

Chemistry of carbon in carbonates at the Earth's mantle conditions

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Carbonates play a major role in the return of carbon into the mantle, but are very reactive and prone to pressure-induced phase transitions. Of particular importance are the theoretically predicted phase transitions from structures with trigonally-coordinated (sp^2) to tetrahedrally-coordinated (sp^3) carbon, as these may promote carbon solubility in the mantle and lead to contrasting carbonate chemical and physical behavior with depth. Despite the importance, experimental evidence for the stability of sp^3 -carbonates at lower mantle conditions has been incomplete. Here we use laser-heated diamond anvil cells combined with synchrotron x-ray diffraction (XRD), Raman spectroscopy, and first-principles calculations to identify phase transitions in CaCO_3 at high pressure. As we show that post-aragonite CaCO_3 transforms to $P2_1/c$ - CaCO_3 with sp^3 -hybridized carbon at 105 GPa, this supports a crossover to Ca-rich carbonates in the lowermost mantle, which may contribute to the seismic complexity of the region. We have also studied the Mg-carbonate – Fe interactions using synchrotron XRD. This study demonstrates the interaction of carbonates with Fe or Fe-bearing materials that produces Fe-carbide and excessive diamond, which can be accumulated near the core-mantle boundary depending on the balance between carbon and Fe.