Probing carbon-bearing species and CO\textsubscript{2} inclusions in amorphous carbon-MgSiO\textsubscript{3} enstatite reaction products at 1.5 GPa: Insights from \textsuperscript{13}C 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 \textsuperscript{13}C 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 \textsuperscript{13}C-enriched amorphous carbon and MgSiO\textsubscript{3} enstatite synthesized at 1.5 GPa and 1400 °C using \textsuperscript{13}C MAS NMR spectroscopy and Raman spectroscopy. The Raman spectra for the fluid inclusion show the presence of multiple molecular species (e.g., CO\textsubscript{2}, CO, CH\textsubscript{4}, H\textsubscript{2}O, and H\textsubscript{2}) and reveal heterogeneous distribution of these species within the inclusion. \textsuperscript{13}C MAS NMR results show that the sharp peak at 125.2 ppm is dominant. While the peak could be assigned to either molecular CO\textsubscript{2} in the fluid phase or fourfold-coordinated carbon (\textsuperscript{13}C\textsuperscript{4}C), the peak is likely due to fluid CO\textsubscript{2} 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 \textsuperscript{13}C NMR spectrum correspond to the carbonate ions (CO\textsubscript{3}\textsuperscript{2–}) and additional small peak at 184.5 ppm can be attributed to carbon monoxide. Based on the established relationship between \textsuperscript{13}C abundance and peak intensity in the \textsuperscript{13}C MAS NMR, the estimated \textsuperscript{13}C amounts of CO\textsubscript{2}, CO\textsubscript{3}\textsuperscript{2–}, 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 \textsuperscript{13}C 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\textsuperscript{2} to sp\textsuperscript{3} hybridization and/or pressure-induced changes in sp\textsuperscript{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: \textsuperscript{13}C MAS NMR, enstatite, carbon speciation, amorphous carbon

Introduction

Understanding the carbon speciation in Earth materials is important to unravel the geochemical evolution of the Earth’s atmosphere, composition of 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 \textsuperscript{13}C 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 \textsuperscript{13}C-enriched amorphous carbon and MgSiO\textsubscript{3} enstatite synthesized at 1.5 GPa and 1400 °C using \textsuperscript{13}C MAS NMR spectroscopy and Raman spectroscopy. The Raman spectra for the fluid inclusion show the presence of multiple molecular species (e.g., CO\textsubscript{2}, CO, CH\textsubscript{4}, H\textsubscript{2}O, and H\textsubscript{2}) and reveal heterogeneous distribution of these species within the inclusion. \textsuperscript{13}C MAS NMR results show that the sharp peak at 125.2 ppm is dominant. While the peak could be assigned to either molecular CO\textsubscript{2} in the fluid phase or fourfold-coordinated carbon (\textsuperscript{13}C\textsuperscript{4}C), the peak is likely due to fluid CO\textsubscript{2} 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 \textsuperscript{13}C NMR spectrum correspond to the carbonate ions (CO\textsubscript{3}\textsuperscript{2–}) and additional small peak at 184.5 ppm can be attributed to carbon monoxide. Based on the established relationship between \textsuperscript{13}C abundance and peak intensity in the \textsuperscript{13}C MAS NMR, the estimated \textsuperscript{13}C amounts of CO\textsubscript{2}, CO\textsubscript{3}\textsuperscript{2–}, 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 \textsuperscript{13}C 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\textsuperscript{2} to sp\textsuperscript{3} hybridization and/or pressure-induced changes in sp\textsuperscript{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.

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H\textsubscript{2}O and CO\textsubscript{2} are the most abundant volatile components in the Earth’s interior. Additional species such as CH\textsubscript{4}, H\textsubscript{2}, and CO can be formed depending on total bulk chemistry of inclusion, f\textsubscript{02} condition, as well as temperature and pressure (e.g., Morizet et al. 2010; Mysen and Richet 2005; Pawley et al. 1992). While the CO\textsubscript{2} inclusions are not included in an estimate of carbon solubility into silicate crystals and melts, they can contribute to the total bulk carbon contents of magma chambers, thereby affecting their buoyancy and rising speed (Blundy et al. 2010; Burton et al. 2013; Dixon and Clague 2001; Gerlach et al. 2002; Kaminski and Jaupart 1997; Lloyd et al. 2014; Parfitt and Wilson 2008; Rust and Cashman 2011; SugioKA and Bursik 1995). For example, the exsolved CO\textsubscript{2} in Kilauea magma was estimated to be ~0.61 wt%, which is approximately 87% of the total CO\textsubscript{2} emitted from the volcanic eruption, while that of dissolved (and thus structurally bound) CO\textsubscript{2} is ~0.09 wt% (Gerlach et al. 2002), indicating that the exsolved CO\textsubscript{2} in the glasses is among the important carbon reservoirs. Together with CO\textsubscript{2} inclusions in the glasses, carbon species in crystalline silicates has been proposed as an additional carbon...