

## Dissolution mechanisms of CO<sub>2</sub> in silicate melts

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Carbon dioxide is one of abundant volatile components in natural magmas. It is generally known to dissolve in silicate melts/glasses as molecular CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> species, but how the latter group is incorporated and its effect on the silicate structure are less known. Recently, we started a comprehensive study on silicate glasses (quenched melts) using advanced solid-state NMR techniques combined with Raman spectroscopy and first-principles calculations to better understand this issue. Here we give a preliminary report of the results.

CO<sub>2</sub>-bearing glasses (1 to 10 wt%, all undersaturated) were prepared by quenching melts at 1.0 to 1.5 GPa and 1400 to 1600 °C using a non-endloaded piston cylinder apparatus. <sup>13</sup>C-enriched carbonate (CaCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>) was used as the <sup>13</sup>C source. The starting material was sealed in Pt capsule, and Fe<sub>2</sub>O<sub>3</sub> disk was placed near the capsule to avoid reduction of CO<sub>2</sub>.

Three silicate compositions have been examined by NMR thus far: diopside (CaMgSi<sub>2</sub>O<sub>6</sub>), Ca-melilite (Ca<sub>1.5</sub>AlSi<sub>2</sub>O<sub>7</sub>) and jadeite (NaAlSi<sub>2</sub>O<sub>6</sub>). The <sup>13</sup>C MAS NMR spectrum of the diopside glass contains a nearly symmetric peak near 167.2 ppm. That of the Ca-melilite glass exhibits a similarly narrow peak near 167.8 ppm with a tail to lower frequency. Both peaks are attributable to dissolved CO<sub>3</sub><sup>2-</sup> group. The <sup>13</sup>C MAS NMR spectrum of the jadeite glass contains a broader asymmetric peak near 164 ppm, a narrower peak near 125 ppm and another weak narrow peak near 185 ppm, resembling that reported previously. These peaks may be attributed to dissolved CO<sub>3</sub><sup>2-</sup>, CO<sub>2</sub> and CO species, respectively. Thus for depolymerized diopside and Ca-melilite compositions, CO<sub>3</sub><sup>2-</sup> species is predominant, but for fully polymerized jadeite composition, CO<sub>3</sub><sup>2-</sup> and CO<sub>2</sub> species coexist, consistent with previous reports. The presence of CO molecules indicates somewhat reduced condition. Preliminary speculation on the environments of the CO<sub>3</sub><sup>2-</sup> groups may be made from the <sup>13</sup>C NMR spectra. The narrowness and closeness in peak position to crystalline CaCO<sub>3</sub> (168.6 ppm) for the two depolymerized compositions may indicate that both are dominated by free CO<sub>3</sub><sup>2-</sup> species (i.e. linked only to network modifiers). Formation of free CO<sub>3</sub><sup>2-</sup> will polymerize the melt structure. The asymmetric peak shape for the Ca-melilite glass could be a sign for additional species. For this sample, <sup>27</sup>Al 3Q MAS NMR revealed small amounts of penta-coordinated and octahedral Al, in addition to tetrahedral Al. It is interesting to know whether these high-coordinated Al are related to CO<sub>3</sub><sup>2-</sup> speciation. The <sup>13</sup>C NMR peak of CO<sub>3</sub><sup>2-</sup> in the jadeite glass is much broader and more shifted from that of crystalline carbonate, suggesting that these species could be part of the aluminosilicate network. More definite peak assignment awaits further <sup>29</sup>Si-<sup>13</sup>C and <sup>27</sup>Al-<sup>13</sup>C double-resonance NMR measurements that can directly probe C-O-Si(Al) linkages. Raman spectroscopy will be also used to obtain information regarding symmetry of CO<sub>3</sub><sup>2-</sup> species. First-principles calculations are underway to gain better insights into the chemical shifts and J couplings for candidate local structures. The latest results will be presented at the meeting.

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