Experimental constraints on the fate of $MgCO_3$ and $CaCO_3$ subducted into Earth's lower mantle

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Carbonates are the main phases that transport carbon from the Earth's surface to its interior through subduction. Evidence from thermodynamic modeling, ab initio calculation, high pressure and temperature experimental observations, and diamond inclusions indicate that both magnesium and calcium carbonates can be transported to at least transition zone depths, and carbonates may thus host carbon in the lower mantle. To determine whether $MgCO_3$ and $CaCO_3$ are present in the deep mantle, a key issue is the thermodynamics and kinetics of reactions of these carbonates with major lower mantle phases bridgmanite and Ca-perovskite. However, the effects of carbonate polymorphism on phase equilibrium between carbonates and silicates are poorly constrained. Here, we report a series of high pressure and temperature experiments exploring the following reaction and its reversal:

$CaCO_3 + MgSiO_3 \leftrightarrow MgCO_3 + CaSiO_3$,

at conditions ranging from the topmost lower mantle to the core-mantle boundary. Reaction products were determined in-situ by synchrotron X-ray diffraction and ex-situ by transmission electron microscopy with energy-dispersive X-ray spectroscopy. The results show that at shallow lower mantle pressure of 33 GPa, $CaCO_3$ + $MgSiO_3$ react to produce $MgCO_3$ and $CaSiO_3$, whereas at middle lower mantle pressure of 88 GPa, the reaction reverses to stabilize $CaCO_3$ + $MgSiO_3$. This pressure corresponds to the phase transition reported in recent experimental and theoretical studies of $CaCO_3$ from an orthorhombic post-aragonite structure with CO_3-coordination to a monoclinic $P2_1/c$-h structure with CO_4-coordination. At core-mantle boundary pressure of 137 GPa, we observe $CaCO_3$ in contact with Fe-rich post-perovskite. Therefore, the major change in the $CaCO_3$ structure controls the fate of $MgCO_3$ and $CaCO_3$ in the deep lower mantle.