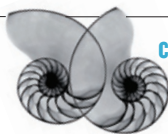


COMMENT

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The impressive front of the Perito Moreno Glacier in southwest Argentina, part of the vast South American icefields.

Ten things we need to know about ice and snow

Understanding the molecular behaviour of frozen water is essential for predicting the future of our planet, says **Thorsten Bartels-Rausch**.

Ice is central to climate, geology and life. Understanding its behaviour is essential for predicting the future of our planet and unravelling the emergence of life in the Universe¹. Water ice frosts planets, moons and comets in our Solar System. On Earth, white polar ice caps reflect up to 90% of the Sun's incoming radiation. On average, 7% of the ocean's surface is frozen; sea ice alters ocean currents and limits the exchange of gases with seawater. Ice and snow coat 10% of the land permanently and up to half of the Northern Hemisphere in midwinter. These blankets of frozen water insulate the ground and the oceans.

Ice clouds concentrate airborne chemicals and are sites for atmospheric chemistry. Above the poles, clouds of ice grains host ozone-depleting reactions, forming holes in the stratospheric ozone layer at high latitudes that expose millions of people to increased ultraviolet radiation. Chemical reactions in snow on the ground can produce ozone and other environmental pollutants. Organic toxins and mercury accumulate in snow and can be released into rivers and oceans when the snow melts, where they enter the food web.

Yet the molecular mechanisms underlying these processes remain largely unknown². Without knowing more about how chemical

reactions proceed in ice and snow, and where they occur within the grain and crystal structure, it is impossible to build snow or ice-cloud modules for atmospheric and climate models or to extrapolate laboratory studies to environmental conditions with enough confidence.

In my view, the chemistry and physics of ice need to be studied more on a molecular scale if we are to address the massive environmental problems we face. Recent advances in computer simulations and in experimental techniques such as surface-sensitive spectroscopy, which can now be operated at temperatures and pressures ►

► relevant to ice in the environment, open the door to exciting future studies. Here, I summarize ten open questions about ice.

TEN QUESTIONS

How does ice form? Much about how and when water freezes is still unclear, even though this is essential for understanding Earth's climate and water cycle. We cannot predict with certainty when and where ice clouds will form in the atmosphere; areas of the sky remain humid when we would expect them to freeze. Do water droplets freeze from the surface first or crystallize from within? Which form of ice will they make?

Ice often forms easily on solid surfaces. To understand why that happens, the molecular bases of the interaction of water molecules with such surfaces need to be studied.

How does ice structure change? Ice crystals are composed of water molecules held in a regular tetrahedral arrangement by hydrogen bonding. Many crystalline structures of water are known, the most familiar being the hexagonal ice that forms snowflakes. As pressure and temperature vary, the water molecules adapt their arrangement to minimize energy, producing the different phases of ice.

These phase transitions are well understood macroscopically. Next, we need to be able to reproduce the molecular processes in those transitions in computer simulations or quantum-chemistry calculations over the whole temperature and pressure range. With these optimized models we might then tackle other questions such as the surface structure and how impurities react in ice.

How do different ice structures behave? In addition to ordered crystals, ice also comes in amorphous and 'metastable' forms — molecular arrangements that are long lived but not at minimum energy. This structural variety widens the possibilities for how readily ice crystals form, the chemical reactivity of ice clouds, how impurities are captured in comets, and the mechanical strength of icy bodies in space. Yet we know little about how these ices are structured, whether they mix with crystalline ice and where they occur.

Amorphous ice — loosely tetrahedral in molecular structure but not crystalline throughout — might form on comets when water condenses at extremely low temperatures. Metastable cubic ice, which seeds more readily than the hexagonal arrangement, can form in ice clouds. Examining these phases is tricky as they are difficult to access and are optically indistinguishable. In the laboratory, X-ray and neutron diffraction studies might be the answer.

What is the surface structure of ice? Molecular order breaks down at crystal surfaces. Hydrogen bonds exposed to the air also bind

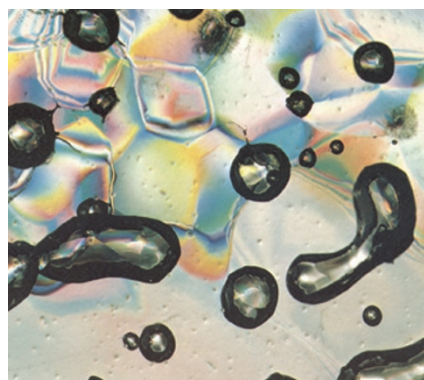
pollutants such as methanol, acetone, nitric acid and hydrochloric acid. The resulting networks of water molecules are irregular and difficult to describe, especially in ice that is warm and near its melting point, when the disorder spreads deep into the crystal.

We need to know the most essential things about this layer, such as its molecular structure and how that changes with temperature. And the layer's role in hosting impurities and chemical reactions is not clear. Surface-sensitive spectroscopy that can probe the bonding network of water molecules at near-ambient pressure, and thus of ice close to its melting point, could help answer these questions.

Where do impurities lie within ice? In the upper atmosphere and in space, water ice is often mixed with carbon monoxide, carbon dioxide, methane, sulphuric acid and nitric acid. Ice on the Earth's surface holds chemicals from sources such as sea salt, dust and pollution. Different impurities have been observed to boil off together from comets approaching the Sun, which suggests that they are trapped within the frozen material until the ice matrix vaporizes. But we don't know how these impurities are mixed in with the ice, or whether different types of ice, such as soft snow and compacted glaciers, hold contaminants in similar ways.

Some common crystalline structures associated with impurities have been identified in the laboratory. For example, nitric acid forms solid hydrates with frozen water that are crucial for ozone depletion in Earth's stratosphere. We must identify the phase, location and chemical environment of impurities within ice matrices in space, in clouds and on the ground. Surface-sensitive spectroscopy and diffraction are promising techniques in this regard.

How do reactions proceed in ice? At the South Pole, reactions of nitrous oxides released from snow produce enough ozone to raise the local concentration to levels seen in industrial areas. In the Arctic, mercury ions deposited from the atmosphere into the snow cover are chemically converted before



Ice core air bubbles capture ancient atmosphere.

being released back to the air. In space, molecules such as hydrogen, water, methanol, carbon oxides, ammonia and amino acids form on the surfaces of icy grains.

To get a better understanding of the chemical reactions that occur on surface films and in complex ice matrixes, we need to identify the dominant pathways and the locations of the impurities involved, given that reactivity on ice surfaces differs greatly from that within micro-pockets or bulk ice. Classical kinetic experiments could identify the chemical states of reactants.

Are there pockets of liquid in ice? Brine fills the pores and channels in sea ice, and sea salt in snow and impurities along grain boundaries in glacial ice can cause local melting to form internal pools. The presence of liquid changes the fate of impurities and the phase stability of ice, but in environmental ice we do not know how much liquid is trapped or where it is held.

In the lab, liquids in tiny ice pockets nanometres across freeze at temperatures tens of kelvin lower than normal. But whether such pockets exist in nature, and how much of the impurities they might capture, is not known. Observations are difficult at such small scales and it is hard to differentiate liquid and solid water optically. Microscopy using chemicals that enhance the contrast between liquid and solid phase could tackle these questions.

How do physical processes affect ice impurities? Chemicals from the atmosphere are absorbed rapidly by snow and creep deeper into glacial ice over centuries, altering the chemistry of air, snow and ice over time. Fluctuations in the levels of slowly diffusing pollutants, such as fluorides and methane-sulphonates, complicate the dating of the environmental record from ice cores.

The processes that dominate the spread of impurities in ice and snow, and their exchange with the atmosphere in clouds and on the ground, must be determined by measuring exchange rates and where exchange occurs within the ice structure. Surface adsorption, diffusion into the ice crystal or along grain boundaries, and trapping by liquid all affect the migration and fate of impurities. We can use spectroscopic techniques to follow these interactions at the molecular level.

How does ice growth affect impurities? Water molecules in the surface layers of ice and snow are continually evaporating and re-freezing. During the course of a day, as temperatures cycle between warm and cold, up to 60% of the molecules can be redistributed.

How do impurities respond when the shape, surface area and volume of the ice

changes so drastically? Laboratory and field studies reveal that mercury, hydrogen peroxide, hydrochloric acid and nitric acid are taken up more readily by growing than by stable ice. Experiments are needed to measure this uptake accurately and over a range of growth rates. Tracking uptake in individual growing ice crystals would be a good start.

How long will ice last? Satellite data indicate that the Arctic perennial sea-ice cover is declining by around 10% per decade. Glacier shrinkage at the Greenland and Antarctic ice sheets is accelerating. Our understanding of the observations is insufficient for us to predict the rate at which snow and ice could disappear from our planet in this century. Studying the impact of ice chemistry on molecular-scale melting processes will help us to predict the fate of Earth's snow and ice.

BACK TO THE LAB

How shall we answer these questions? Good starting points are existing research networks, such as the Air–Ice Chemical Interactions programme of the International Global Atmospheric Chemistry project, with which I am involved, the European Science Foundation's network on the microdynamics of ice, Micro-DICE, and the Arctic health-risks project ArcRisk, which is supported by the European Community.

These collaborations of scientists from different disciplines and countries should be broadened. We need to bring in materials scientists working on crystal and surface structures in metals, cell biologists who study the biota of frozen environments and food scientists who study how compounds change during freezing.

More funds for fundamental, laboratory-based experiments must be raised. I believe that all ten questions could be answered with an investment of €5 million (US\$7 million). Sadly, this will be difficult to find, but now that we have identified basic key questions, the time has come for complex, well-defined experiments in laboratories using sophisticated analytical techniques, including synchrotron facilities. Lack of recognition of the importance of ice chemistry may be one reason why many ice and snow research groups have moved into field studies. We need to reverse this flight and use the expertise gained over the past decades to understand the role of ice in the global Earth system — before it vanishes. ■

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1. Bartels-Rausch, T. *et al. Rev. Mod. Phys.* **84**, 885–944 (2012).
2. Bartels-Rausch, T. *et al. Atmos. Chem. Phys. Discuss.* **12**, 30409–30541 (2012).



STEPHANIE MAZE/NATL GEOGRAPHIC/GETTY

Brazil distils vast quantities of fermenting sugarcane into alcohol for fuel.

Build a biomass energy market

Governments must offer incentives to drive a switch to biofuels and other renewables, argues **Heinz Kopetz**.

Biofuels — which include wood, straw, charcoal, ethanol derived from corn (maize) and methane-rich biogas — currently generate about 10% of the world's energy, or 53 exajoules¹. The majority goes towards heat, with the rest used for electricity and transportation (see 'Biomass boost'). But biofuels hold the potential to deliver at least one-quarter of the world's projected energy needs of 623 exajoules by 2035 (ref. 2). This would

help to limit global warming, create jobs in rural areas and improve energy security. To achieve it, countries will need to dramatically accelerate their development of biofuel technologies.

Some countries have made huge strides in this respect, notably Sweden, Austria, Brazil and China. Many others are not making the most of their resources: in Australia, for example, millions of tonnes of straw are still burned in fields after ▶