

## Interactions between network cation coordination and oxygen speciation in oxide glasses

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Recent experimental studies of aluminosilicate glasses and melts have greatly enhanced our information on the details of network structure that supersede conventional approximations, notably the presence of non-bridging oxygens (NBO) in metaluminous and even peraluminous compositions, and the widespread presence of significant concentrations of five-coordinated Al even in highly peralkaline (and peralkaline-earth) regions. Especially as Al, Si, (and B) coordination increase at high pressures, the interactions of these species become important for melt properties (e.g. density, viscosity, configurational entropy) and component activities. This interplay can sometimes be more apparent in borosilicate and germanate analog systems, even at ambient pressure, as composition and temperature have now well-known, large effects on structure. For example, the sizes and charges of the network modifier cations can have strong effects, as smaller and/or higher-charged cations often favor the formation of NBO and/or BO such as Al-O-Al linkages, both of which serve as relatively concentrated negative charge that can more effectively coordinate the modifier cations. We will compare results on such speciation reactions for a variety of oxide melt systems, note similarities and differences, and suggest important areas for future investigation.

## Diffusion versus surface reaction control of mineral precipitation and dissolution kinetics at the pore scale

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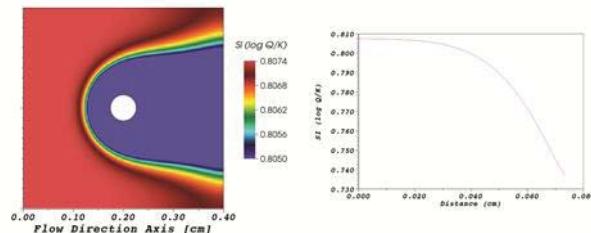
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### Introduction

The rates of mineral precipitation are important as a subsurface carbon sequestration mechanism in the case of carbonates, while mineral dissolution is important as a source of both metal cations and alkalinity for precipitation. Pore scale flow and transport processes within the complex pore structure of the subsurface can lead in some cases to a complete or partial control of reaction rates by molecular diffusion. The extent to which a diffusion control develops depends on the rates of local surface reaction, but also on the pore geometry and the rate of flow, since these effects influence the width of diffusion boundary layers that develop adjacent to reactive mineral surfaces.

### Approach and Results

In this study, we use Direct Numerical Simulation of pore scale reactive transport processes to investigate the effect of a complete or partial limitation of rates by molecular diffusion through a hydrodynamic boundary layer (Figure 1). We focus here on the dissolution and precipitation of carbonate phases, with rates at the mineral surface taken from experimental studies in which a complete surface reaction control can be demonstrated. The partial control of rates by molecular diffusion, which is particularly pronounced for larger grain sizes within porous subsurface materials, is investigated as a function of the saturation state of the bulk solution with respect to the carbonates, as well as temperature and pH, since these can influence both the rate of surface reaction and multicomponent diffusion. The simulations are combined with selected microfluidic reactor experiments in which hydrodynamic boundary layers and surface reaction can be rigorously quantified. The simulations demonstrate that a partial diffusion control of reaction rates in medium to coarse grained materials is much more prevalent than is commonly thought.



**Figure 1:** Left: Contour plot of calcite supersaturation surrounding a spherical calcite grain. Right: Profile of supersaturation with respect to calcite across a diffusion boundary layer, with mineral grain on the right, bulk solution on the left.