

Figure 1 Phase diagram for the CO_2 -[BMIM][PF6] system. CO_2 solubility in the ionic liquid-rich liquid phase at CO_2 mole fractions up to 0.75 was determined using a high-pressure view cell¹¹ rated to 8.3 MPa. The number of moles of CO_2 in the liquid phase at a given temperature and pressure was determined by difference, using IUPAC pure CO_2 density data¹² to obtain the number of moles of CO_2 in the vapour phase (assumed to be pure CO_2). Cloud points of dilute mixtures (1.3–7.2% ionic liquid) were determined using a variable-volume view cell¹³ rated to 40 MPa. The solubility of the ionic liquid in the CO_2 -rich phase was checked with an ISCO 220SX high-pressure extraction apparatus. A small quantity of ionic liquid was loaded onto a polyurethane foam sponge and extracted with CO_2 at 13.8 MPa and 40 °C. The saturated CO_2 phase leaving the system was depressurized through a heated restrictor and slowly bubbled through a flask of ethanol. Ultraviolet and visual absorption of the collection solvent was used to determine that no ionic liquid was extracted. The circles and squares indicate two separate, replicate experiments.

liquid does not dissolve in carbon dioxide, so pure product can be recovered.

We synthesized⁷ the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF6], which is stable in the presence of either oxygen or water. Our primary objective was to show that CO_2 could be used to extract naphthalene, our low-volatility model solute, from an ionic liquid, but it was important to show that the CO_2 -rich phase is not significantly contaminated by the ionic liquid, as would be expected during contact of CO_2 with any conventional organic solvent. We therefore investigated the phase behaviour of [BMIM][PF6] with CO_2 , as well as with naphthalene, and finally that of the [BMIM][PF6]- CO_2 -naphthalene ternary.

CO_2 is highly soluble in [BMIM][PF6] (Fig. 1), reaching a mole fraction of 0.6 at 8 MPa, yet the two phases are not completely miscible: cloud points of mixtures ranging from 1.3 to 7.2 mole % of ionic liquid at 25 °C could not be found at pressures up to 40 MPa, the highest pressure accessible with our equipment. The composition of the CO_2 -rich phase is essentially pure CO_2 . After extracting the ionic liquid with 55 g

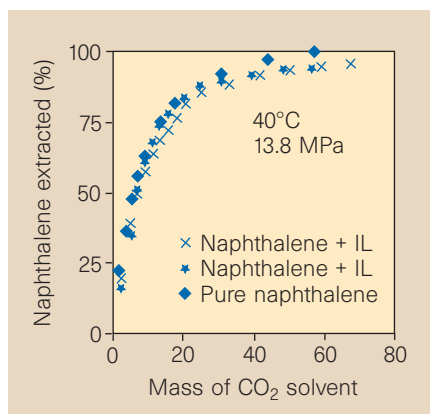


Figure 2 Extraction of naphthalene from the naphthalene/[BMIM][PF6] mixture using CO_2 at 40 °C and 13.8 MPa. The ISCO extractor was the same as that in Fig. 1. The naphthalene concentration in the ethanol collection solution was determined by ultraviolet and visual spectroscopy, using peaks at 267, 276 and 285 nm. Replicate experiments indicate 96% recovery (crosses) from a 0.0431 g sample (containing 0.00265 g naphthalene) contacted with 67 g CO_2 , and 94% recovery (stars) from a 0.0409 g sample (containing 0.00252 g naphthalene) contacted with 56 g CO_2 . Data for the dissolution of an equivalent amount of solid naphthalene into CO_2 , using the same extractor and analytical technique, are also shown (diamonds).

CO_2 at 13.8 MPa and 40 °C, there was no detectable [BMIM][PF6] in the extract, indicating that the solubility is less than 10^{-5} mole fraction. In contrast, a mixture of CO_2 with a conventional organic liquid results in significant solubility of the liquid in the CO_2 -rich phase. The phase behaviour of the ionic liquid- CO_2 system resembles that of a cross-linked polymer-solvent system⁹, even though [BMIM][PF6] is a low-viscosity, low-molecular-weight liquid. The liquid phase increased in volume by only 10–20% when 8 MPa of CO_2 pressure was applied, perhaps because it is ionic; this corresponds to a more than twofold decrease in the molar volume.

Naphthalene was chosen as our model non-volatile organic solute because it dissolves readily in [BMIM][PF6] (maximum solubility of 0.30 mole fraction at 40 °C) and in CO_2 (with a solubility of 0.013–0.017 mole fraction at 35 °C and pressures of 12.2–20.4 MPa; ref 10). A mixture of 0.12 mole fraction naphthalene in [BMIM][PF6] was extracted with CO_2 at 13.8 MPa and 40 °C with recoveries of 94–96% (Fig. 2). This near-quantitative recovery compares favourably with the dissolution of a similar amount of pure solid naphthalene with comparable amounts of CO_2 (Fig. 2). It is therefore possible to quantitatively extract a non-volatile organic solute from an ionic liquid using CO_2 without any contamination. Moreover, the dissolution of CO_2 in the ionic liquid is completely reversible: pure ionic liquid

remains after extraction of the naphthalene and depressurization.

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Long-distance transport of pollen into the Arctic

Airborne particulates can be carried over long distances, but for significant quantities of particulates larger than a few micrometres in diameter to be transported more than a few kilometres usually requires a means of injecting the material high into the atmosphere, such as a volcanic eruption, forest fire or desert windstorm. But an unusual event occurred in the Canadian Arctic last year, in which significant amounts of pine and spruce pollen (30–55 μm long) were transported roughly 3,000 km.

On the night of 5 June 1998 and the following morning, local hunters noticed an unusual concentration of pollen at the edges of ponds on Arctic Ocean ice near Repulse Bay, Northwest Territories, Canada (Fig. 1). Similar deposits were also reported in Pelly Bay, northwest of Repulse Bay, but not in other Arctic communities. The material is a remarkably pure pollen concentrate containing 92% jack pine (*Pinus banksiana*) and 8% white spruce (*Picea glauca*). An examination of more than 1,500 pollen grains revealed no pollen from alder (the most common exotic pollen in the eastern Arctic¹) or other taxa, no large organic debris and no charcoal. The pollen is in excellent condition, most of it having unbroken walls and intact cytoplasm, unlike the ‘yellow rain’ reported in south-

east Asia in the late 1970s and early 1980s, which proved to be bee faeces².

Pine pollen is known to traverse great distances, and is often found as a component of both pollen rain and stratigraphic pollen assemblages well beyond the tree line³. Spruce pollen, being much larger, does not transport as readily but can nevertheless form a significant proportion of the tundra pollen assemblage³. Typically, boreal forest pollen deposit in the high Arctic at a rate of less than 1 grain per species per cm² per year¹. The influx rate in Repulse Bay during this event was not measured, but must have been of the order of hundreds of grains per cm² in only a few hours.

The timing of the deposit and its geographic coverage indicate that the event was the result of an unusually strong low-pressure system that developed over Repulse Bay on 5 June. A three-dimensional back-trajectory analysis indicates that winds arriving at Repulse Bay on 6 June would have been near ground level in central Quebec on 1 June. Pine, spruce and alder may all be in flower at this time of year, depending on weather conditions⁴. High surface winds (up to 24 km h⁻¹) lofted the pollen into the air, and this pollen-laden air mass travelled at approximately the 850 hPa level

(~1,300 m) northeast over Labrador, north over the Labrador Sea, and west over southern Baffin Island, arriving at Repulse Bay late on 5 June and in the morning of 6 June. The wind speed dropped to less than 20 km h⁻¹, allowing the pollen to settle out. This event lasted an unusually long time (turbulence in the airflow causes most grains to remain airborne for less than a day⁵) and covered a remarkable distance (nearly 3,000 km).

That lifetime residents of the area have never seen anything similar demonstrates the rarity of this type of pollen transport event. As stratigraphic pollen data often integrate several decades in a single sample, however, such rare events may account for some of the variability often seen in the records of high Arctic regions. Similar rare transport events may account for some of the noise in ice-core records of pollen, dust, charcoal and other particulates and aerosols.

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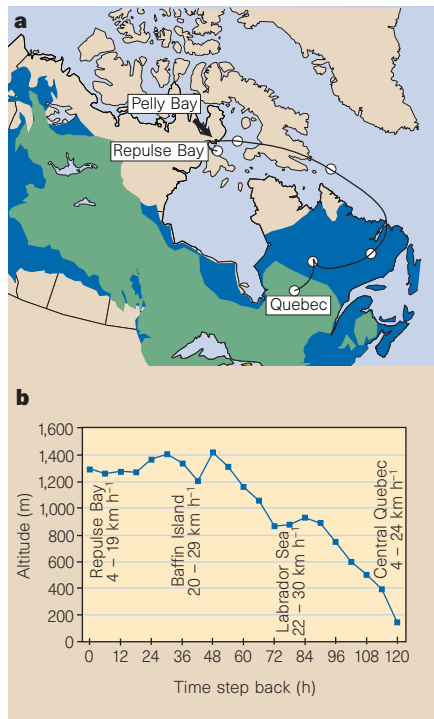


Figure 1 Movement of pollen. Back-trajectory analysis indicates that the pollen was picked up by strong surface winds on 1 June in central Quebec and lifted to and transported at the 850-hPa level to Repulse Bay, where it was deposited in calmer air developed by a low-pressure system on the night of 5 June and early morning of 6 June. **a**, Shading indicates ranges of *Pinus banksiana* (green) and *Picea glauca* (dark blue). The solid line is the 850-hPa trajectory; symbols on the trajectory line mark 24-hour intervals. **b**, Altitude of trajectory from 1 to 6 June.

Cause and effect in evolution

The need to see ‘purpose’ in evolution, or at least some internal drive to help the blind processes of random variation and natural selection, is remarkably resilient¹. Recent manifestations in the scientific literature imagine evolved mechanisms that actively promote further evolution or that facilitate rapid response to changed conditions. For example, Rutherford and Lindquist² (and the authors of related commentaries^{3,4}) suggest that the heat-shock protein Hsp90, by stabilizing developmental pathways, fosters the accumulation of hidden variants that can be exposed by environmental challenges and subsequently fixed by selection.

This is interpreted as “an explicit molecular mechanism that assists the process of evolutionary change”² (or even “a way of saving up mutations for a rainy day”⁴). Similarly, it is widely believed that organisms

increase mutation rates under stressful conditions to improve their chances of hitting on appropriate adaptations⁵.

Such interpretations seem to call for the evolution of properties that anticipate future needs. But selection lacks foresight, and no one has described a plausible way to provide it. In principle, group selection might produce results that seem to escape this limitation. For example, increased mutation rates may indeed allow populations to adapt more quickly to changed conditions, even though they harm most individuals. The evolutionary problem is that such group benefits are usually weaker than individual costs, in a well-defined sense that makes group selection effective only under very restrictive conditions⁶. So, in general, we need explanations that are based on individual fitness differences⁷.

From this perspective, the obvious function of Hsp90 is to prevent abnormalities of the kinds that appear when it is compromised. Up to a few per cent of adults heterozygous for a mutation that inactivates Hsp90 display significant morphological abnormality, so clearly there is selection to maintain its function. Likewise, increased mutation under stress might plausibly arise from trade-offs affecting individual fitness: stressed cells may simply be unable to maintain normal DNA repair without sacrificing other vital functions.

In the natural world, only living things (and their artefacts) have ‘purposes’, and natural selection is the ultimate source of all such ‘purposeful’ design⁸. When speaking of the function or purpose of some feature of an organism, we are therefore referring to the selective advantages that brought the feature into being and that maintain it in the face of recurrent damaging mutations. It is especially important, in any discussion of evolutionary processes, to observe the distinction between function or purpose on the one hand, and effect or consequence on the other. This is not a semantic quibble. Cosmic rays affect evolution by causing mutations, but we would not claim that they exist for that purpose. Similarly, developmental buffering and variable mutation rates may influence the course of evolution, but this does not mean that they evolved to that end.

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