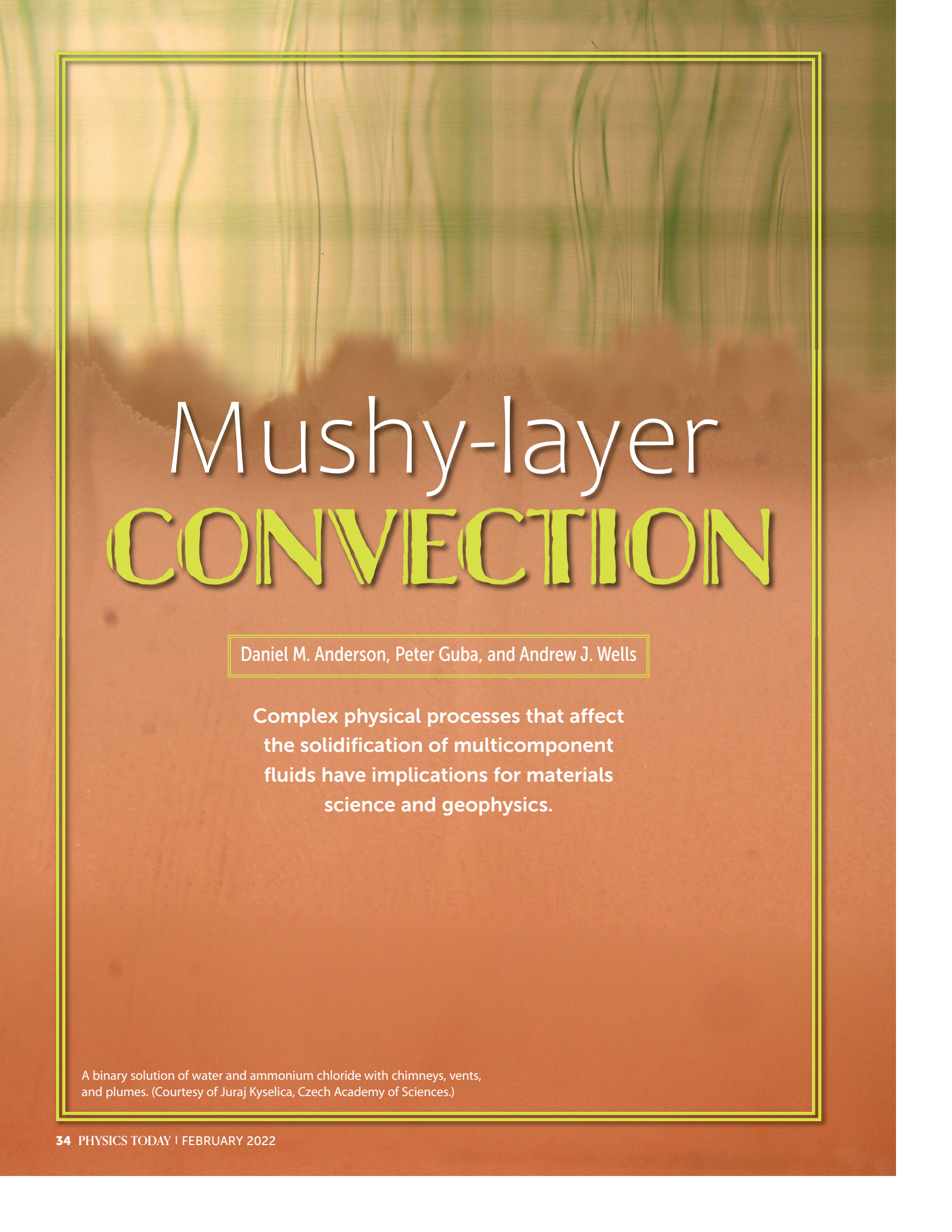




# Mushy-layer CONVECTION

Daniel M. Anderson, Peter Guba, and Andrew J. Wells

Complex physical processes that affect the solidification of multicomponent fluids have implications for materials science and geophysics.

A binary solution of water and ammonium chloride with chimneys, vents, and plumes. (Courtesy of Juraj Kyselica, Czech Academy of Sciences.)



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**S**ea-ice formation in freezing polar oceans and defect development in metal alloys may seem like disparate processes, but they share one important feature: a so-called mushy layer. Such porous media host complex fluid mechanical activity, thermal and chemical transport, phase transformations, nonlinear dynamics, and pattern formation. And the effects can be dramatic: Mushy-layer dynamics are implicated in the demise of industrially cast turbine blades and dynamics of the global climate.

Directly observing real-world mushy layers is a challenge. Industrial alloys, for example, are cast from high-temperature melts that pass through a porous, or mushy, state as they cool, and crystallization patterns that form during cooling control the material properties. But the materials are opaque, so their internal features remain inaccessible to visual inspection until they are cooled and sectioned.

Under quite different thermal conditions, sea ice forms when water freezes in the inhospitable polar oceans. Although the expanse of polar ice can be imaged remotely by satellites, directly probing dynamics inside the sea ice is a formidable challenge for even the most intrepid field researchers.

Earth's mantle and core have their own phenomena linked to mushy layers, but the deepest parts of our planet remain unreachable to direct exploration. Observations rely on inverse techniques, such as interpreting the propagation of seismic waves.

This article aims to provide a physical understanding of mushy layers by describing the mechanisms behind their convective processes. The synergy between analytic models, laboratory experiments, and computational simulations has been instrumental in developing a comprehensive picture. We feature two ubiquitous examples—one from Earth's cryosphere and another from metallurgy—and conclude by highlighting new insights into convective phenomena in ternary systems. But first, we explain how mushy layers form.

## Reactive porous media

A mushy layer is a mixed-phase region composed of a solid matrix surrounded by a melt phase. When a solid-liquid interface freezes, such layers can appear as a result of the Mullins-Sekerka instability, in which constitutional supercooling—the cooling of a multicomponent fluid below its local equilibrium freezing temperature—drives perturbations on the interface to grow.<sup>1</sup> Small perturbations develop into dendritic structures that form a porous region of solid crystals in the parent liquid phase. The mushy layer is reactive in that the solid matrix will

melt, dissolve, or grow in response to its local thermal and chemical environments.

Buoyancy forces tied to the fluid density's dependence on temperature and composition drive the motion of the interstitial fluid. The resulting heat and solute transport can cause the solid matrix to melt or dissolve, even to the point of complete local erosion. A striking consequence of that erosion is so-called chimney convection, shown in the opening image, in which fluid

flow is strongly focused into channels devoid of solids.

Chimney convection during the industrial casting of an alloy can cause macrosegregation—the macroscale redistribution of the alloy's components. It can also lead to the appearance of chains of equiaxed grains known as freckle defects that punctuate the final solidified product. Freckle defects and other chemical inhomogeneities can weaken materials used in, for example, high-performance aeronautical turbine blades (see figure 1). It is therefore necessary to understand and prevent their formation in solid manufacturing processes.

Sea ice solidifies because of heat loss to the atmosphere at the sea surface.<sup>2</sup> Its chimneys are known as brine channels and, importantly, provide a direct source of salt flux into the underlying ocean.

To understand mushy layers in metallurgical and geophysical systems, one must come to grips with their phase diagram. Figure 2a shows a phase diagram for a simple binary alloy of components A and B with composition C and temperature T. Typically, A represents a solvent, such as water; B represents a dissolved solute, for example, salt; and C is the mass fraction of B in the system. Here we consider the case where the melt's density increases with C.

Two features of the phase diagram become immediately apparent: the liquidus, a line above which the system is entirely liquid, and the eutectic, a line below which a mixed solid forms. The liquidus temperatures of the components simultaneously reach their lowest values at the so-called eutectic concentration  $C_E$ . Between the liquidus and the eutectic exists a two-phase equilibrium mixture of solid dendritic crystals and interstitial fluid. The initial liquid composition determines which of the two chemical components forms the solid matrix: an alloy with subeutectic composition  $C < C_E$  yields a mushy layer with solid A, whereas a supereutectic composition produces a mushy layer with solid B. At a given temperature, the liquidus defines the composition of the interstitial liquid.

The dendritic mushy layer has large surface-area-to-mass

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ratio, so pore-scale transport and internal phase transformations act rapidly to maintain thermodynamic equilibrium. Phase transformation is critical for maintaining the thermal and solutal balances in the mushy layer.

### Buoyancy, instability, and convection

Because of density variations in the interstitial liquid, gravity can generate flows during mushy-layer solidification. Consider, for example, a common scenario in which the liquid density increases strongly with concentration and decreases weakly with temperature over the relevant ranges. A solidifying subeutectic alloy cooled from below (see figure 2b) generates a solute-enriched interstitial fluid, thereby developing temperature and concentration fields that are both stabilizing; the cold solute-rich fluid near the mushy bottom is denser than the warm solute-poor fluid above, so no convection occurs.

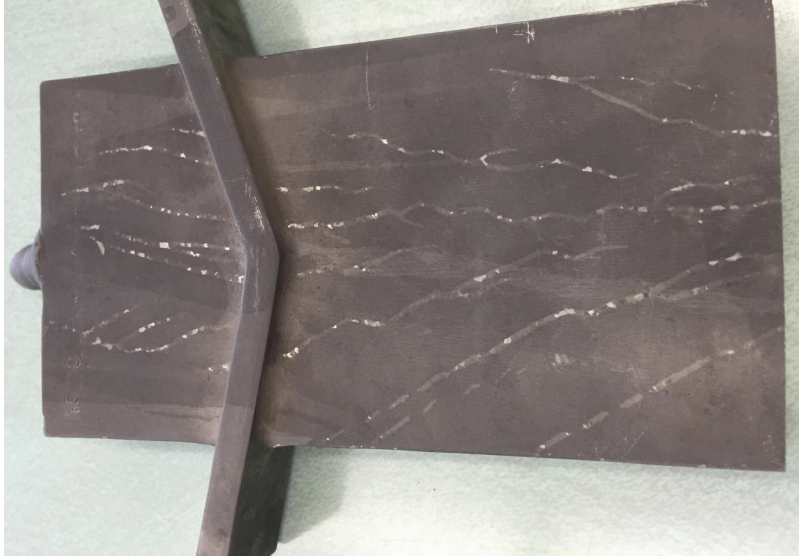
By contrast, a supereutectic alloy cooled from below (see figure 2c) releases solute-depleted fluid. The stabilizing thermal field is overcome by a much stronger destabilizing concentration gradient—the solute-poor cold fluid below is less dense than the solute-rich warm fluid above—and the interstitial fluid in the mush undergoes composition-driven convection.

The tables are turned when cooling occurs from above. In the case of sea ice, for instance, both the thermal and compositional fields drive convection in the mush. As the brine is cooled from above, the growing ice rejects salt, which makes the interstitial fluid denser.

The above classification can be guessed on purely static grounds, but dynamics must be considered to explain the onset of convection. The process is usually delayed until the density drop across the mush reaches a dynamically predicted critical value.<sup>3</sup> Potential energy must be released from the background state faster than it is dissipated to allow instabilities to grow and fluid to flow.

Quantitative representations of the critical conditions use the Rayleigh number, a dimensionless parameter that represents the ratio of buoyant mechanisms to dissipative ones. The liquid adjacent to the mush may also be prone to convection, and the different rates of heat and solute diffusion may drive double-diffusive fingering convection, known to oceanographers as salt fingers (see box 1). Interestingly, double diffusion plays no role in binary mushy layers because the liquidus constraint—the maintenance of phase equilibrium in the mush—prevents the temperature and the solute concentration from evolving independently. Related double-diffusive-type mechanisms for convection, however, are a necessary part of the conversation about ternary systems.

A conceptual tool known as a parcel argument (see box 2) explains a mechanism behind the formation of liquid inclusions, or nascent chimneys, in configurations like the one in figure 2c. The mechanism lies at the heart of all studies



**FIGURE 1. A TURBINE BLADE** can be weakened by defects like those in this test cast. The growth direction of the freckle defects shown here is right to left, which was against gravity during the growth process. (Courtesy of Boyd Mueller of Howmet Aerospace and William Boettinger of NIST.)

of near-onset convection regimes. Using techniques of bifurcation theory, Grae Worster at the University of Cambridge and one of us (Guba) found that positive nonlinear feedback can focus flow to form liquid inclusions. The feedback is associated with a decrease in the solid fraction and leads to increased permeability to fluid flow. The findings also demonstrate how experimental conditions—namely, the freezing speed and initial solution concentration—control the various stable convective flow patterns in mushy layers.<sup>4</sup>

Although they show only the near onset of chimney flow and not fully developed chimneys, the findings do hint at the experimental parameters one might tune to stimulate or avoid the emergence of chimneys. The phenomenon is highly nonlinear, so modelers have turned to approximate nonlinear models and simulations.<sup>5,6</sup> Numerical studies in which a single liquid inclusion or a chimney was isolated have helped explain convection in steadily propagating mushy layers.<sup>7</sup> Single-domain enthalpy methods for simulating flows and phase changes during mushy-layer evolution serve as versatile, less

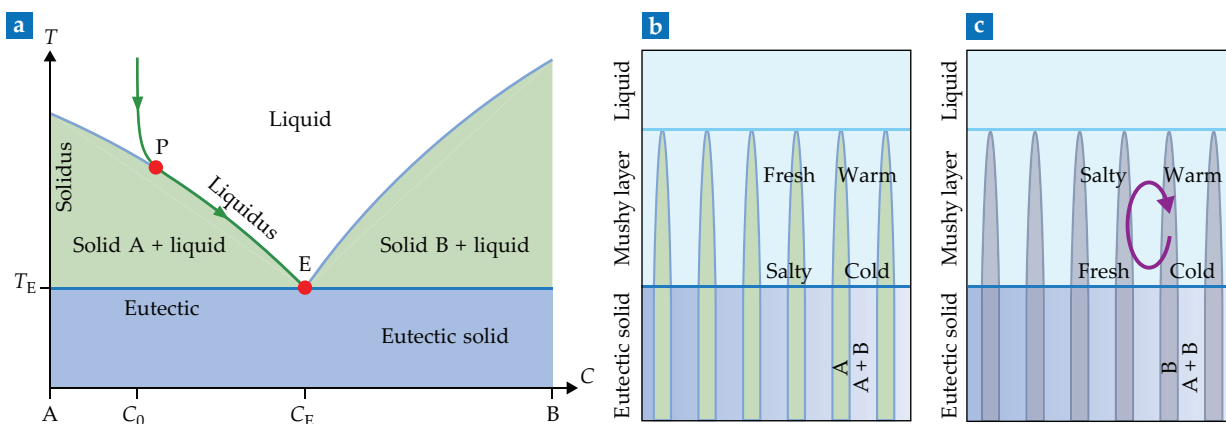
### BOX 1. DOUBLE-DIFFUSIVE CONVECTION IN BINARY FLUIDS

A classic example of double-diffusive convection occurs when a layer of warm, salty water is adjacent to one of cold, fresh water.<sup>16</sup> The underlying instability can be traced to the different rates of heat and solute diffusion, hence the term double-diffusive convection.

If the warm, salty layer is above the cold, fresh water, a parcel of fluid displaced upward warms rapidly because its thermal diffusivity is large relative to its solute diffusivity. The parcel is fresher and therefore lighter than its surroundings and continues to rise. By the same argument, a parcel displaced downward would continue to fall. The potential energy in each case is supplied by the unstable liquid-density stratification generated by the destabilizing process of thermal diffu-

sion. Such double-diffusive convection occurs in what is often referred to as the fingering regime. Salt fingers influence the dynamics of such natural hypersaline environments as the Dead Sea.<sup>16</sup>

In the reverse situation—cold, fresh water on top—a parcel of fluid displaced upward cools but retains its salt content. Being heavier than its surroundings, the parcel falls back toward its original position. But a temperature lag allows the parcel to return with more inertia than it had before, and an overstable oscillatory motion persists against the stable compositional stratification. The regime is usually referred to as diffusive, and the mechanisms are fundamentally the same as those seen in nonreactive porous media.<sup>17</sup>



**FIGURE 2. A BINARY EUTECTIC ALLOY** with components A and B can be understood using a two-dimensional phase diagram. **(a)** A solution with initial composition  $C_0$  lower than the eutectic composition  $C_E$  follows path P–E along the liquidus as it gradually cools. **(b)** If  $C_0 < C_E$ , the residual liquid is denser than the initial melt and the mushy layer is stable. **(c)** If  $C_0 > C_E$ , the residual liquid is lighter, which drives convection in the mushy layer.

computationally expensive alternatives to the classical front-tracking approach and have been applied to study solidification of metals and sea-ice dynamics.<sup>6</sup> Still, a complete picture remains elusive of how liquid inclusions develop into chimneys in time-evolving mushy layers.

## Sea ice and brine channels

Sea ice is a geophysically important mushy layer formed by freezing seawater. More than  $10^7$  km<sup>2</sup> of Earth's polar oceans freeze over each year (see the article by Ron Kwok and Norbert Untersteiner, *PHYSICS TODAY*, April 2011, page 36). Convective motions in the mushy layer are crucial for understanding the salt flux to the underlying ocean, which affects the water's buoyancy and has implications for circulation and water-mass transformation. Desalination and convective flow also affect the material properties of the porous sea ice. Further, the liquid-filled pores provide a natural biogeochemical reactor that supports life, such as photosynthetic algae, in sea ice. (See references 2 and 6 for broader reviews.)

Brine channels, the convective chimneys in mushy sea ice, are the primary conduits for saline water expelled from sea ice into the upper ocean. Convection is suppressed in thin mushy layers, but it is initiated above a certain thickness, thereby driving brine-channel growth and gravitational drainage through high-salinity plumes. That behavior is consistent with the idea of a critical Rayleigh number and the layer storing increasingly more potential energy until it exceeds its convective-stability threshold. The brine-channel pattern evolves in space and time as a sea-ice layer grows (see figure 3), with extinction of flow in some channels and a coarsening of their spacing.

It is natural to wonder about what controls the selection and evolution of the convection pattern in such a nonlinear dissipative system. John Wettlaufer, Steven Orszag, and another of us (Wells) postulated a variational principle by which the brine-channel spacing maximizes the outward flux of potential energy in response to buildup driven by cooling, ice growth, and brine segregation in the pore space.<sup>8</sup> Several groups have used that principle to build simplified models of mushy-layer convection with brine channels to predict salt fluxes from ice and flow patterns.<sup>6</sup> The results agree with laboratory observa-

tions over relatively short time scales on the order of days.

Longer-term observations of sea ice are more challenging, and researchers have historically relied on *in situ* techniques, such as collecting ice-core samples and inferring attributes from electromagnetic properties.<sup>2</sup> Alternatively, computational simulations with an enthalpy method can be used to evaluate the complexities caused by permeability evolution as ice desalinates.

In addition to affecting the surrounding ocean water, salt fluxes influence the physical and biogeochemical properties of polar ice. Many biogeochemically active tracers, such as nitrates and phosphates, are rejected from the solid-ice matrix and segregated into the liquid-brine-filled pore spaces alongside other salts. That process can lead to chemical concentrations much higher than those in the ocean, and the ice can therefore act as a substrate for significant biogeochemical processes.<sup>2</sup> When convection occurs, the turnover continually replenishes pore water with nutrients. The pores can thus provide a habitat for bacteria, photosynthetic algae, and other life.

## Freckle prediction in metallurgy

Sea ice has been freezing and thawing for eons. Metallurgical history spans millennia. But understanding their link is a modern development. A little more than half a century ago, metallurgists working at Bell Labs in Murray Hill, New Jersey, recognized the utility of using transparent compounds as proxies for metals in solidification experiments.<sup>9</sup> The researchers studied solidification in transparent aqueous systems, such as ammonium chloride solutions, because they were more easily managed and visualized in the laboratory. Other metallurgists from the University of Oxford, MIT, Pratt & Whitney Aircraft Company, and other institutions successfully used the systems to trace the origins of macrosegregation in cast alloys, along with freckle and other channel-type defects, back to interdendritic convection during growth.<sup>10</sup> The juncture was also notable because those metallurgists appear to have coined the term “mushy” to describe mixed-phase solid–liquid regions.<sup>11</sup>

Experiments, modeling, and simulations of aqueous systems have since been used extensively to identify conditions under which defects can be avoided and to explore such mitigation strategies as rotation, application of magnetic fields, and forced



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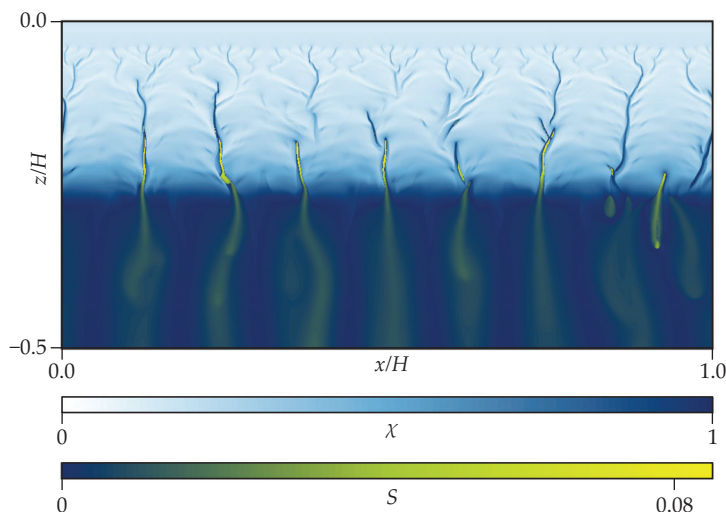
convection. One strategy involved adding a third component—zinc chloride—to a solution of water and ammonium chloride.<sup>12</sup> In that case, the added component increased the density of the fluid released upon solidification. The denser fluid promptly shut off the convective instability and the related formation of unwanted freckles.

Although adding an extra component to a metallurgical process may make forming a solid product easier, the most important consideration is whether that product still has the desired properties. Thus, to make quantitative predictions for multicomponent alloys of metallurgical interest, one must address their increasingly complex phase diagrams. That need led metallurgists at NIST to team up in the 1990s with researchers at the University of Iowa and develop the freckle-predictor criterion, a Rayleigh number-based measure for predicting whether freckles will form in different nickel-based superalloys.<sup>13</sup> Because of their complexity, multicomponent systems are typically studied using continuum models<sup>14</sup> based on conservation of mass, momentum, energy, and species, all coupled to phase transformations. The models are amenable to computer simulations like the one shown in figure 3.

### Ternary systems and distinct mushy layers

Research on aqueous ternary systems constitutes a small but important step toward understanding complex multicomponent systems. Recent studies of systems with relatively simple phase diagrams have revealed new, and in some cases unexpected, mechanisms associated with convection in mushy layers.

As with binary systems, the first ingredient for understanding ternary-mixture solidification is the ternary phase diagram. The sketch in figure 4a is for a system with components A, B, and C. Suppose that A represents a solvent, such as water, and B and C two solutes, such as salts. Upon cooling from below,



**FIGURE 3. SEA-ICE GROWTH** is simulated here using an enthalpy method in an effectively two-dimensional Hele-Shaw cell of depth  $H$ . The cell is cooled from above.<sup>15</sup> Salt-enriched plumes (yellow) with dimensionless salinity  $S$  drain from brine channels in sea ice with porosity  $\chi$  into the underlying liquid (blue).

A solidifies at point P to form single-phase dendrites in a primary mushy layer, shown in figure 4b, with B and C left in the liquid. The liquid mass fractions of both B and C increase with depth in the primary mushy layer as A is removed from the liquid phase to form the dendrites. At point S, components A and B solidify together, forming two-phase dendrites in a secondary mushy layer, with component C rejected. The liquid phase in the secondary mushy layer is further enriched in component C and depleted in component B.

Even for the relatively simple phase diagram shown in figure 4, one can also envision adjusting the initial liquid compo-

### BOX 2. PARCEL ARGUMENTS

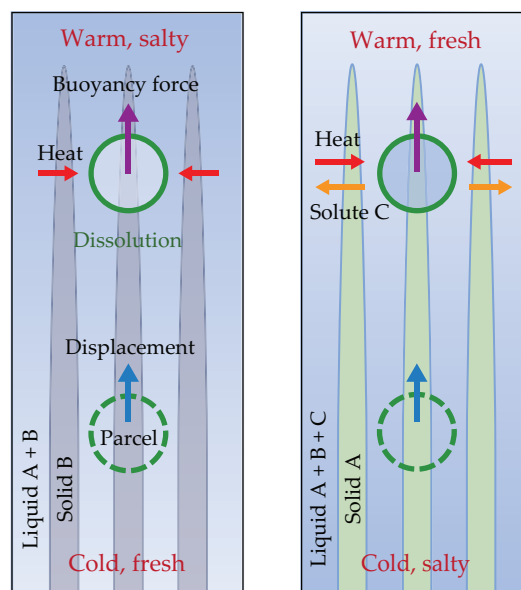
Consider a binary mushy layer with cold, fresh water sitting below warm, salty water, as shown in the left diagram. The layer is thermally stable and solutally unstable, a typical situation in supereutectic growth. The lighter component is water, or solvent A, and is released upon solidification; the heavier component is salt, or solute B, and forms dendrites. Assume that heat diffuses much faster than solute B.

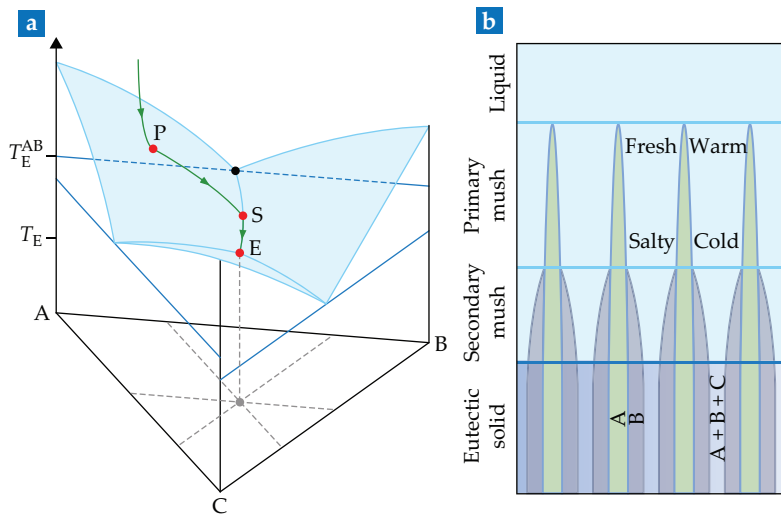
An upwardly displaced fluid parcel warms rapidly in response to its new environment. To maintain thermodynamic equilibrium and achieve the composition required by the liquidus constraint, the parcel dissolves some of the surrounding matrix. Such dissolution may lead to a nascent chimney; the accompanying permeability increase, although secondary to the solid-fraction erosion, generates nonlinear focusing of the flow into narrow buoyant plumes.

Now consider a ternary mixture whose primary mushy layer is thermally and solutally stable—specifically, the bottom is cold and rich in two salts, solutes B and C, as shown in the right diagram. Assume heat diffuses much faster than solutes and that solute C diffuses much faster than solute B. For simplicity, suppose that buoyancy forces act only with respect to solute C.

An upwardly displaced fluid parcel warms rapidly but remains relatively rich in the slowest-diffusing component, solute B. Thermodynamic equilibrium—the ternary liquidus constraint—is maintained by a relative depletion of solute C through solutal diffusion. The parcel is thus fresher in solute C and lighter than its local environment, so

it experiences an upward buoyancy force that drives an instability, despite the apparently stable background stratification.





**FIGURE 4. A TERNARY EUTECTIC ALLOY** with components A, B, and C can be understood using a three-dimensional phase diagram. **(a)** The temperature  $T$  is plotted on the vertical axis and the composition is represented on the triangular base. Each corner represents a pure component. Points on the sides correspond to binary alloys. Points in the triangle correspond to ternary alloys. Liquidus surfaces from the binary vertical sides meet at a ternary eutectic point E. Points P and S represent the thermodynamic states in the primary and secondary mushy layers formed by the ternary alloy. (Adapted from ref. 5.) **(b)** This schematic shows the dendritic microstructure in primary and secondary mushy layers. A novel mechanism behind the unexpected convection that can occur in the primary mush is explained in box 2.

sition to instead produce a secondary mush with solids A and C. Whereas a binary eutectic system could be characterized into subeutectic and supereutectic cases, the simple ternary eutectic system has six such categorizations, two for each of the three corners of the phase diagram.

As with the binary-alloy case, the preferential rejection of one or more components upon solidification generates potential energy that can fuel buoyancy-driven convection. A hypothesis based on the static density profile in a ternary mixture is that convection could be triggered in either, neither, or both of the mushy layers. Exploration has begun in laboratory experiments and in analytic and computational models. Still, the interaction between convection in primary and secondary mushy layers is far from being completely understood.<sup>5</sup>

Even in isolation, however, the primary mushy layer of a ternary system reveals new features and convective-instability mechanisms distinct from any known to operate in binary mushy layers, and the ternary liquidus constraint plays a central and somewhat unexpected role. As outlined earlier, the local composition and temperature are directly linked in a binary mushy layer. In the primary layer of a ternary system, only the combination of two solute compositions is linked to the temperature.

The additional degree of freedom afforded to the temperature and composition in the ternary system calls back into question the possibility of double-diffusive-type instabilities driven from inside the primary mushy layer. Indeed, convective instabilities are predicted when temperature and composition fields have different diffusion rates and make opposing contributions to an otherwise static density profile. More surprising are the instabilities observed in models without any destabilizing contribution to the static density profile when differences in diffusion rates, solute rejection rates, or other imbalances related to the solute fields are present. The mechanism driving such instabilities is outlined for a special case in box 2. Further details can be found in reference 5.

Over the past half century, convection in mushy layers undergoing multicomponent solidification has developed from a hypothesis to a well-documented phenomenon. Careful laboratory experiments have revealed its striking features, mathematical models and analyses have cemented a physical understanding of mushy-layer dynamics and the mechanisms that trigger convective processes, and computer simulations have

quantified fully developed chimney convection. With their importance in metallurgy and geophysical systems, the multi-scale, multiphase, multicomponent, multiphysics systems that host mushy layers continue to offer exciting opportunities for physics-based research.

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