Synthesis of calcium orthocarbonate, Ca$_2$CO$_4$-Pnma at P-T conditions of Earth’s transition zone and lower mantle

Carbonates play a crucial role in the long-term global carbon surface and in its crust (Hirschmann 2018; McKenzie et al. 2016; Ridgwell 2005; Wallmann 2001). As carbonates are partly incorporated into oceanic lithosphere, they may be transported into the deep mantle via subduction (Clift 2017; Kelemen and Manning 2015; McKenzie et al. 2016). Models propose a carbon influx on the order of several tens of megatons per year, which is mainly due to the contribution of carbonate sediments and altered carbonaceous oceanic crust (Hirschmann 2018; Kelemen and Manning 2015). Within the last two decades, several studies showed that all major carbonates, such as CaCO$_3$ (Bayarjargal et al. 2018), MgCO$_3$ (Binck et al. 2020b), FeCO$_3$ (Cerantola et al. 2017), and CaMg(CO$_3$)$_2$ (Binck et al. 2020a; Merlini et al. 2017), may be stable at the P-T conditions of the Earth’s mantle, while displaying a variety of different high P-T structures (e.g., Binck et al. 2020a; Cerantola et al. 2017; Chariton et al. 2020; Merlini et al. 2017; Gavryushkin et al. 2017; Ono et al. 2007). It has been proposed that carbonates in contact with mantle silicates and metals in the deep Earth are reduced and, depending on the stage of reduction, form metal carbides, or diamonds (Palyanov et al. 2013; Rohrbach and Schmidt 2011; Stagno et al. 2011, 2013). However, carbonate inclusions in diamonds originating from the deep mantle offer direct evidence for the presence of oxidized carbon in the form of carbonates in at least some regions of the mantle (Brenker et al. 2007; Kaminsky et al. 2016). Cold oxidized subducting slabs with slow reaction kinetics are believed to provide suitable conditions for hosting carbonates even at depths of the lower mantle (Maeda et al. 2017; Martirosyan et al. 2016; Walter et al. 2011).

A recent remarkable discovery are carbonates, in which $sp^3$-hybridization of carbon leads to the formation of CO$_4$ tetrahedra instead of triangular $sp^3$-hybridized CO$_4$-groups (Binck et al. 2020b; Bouard et al. 2011, 2012, 2015; Cerantola et al. 2017; Merlini et al. 2015, 2017; Lobanov et al. 2017). It is now of great interest to determine whether carbonates with $sp^3$-hybridized carbon form solid solutions with their silicate analogs and thus provide an alternative major host of carbon in the deeper mantle regions. Up to now, carbonates with CO$_3$-groups were synthesized at pressures >70 GPa, which led to the conclusion that only the deep lower mantle may provide the required thermodynamic conditions for their occurrence (Binck et al. 2020b; Bouard et al. 2011, 2012, 2015; Cerantola et al. 2017; Merlini et al. 2015, 2017; Lobanov et al. 2017).

Recent theoretical studies, however, have indicated that carbonate polymorphs in the system CaO-CO$_2$, which contain CO$_4$-groups may be stable at pressures and temperatures corresponding to the conditions of Earth’s transition zone and uppermost lower mantle (Sagatova et al. 2020; Yao et al. 2018). Specifically, Yao et al. (2018) predicted that Ca$_2$CO$_4$-Cmcn and CaC$_2$O$_4$-Pc may be stable phases at pressures >11 and >33 GPa, respectively, while Sagatova et al. (2020) found Ca$_2$CO$_4$-Pnma to be a stable phase at pressures >13 GPa.

While the phase diagram of CaCO$_3$ is well constrained for...