High Pressure Changes to the Carbonate Ion: Implications for Carbon Retention in the Mantle

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The stability and structure of carbon bearing minerals under pressure governs carbon induced melting, carbon-rich magma generation (e.g. carbonatite and kimberlite) and carbon’s retention time in the deep Earth. There has been considerable interest to the high-pressure phases of carbonates recently, as they have been identified as the source of carbon into the deep Earth and are considered the stable form of carbon in oxidized regions of the mantle. We have probed the high-pressure phases of two carbonates, shortite (Na$_2$Ca$_2$(CO$_3$)$_3$) and dolomite (CaMg(CO$_3$)$_2$) to 26 and 86 GPa, respectively. We have used both Raman spectroscopy and single crystal X-ray diffraction for shortite and Raman spectroscopy for dolomite. We have observed a similar distortion to a portion of the carbonate ions within the unit cells of the two minerals at high pressures: dolomite at 63 GPa and shortite at 15 GPa. This distortion is manifested by an extremely non-planar carbonate ion with a fourth oxygen approaching from another carbonate ion, termed “3+1” coordination. In shortite, we have observed an apparent dimerization of two of the carbonate groups. This is compelling evidence for an increase in coordination of carbon at depth, which could change our understanding of carbon-retention in the Earth and indicates a complexity of carbonate bonding that has previously been unobserved.