

## High-Pressure/Temperature Behavior of the Alkali/Calcium Carbonate Shortite ( $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ): Implications for Carbon Sequestration in the Deep Earth

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The behavior of shortite ( $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ) has been investigated using synchrotron-based single crystal x-ray diffraction and Raman spectroscopy at room temperature at high pressures. The high-pressure structure of shortite has geological implications: carbonate minerals are suspected to be present in the upper mantle and are likely protoliths for carbon rich eruptions (e.g. carbonatites and kimberlites). Additionally, understanding the high-pressure structures of carbon rich minerals, we are able to better understand carbon retention within the deep earth, which has implications for the evolution of and changes to our atmosphere. We observe three phases of shortite: shortite-I from 0 to 14 GPa (at 300K); shortite-II above 15 GPa (at 300 K); an amorphous phase at pressures above  $\sim 22$  GPa (at 300 K). X-ray data demonstrate that shortite remains in the orthorhombic-C crystal system ( $Amm2$ ) up to 14 GPa; diffraction data yield a bulk modulus of  $56.6 (\pm 3.9)$  GPa with a pressure derivative of  $4.8 (\pm 1.1)$ . Compression is highly anisotropic, with the  $c$ -axis being twice as compressible as the  $a$ - and  $b$ -axes; this anisotropy appears to be governed by highly compressible sodium and calcite sites in the structure. Above 15 GPa, a phase change, likely driven by cation-cation repulsion occurs; shortite-II crystalizes in the  $Pm$  space group. This phase was solved in situ, at 15 GPa, and is novel in that it involves a large distortion of the carbonate groups, with an onset of 3+1 coordination and near-dimerization. This dimerization is observed at lower pressures than other systems to date: this coordination could become important in complex carbonate solids and liquids in the deep earth, at lower depths than previously anticipated.