

***Ab initio* study of the structure and stability of high-pressure iron-bearing dolomite**

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Carbon is subducted into the mantle primarily in the form of metasomatically calcium-enriched basaltic rock, calcified serpentinites and carbonaceous ooze, all of which often contain dolomite. End-member $\text{CaMg}(\text{CO}_3)_2$ dolomite typically breaks down into two carbonates at 2-7 GPa. However, high-pressure x-ray diffraction experiments have recently shown that the presence of iron may be sufficient to stabilize high-pressure dolomite over single-cation carbonates above 35 GPa [1,2]. The structure and equation of state of high-pressure dolomite phases have been debated, creating a need for theoretical calculations. Using density functional theory interfaced with a genetic algorithm that predicts crystal structures (USPEX), we have found a monoclinic phase with space group $C2/c$. The $C2/c$ structure has a lower energy than previously reported dolomite structures at relevant pressures. It is possible that this phase is not achieved experimentally due to a large energy barrier and a correspondingly large required volume drop, resulting in the transformation to metastable dolomite II. We calculate the equation of state of trigonal dolomite, triclinic dolomites II and III, and monoclinic $C2/c$ dolomite to 60 GPa with 0, 50 and 100 mol% $\text{CaFe}(\text{CO}_3)_2$ and compare their enthalpies to single-carbonate assemblages. Although end-member $C2/c$ $\text{CaMg}(\text{CO}_3)_2$ dolomite is not stable relative to single-cation carbonates, $C2/c$ $\text{Ca}(\text{Mg}_{0.5}\text{Fe}_{0.5})(\text{CO}_3)_2$ and $\text{CaFe}(\text{CO}_3)_2$ are preferred over single-cation carbonates at high pressures. Thus, iron-bearing $C2/c$ dolomite may be an important host phase for carbon in slabs subducted into the lower mantle.

[1] Mao, Z. *et al.* (2011) *Geophysical Research Letters*, **38**. [2] Merlini, M. *et al.* (2012) *Proceedings of the National Academy of Sciences*, **109**, 13509-13514.