + armalcolite phase assemblage (solid red line, dT/dP ~ 120°C/GPa).

At pressures greater than 1.3 GPa, ilmenite is stabilized in the harzburgite assemblage, at least at temperatures near its solidus (half-filled blue squares in Fig. 1). The solidus of the olivine + opx + ilmenite cumulate has a slope similar to that of the olivine + ilmenite mixture, i.e., dT/dP ~ 70°C/GPa (solid blue line in Fig. 1).

Discussions: The phase assemblage and reaction relationship for the ilmenite-, armalcolite-, and ulvöspinel-bearing dunite or harzburgite shown in Fig. 1 can be easily understood with aid of the pseudo-ternary compositional diagram of (Mg, Fe)O-TiO_2-SiO_2 (Fig. 2). Hence armalcolite can be formed by reacting ilmenite with opx (at P < 1.4 GPa), while ulvöspinel can be formed by reacting ilmenite with olivine (at high T and high P). Based in part on the phase equilibrium work of Wagner and Grove [13] for Apollo 14 black glass and our olivine + ilmenite run at 1475°C and 2 GPa, we suggest that ilmenite in an olivine + opx mixture may become unstable and transform into ulvöspinel at higher temperatures and pressures (> 1350°C and 1.4 GPa, dashed blue line in Fig. 1). It is also possible that armalcolite may react with opx to form olivine + rutile, as observed in the ternary MgO-TiO_2-SiO_2 at 1.4 GPa [14]. Clearly more experiments are needed to confirm these transformations in cumulate assemblages relevant to lunar mantle overturn.

We should point out that the solidi reported in Fig. 1 should be viewed as upper bounds because clinopyroxene (cpx) has not been include in the present study. The presence of cpx, either from the sinking ilmenite-rich cumulate layer or cumulate harzburgite or lherzolite will likely lower the solidi of the dunite and the harzburgite. Figure 1 shows that the solidus of an ilmenite + cpx assemblage [11] is about 60°C lower than our reported solidus for the ilmenite-bearing harzburgite at 2 GPa. Nevertheless, the depth at which armalcolite is stable may not be significantly affect by the presence of cpx.

Lunar applications: Results from the present study have important implications for the distribution of high Ti oxides during lunar mantle overturn and for the generation of high Ti magmas in the lunar mantle. According to Fig. 1, ilmenite in the sinking ilmenite-rich layer will first transform into armalcolite when in contact with harzburgite cumulate at depth less than 270 km in the lunar mantle. If convective mixing during lunar mantle overturn is not efficient and mass distribution is somewhat heterogeneous, it is possible that some isolated pockets of armalcolite-bearing harzburgite be left behind in the lunar upper mantle. An ilmenite-bearing lunar lower mantle overlaid by a heterogeneously distributed armalcolite-bearing harzburgitic upper mantle can serve as potential high-Ti sources for ilmenite and armalcolite assimilation during transport of low Ti picritic magmas in the lunar mantle. The mechanisms and consequences of ilmenite and armalcolite assimilation are discussed in a companion paper [15].

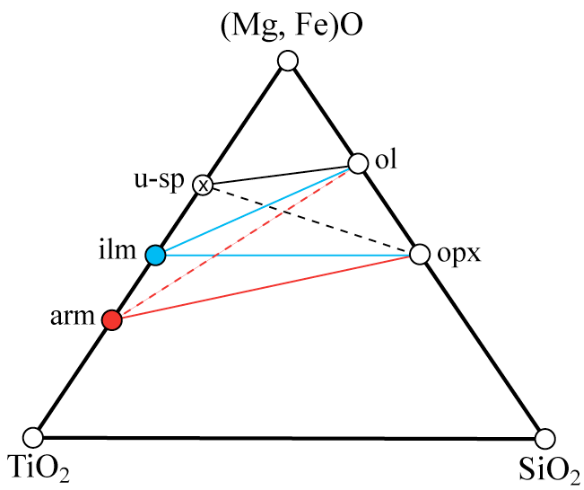

Figure 2. Tie-lines illustrating possible phase assemblage and reaction relationships of armalcolite (arm), ilmenite (ilm), and ulvöspinel (u-sp) coexisting with olivine (ol) or olivine + opx in the pseudo-ternary system (Mg, Fe)O-TiO_2-SiO_2. One of the high-Ti oxides can coexist with olivine + opx, depending on T and P.

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