Detection of a Non-Classical, Prenucleation, Liquid Phase of Calcium Carbonate

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Introduction

Recently, it has been found that calcium carbonate biominerals are formed through a non-classical, multi-step, precursor process (1-3). Specifically, calcium carbonate is suspected to transition through an intermediate liquid phase prior to solid nucleation (4-5). The current thrust of this collaborative research is to demonstrate the presence of the liquid phase precursor using nuclear magnetic resonance

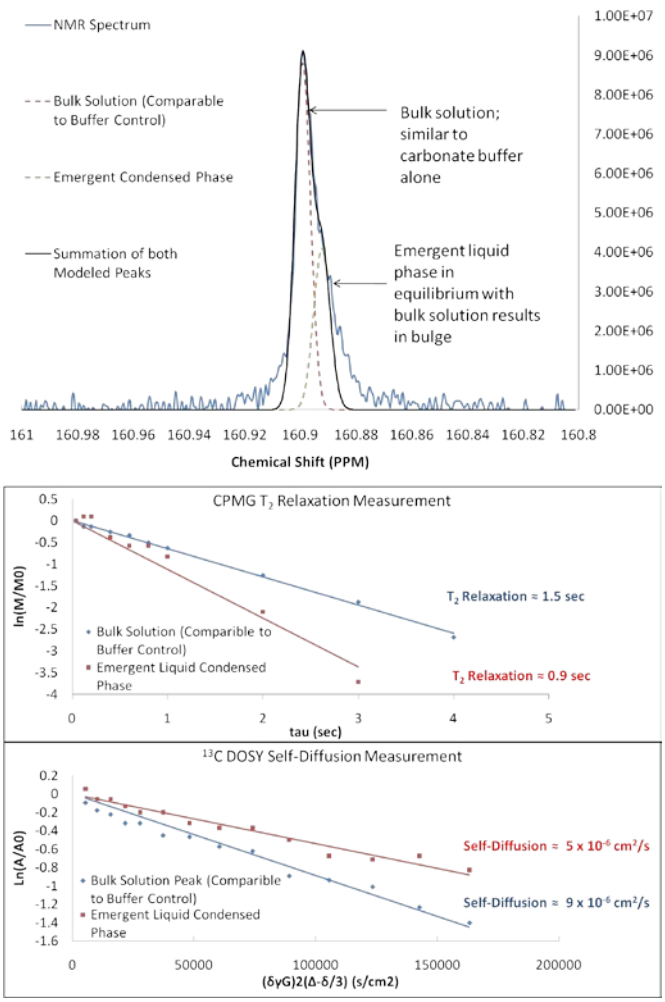

Figure 1. (Top) A liquid-liquid phase separation leads to a bulge in the NMR spectrum. (Bottom) There are two distinct T_2 relaxation times and diffusions, suggesting that there is an emergent phase.

Experimental

We are using ^{13}C NMR at the NHMFL at the University of Florida to identify liquid-liquid phase separation processes occurring in supersaturated calcium carbonate solutions. We are characterizing the presence of prenucleation phases using ^{13}C Pulse-Field Gradient Spin Echo (PFGSE) diffusion nmr and Carr-Purcell Meiboom-Gill (CPMG) T_2 measurements.

Results and Discussion

The onset of phase separation is detected based on the biased broadening (bulging) of the NMR spectrum for the solution (see **Figure 1**) We are able to demonstrate differences in diffusion and T_2 relaxations between the two phases (see Figure 1), verifying the presence of a two state system.

Conclusions

Our results suggest that there is a liquid-liquid phase separation occurring and that the emergent liquid precursor to calcium carbonate is more viscous than the bulk solution.

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References

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