

Probing carbon-bearing species and CO₂ inclusions in amorphous carbon-MgSiO₃ enstatite reaction products at 1.5 GPa: Insights from ¹³C high-resolution solid-state NMR

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ABSTRACT

Understanding carbon speciation in Earth materials is important to unravel the geochemical evolution of the Earth's atmosphere, the composition of mantle partial melts, and the overall distribution of carbon in the deep mantle. In an effort to provide the systematic protocols to characterize carbon-bearing fluid inclusions and other carbon-bearing species using high-resolution ¹³C solid-state NMR, one of the element-specific probes of local structure around carbon, we explore the atomic configurations around the carbon species formed during the reaction between ¹³C-enriched amorphous carbon and MgSiO₃ enstatite synthesized at 1.5 GPa and 1400 °C using ¹³C MAS NMR spectroscopy and Raman spectroscopy. The Raman spectra for the fluid inclusion show the presence of multiple molecular species (e.g., CO₂, CO, CH₄, H₂O, and H₂) and reveal heterogeneous distribution of these species within the inclusion. ¹³C MAS NMR results show that the sharp peak at 125.2 ppm is dominant. While the peak could be assigned to either molecular CO₂ in the fluid phase or fourfold-coordinated carbon (⁴C), the peak is likely due to fluid CO₂, as revealed by Raman analyses of micrometer-sized fluid inclusions in the sample. The peaks at 161.2, 170.9, and 173.3 ppm in the ¹³C NMR spectrum correspond to the carbonate ions (CO₃²⁻) and additional small peak at 184.5 ppm can be attributed to carbon monoxide. Based on the established relationship between ¹³C abundance and peak intensity in the ¹³C MAS NMR, the estimated ¹³C amounts of CO₂, CO₃²⁻, and CO species are much larger than those estimated from carbon solubility in the crystals, thus, indicating that those carbon species are from external phases. The ¹³C NMR spectrum for amorphous carbon showed a peak shift from ~130 to ~95 ppm after compression, thereby suggesting that the amorphous carbon underwent permanent pressure-induced densification, characterized by the transition from *sp*² to *sp*³ hybridization and/or pressure-induced changes in *sp*² carbon topology. While direct probing of carbon species in the crystalline lattice using NMR is challenging, the current results and method can be utilized to provide quantitative analysis of carbon-species in the fluid-inclusions in silicates, which is essential for understanding the deep carbon cycle and volcanic processes.

Keywords: ¹³C MAS NMR, enstatite, carbon speciation, amorphous carbon