# Brinicles as a Case of Inverse Chemical Gardens

Julyan H. E. Cartwright,[†] Bruno Escribano,[*,‡] Diego L. González,[§] C. Ignacio Sainz-Díaz,[†] and Idan Tuval[‖]

[†]Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC−Universidad de Granada, Armilla, Granada, Spain
[‡]Basque Center for Applied Mathematics (BCAM), Bilbao, Spain
[§]Istituto per la Microelettronica e i Microsistemi (IMM), CNR, Bologna, Italy
[‖]Mediterranean Institute for Advanced Studies (IMEDEA), CSIC−Universitat de les Illes Balears, Mallorca, Spain

ABSTRACT: Brinicles are hollow tubes of ice from centimeters to meters in length that form under floating sea ice in the polar oceans when dense, cold brine drains downward from sea ice to seawater close to its freezing point. When this extremely cold brine leaves the ice, it freezes the water it comes into contact with: a hollow tube of ice—a brinicle—growing downward around the plume of descending brine. We show that brinicles can be understood as a form of the self-assembled tubular precipitation structures termed chemical gardens, which are plantlike structures formed on placing together a soluble metal salt, often in the form of a seed crystal, and an aqueous solution of one of many anions, often silicate. On one hand, in the case of classical chemical gardens, an osmotic pressure difference across a semipermeable precipitation membrane that filters solutions by rejecting the solute leads to an inflow of water and to its rupture. The internal solution, generally being lighter than the external solution, flows up through the break, and as it does so, a tube grows upward by precipitation around the jet of internal solution. Such chemical-garden tubes can grow to many centimeters in length. In the case of brinicles, on the other hand, in floating sea ice we have porous ice in a mushy layer that filters out water, by freezing it, and allows concentrated brine through. Again there is an osmotic pressure difference leading to a continuing ingress of seawater in a siphon pump mechanism that is sustained as long as the ice continues to freeze. Because the brine that is pumped out is denser than the seawater and descends rather than rises, a brinicle is a downward-growing tube of ice, an inverse chemical garden.
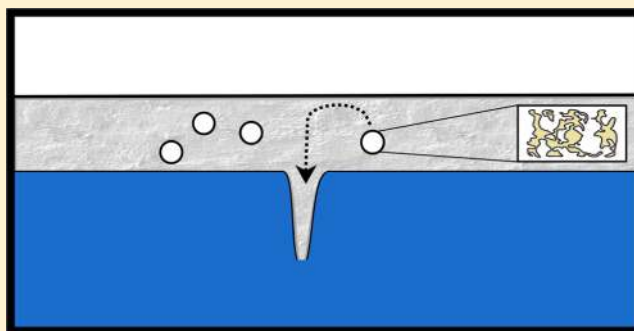
INTRODUCTION

Chemical gardens (Figure 1a) are tubular structures that are formed when a metal salt crystal is immersed in a solution of silicate or other anions.[1−3] As the metal ion salt starts to dissolve, it forms a semipermeable membrane about itself. The difference in osmotic pressure on the two sides of this semipermeable membrane forces water molecules to pass from the more dilute silicate solution outside to the more concentrated metal-ion solution inside, forming an osmotic pump. The flow of water molecules inflates the membrane until it ruptures, expelling a jet of metal-ion solution. When the metal-ion solution is in contact with the alkaline silicate solution, it precipitates, forming a tube around the jet. Thus, a chemical garden combines two aspects—the osmotic pump and tube formation—that may be found separately in other phenomena and, more rarely, combined in the same fashion. Examples of such chemical-garden systems outside the laboratory are to be found in cement hydration[4] and in corrosion processes.[5]

There are several geological structures that grow in a similar way into chemical gardens. Examples include hydrothermal vents,[6] soda straws,[7] and mud volcanoes.[8] All of these tubular geological formations are a consequence of physical and chemical interactions that combine a membrane or another sort of filtering mechanism and tubular precipitation, solidification, or sedimentation about a fluid flow.

Brinicles (Figure 1b)—tubes of ice that are found under the pack ice of the Antarctic ocean—are less-well-known examples of tubular patterns in geology. Brinicles grow around cold streamers of brine beneath sea ice, and their size ranges from a few centimeters up to a few meters in length. They have also been termed sea-ice stalactites,[9−11] but because an icicle is the icy form of a stalactite and both stalactites and icicles grow in a different fashion to these structures,[12,13] we prefer the term brinicle.

Brinicles are found only during the winter in the Antarctic regions. As the polar winter progresses, the air temperature above the sea ice drops from −10 °C to at least −40 °C whereas the sea temperature beneath the ice remains at −2 °C; see Figure 2. This produces an increasing temperature gradient across the sea ice, and heat flows from the sea to the atmosphere. As the seawater loses heat, ice crystals begin to
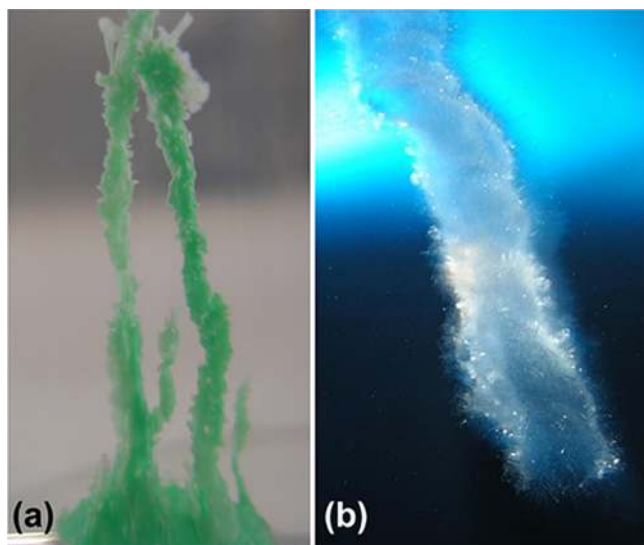
Figure 1. (a) Example of chemical gardens grown from nickel sulfate crystals in a sodium silicate solution, typically 1−10 cm long. (b) Brinicle off Ross Island, Antarctica, typically 10−100 cm long. Photography by Rob Robbins on the GOLF 4-3-9 Antarctica Expedition 2010. Image archived by EarthRef.org.[14]
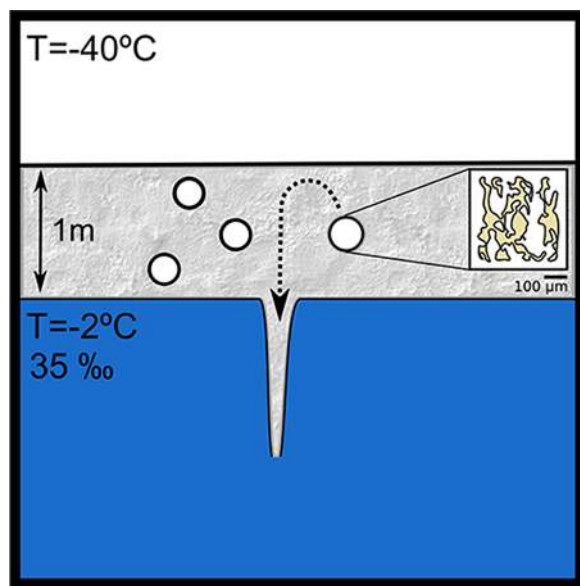

Figure 2. Cross section through sea ice illustrating brinicle formation. The temperature in the ice is defined by a gradient between the temperatures of the air and the sea. The brine inside the ice is siphoned through the channel network and ejected through a single opening, forming a tubular brinicle.

nucleate in the region directly beneath the ice pack. Ice formed under these conditions usually grows in a bidimensional way, forming what are referred to as ice platelets.[15] Because ice is less dense than liquid water, these platelets float upward and accumulate under the ice pack, forming a porous polycrystalline layer known as the skeleton layer.[16] Within this layer some seawater becomes trapped, and as the heat flow toward the air continues, it begins to freeze, adding its water molecules to the crystal structure that forms the skeleton layer. As a result, the trapped seawater becomes a progressively more concentrated solution of brine. The trapped brine continues to concentrate, and as it does so, it becomes denser and colder as it equilibrates

with the temperature of the surrounding ice. At some point, this dense cold brine finds a way to escape from the ice into the seawater below. Because brine is denser than water, it flows downward, and because it is colder, it absorbs heat from the surrounding water, which is already near its salinity-determined freezing point. The consequence is that the brine streamer forms a tube of ice, a brinicle, around itself by freezing the surrounding seawater. The brinicle continues to grow downward as long as there is brine flowing and as long as there are no strong currents in the sea beneath the ice or movements of the sea ice itself to dislodge it. This growth process was recently filmed in situ in Antarctica for the first time in a BBC documentary film, "Frozen Planet".[17]

GROWTH PROCESS OF BRINICLES

The brinicle growth process (Figure 2) begins with the formation of the skeleton layer beneath sea ice. This is a porous polycrystalline mass, like a soaked sponge, that has been termed a mushy layer.[18] The characteristic pore size is small enough to inhibit convective fluid exchange with the seawater beneath.[16] This inhibition is a necessary condition for brine entrapment, otherwise the heavier concentrated brine would simply flow into the sea by free convection. As the ice pack increases in thickness, brine gets colder and more concentrated. When most of the water has frozen, the remaining superconcentrated brine is trapped in a network of so-called brine channels. These compartments are roughly cylindrical, with thin branches with a typical diameter of ∼0.1 mm that interconnect with others.[19,20] The development of the brine-channel network is a self-organized process in which the vertical temperature gradient through the ice favors the formation of compartments where brine remains trapped.

There are several candidate mechanisms for brine migration within the ice pack.[21] Brine might diffuse from one inclusion to another through the solid ice, but the velocity of surface diffusion is $\sim 1\ \mu m^2/h$, which makes it negligible. Density-driven convection can occur only once the density gradient is strong enough to provoke an instability, which is a function of the radius of the brine channels: $\Delta \rho > f(1/r^4)$. Because the typical radius r of the channels is ∼0.1 mm, this mechanism is effective only on the wider channels and only once the ice fracturing has opened enough connections through the channel network.

The mechanism that starts the growth of a brinicle necessarily implies releasing this trapped brine. A plausible trigger involves cracks that appear in the ice when the water in the brine inclusions freezes, increasing in volume and building up internal pressure in the crystal lattice. Cracks in the ice will follow lines of natural weakness, which in the case of a polycrystalline material are the boundaries between crystal grains. Those cracks will continue to propagate until they find a hole in the lattice, which would stop the fracture. In the case of sea ice, such holes would be the brine channels. The self-organized structure of the channel network will now guide the fracture along the thinner channels toward wider ones, until it reaches an opening wide enough that the weight of the brine column is enough to lead to convective instability in the skeleton layer. It has been found in field observations that one larger channel several millimeters in diameter appeared on average every 180 cm². [16] This sparsity and the idea of fracture propagation help explain why brinicles are often found growing only from the widest brine channels in the surrounding ice.[10]
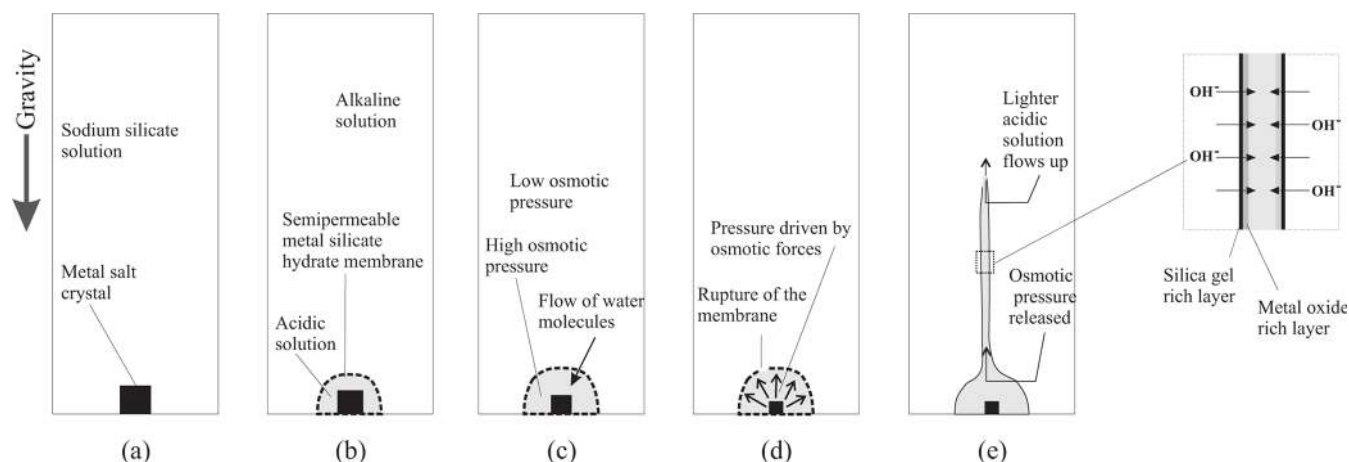
Figure 3. Chemical-garden growth. (a) Setup at the start of the reaction. (b) Membrane formation between acidic and basic solutions. (c) Osmotic pressure is higher within membrane than outside it, so it expands. (d) Under osmotic forces, the membrane ruptures. (e) A tube forms.

Such a wide opening is commonly referred to as a "chimney" in mushy layers.[18,22,23]

Once the concentrated brine has found a way to escape from the ice, it starts to flow into the seawater below and gains heat by freezing the water around it. A nearly cylindrical, externally slightly tapering tube then starts to form, growing from the base of the ice downward into the sea. This brinicle drains the brine in the surrounding ice pack and produces an inhibiting effect whereby the appearance of one brinicle inhibits the growth of others in the nearby area. It has been reported that only one major brinicle can be found for every 6−8 m² of ice.[9] This inhibition effect is common in other mushy layers, leading to spatial patterns such as bidimensional square and hexagonal lattices.[24]

The seawater outside the brinicle is warmer than the brine flowing through the inside, so there is heat transfer through the tube walls, freezing more water on the outside and melting it on the inside. The brinicle thus increases in length and in diameter by the ablation of the inner wall and accretion at the outer wall; this explains the slightly conical form of a brinicle. However, this growth implies that as ice on the inner wall is melting it is reducing its volume and creating a volume deficit inside the tube. Therefore, there has to be more brine coming into the tube from the ice sheet than there is leaving the tube at the tip. Furthermore, the fluid closer to the inner wall is warmer and lighter than the brine, meaning that the flow inside the tube can be convectively unstable. If overturning occurs inside the brinicle, then there could be freezing in the brine channels and the growth would be interrupted. The condition for this not to happen is that the pressure-gradient force inside the tube is always greater than the buoyancy force generated by the melting of the inner wall.[11] The satisfying of this condition demands that the volume flux be continuous and always above some minimum value, which requires a large amount of brine.

Some brinicles reach lengths of several meters and grow for several hours or days. We can estimate how much brine is required to grow such a brinicle. If we consider the brinicle to be a hollow cylindrical shell, its mass is $\pi(r_2^2 - r_1^2)L\rho_{ice}$, where L is the length of the brinicle, r_1 and r_2 are the inner and outer radii, and ρ_{ice} is the density of the ice. Considering the latent heat of fusion for water, $L_f = 333.7$ J g⁻¹, we can estimate how much heat it must absorb in order to freeze such a mass of ice. And we can consider how much heat the brine is able to absorb if we assume that its specific heat is similar to that of water (c_p

≈ 4.18 J g⁻¹ K⁻¹) and that it is flowing into a sea with a temperature difference of $\Delta T \approx 20$ K. With such an estimation, we calculate that the total volume of brine necessary to grow a brinicle of ~1 m in length is on the order of ~10² L. This implies that the flow needs to be ~1 L/min, which is consistent with field observations.[10] If we estimate how much seawater is necessary to generate this volume of brine, considering that seawater has a salinity of 35‰ at −2 °C and that brine has a salinity of 224‰ at −20 °C, we come up with ~10 L of seawater/L of brine. This amount of liquid will dictate the typical spacing between brinicles.

■ BRINICLES AS CHEMICAL GARDENS

The formation process of a chemical garden is described in detail in Figure 3. The setup for the reaction is a metal salt crystal immersed in a sodium silicate solution (Figure 3a). As soon as the seed crystal comes into contact with the aqueous solution, it begins to dissolve and at the same time is covered with a colloidal coating (Figure 3b). This material acts as a semipermeable membrane. As a consequence of the different osmotic pressures inside and outside the membrane, water is drawn osmotically from the outside, permitting the further dissolution of the crystal (Figure 3c). The entry of water causes the membrane to dilate under osmotic pressure until it ruptures (Figure 3d). This provokes the injection of the salt solution in its interior into the silicate solution. Because the jet of solution is generally lighter than the fluid around it, it flows upward by buoyancy and an upward-pointing tube grows around the expelled jet (Figure 3e). However, chemical gardens can also grow downward under conditions in which the density difference is reversed and the jet is denser than the surrounding liquid.[26,27] Such downward-growing tubes have been termed reverse or inverse chemical gardens.

At this point, to compare the filtering mechanisms of chemical gardens and brinicles, it is important to consider the process of salt rejection by sea ice and to compare it to the semipermeable membrane of a chemical garden that filters out solute particles that are too large to go through its pores and allows only water molecules to pass (Figure 4). The polarity of water molecules determines that they will crystallize into a hexagonal crystal lattice.[28] This is crucial for our planet because hexagonal ice is less dense than liquid water and hence floats on the sea. Without this unusual property of water, our oceans would have frozen from the bottom up during glaciations and
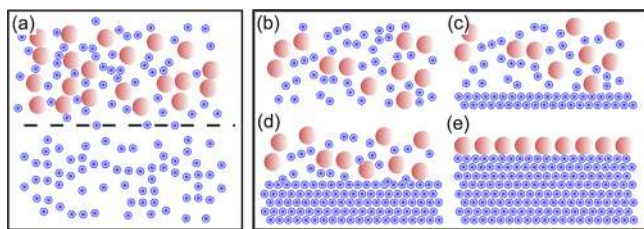
Figure 4. Filtering mechanisms: osmosis across a semipermeable membrane (left) and salt rejection (right).

life as we know it would not exist. But the hexagonal crystal lattice also plays an important role in salt rejection of sea ice. When water molecules start to crystallize, everything that does not enter the lattice is pushed away from the solid−liquid interface. Hence, this is a process of purification on the molecular level, very much like the filtration process through a semipermeable membrane but in an inverse sense. In a classical chemical garden, there are two solutions with different concentrations separated by a semipermeable barrier with a flow of water from smaller to greater concentration, which provides energy for an osmotic pump. A similar osmotic pump mechanism makes brinicles equivalent to chemical gardens: the higher osmotic pressure of the concentrated brine in the mushy layer, which acts as a semipermeable membrane,[25] will cause an inflow of water, and it is this continual inflow—continual for as long as the osmotic pressure imbalance remains, owing to salt rejection during crystallization—that maintains the osmotic pump of the brinicle.

The growth of chemical gardens grown on earth is driven by a combination of the potential energies from an osmotic pump and density-driven convection.[2] Likewise, density-driven convection as well as osmosis is important in brinicles; however, with a brinicle, the density difference is reversed from that of a classical chemical garden, so the brinicle grows downward. We may view this convection through the brinicle as a type of siphon: as long as the brinicle's tip is at a lower height than the bottom of the ice sheet, the brine will continue to flow and, considering Bernoulli's equation, the flow will be nearly constant (Figure 2). Seeing the brinicle system as a siphon solves the problem of explaining how the flow remains constant for the long times required for brinicle growth. It also explains where all of the brine comes from because one open channel can siphon the brine out of all surrounding channels that are connected through the network, even if they are at a lower height than the siphon's neck. Furthermore, if one open channel can siphon all of the brine from several square meters around it, then it justifies the inhibition effect producing the sparsity reported in field observations.[9,10] Density-driven convection in a chemical garden may also be considered to be a siphon in which the fluid being siphoned is less dense than the surrounding fluid and so the siphon there operates upward, in reverse. This siphon effect disappears when growing chemical gardens in microgravity,[29,30] when the osmotic force alone drives growth, and it would likewise disappear if brinicles were grown in the absence of gravity.

◼ CONCLUSIONS

The formation process of brinicles remains little studied because of the difficulties of field observations: they grow only in polar regions, in calm waters, and under the ice sheet. They do not appear to have been observed hitherto in the Arctic, but

presumably should be found under similar conditions in the Antarctic, in still waters; such conditions may, however, be rarer in the Arctic. In common with other unusual types of ice formed under polar conditions, such as anchor ice,[31] there is not a great deal of published work, and there are many questions that remain to be answered. Here we have placed brinicles within the framework of chemical gardens. Future work should include quantitative modeling and theory as well as laboratory experiments on both brinicles in particular and chemical gardens in general as part of this new research area of chemobrionics.[32]

Like some other tubular formations in geology, brinicles can be understood as a form of chemical garden, in this case, an inverse chemical garden. The crystal lattice of sea ice can filter out water molecules and accumulate highly concentrated brine in the opposite way in which an osmotic membrane can filter out the solute and accumulate water molecules in the case of chemical gardens. Once the filtering and concentrating are finished, the resulting brine solution will be expelled into the sea, and the growth of a brinicle begins by freezing water around the brine streamer. In the case of chemical gardens, a similar hollow tube is formed, generally growing upward in this case, by the precipitation of metal silicate around a jet of metal salt solution. But both freezing and precipitation can be regarded as parallel processes if we consider that both systems are losing energy to become more stable. Both osmosis and density-driven convection contribute to the self-organized formation of self-assembled tubular precipitation structures.

Understanding the formation of brinicles goes hand in hand with understanding the process of salt rejection in sea ice. The concept that salt rejection works in a similar way to semipermeable membranes is an idea that can have several implications in many related processes. Reverse osmosis is currently used in desalination plants[33] to achieve basically the same effect that is achieved in sea ice: purifying salt water. The rejection of impurities in sea ice is also very similar to industrial processes related to metallurgy, where impurities in the solidifying metal can affect its mechanical properties.[34] It also has medical implications in the fields of biocompatible materials[35,36] and in the controlled freezing of biological tissues.[37]

We have seen that brinicles affect brine and heat fluxes in the ice pack. Might brinicles then have importance in understanding climate and possible climate change? Small-scale processes are known to be important also at the climate scale, but these processes are usually neglected or poorly parametrized in the large-scale models, and the phenomena they generate have received hardly any attention.[15] An understanding of brinicle dynamics and its role in brine and heat flow might allow an improved statistical-dynamical parameterization of the sub-grid scale processes in climate models.

But perhaps the most important application of salt rejection is that related to the theories for a cold origin of life on our planet or elsewhere in the universe. The origin of life is often proposed to have occurred in a hot environment, such as the one found in hydrothermal vents.[6] It is proposed that chemical-garden processes are involved in the mechanism.[38,39] But there is a different school of thought that presents sea ice as a promoter of the emergence of the first life.[15,40] Brine rejection in sea ice produces all of the conditions that are considered necessary for life to appear. We have mentioned the enrichment of chemical compounds that occurs in brine entrapment between ice-crystal grains, but there is also membrane

formation by the deposition of lipids, today originating from extracellular polymeric substances (EPS) generated by phytoplankton[41] and perhaps produced by complex prebiotic molecules at the dawn of life. There are electric potentials and pH gradients across the interface of ice and brine, and the surface of ice has been proven to have catalytic effects.[40] Because brinicles play an important role in the dynamics of brine transport through sea ice, they might also play a role in this scenario of a cold origin of life, just as hydrothermal vents do in the hot environment theories, and in both instances chemical-garden processes are fundamental.

Beyond earth, the brinicle formation mechanism may be important in the context of planets and moons with ice-covered oceans. As for brinicles similar to those on Earth, under astrophysical conditions of different temperatures and pressures, there also exists the possibility of brinicles forming from other ice phases beyond the familiar hexagonal ice I_h, including high-pressure ice phases that are more dense than water,[15] such that such a brinicle, say, on Ganymede or Callisto might grow upward from the ocean floor rather than downward from above. One might speculate that brinicles might play a similar role on such icy bodies as hydrothermal vents are proposed to have played in the origin of life on earth.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: bescribano@bcamath.org.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Coatman, R. D.; Thomas, N. L.; Double, D. D. Studies of the growth of 'silicate gardens' and related phenomena. *J. Mater. Sci.* **1980**, *15*, 2017−2026.

(2) Cartwright, J. H. E.; Garcia-Ruiz, J. M.; Novella, M. L.; Otalora, F. Formation of chemical gardens. *J. Colloid Interface Sci.* **2002**, *256*, 351−359.

(3) Cartwright, J. H. E.; Escribano, B.; Khokhlov, S.; Sainz-Daz, C. I. Chemical gardens from silicates and cations of group 2: a comparative study of composition, morphology and microstructure. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1030−1036.

(4) Double, D. D.; Hellawell, A. The hydration of Portland cement. *Nature* **1976**, *261*, 486.

(5) Fontana, M. G. *Corrosion Engineering*, 3rd ed.; McGraw-Hill: New York, 1986.

(6) Corliss, J. B.; Dyamond, J.; Gordon, L. I.; Edmond, J. M.; Herzen, R. P. V.; Green, K.; Williams, D.; Bainbridge, A.; Crane, K.; Van Andel, T. H. Submarine thermal sprirngs on the Galápagos rift. *Science* **1979**, *203*, 1073−1083.

(7) Hill, C.; Forti, P. *Cave Minerals of the World*; National Speleological Society: Huntsville, AL, 1997.

(8) Alvisi, F.; Cartwright, J. H. E.; Escribano, B.; González, D. L.;Sainz-Daz, C. I. Dynamics of mud volcanoes: An osmotic pump mechanism. 2012, unpublished work.

(9) Paige, R. A. Stalactite growth beneath sea ice. *Science* **1970**, *167*, 171−172.

(10) Dayton, P. K.; Martin, S. Observations of ice stalactites in McMurdo Sound, Antarctica. *J. Geophys. Res.* **1971**, *76*, 1595−1599.

(11) Martin, S. Ice stalactites: comparison of a laminar flow theory with experiment. *J. Fluid Mech.* **1974**, *63*, 51−79.

(12) Neufeld, J. A.; Goldstein, R. E.; Worster, M. G. On the mechanisms of icicle evolution. *J. Fluid Mech.* **2010**, *647*, 287−308.

(13) Chen, A. S.-H.; Morris, S. W. Experiments on the morphology of icicles. *Phys. Rev. E* **2011**, *83*, 026307.

(14) Robbins, R. *Earth Reference and Data Models. GOLF 4-3-9 Antarctica Expedition 2010*; http://earthref.org.

(15) Bartels-Rausch, T.; Bergeron, V.; Cartwright, J. H. E.; Escribano, R.; Finney, J. L.; Grothe, H.; Gutiérrez, P. J.; Haapala, J.; Kuhs, W. F.; Pettersson, J. B. C.; Price, S. D.; Sainz-Diaz, C. I.; Stokes, D. J.; Strazzulla, G.; Thomson, E. S.; Trinks, H.; Uras-Aytemiz, N. Ice structures, patterns, and processes: a view across the icefields. *Rev. Mod. Phys.* **2012**, *84*, 885−944.

(16) Lake, R. A.; Lewis, E. L. Salt rejection by sea ice during growth. *J. Geophys. Res.* **1970**, *75*, 583−597.

(17) Jeffs, K. 'Brinicle' ice finger of death, in Frozen Planet. *BBC documentary film*, 2011

(18) Feltham, D. L.; Untersteiner, N.; Wettlaufer, J. S.; Worster, M. G. Sea ice is a mushy layer. *Geophys. Res. Lett.* **2006**, *33*, L14501.

(19) Weissenberger, J.; Dieckmann, G.; Gradinger, R.; Spindler, M. Sea ice a cast technique to examine and analyze brine pockets and channel structure. *Limnol. Oceanogr.* **1992**, *37*, 179−183.

(20) Eide, L. I.; Martin, S. The formation of brine drainage features in young sea ice. *J. Glaciol.* **1975**, *14*, 137−154.

(21) Untersteiner, N. *Phys. Snow Ice, Conf. Proc.*; Oura, H., Ed.; 1967; Vol. 1, Part 1, p 569.

(22) Worster, M. G. Natural convection in a mushy layer. *J. Fluid Mech.* **1991**, *224*, 335−359.

(23) Schulze, T. P.; Worster, M. G. Weak convection, liquid inclusions and the formation of chimneys in mushy layers. *J. Fluid Mech.* **1999**, *388*, 197−215.

(24) Worster, M. G. Convection in mushy layers. *Annu. Rev. Fluid Mech.* **1997**, *29*, 91−122.

(25) Miller, R. D. Ice sandwich: functional semipermeable membrane. *Science* 1970; Aug 7; 169(3945):584-5.

(26) Jones, D. E.; Walter, U. The silicate garden reaction in microgravity: a fluid interfacial instability. *J. Colloid Interface Sci.* **1998**, *203*, 286−293.

(27) Pagano, J. J.; Bansagi, T.; Steinbock, O. Tube formation in reverse silica gardens. *J. Phys. Chem. C* **2007**, *111*, 9324−9329.

(28) Petrenko, V. F.; Whitworth, R. W. *Physics of Ice*; Oxford University Press: New York, 1999.

(29) Cartwright, J. H. E.; Escribano, B.; Sainz-Daz, C. I. Chemical-garden formation, morphology, and composition. I. Effect of the nature of the cations. *Langmuir* **2011**, *27*, 3286−3293.

(30) Cartwright, J. H. E.; Escribano, B.; Sainz-Daz, C. I.; Stodieck, L. S. Chemical-garden formation, morphology, and composition. II. Chemical gardens in microgravity. *Langmuir* **2011**, *27*, 3294−3300.

(31) Denny, M.; Dorgan, K. M.; Evangelista, D.; Hettinger, A.; Leichter, J.; Ruder, W. C.; Tuval, I. Anchor ice and benthic disturbance in shallow Antarctic waters: interspecific variation in initiation and propagation of ice crystals. *Biol. Bull.* **2011**, *221*, 155−163.

(32) Barge, L. M.; Cartwright, J. H. E.; Cooper, G. J. T.; Cronin, L.; Doloboff, I. J.; Jones, D. E. H.; Maselko, J.; Pagano, J. J.; Pantaleone, J.; Russell, M. J.; Sainz-Díaz, C. I.; Steinbock, O.; Stone, D. A.; Tanimoto, Y. From chemical gardens to chemobrionics. To be submitted for publication, 2013

(33) Fritzmann, C.; Löwenberg, J.; Wintgens, T.; Melin, T. State-of-the-art of reverse osmosis desalination. *Desalination* **2007**, *216*, 1−76.

(34) Wettlaufer, J. S.; Worster, M. G.; Huppert, H. E. Natural convection during solidification of an alloy from above with application to the evolution of sea ice. *J. Fluid Mech.* **1997**, *344*, 291−316.

(35) Deville, S.; Saiz, E.; Nalla, R. K.; Tomsia, A. P. Freezing as a path to build complex composites. *Science* **2006**, *311*, 515−518.

(36) Wegst, U. G. K.; Schecter, M.; Donius, A. E.; Hunger, P. M. Biomaterials by freeze casting. *Philos. Trans. R. Soc. A* **2010**, *368*, 2099−2121.

(37) Rall, W. F.; Fahy, G. M. Ice-free cryopreservation of mouse embryos at −196°C by vitrification. *Nature* **1985**, *313*, 573−575.

(38) Russell, M. J.; Hall, A. J. The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *J. Geol. Soc. London* **1997**, *154*, 377−402.

(39) Martin, W.; Russell, M. J. On the origin of biochemistry at an alkaline hydrothermal vent. *Philos. Trans. R. Soc. B* **2007**, *362*, 1887−1926.

(40) Trinks, H.; Schröder, W.; Bierbricher, C. K. Sea ice as a promoter of the emergence of first life. *Origins Life Evol. Biospheres* **2005**, *35*, 429−445.

(41) Krembs, C.; Eicken, H.; Deming, J. W. Exopolymer alteration of physical properties of sea ice and implications for ice habitability and biogeochemistry in a warmer Arctic. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 3653−3658.