

## Analogue experiments on volatile escape from crystal-rich magmas

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The low water content of granitoid bodies requires effective escape of the volatile phase during crystallization of mushy magma. We explore the physical mechanisms for volatile migration in crystal-rich magmas with experiments on three-phase analogue mixtures of syrup, solid particles and gas. The liquid+particles was either placed in a vertical tube or sandwiched between two glass plates; gas was injected into the suspension, or generated throughout the suspension by chemical reaction or by decompression. The proportions of phases, syrup viscosity, particle sizes, and rate of gas injection/expansion were varied. Experiments were videoed and monitored with gas pressure data.

Comparisons with crystal-free experiments indicate that crystals in mushes strongly inhibit buoyancy-driven bubble migration, but can facilitate the formation of temporary connected gas pathways, allow degassing of permeable gas flow at much lower volume fractions of gas than the crystal-free system. The experiments with parallel glass plates facilitate visualization of the gas phase. Three regimes are identified by gas distribution patterns, and are found to be related to the volume fraction of solids: (1) At low particle concentrations the gas forms smooth fingers that intrude steadily; (2) At ~55% particles, the gas penetrates the suspension in bursts, and forms thin "fractures"; (3) At solid fractions sufficient to lock the particles in place, the gas pushes liquid out through the particle network.

In all three regimes the measured gas pressure increases smoothly and does not decrease until, or shortly before, the gas reaches the edge of the liquid+particle mixture. In the fracturing regime, the pressure increase is steady even during bursts of motion; this indicates that the ductile but sudden fracture formation rearranges the gas phase but does not create episodes of pressure buildup and release. Once a fracture has released gas to the outside, however, there are subsequent fluctuations in pressure as the initial fracture heals (viscously) and closes the system until a new fracture reaches the suspension boundary, at which point the process is repeated in a new location (because in heterogeneous suspensions fractures preferentially propagate into areas with relatively high solid contents). This mechanism would allow effective open-system degassing of crystallizing volatile-saturated magma, without leaving textural evidence of the volatile phase.

## Calculation of Mass-Dependent Isotope Fractionation in Aqueous-Mineral Systems: In Pursuit of 1-permil Accuracy

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Calculation of mass-dependent isotope fractionation in geochemical systems is probably the single most successful application of computational chemistry to geochemistry. The accuracy of these calculations is highly system dependent. For heavy isotopes with fractionations between minerals and aquo ions on the 1-2 permil level, first principles calculations are highly challenging, and computational requirements differ considerably between anionic and cationic systems. Aquo ions need large basis sets, particularly anions, which require basis sets of aug-cc-pVTZ (or better) quality. Aquo cations can be represented using continuum solvent models beyond the second shell, while aquo anions cannot. When density functional theory is used, the choice of the exchange-correlation functional has a strong effect on the results. This exchange-correlation variation, together with the basis set variation, can easily result in steps taken through basis-set XC functional that vary over a range of more than ~3 permil, with no apparent consensus on which functionals work best. Thus while past success has often been impressive, reliable prediction of fractionation at the sub-1 permil level will remain a highly challenging, though not unattainable, goal. Examples are taken from  $\text{BOH}_3(\text{aq})$ - $\text{BOH}_4(\text{aq})$ ,  $\text{Mg}^{2+}(\text{aq})$ -calcite,  $\text{Ca}^{2+}(\text{aq})$ -calcite,  $\text{Fe}^{3+}(\text{aq})$ -hematite,  $(\text{H})\text{CO}_3(\text{aq})$ -carbonate, perovskite-ferropericlae, chlorophyll, and amino acid systems.