The birth of bubbles by spinodal decomposition: Solving the tiny bubble paradox

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Abstract

Energetic ash-producing volcanic eruptions are driven by the diffusive and decompressive growth of bubbles (mostly water) during ascent in a magma conduit. The spatial distribution of bubble nucleation sites is one of the primary controls on ash-forming fragmentation. However, the initial formation of bubbles in a supersaturated magma is problematical, especially for homogeneous nucleation. Excessive surface tension pressure should preclude the existence of small bubbles, because exsolved water is driven back into the melt. This is the "tiny bubble paradox."

We suggest that—under special circumstances—the tiny bubble paradox may be circumvented by spinodal decomposition, a process in which uphill diffusion enables spontaneous unmixing of phases to reduce the free energy of the system. As spinodal decomposition progresses, three dimensional, quasi-spherical, zones of water-rich magma develop. These zones are characterized by an increasingly high concentration of dissolved water at the centers and reducing concentration at the margins. Bubbles are born when the concentration of water in the interior of the water-rich zones goes to 100% and the concentration of melt goes to zero. The small, nascent, bubbles that emerge will be buffered from melt by water-rich shells with increasing melt concentration away from newly formed bubbles. This diffuse concentration gradient of water means that there is no surface, per se, for surface tension to arise. This is the crux of the solution of the tiny bubble paradox.

Particle morphology may be used to distinguish ash with spinodal origins from ash associated with typical (metastable) bubble nucleation. Spinodal decomposition occurs at a wavelength determined by the pressure, temperature, and viscosity of the magmatic system. This wavelength should create bubbles of uniform size and bubble walls of equal strength in a fragmenting magmatic foam, leading to sharply mono-modal vesicle and ash particle size distributions. Classical bubble nucleation should create more-variable bubble sizes and bubble wall strengths, leading to a broader particle size distribution. Better understanding the mechanism of bubble formation in magmatic systems will, in turn, enable better understanding of hazardous, explosive, eruptions.

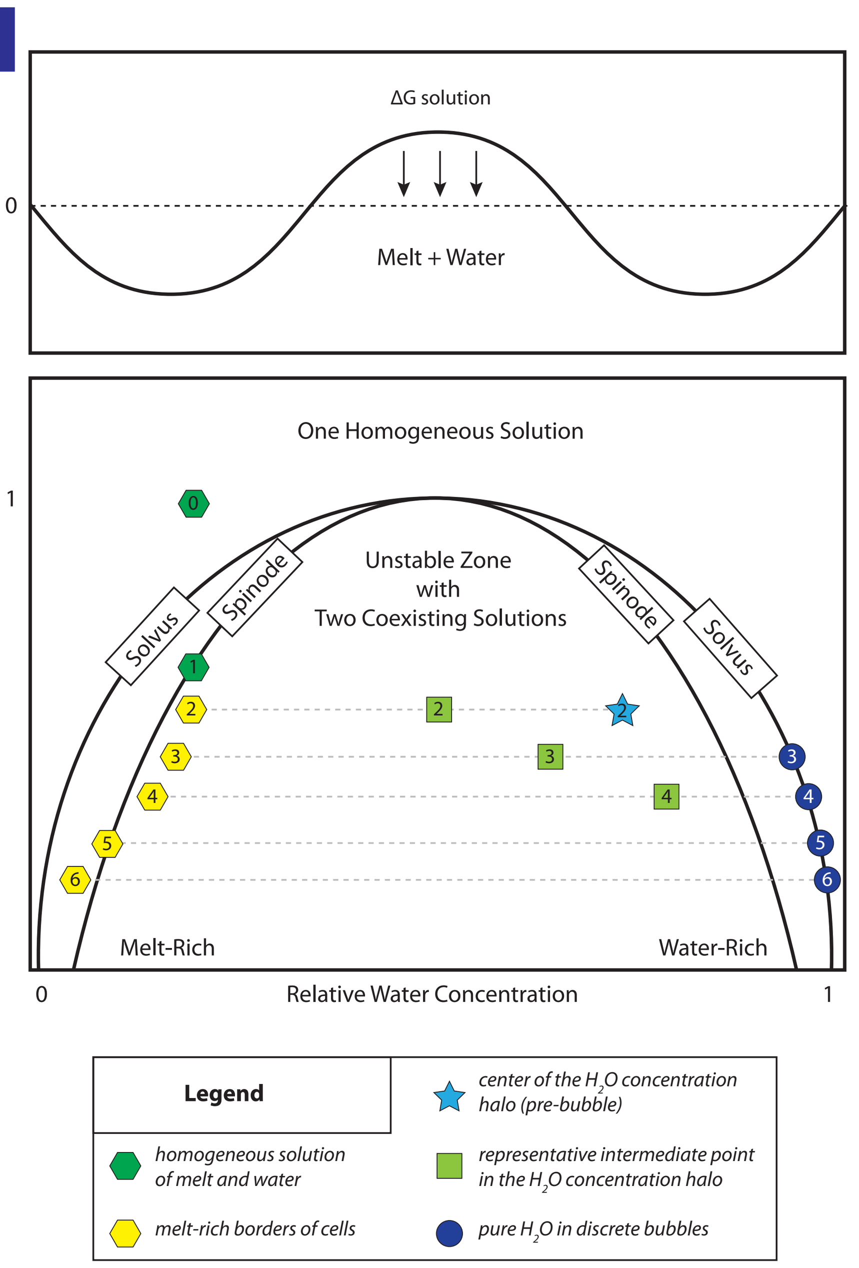


Figure 1: Conceptual phase diagram for spinodal decomposition in decompressing magma Above the binode (solvus) the system is undersaturated. Continuous decompression drives the melt into a metastable zone between the binode and spinode. Here, sufficient perturbation of the system can overcome the energy barrier associated with bubble nucleation. With continued decompression, compositional unmixing of melt and water occurs via uphill diffusion (spinodal decomposition; times 2-5). Eventually, further decompression and oversaturation bring the system back to the metastable region and "normal" downhill diffusion commences (time 7). The panels to the right (Figure 2) offer a spatial perspective of this process.

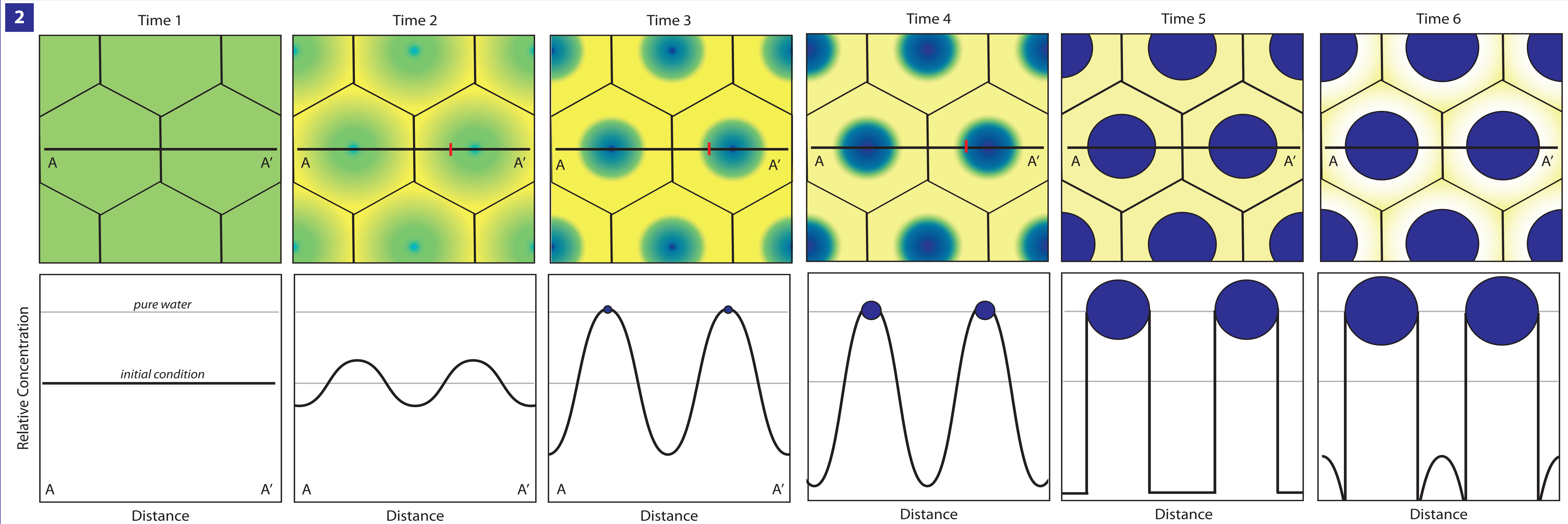


Figure 2: Spatial perspective of spinodal decomposition and bubble formation in decompressing magma.

At time 1, the decompressed and oversaturated magma has passed through the metastable region (Fig. 1), achieving the initial conditions for spinodal decomposition.

At time 2, beyond the spinode, the Gibbs free energy of the system is reduced by uphill diffusion and phase separation, leading to higher and lower water concentrations across the profile A-A'. The wavelength of separation between water rich zones is controlled by diffusion rates and water concentration.

At time 3, progressive phase separation leads to small spherical regions of essentially pure water (recognizable bubbles). The magma immediately adjacent to the nascent bubble is almost pure water, with water concentration decreasing away from the newly formed bubble. As such, there is no surface, per se, for surface tension to be a barrier to bubble formation. This is the crux of the solution of the "tiny bubble paradox."

At time 4, decompression and uphill diffusion lead to a lower water concentration in the melt surrounding the growing bubble (paler yellow than time 4). The concentration gradient steepens as phase separation continues.

The "distance" scale is renormalized as bubbles grow; bubbles draw water from increasingly expanded unit cells between each time step.

At time 5, a sharp interface develops between "pure" water and water-saturated melt (a bubble wall). The dissolved water concentration in the melt (which is now uniformly supersaturated between bubbles; uniform yellow) has reduced enough to drive the system from the sub-spinodal region and back into the metastable region. Uphill diffusion ceases and surface tension temporarily inhibits further bubble growth.

At time 6, increasingly rapid decompression and low-pressure oversaturation overcome surface tension. Water enters the bubble via standard downhill diffusion, leading to a gradient with lower water concentration at the bubble wall (reversal of yellow intensity; the "typical" visualization of bubble growth). As bubbles continue to grow by decompression and downhill diffusion, the magma experiences volumetric expansion—and thus accelerating ascent and decompression.

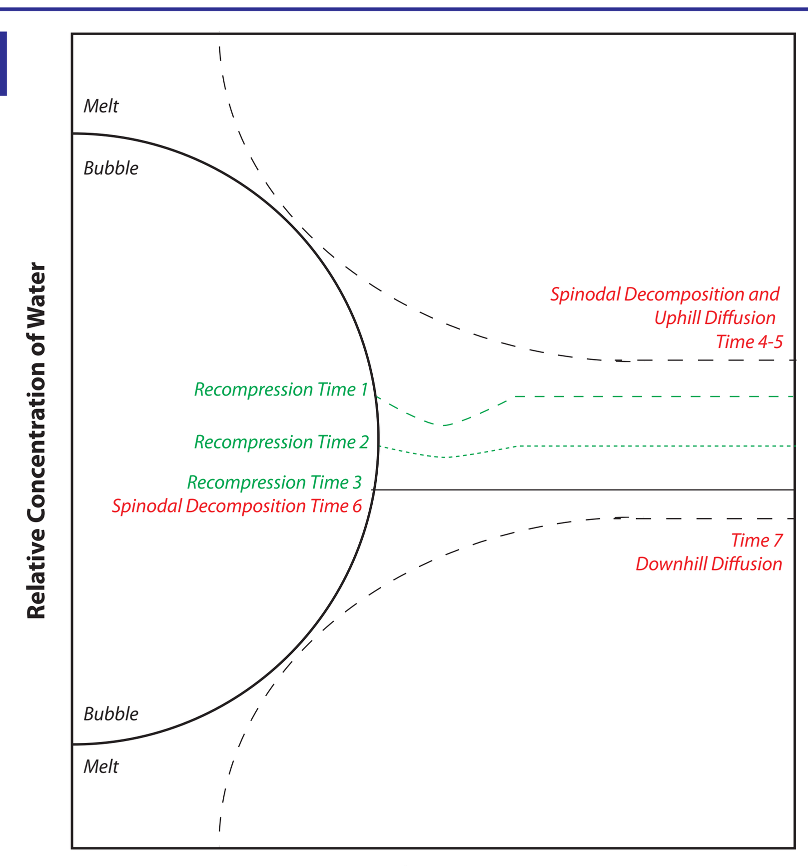


Figure 3: Evolution of concentration profiles approaching the bubble-melt interface. Concentration profile evolution involved in spinodal decomposition and the transition to more-typical downhill diffusion. With spinodal decomposition, a monotonic increase of water concentration is expected toward the bubble as long as the system is beneath the spinode (Fig 1).

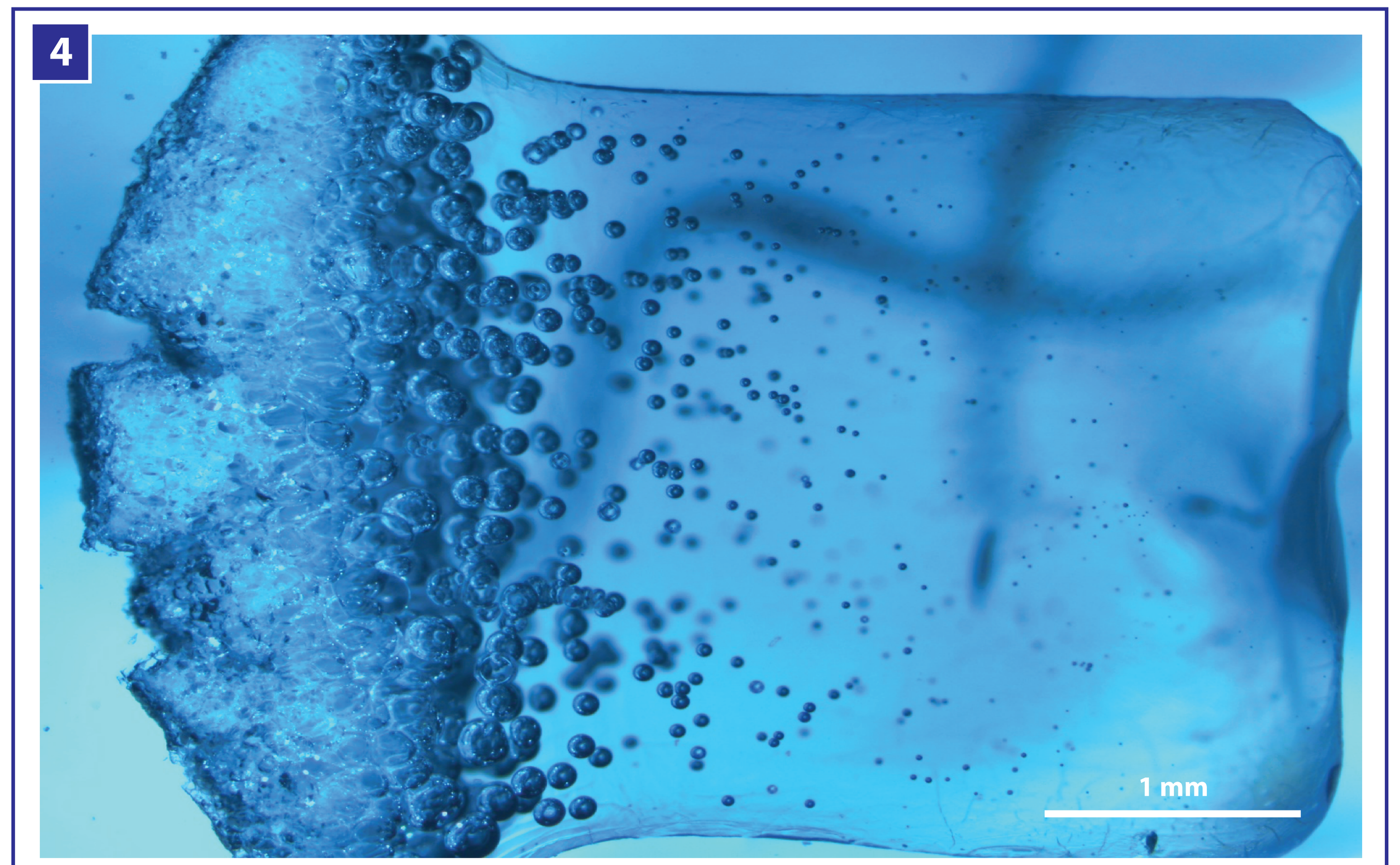


Figure 4: Phonolitic sample (AOQ; 5% water) formed from glass (not powder), and hydrated at 1250˚C and 200 MPa. It was quenched at pressure then slowly decompressed to 1 bar. Then it was placed on a hot plate at 550˚C for 2 minutes, during which time the hot end vesiculated, but the cool end did not. This created a gradient in which it is most likely to find water concentration variations caused by spinodal decomposition. Analysis of this and other samples is ongoing.

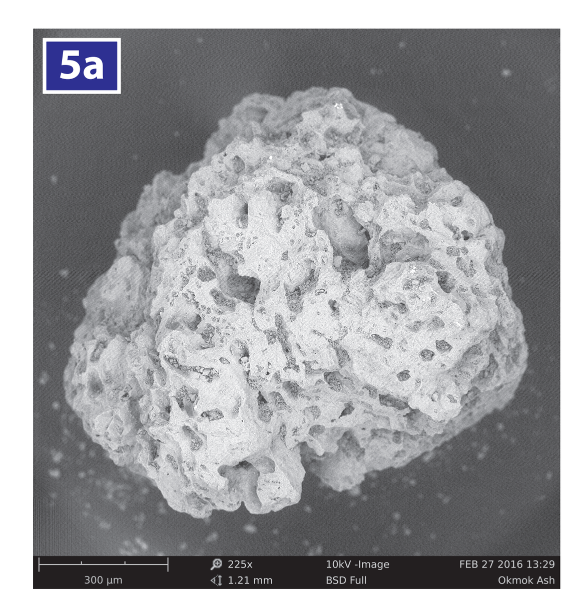
Catching it in the Act

Even if spinodal decomposition is responsible for the initial formation of bubbles in natural systems, it is expected that the bubbles will evolve and reach "time 6" (Figs. 1 and 2) and continue to grow by normal downhill diffusion (Fig. 3). Consequently, there may be no conclusive record of spinodal decomposition in natural ashes. In order to catch spinodal decomposition" in the act," it is thus necessary to create conditions under which the process occurs in the lab, and quench before there is time to complete the evolution of bubbles. Samples have been created for this purpose with phonolitic (Tuebingen) and rhyolitic (Texas) compositions, with dissolved water concentrations ranging from 1 to 6 wt% (Fig. 4). The next steps are to examine these samples with various tools (e.g., SEM, Raman, CXT) to measure water concentration variations within the samples. Concentrations greater than initial will indicate uphill diffusion. Further, the wavelength of variability will shed light on the parameters involved in phase separation in hydrous melts, for which an equation of state does not yet exist.

Significance to Explosive Eruptions

The explosivity of an eruption is controlled, in part, by the uniformity of bubble size and distribution in a fragmenting foam. In a foam with a broad bubble size (and thus space) distribution, bubble walls will have a range of strengths; fragmentation will occur over an extended time. This promotes the formation of "compound ash," with relatively large clasts containing many internal vesicles. Conversely, if bubbles are uniform in size (and space) distribution, bubble wall disruption will occur simultaneously throughout the foam, causing a sudden explosive release of gas and a more violent eruption.

One way to achieve uniform distribution in a bubbly foam is spinodal decomposition, which yields a characteristic wavelength of phase separation between water and melt. More explosive eruptions that produce a greater fraction of simple ash may be driven by simultaneously fragmenting uniform bubbles originally formed by spinodal decomposition. Further understanding the mechanisms of bubble formation in magmatic systems may thus enable better prediction of the hazards accompanying explosive eruptions.



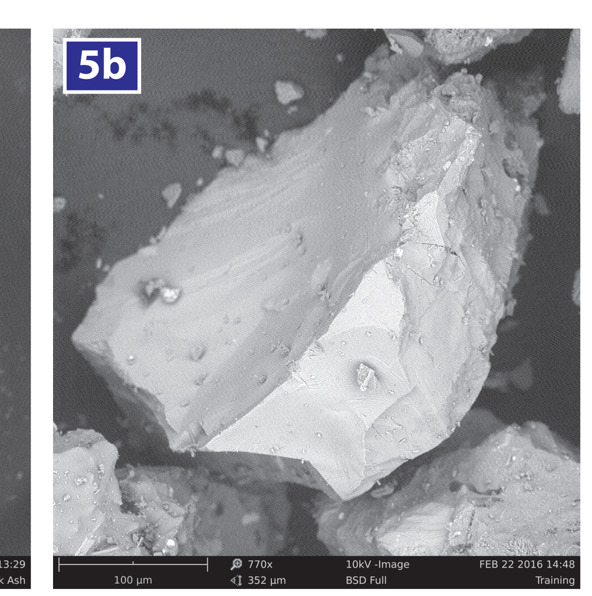


Figure 5: (A) An example of a "compound" ash particle, which contains imprints of many partial bubbles on its surface, and is filled with whole bubbles internally. (B) An example of a "simple" ash particle, composed of a single fragmented bubble wall or plateau border. When compound ash forms, some bubbles are disrupted, while others remain intact, resulting in a wide range of bubble sizes and bubble wall strengths. This morphology results from a diverse distribution of bubble sizes and spacing. If all bubbles form simultaneously at a fixed distance apart, as may happen during spinodal decomposition, one would expect fragmentation to occur suddenly and uniformly (creating simple ash). (C) The eruption of Mt. Redoubt, Alaska, in 1990 is an example of an ash-generating event that motivates this study (Photograph by R. Clucas, April 21, 1990, found at https://geology.com/volcanoes/redoubt/).

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