

LETTER

^{17}O NMR evidence of free ionic clusters $\text{M}^{\text{n}+} \text{CO}_3^{2-}$ in silicate glasses: Precursors for carbonate-silicate liquids immiscibility

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ABSTRACT

Carbon dioxide is a ubiquitous component of low-silica melts such as kimberlites or melilitites. It is currently assumed that CO_2 molecules dissolving in low-silica melts as carbonate groups (CO_3^{2-}) induce a strong polymerization of the silicate network; however, the exact molecular configuration of this dissolution mechanism is still debated.

Using ^{17}O MAS NMR spectroscopy, we have investigated the carbonate molecular environment in a series of synthesized low-silica (31–41 wt% SiO_2), CO_2 -bearing (from 2.9 to 13.2 wt% CO_2) silicate glasses analogous to melilitites and kimberlites. With the selective $\{^{13}\text{C}\}$ -, $\{^{27}\text{Al}\}$ -, and $\{^{29}\text{Si}\}$ - ^{17}O JHMQC NMR method, we show that CO_2 dissolved in the studied low-silica glasses is totally disconnected from the silicate network, forming free ionic clusters (FIC) $\text{M}^{\text{n}+} \text{CO}_3^{2-}$ with $\text{M}^{\text{n}+}$, a charge compensating cation.

The $\text{M}^{\text{n}+} \text{CO}_3^{2-}$ FIC are considered as precursors to immiscibility in between carbonate and silicate liquids. Observed in all studied compositions, we suggest that this immiscibility can be produced from moderately to strongly depolymerized silicate melt compositions.

Keywords: ^{17}O NMR spectroscopy, CO_2 dissolution mechanism, free ionic clusters, silicate glasses, immiscibility