20 Years as a Material Witness



A selection of columns from *Nature Materials* By Philip Ball

December 2002

The stuff of youth

There's scarcely any scientist, with the possible exception of geneticists and cosmologists, who feels that his or her discipline gets its fair share of the limelight. But materials scientists have the added disadvantage that their science runs perilously close to engineering—and when was the last time you saw a popular TV programme on engineering?

So it is good news that this year's Christmas Lectures for children at the UK's Royal Institution in London, entitled Smart Stuff, will have a heavy focus on materials. Not only that, but they will show something of the grand sweep and diversity of today's materials science, ranging from photonics to biomedical materials to food science.

The lecturer is Tony Ryan of Sheffield University, who is especially well-situated to explain the importance of polymers in modern science and technology—illustrated in this case with reference to that icon of youthful cool, the training shoe.

If there is an older tradition of communicating science to the public, I do not know of it. The Christmas Lectures at the Royal Institution begun in 1825, and became legendary through the pedagogical genius of Michael Faraday, who delivered them regularly until 1860.

Faraday established the model that Tony Ryan will adopt this Christmas: to illustrate the unfamiliar by means of the familiar. For Faraday, the famous leitmotif was the candle; now mobile phones and ice creams are likely to capture the attention of a young audience more effectively.

The Christmas Lectures have always reflected the Royal Institution's strong tradition in the chemical and practical sciences, with recurring themes such as electricity, light, photography and radio communications. The glittering array of speakers has included John Tyndall, James Dewar, William Bragg, D'Arcy Thompson and the late George Porter. The more recent decades have been delightfully egalitarian, embracing geology, music and mathematics, alongside more familiar topics.

Because the Christmas Lectures are televised, they reach out to more than a few hundred school children: there were 1.5 million viewers last year. And one must suspect that it is not just children who watch. The appeal of the lectures is that, by having to address themselves to a young audience, they are highly visual, participatory and free from earnestness: qualities just as attractive to adults.

This need not mean that fun eclipses any real instruction. There is little, if anything, that we might wish the adult public to understand about science that cannot be readily assimilated by a ten-year-old child. It's just that, to communicate to the latter, we are forced to say what we mean in simple words and short phrases, knowing that attempts to impress will fall on deaf ears. This is a principle that could be usefully employed more widely than in lectures for children. Peter Goodhew of the UK Centre for Materials Education has asked why under-graduate lecture courses or book chapters have to be called 'Metallurgical thermodynamics' or 'Microstructure 1', rather than 'Why reactions work' or 'How far can we bend a beam?' Can anyone see a reason?

March 2003

Keeping art alive

Field for the British Isles, by contemporary artist Antony Gormley, which I saw recently, is a wonderful sculpture: accessible, resonant and poignantly beautiful. But it must be a curator's nightmare. All those thousands of little terracotta figures, as brittle as prehistoric pots — how many relocations will they survive?

At least museums and galleries have plenty of experience with terracotta. Gormley, like many modern sculptors, has often been experimental with his materials, throwing up challenges that never faced the conservators of stone and bronze statuary.

Take his early work *Natural Selection* (1981). Here are 24 objects, some natural, some man-made, each encased in lead. There is a pea, a banana, a goose egg, a grenade, a light bulb, a coconut. Lined up in ascending size, they present a study in the evolution of form and the relationship of natural to artificial.

Why lead? "It is the best possible material", Gormley has said, "It's the most female metal, the most malleable and the densest." (Wait till he gets hold of osmium!) But although Gormley also likes lead's "impenetrability", his casings proved not quite as impermeable as he'd hoped.

The objects containing fruits and vegetables soon started leaking, forcing Gormley to unsolder the seams and dry the organic contents before resealing them. The goose egg started emitting the unpleasant rotten odour of hydrogen sulphide. The casing was cut apart and the eggshell cleaned.

As the sculpture's conservators pointed out, Gormley's prized impenetrability of lead prevented them from using X-rays to study the state of the casings' contents nondestructively. The coconut was a particular problem: its organic acids were corroding the metal, and the conservators at the Tate Gallery in London were compelled to seek safety advice from the Natural History and Science Museums.

The coconut proved to have produced a thick layer of basic lead carbonate inside its casing. The shell was carefully sawn in half, cleaned and chemically treated. (All concerned were determined that the original objects should not be replaced by new ones.) The pitted lead was filled with polyester resin coloured with graphite. When not on display, the work is now stored in a sealed, desiccated container.

The issues that arise in conserving modern sculptures like this are quite different from those for older works. "No-one knows what an ancient sculpture looked like when first made", conservator Jackie Heuman points out. Moreover, ageing of old materials, like the patination of bronze, may be aesthetically pleasing, as well as providing a record of the history of the work.

Restoration of modern works is often much more radical. Sometimes they are entirely remade, as was the case for Naum Gabo's *Linear Construction No. 2*, made from strung nylon threads that slackened when the work was rehung in 1970. Gabo, one of the first to

use plastics in his sculpture, accepted such problems as the price of innovation. "The genesis of a sculpture is determined by its material", he said, adding "there is no limit to the variety of materials suitable for sculpture."

September 2003

Space myths

Thank goodness for space exploration, which has given us that vital ingredient of modern life: the perfect fried egg.

Or has it? Never mind the bathos, what about the facts? The idea that DuPont's Teflon was a spin-off from research on space technology is one of the most pervasive myths about today's materials. But it was nothing of the sort.

Polytetrafluoroethylene was in fact the serendipitous offshoot of research on refrigerators. When Roy Plunkett and his co-workers stumbled across it in 1938, they were attempting to make a new CFC refrigerant. This white plastic that resisted water, acids, organic solvents and fungus clearly had something going for it, and DuPont patented it in 1941.

The real boost for applications of PTFE came from the Second World War, when it was used under the code-name K416 as a protective coating against corrosive uranium hexafluoride in isotope separation for the Manhattan Project, as well as in aircraft engines and explosives manufacture. Seeing its commercial potential, DuPont registered the Teflon trademark in 1944 and developed mass-production methods. By 1950 the company's Teflon plant in Virginia was producing a million pounds in weight of the material a year, used largely as an insulator and sealant. Non-stick cooking equipment followed soon after, although DuPont was cautious about introducing it for domestic use until its safety had been established. Teflon-coated pans were all the rage by the time Yuri Gagarin flew in space in 1961.

So although PTFE featured in the space suits, blankets, heat shields and insulation of the lunar module in which Neil Armstrong and colleagues landed on the moon in 1969, such space applications were a minor sideline in the burgeoning Teflon market.

And yet the myth continues. US senator Kay Bailey Hutchison claimed only last February in the *Dallas Morning News* that not only Teflon but also Velcro "were developed through our space programme".

Why does this notion persist? One can't blame an over-zealous NASA press agency; indeed, it gives the impression that it would be relieved not to have to keep denying the tale. "There was a guy last week who was assuring me that Teflon was a NASA product", said a NASA spokesman earlier this year, "and I kept saying to him 'Show me the documentation'." The same is true of several other putative spin-offs, such as the instant fruit-drink Tang. "We didn't develop it", says the man from NASA, "we just bought it off the shelf like everyone else."

Partly this stems from a refusal to believe that wonderful modern materials can have such prosaic origins. But some banging of the spin-off drum is for propaganda purposes, as a way to revitalize the moribund and obsolete vision of manned spaceflight. Setting foot on Mars, claims Robert Zubrin of the Mars Society, would produce an even greater spin-off benefit than Teflon. If, in 30 years' time and after astronomical expenditure, that were to

happen, I wonder what products we will be asked to thank it for — carbon nanotubes, perhaps?

October 2003

Portentous polymers

'Mylar' does not appear in my Webster's dictionary, which is nevertheless content to include 'myristic acid' and 'myxomycete'. My Oxford English dictionary acknowledges it ("a form of polyester resin used to make heat-resistant plastic films and sheets"), but I submit that it is not exactly a household word.

Which makes it curious that American novelist Don DeLillo sees fit to refer repeatedly to Mylar in his 1985 book *White Noise*. The neighbourhood of protagonist Jack Gladney becomes haunted by men in Mylar suits testing for toxic fallout from a chemical accident.

He didn't have to specify the Mylar. Indeed, arguably DeLillo would have made himself clearer to many readers by calling the protective clothing simply that. There is no indication of why the properties of Mylar dispose it to such a use, or even any explicit mention that it is protective.

But 'Mylar' is precisely the right choice. It gives readers the frisson of being surrounded with materials the names of which they barely know and the provenance of which they cannot guess. And the capitalization tells us that this is not merely some new word, but a trade name devised, trademarked and marketed by some big corporation. It fits with the novel's themes of alienation and disorientation in contemporary US society.

DeLillo is one of a small, influential group of American writers who insist that chemical and materials technology is one of the pervasive aspects of twentieth century life. Theirs is not the prosaic assertion that 'materials are all around us' (which of course has always been true) but that the textures, the sights and smells of modern life have typically been designed, synthesized and patented. Styrofoam, Kevlar, neoprene. If these writers are not always exactly friendly to the new substances — which often appear in ominous contexts — they do recognize and in some sense embrace them.

Thomas Pynchon's *Gravity's Rainbow* (1973) is the most remarkable fable of materials chemistry in the English language, laced with the tale of a sinister and sensual polymer called Imipolex G: "the first plastic that is actually erectile". Having studied engineering at Cornell before working at Boeing, Pynchon knows what he is talking about when he mentions "aromatic polyamides, polycarbonates, polyethers."

But crucially, he does not much care whether his readers know what he means by "giant heterocyclic rings" and so on: these words and phrases are talismans, half-glimpsed clues to a world of power, commerce and arcane knowledge. DeLillo too is interested not in dispelling this bewilderment but in exploring it.

A more recent initiate into this group is Richard Powers, whose 1998 novel *Gain* recounts the development of a Boston chemicals company. Again, the uncompromising details: page 171 has no text but a diagram showing the synthesis and uses of Glauber's salt.

We should be heartened by this. Patiently demystifying materials technology is one way to disseminate it. But for writers like DeLillo, Pynchon and Powers, it is already here, seamlessly embedded in our cultural experience, and we had better get used to it.

November 2003

Freedom to build

In what style should we build? Now that architecture claims to have broken free of rule books, this question is more urgent than ever. Architects such as Charles Jencks, Frank Gehry and Daniel Libeskind have found one answer in a startling asymmetry, which Jencks justifies with reference to the physics of phase transitions and symmetry breaking.

It is popular to explain the liberty that architects now enjoy by invoking cultural trends, particularly the post-modernist determination to avoid prescriptive dogmas. But the dramatic, sometimes unearthly edifices that have appeared in the past decade, such as Gehry's Guggenheim Museum in Bilbao and Libeskind's Jewish Museum in Berlin, are made possible largely by technological advances.

Thanks to these changes, just about anything seems possible. No longer do walls have to be flat, rectilinear or assembled from identical small units. Buildings may have not doors and windows but simply 'orifices'. Rather than being most substantial at their base, towers can balloon outwards as they rise up, like the inverted bell figures of marine tunicates. Such freedom might seem a gift to architects, but it can also be artistically paralysing: invention is rendered motherless.

Computerization of the design and the manufacturing processes has been responsible for much of the expansion in architectural possibilities. But equally significant is the advent of new materials and methods of processing them. Lightweight plastic film can clad buildings in a skin lighter than the air they contain. Self-cleaning glass enables vast or inaccessible areas to be glazed without worrying about maintenance.

Not all of this new architecture is rootless, however. The plastic domes of the Eden Project, an ecology centre and botanical park in Cornwall, England, throw a nod towards two great pioneers of radical architectural design: Buckminster Fuller and Frei Otto. Otto based many of his designs on the shapes of soap films and bubbles, and his tent-like plexiglass roof for the Munich Olympic stadium in 1972 established a curved, airy, 'organic' architectural language that has been reworked on countless occasions — notably in Norman Foster's roof for the Great Court of the British Museum.

Otto's work, and the influence of new materials, lurk in the background of an exhibition entitled Zoomorphic at London's V&A Museum, which explores the use of animal motifs in architecture. The title is interpreted loosely, encompassing anything from Gehry's explicitly fish-shaped Fishdance restaurant in Kobe, Japan, to buildings based on 'animal architecture' such as nests (a topic explored by ethologist and Nobel laureate Karl von Frisch) or ones that simply display suggestive, 'organic' curves.

One such is the Weald and Downland Museum's Jerwood Gridshell in West Sussex, England. This is basically a wooden barn, acting as a storehouse and conservation workshop. But the undulating body evokes a living form, and its fabric shows the versatility of some traditional materials: the skeleton is a lattice of local oak beams, shaped and moulded while still 'green'. In other words, not all eye-catching new architecture has to be post-modernist or use fancy new materials.

January 2004

A matter of taste

Do materials have a personality? Mike Ashby and Kara Johnson ask this question in the December issue of *Materials Today*, and their answer is: of course they do. Metals are 'cold, clean, precise': strong and reliable, but impersonal. Wood is warm, soft and associated with good craftsmanship. Plastics are cheap, fun, gauche, synthetic, chameleon-like.

Well, this much seems obvious. Designers have long used their choice of materials to say something about their products, from the filigree of Celtic goldsmiths to the wooden furniture of the Arts and Crafts movement and the insoluciant plastics of the Pop Art style. What is curious is that these associations transcend instances of contradictory materials usage: wood appears in most uncraftsman-like contexts such as cheap packaging, whereas plastics house expensive, high-tech electronic products and feature in cutting-edge biomedicine.

Ashby has been a pioneer in the business of materials selection: how to choose materials in engineering so that they represent the best compromise between potentially conflicting criteria such as strength, lightness and cost. For an engineer, that is often where the story starts and ends: aesthetics rarely enter the equation. Or if they do, the aesthetic of the engineer often expresses itself in the intrinsic quality of the design: a well-built bridge is automatically beautiful, as Brunel believed.

However, because not everyone shares that belief, products that are designed to be sold – that is to say, to capture a consumer market – have to acknowledge a wider vision of aesthetic appeal. Part of that appeal is purely functional: how well does the product work, and for how long? Much of it, however, is bound up with the 'personality' of the material components and their manner of processing and assembly. What is their shape, colour, texture, their cultural associations? Then it becomes harder to unravel cause and effect. Did the flat, economical contours of Bauhaus design precede a material in which they could be economically realised, or did the use of moulded plywood help to determine that aesthetic?

I'm not sure we recognize how deeply ingrained materials' personalities are in our cultural preferences. Plastics can mimic the appearance of other materials so closely as to be sometimes all but indistinguishable, and yet (as Ashby and Johnson point out), many people would baulk at being buried in an imitation-wood plastic coffin, even if it were biodegradable. It would feel like being thrown away in disposable plastic packaging. These non-material connotations of materials are reminiscent of how painters once insisted on using precious ultramarine for religious iconography.

What this means is that anyone who is going to use materials science in industrial design, from computers to construction machinery (for even that has to be sold in a competitive market), could surely benefit from instruction in the role and history of materials in art and culture. That is why initiatives like the one developed by Mark Miodownik at King's

College London to bring engineers into contact with the arts (see www.eee.kcl.ac.uk/mecheng/mam/engart.html) are well worth encouraging.

February 2004

Designing with complexity

When I hear the word 'complexity', I don't exactly reach for my hammer, but I suspect my eyes narrow. It has the dangerous allure of an incantation, threatening to acquire the same blithe explanatory role that 'adaptation' once did in biology.

But whereas there is no denying that certain 'complex systems' of many interacting parts do seem, in the natural world, to have an uncanny ability to self-organize into coherent modes of behaviour, the intersection of complexity with engineering has the potential to generate friction.

For one thing, the notion that complex systems have discrete 'attractors' or stable modes of behaviour could be deemed to constrain the engineer's freedom to design. Not only does it imply that not all designs are possible, but it might imbue small changes with disproportionate consequences.

There seems no question that studies of complexity have a place in materials science and engineering — for example, in the behaviour of granular media, complex fluids and colloidal crystals. Even old-fashioned crystallization is arguably a process of complex pattern formation arising from cooperativity between the components, and it remains a hard thing to predict.

But can engineers and materials designers make rational use of the sorts of phenomena that complex systems produce? Self-assembly, now widely used in materials synthesis, need not be inherently complex, in that the final state of a multicomponent system may be uniquely specified by the design of the components and thus not really an emergent property at all. But some researchers, like George Whitesides at Harvard University, are interested in developing non-equilibrium self-assembling materials systems that show dynamic, dissipative ordered states, more akin to the traditional structures of 'complexity science'.

Whitesides described such systems at a conference on complex systems last year that explicitly included engineering and industrial perspectives

(http://complexsystems.mccormick.northwestern.edu). The idea of 'emergence' is being harnessed by others to solve problems in engineering design. One can argue that even well-established finite-element optimization routines for shape engineering embody the spirit of complexity. Some of these draw inspiration from the growth-and-feedback processes evident in nature, for example in the formation of wood and bone. Biology, like engineering, must address the conflict between emergence and function, or spontaneity and purpose.

The engineering of complex systems has been studied for some time now (S. Wolfram *Physica D* **22**, 385–399; 1986). One current example is the European SYNAMEC project for aeronautical engineering, an aspect of which is the use of self-organizing agents for mechanical design (see www.co.umist.ac.uk/~mcaihak2/papers/esao03_5c.pdf). Here a set of components interacts to find the best mechanical design for a job. As yet, there is

no theory that can prove the optimality of these emergent solutions, however — indeed, a general 'theory of complexity' remains perhaps the biggest challenge for the field.

June 2004

What's so pure about science?

One of the intellectual attractions of materials science, it has always seemed to me, is that, rather than sitting at the interface between science and technology, it demolishes conventional attempts to distinguish between them. In principle, this provides an opportunity to reorient the traditional understanding of how the two are related. In practice, it tends to mean that no one — not even scientists — is quite sure how to represent the science of materials: true science, or engineering?

Even so erudite a commentator as Derek de Solla Price, historian of science at Yale University in the 1960s, came unstuck in attempting to differentiate science from technology. While admitting that "easily we can fool ourselves into believing that we know what these terms mean", he went on to offer the usual cliché: "If, when a man [this was 1968] labors, the main outcome of his research is knowledge,... then he has done science. If, on the other hand the product of his labor is primarily a thing, a chemical or a process, something to be bought and sold, then he has done technology."

The same idea was repeated more succinctly by biologist Lewis Wolpert in 1992: "The final product of science is an idea; the final product of technology is an artefact." So most materials science must be technology, never mind the fact that it might be published in such resolutely technical outlets *as Applied Physics Letters* or *Journal of the American Chemical Society (JACS)*. Such definitions insist that almost all chemistry (my crude estimate from surveys of issues of *JACS* is 96 per cent) is not real science but technology. And to judge from *Physical Review Letters*, less than half of physics is about understanding 'how nature works'.

Perhaps Price and Wolpert would be content to carve up the disciplines this way. But such an arbitrary and intricate division seems hardly likely to prove valuable, intellectually meaningful or even comprehensible to non-scientists, any more than Europeans can understand the rules of baseball.

I suspect that Peter Medawar put his finger on what is going on here. Francis Bacon, he said, made a clear distinction between 'pure' and 'applied': "between research that increases our power over nature and research that increases our understanding of nature." "Unhappily", Medawar goes on, "Bacon's distinction is not the one we now make... The notion of purity has somehow been superimposed upon it, and in a new usage that connotes a conscious and inexplicably self-righteous disengagement from the pressures of necessity and use. The distinction is [now] between polite and rude learning, between the laudably useless and the vulgarly applied, the poetic and the mundane."

It's an old snobbery that refuses to die. Of the philosopher's view of the engineer, Plato said "You despise him and his art, and sneeringly call him an engine-maker, and you will not allow your daughter to marry his son." Rather than trying to draw up pure, abstract and elevated definitions of what science is, might we not simply say that it is whatever scientists choose to do?

September 2004

A blast from the past

Sometimes you never know when a material will come into its own. Fifty years ago there was a small flurry of work on a rather obscure class of metal oxides, manganites with a perovskite structure. These materials had interesting magnetic properties: they exhibited a phenomenon dubbed double exchange, wherein electron spins on adjacent mixed-valence metal ions are coupled by delocalization of an electron between them.

This process, explained by Clarence Zener (of Zener diode fame) in 1951, posed a nice theoretical challenge, and it drew the attention of two future Nobel laureates (Philip Anderson and Pierre-Gilles de Gennes) as well as John Goodenough, now arguably the world's leading expert on the behaviour of metal oxides. But despite the calibre of the researchers, no one would have guessed that papers with titles like 'Interaction between *d*-shells in transition metals. II. Ferromagnetic compounds of manganese with perovskite structure.' were destined for great things.

Yet this, Zener's original paper on double exchange in manganites (*Physical Review* 82, 403–405; 1951), has just been ranked as the paper with the sixth highest impact among all the publications in the *Physical Review* (*PR*) journals since 1893. A publication on the subject by Anderson ranks at number 19, de Gennes' at 21, and Goodenough's at 37.

Even more remarkably, all four papers, along with one by E. O. Wollan and W. C. Koehler on neutron diffraction from manganites (published in 1955, ranked 37), made very little impact at the time of publication. They were cited just a few times a year, if at all, until the mid-1990s, when the citation statistics for all of them soared. In 2000, Zener's paper was cited over 100 times within the *PR* journals alone.

They were classic 'sleepers'. These papers suddenly became hot when it was discovered in 1993 that thin films of manganite materials exhibit so-called colossal magnetoresistance: their electrical resistance changes dramatically in the presence of a magnetic field. This is the crucial characteristic of readout heads for magnetic data storage, and the manganites were suddenly of vast technological interest.

This history of the early work on manganites emerges from a fascinating analysis by Sidney Redner of Boston University of the citation statistics of all the papers published in the *PR* journals since they began 111 years ago (xxx.arvix.org/abs/physics/0407137). The extraordinary burst of citations of the manganite studies, 40 years after their first appearance, is 'unique in the entire history of *PR* journals', Redner says.

Nonetheless, the significance of that work fits within the general consensus from Redner's list of highest-impact papers in *PR* journals, which is to say that twentieth-century physics was largely about condensed matter, and more specifically about the quantum-mechanical theory of electronic and magnetic properties in the solid state. The top two papers, both co-authored by future Nobel laureate Walter Kohn, established the density-functional theory by which means electronic band structures are typically calculated. The story Redner's study tells is one of physics' persistent engagement with materials and technology.

November 2004

The myth and magic of plastic

When the French writer Roland Barthes went to a plastics exhibition in the mid-1950s, he interpreted what he saw in mythical terms. Not only did these substances have "names of Greek shepherds (Polystyrene, Polyvinyl)", but they were the products of a kind of alchemy: "the public waits in a long queue in order to witness the accomplishment of the magical operation par excellence: the transmutation of matter."

This was not an overly florid imagination at work. Magic and wonderment were indeed the qualities used to sell plastics to the public. As David Rhees of the Bakken Library and Museum in Minneapolis pointed out at a recent conference in Paris (*The Public Image of Chemistry in the 20th Century*, 17–18 September 2004) from the 1930s DuPont marketed its products, and plastics in particular, as 'miracles'.

In part, DuPont's beguiling salesmanship was a response to accusations made in the 1930s that the company encouraged the USA to enter the First World War to create a military market for its products: DuPont was accused of being 'merchants of death'. That was when the company launched its famous slogan "Better things for better living through chemistry" — the white-coated boffins who took the podium at trade shows were making things for life, not death.

DuPont did not, however, foresee its most potent consumer snare. At the New York World's Fair in 1939, public demand forced the company to move to centre stage the young women modelling slinky stockings made from a new wonder fibre: nylon, which Wallace Carothers devised five years earlier. In next year's fair, DuPont exploited nylon's popularity to the full, as a nylon-stockinged Miss Chemistry emerged from a giant test tube.

War undoubtedly shaped the fortunes of plastics. As nylon was diverted to military uses such as parachutes, its rarity in the public sphere lent it glamour. When nylon stockings were reintroduced into stores after the war, there were riots among buyers. Acrylic aircraft canopies left people anticipating futuristic cars with plastic bubble-shaped windshields. Plastics were now the materials of tomorrow.

As Jeffrey Meikle of the University of Texas at Austin explained at the Paris conference, post-war plastics promised easy domesticity: they were marketed to housewives as easy to clean: fit out your house with plastic surfaces and you could virtually hose it down. Monsanto erected an all-plastic 'house of the future' at Disneyland.

And plastics could mimic the appearance of other, more luxurious materials, such as leather, wood and gemstones, enabling everyone to enjoy the superficial opulence of the rich. It was precisely this quality that dazzled Barthes: "The hierarchy of substances is abolished: a single one replaces them all." Indeed, he concluded, "the whole world can be plasticized."

But by the end of the 1960s, the romance was over. To the sixties generation, 'plastic' meant fake, worthless: an association crystallized in *The Graduate* in 1968, when all the

hollowness of American consumerist society is revealed to Dustin Hoffman through the famous career advice: "I just want to say one word to you ... plastics."

April 2005

Lost in translation

De rerum natura, by the Roman writer Lucretius, is one of the classic ancient works on the composition of the Universe. Written around 56 BC, it outlines the atomistic philosophy of Epicurus (341-270 BC) and was a major influence on the mechanistic world-view of Cartesians such as Pierre Gassendi in the seventeenth century.

But this book reached the early Enlightenment by the skin of its teeth. In the Middle Ages, Lucretius's atomism was considered anti-Aristotelian – then almost tantamount to heresy – and religious zealots nearly eradicated all copies of his manuscript. It resurfaced only in 1414, and a printed version appeared in 1473.

Many works of the ancient philosophers were less fortunate. The reputation of Pliny the Elder rests on just one seventh of his total oeuvre. For his encyclopaedic *Natural History*, Pliny drew on around 2,000 manuscripts from antiquity, of which very few now survive. Our knowledge of what the ancients knew will forever be woefully incomplete.

John Cisne of Cornell University has developed an original perspective on this decimation of antique manuscripts by comparing it with the growth and extinction of biological populations (*Science* **307**, 1307; 2005). The rationale is that until the explosion of book-making that followed the introduction of printing in the mid-fifteenth century, manuscripts propagated much as organisms do: by spawning copies, generated at the hands of monks.

Cisne's conclusion is somewhat cheering. His calculations, based on Markovian modelling of the 'growth' and 'decay' of manuscripts, suggests that any that survived from antiquity to enter the workshops of the ninth-century Carolingian empire – arguably the 'first Renaissance', when attempts were made to mass-produce the great works of the ancients – had a good chance of persisting until printing began.

Thus, he says, many if not most of the leading technical manuscripts circulating in the early Middle Ages probably exist today. But Cisne's analysis does not reach back into 'antiquity'- that is, before the latter days of the Roman Empire in the third century AD. The surviving fraction of works from this earlier time is evidently far smaller. Why so?

The answer, Cisne, suggests, might lie with a change in material. The principal material used for manuscripts in antiquity was papyrus. It was gradually replaced by parchment or vellum: untanned leather from the skin of a calf or young goat, shaved, stretched and rubbed down to provide a smooth writing surface.

The use of parchment may have begun as early as the third century BC, when the Egyptian ruler Ptolemy Epiphanes banned the export of papyrus in the hope of checking the growth of a library at Pergamum that rivalled his own. Parchment was expensive, but it was a superior and more durable material, and became commonly used by the third century AD.

The import of paper-making technology to the West around the twelfth century, followed by the later appearance of the printing press, are often cited as key factors in the growth of learning. But it seems that another aspect of materials culture may have been one of the earliest drivers of the information revolution.

June 2005

Casting problems

'It's time we got away from the idea that, unless an artist makes every last bit of his work himself, it's not art.' This was the exasperated assertion of one participant in a recent gathering of artists, scientists, engineers and designers at London's Tate Modern art gallery*. An artist herself, the speaker claimed that she did not want her creativity to be impeded by the need for technical knowledge about the materials she uses.

One can sympathize with that point of view. While it is all very well to point to the intimate relationship between the medieval metalsmith or painter and his materials – painters might grind their own colours from the raw materials – later artists would not have been able truly to understand their materials without considerable scientific training.

The advent of coal-tar and other synthetic organic colorants, for example, as well as new synthetic inorganics such as copper aceto-arsenite ('Emerald Green'), made unfair demands on the chemical knowledge of the painters using them. So they relied increasingly on technical experts (colourmen) both for access to and information about their materials. The introduction of synthetic polymer resins like acrylics as paint media added to this distancing of artist from material.

But the comment at the Tate event betrayed the fact that what was once an unfortunate inevitability, which artists tried to alleviate by consultation with specialists, has sometimes now given rise to indifference to, even contempt for, the question of what one should make one's art *from*.

That was evident in the way Mark Rothko once claimed (perhaps mischievously) that he simply bought his paint from Woolworths, not caring what was in it. (Some of Rothko's work have paid a heavy price for that lack of curiosity.) There was a sense of this blithe attitude to materials also in the account at the Tate by Mike Smith of his fabrication studio's struggles to meet the requirements of British artist Rachael Whiteread for her sculpture *Monument* in 2001.

Whiteread, one of the most inventive of young British contemporary artists, told Smith that she wanted to make a cast in 'water-clear' polyurethane of the plinth on which her commissioned work would stand. The problem was that polyurethane is poisonous, expensive and unstable against photodegradation – and worst of all, it shrinks as it cures. For that reason, no one had previously cast it at such a literally monumental scale, and Smith's initial attempts to find a supplier were treated as hoax calls once he explained what the 11 tons of resin were for. But he persevered, accommodating the predicted shrinkage by creating an aluminium mould that was systematically too large, controlled by a hydraulic system that altered the dimensions gradually as the resin slowly cured.

It was little short of miraculous that the final sculpture emerged, uncracked and undistorted, 18 months later. Smith appeared to relish the challenge; others might wonder whether the artist's choice of material would have benefited from a little more technical input. *Engineering Art, Tate Modern, London, 15 April 2005.

January 2006

Everything must change

No one finds it easy to come to terms with death, and for the materials scientist the death of their materials is still traumatic. They may feel let down, as the bereaved often do; they say that the material 'failed'. And so they battle against entropy, struggling to achieve permanence in a world where impermanence is one of the fundamental laws.

For artists and designers, however, their relationship with impermanence isn't what it used to be. Some of them embrace change and decay, as the artist Joanna Greenhill explained at a recent discussion meeting at London's Tate Modern gallery, convened to look at 'the art and science of impermanence'*. While painters, clothiers and sculptors once fretted over whether their pigments and dyes would fade or their metals corrode, now artists use materials that cannot possibly last long: milk, mud, snow and ice.

Artist Cornelia Parker goes further: she confessed that many of her works are concerned with "killing off the object", which she then 'resurrects' in another form. She explodes sheds, steamrollers silverware, throws teapots off cliffs – and then arranges the remains in a way that speaks of this process of change.

And as designer Chris Lefteri showed, the issue of decay in many commercial products has been sidestepped by the shrinking of product lifetimes due to the dictates of fashion and technological progress. Today products are discarded not when they are worn out but when they are obsolete: when we decide we need to upgrade. As a result, perfectly functioning items are sent to the landfill, unless they can somehow be recycled. "We have reached a point", Lefteri said, "where the unmaking of products is as important as the making of them."

One answer is of course to make the products biodegradable, and there are now some ingenious materials solutions to that – such as a water-soluble plastic used for food packaging, or artificial snow for movie sets made from starch. Lefteri pointed to how the cell phone company Nokia is using shape-memory alloys for the screws holding their phones together, which automatically unscrew when placed in hot water. This makes disassembly and recycling of materials much easier.

But to a designer like Lefteri, environmental consideration isn't the only factor raised by short product life cycles. We seem prone to forming an emotional attachment to even the most mundane objects if we possess them for long enough. It's understandable perhaps that we might grow to love our car, but we even feel fond of our favourite coffee mug. If ownership becomes so fleeting, how must the designer respond? Does design itself then risk becoming redundant?

All this is a long way from the traditional concern of the materials scientist to fight decay: to foil cracks, to prevent corrosion and fatigue and wear, like modern Canutes hoping to hold back the tide of change. As materials scientist Mark Miodownik pointed out, this isn't how nature copes with impermanence. Instead, it constantly renovates and replaces by reproduction. But that's difficult.

*Fugitive Materials, Tate Modern, London, 29 November 2005.

March 2006

Cold comforts

The use of ice formation to produce biomimetic microstructures in ceramic materials, reported by Sylvain Deville and colleagues at the Lawrence Berkeley National Laboratory in California (S. Deville *et al.*, *Science* **311**, 515-518; 2006) is not only an ingenious use of spontaneous self-organization but a reminder of the potential value of ice to materials scientists.

Deville and colleagues show that the crystallization of ice platelets as water freezes, coupled with the expulsion of solute particles from the ice phase, can be exploited to create porous and lamellar structures toughened in the same way as natural hard materials such as nacre. The researchers froze concentrated suspensions of ceramic microparticles to produce layered ceramic/ice composites. The ice was subsequently removed by freeze drying, and the space filled with a second phase such as epoxy resin or metal.

These composites are toughened by deflection of cracks due to delamination at the interfaces. Applying this technique to a slurry of hydroxyapatite powder generated a material four times stronger than conventional porous hydroxyapatite, which could act as a bone substitute.

Here ice is acting as a self-organizing, removable template. But it's tempting to speculate that the layered ice composite might itself have interesting mechanical properties. As well as ice determining the morphology of the suspended material, the reverse can be true. The most striking example of this was discovered in 1942 in an extensive and almost unique investigation of ice as a structural material.

This was Project Habbakuk, one of the most extraordinary examples of how war can fertilize technological creativity (L. W. Gold, *Interdiscipl. Sci. Rev.* **29**, 373-384; 2004). Habbukuk is often regarded now as a quixotic act of lunacy, but at the time it was supported by Winston Churchill and engaged leading scientists including J. D. Bernal and Max Perutz.

It was the brainchild of an eccentric scientific adviser to Britain's war office, named Geoffrey Pyke. He proposed that immense aircraft carriers might be constructed cheaply from ice, which would be extremely resistant to explosives. This led to testing of the mechanics of ice beams in Canada in 1943, which laid the foundations for much of the current understanding of ice as a material (E. M. Schulson, *JOM* **51**, 21-27; 1999).

It's a curious substance – plastic and ductile at low strain rates (that's why glaciers flow) but brittle at higher rates. Tests of how the strength of ice could be enhanced by additives tried cardboard, clay and cloth, but the best material was wood pulp. This was partly a result of crack arrest in a manner similar to Deville's composites; but Bernal pointed out that it could also be due to changes in the grain shape and size of ice, an effect known in metals. The composite was named Pykrete.

Project Habbukuk came to nothing; but the construction of oil rigs on ice platforms and of roads and airstrips on ice cover leaves ample reason to be interested in ice mechanics. Pykrete didn't win the war, but it deserves to be taken seriously.

April 2006

Sonic sense

In ancient China, one of the most acoustically sensitive of world cultures, materials such as metal, wood and stone were classified by what they sounded like. The Chinese recognized that metal creates a very different sound from wood, just as the timbres of the brass and woodwind sections in today's orchestras fulfil very specific roles in painting images with sound.

But the acoustic fingerprints of materials remain underexplored. It is straightforward to measure the acoustic signals produced by, say, striking an object; but how this translates into a perception of timbre and then into an interpretation of the source is poorly understood. A listener's ability to distinguish the same pitch played on a trumpet and a clarinet obviously has something to do with both the harmonic content of the sound and its time variation. Yet our acoustic 'material sense' seems to be considerably more fine-tuned than that.

For instance, people have been shown to estimate accurately the elasticity of bouncing balls merely by hearing the sound of a single bounce. Some sounds with extremely complex time–frequency signals are experienced as single, clearly identifiable events, such as the smashing of glass. There seem to be particular acoustic signatures of 'glassness' and 'wood-ness' that create a perceptual link between very different sounds.

At the same time, our auditory sense of material can be fooled by context. Movie makers rely on this, which is why we wince at the sound of a cabbage being split in half when in a movie it accompanies an image of bones breaking. It's an example of so-called Foley sound, named after the 1950s pioneer of film sound Jack Foley, in which sounds made artificially by simple mechanical means 'stand in' for those associated with images in the film. Footsteps, rustling, jangling keys and creaking doors are reproduced live in a studio by 'Foley artists' as they watch the footage on a screen.

Clearly, the sound of jangling keys can be made by metal objects that are not real keys, but not by plastic ones. What are the limits of this mimicry? Bruno Giordano and Stephen McAdams have recently tried to map out the boundaries of our acoustic identification of materials by measuring the ability of a group of listeners to recognize sheets of plastic (plexiglass), steel, glass and wood from the sound when sheets of different sizes are struck (*J. Acoust. Soc. Am.* **119**, 1171–1181; 2006). Steel and glass could readily be distinguished from wood and plastic, but it was harder to differentiate within each pair.

Giordano and McAdams suggest that our recognition is based not so much on pure acoustic differences but on environmental 'training': for example, we tend to hear impacts on smaller objects of glass (such as tumblers) than of metal (pots and pans), and for thicker objects of wood than of plastic. This learning generally serves us well, but it means we can be fooled by sound when the material sources come in unfamiliar shapes and sizes.

July 2006

Platinum sales

We all know that platinum is a precious metal, but paying close to \$3 million for a few grams of it seems excessive. Yet a private art collector has done just that. The high price stems from how the metal is arranged: as tiny black particles scattered on gummed paper, portraying an image of the moon rising over a pond on Long Island in 1904. This is, in other words, a photograph, defined in platinum rather than silver. It was taken by the American photographer Edward Steichen, and in February it sold at Sotheby's of New York for \$2,928,000 — a record-breaking figure for a photo.

At the same sale, a photo of Georgia O'Keeffe's hands recorded in a palladium print by Alfred Stieglitz in 1918 went for nearly \$1.5 million (*Platinum Met. Rev.* **50**, 78; 2006). Evidently these platinum-group images have become collector's items.

The platinotype process was developed (excuse the pun) in the nineteenth century to address some of the shortcomings of silver prints. In particular, although silver salts have the high photosensitivity needed to record an image 'instantly', the metal fades to brown over time because of its conversion to sulphide by reaction with atmospheric sulphur gases. That frustrated John Herschel, one of the early pioneers of photography, who confessed in 1839 that "I was on the point of abandoning the use of silver in the enquiry altogether and having recourse to Gold or Platina".

Herschel did go on to create a kind of gold photography, called chrysotype. But it wasn't until the 1870s that a reliable method for making platinum prints was devised. The technique was created by the Englishman William Willis, and it became the preferred method for high-quality photography for 30 years. A solution of iron oxalate and chloroplatinate was spread onto a sheet coated with gum arabic or starch and exposed to light through the photographic negative. As the platinum was photochemically reduced to the finely divided metal, the image appeared in a velvety black that, because of platinum's inertness, did not fade or discolour. "The tones of the pictures thus produced are most excellent, and the latter possess a charm and brilliancy we have never seen in a silver print", said the *British Journal of Photography* approvingly.

To enrich his moonlit scene, Steichen added a chromium salt to the mix. This was trapped in the gum as a greenish pigment, giving a tinted, painterly image evoking night scenes painted by James McNeill Whistler. Steichen and Stieglitz helped to secure the status of photography as a serious art form in the USA.

Stieglitz's use of palladium rather than platinum in 1918 marks the demise of the platinotype. The metal was used as a catalyst in manufacturing high explosives in World War I, so it could not be spared for so frivolous a pursuit: making shells took precedence over making art.

October 2006

Diamond dreams

When Robert Hazen, geoscientist at the Carnegie Institution of Washington, called his 1993 book on high-pressure research The New Alchemists, it was tempting to see this as yet another flippant use of 'alchemy' to describe any transformation of matter. But Hazen's evocation of alchemy in a story of the high-pressure synthesis of diamond at the General Electric laboratories in the 1950s could hardly be more apt.

For making artificial diamond is the contemporary equivalent of the alchemical quest for gold — and so diamond synthesis has a resonance that goes far beyond its practical utility. It provides an illustration of how seemingly innocuous research can take on an unguessed significance when embedded in a broader cultural context.

Joachim Schummer (Technical University, Darmstadt) has explored the links between diamond-making, alchemy and the public image of the scientist in an analysis of the 19thcentury literary roots of the 'mad scientist' archetype (*Ambix* **53**, 99–127; 2006). The much older image of the avaricious and swindling alchemist had come by then to represent the striving for material goods, and often the attendant atheistic materialism, that was condemned by Romantic writers. So it is perhaps not surprising that diamond, like gold a precious natural material, became another symbol of the chemist's bad intent.

The first literary caricature of this kind is the Faustian hero of *Der Komet oder Nikolaus Marggraf* (1820–1822) by the German writer Jean Paul. *The Diamond Maker* (1894) by H. G. Wells is, as one might expect, less wary of science in general but presents an amateur chemist whose obsession with creating diamond leads to only to poverty in the manner of the medieval mad alchemist.

Balzac's hubristic chemist in *La Recherche de L'Absolu* (1834) also exclaims to his wife that 'I shall make diamonds, I shall be a co-worker with Nature!'— whereupon she scolds him for his pride. These writers often drew on contemporary chemistry to justify the plausibility of their tales — Lavoisier and Smithson Tennant had shown at the end of the eighteenth century that diamond was nothing but pure carbon. By the 1850s, there were several claims that it had been synthesized (Wells mentions that of Henri Moissan in the 1890s).

In due course diamond-making was seen as a regular capitalist pursuit. Karl Marx used it to show how rare materials become fetish objects, divorced from any true measure of value. If with minimal labour we could convert carbon to diamond, he said, 'their value might fall below that of bricks.' Olaf Nissen's 1940s Allied propaganda pamphlet *Germany: Land of Substitutes* accuses the Nazis of producing all manner of fake materials, including gems.

These tales leave their traces in broader culture. They would certainly help to explain why one critic of the GE high-pressure process, announced in 1955, objected that 'You can't make diamonds for they are nature grown.'

January 2007

Virtuosi's choice

As some of the most discriminating materials consumers, musicians have a reputation for conservatism that verges on superstition. The materials scientists who labour to provide instrument-makers with an alternative to a rare traditional material, such as pernambuco — the material of choice for violin bows until the source tree, *Guilandia echinata*, became an endangered species — can expect scant thanks. Try as they might to point out that a carbon-fibre composite bow has superior mechanical properties (and less chance of shearing off at the head), the violinist is sure to insist that it just doesn't 'play' as well.

This acute sensitivity, if not subjectivity, towards musical materials raises the question of how far their selection can be quantified, for example with the materials selection charts pioneered by Mike Ashby at Cambridge University. That is the subtext of a survey of woods used in musical instruments by Ashby's former student Ulrike Wegst, now at the Max Planck Institute for Metals Research in Stuttgart (*Am. J. Bot.* **93**, 1439–1448; 2006).

Materials selection charts are two-dimensional spaces in which the coordinates are two properties – density and Young's modulus, say. Each material has a specific location on this plane. Materials applications often demand a compromise between at least two such quantities, in which case the candidates are those that fall within the appropriate elliptical field on the map.

Wegst shows how the acoustical properties that determine a wood's suitability for a type of instrument – a xylophone bar, say, or a violin's soundboard or a clarinet body – can be classified according to just a few parameters, such as the speed of sound, the density, and the loss coefficient that describes damping.

There are other considerations too, however. Fine-grained woods allow a smooth finish that improves tonal quality and permits accurate cutting. Woodwind instruments must resist significant swelling when exposed to moisture. The woods used in the moving parts of pianos must be tough and wear-resistant. The Darwinian environment of the musical marketplace has usually identified the most suitable materials without the benefit of accurate scientific testing.

Such trial and error has created traditions for which scientific justification, if it exists, remains elusive. The hammershanks — the sticks that hold the hammers — in the finest piano actions are subject to the most exacting selection. Generally made from birch, they are hand-tested for elasticity, then dropped onto a hard surface and classed, according to the sound of the impact, as dark, medium or bright. Different classes are used in different parts of the piano. The instrument-makers insist on the value of this labour-intensive method for sound quality, but we have to take their word for it.

Doubts about the availability of specialist woods — African blackwood, favoured for clarinets, is also endangered — are sometimes forcing acceptance of new materials. Carbon-fibre violin bows have overcome the initial reservations and are now welcomed for more forceful playing. But in other cases there may be a case for trying to understand apparent conservatism before dismissing it.

February 2007

Poison plastic?

Sir Richard Doll, the British epidemiologist who linked smoking with lung cancer, has recently been accused of holding undisclosed contracts with various companies and industries while assessing the safety of their products. The insinuation that this compromised the integrity of his research has been disputed, and certainly it's not clear that Doll, who died in 2005, can be judged by today's standards on conflicts of interest. Quite aside from questions of conduct, however, the affair raises the vexed issue of the toxicology of polyvinyl chloride, arguably the most environmentally controversial polymer in widespread use.

PVC is now ubiquitous. The second most widely used plastic, it is found in everything from house plumbing to biomedical equipment, clothing, and 'vinyl' gramophone records. But the plastic has been under threat ever since it was found in 1972 that its constituent monomer, vinyl chloride, may cause liver cancer.

Fear of regulation led the Chemical Manufacturers Association to commission a safety review of PVC from Doll in the mid-1980s. In 1988 he concluded that there was no evidence that vinyl chloride causes other cancers. Doll's report is still cited today in support of the safety of manufacturing vinyl chloride.

Yet PVC has become a battleground. In 1982 several chemicals companies set up the Vinyl Institute to defend its reputation, while Greenpeace has called PVC the 'poison plastic' and campaigns for its phase-out. It says that both the production and incineration of PVC produce dioxins, which are toxic carcinogens. PVC waste has been implicated in dioxin release from landfills.

That's a criticism not of the plastic itself but the way it is made and disposed of. But products made from PVC have also been attacked because of the plasticizing additives, particularly phthalates, which are again thought to be potential carcinogens. Concerns that these may leach out when children chew soft toys made from PVC led the European Union to ban some such plasticizers from toys in 2006, while some toy companies have stopped using PVC voluntarily. (My child's bath-friendly book comes with the label 'PVC-free'.)

Yet these claims too are disputed. In 1998 the US Consumer Product Safety Commission said that the amount of phthalates that might leach from toys don't even come close to the danger level, and in 1999 the American Council on Science and Health declared vinyl toys safe.

These arguments are going to be resolved not by science but by the marketplace: mere suspicion of danger is now enough to put consumers off. It's surely this that has motivated companies such as Microsoft and Wal-Mart to phase out PVC from their products. 'PVC-free' labels, whether needed or not, send out a clear message that PVC is bad. No one could really call PVC green, and if there are better alternatives, maybe it is good to use them. Yet this seems to be another instance of society wanting to put

materials into boxes labelled 'good' and 'bad' rather than facing the full complexities of their manufacture and use

July 2007

Tendentious tilings

Quasicrystal enthusiasts may have been baffled by a rather cryptic spate of comments and clarifications following in the wake of a recent article claiming that medieval Islamic artists had the tools needed to construct quasicrystalline patterns. That suggestion was made by Peter Lu at Harvard University and Paul Steinhardt at Princeton (*Science* **315**, 1106–1110; 2007). But in a news article in the same issue, staff writer John Bohannon explained that these claims had already caused controversy, being allegedly anticipated in the work of crystallographer Emil Makovicky at the University of Copenhagen (*Science* **315**, 1066; 2007).

The central thesis of Lu and Steinhardt is that Islamic artists used a series of tile shapes, which they call girih tiles, to construct their complex patterns. They can be used to make patterns of interlocking pentagons and decagons with the 'forbidden' symmetries characteristic of quasicrystalline metal alloys, in which these apparent symmetries, evident in diffraction patterns, are permitted by a lack of true periodicity.

Although nearly all of the designs evident on Islamic buildings of this time are periodic, Lu and Steinhardt found that those on a fifteenth-century shrine in modern-day Iran can be mapped almost perfectly onto another tiling scheme, devised by mathematician Roger Penrose, which does generate true quasicrystals.

But in 1992 Makovicky made a very similar claim for a different Islamic tomb dating from 1197. Some accused Lu and Steinhardt of citing Makovicky's work in a way that did not make this clear. The authors, meanwhile, admitted that they were unconvinced by Makovicky's analysis and didn't want to get into an argument about it.

The dispute has ruffled feathers. Science subsequently published a 'clarification' that irons out barely perceptible wrinkles in Bohannon's article, while Lu and Steinhardt attempted to calm the waters with a letter in which they 'gladly acknowledge' earlier work (*Science* **316**, 982; 2007). It remains to be seen whether that will do the trick, for Makovicky wasn't the only one upset by their paper. Design consultant Jay Bonner in Santa Fe has also made previous links between Islamic patterns and quasicrystals (see http://www.bonner-design.com/publications/self-similar.htm).

Most provocatively, Bonner discusses the late-fifteenth-century Topkapi architectural scroll that furnishes the key evidence for Lu and Steinhardt's girih scheme. Bonner points out how this scroll reveals explicitly the "underlying polygonal sub-grid" used to construct the pattern it depicts. He proposes that the artists commonly used such a polygonal matrix, composed of tile-like elements, and demonstrates how these can create aperiodic space-filling designs.

Bonner does not mention quasicrystals, and his use of terms such as self-similarity and even symmetry do not always fit easily with that of physicists and mathematicians. But there's no doubting that his work deepens the "can of worms" that Bohannon says Lu and Steinhardt have opened.

All this suggests that the satellite conference of the forthcoming European Crystallographic Meeting in Marrakech this August, entitled "The enchanting crystallography of Moroccan ornaments", might be more stormy than enchanting — for it includes back-to-back talks by Makovicky and Bonner.

November 2007

The materials of history

While it would be too much to say that the history of materials technology has been largely an amateur pursuit of scientists, it hasn't enjoyed much support from professional historians. Yet the sophistication of some of the field's pioneers, despite lacking any formal grounding in the study of history, is remarkable.

Take the English metallurgist Cyril Stanley Smith, who worked on fissionable metals for the Manhattan Project before making reconstructions of ancient metallurgical techniques and translations of historical crafts manuscripts. With a fluent command of Latin, Smith was a member of both the humanities and metallurgy departments at MIT, and his translation, with John Hawthorne, of the treatise *On Divers Arts* by the twelfth-century Benedictine monk Theophilus remains a central reference on medieval craft methods. (Smith benefited perhaps from marriage to an eminent historian of science, Alice Kimball Smith.)

Then there is Trevor Williams, a chemist at the British chemicals company ICI, who was managing editor of the magisterial five-volume *History of Technology* in the 1950s. And the pre-eminent historian of chemistry in the twentieth century, James Partington, was a chemist who worked for a time with Walther Nernst.

That the history of materials culture has tended to rely on scientists rather than historians obviously has its pitfalls, for not all such enthusiasts acquire the historical *nous* of a Smith or a Partington. As archaeologist Marcos Martinón-Torres of University College London points out in a recent collection of papers on early modern chemistry (*Chymists and Chymistry*, ed. L. M. Principe, Science History Publications, 2007), "Many of the pioneer historians of alchemy and chemistry were chemists with an interest in the past. Most conducted outstanding work but, due to a lack of education as professional historians, sometimes committed oversights or anachronisms."

But Martinón-Torres goes on to say that today the tables are being turned: the study of chemical and materials history tends to focus on texts while "ignoring the fundamentals of chemistry and materials science." Martinón-Torres' own work illustrates what we risk losing with such neglect – his scientific analysis of the renowned crucibles of Hesse used by chemists in early modern Europe shows that they were made from mullerite, a refractory aluminium silicate that was not formally discovered until the twentieth century (M. Martinón-Torres *et al., Nature* 444, 437; 2006).

A disjuncture between historians working from text and image, and scientists and archaeologists using quantitative analytical methods, is no recent complaint – in the 1980s the art historian Jan van der Meulen criticized studies of Gothic buildings for their indifference to the physical evidence. But why does this happen? It's tempting to blame the notorious fear of science in humanities departments, and there is probably some truth in that. But the wider reason is perhaps that an interest in 'materials culture', and a recognition that technologies are not only powerful forces of social and political change

but also shapers of art, literature and philosophy, have not yet reached as far as they might.

February 2008

Greatest hits

Everyone loves lists. Or rather, some love them and others love to hate them, condemning them as invidious, unduly competitive or plain meaningless. But it's hard to deny one thing in their favour: a list is guaranteed to excite debate about what is valued in the topic it tabulates. That, it seems, was what induced the magazine *Materials Today* (11(1-2), 40-45; 2008) to draw up the 'top ten advances in materials science over the last 50 years'.

Being informed by the magazine's editorial advisory panel and 'leaders in the field', the list doubtless has some formidable authority behind it. All the same, you might anticipate that I am going to pour scorn on it. Not at all – it's a very attractive selection, which runs (briefly) as follows: the International Technology Roadmap for Semiconductors, scanning probe microscopes, giant magnetoresistance, semiconductor light sources, the US National Nanotechnology Initiative, carbon-fibre reinforced plastics, lithium ion batteries, carbon nanotubes, soft lithography and metamaterials. The magazine's editor Jonathan Wood admits that some might be dumbfounded by the omission of organic electronics (yes) or high-temperature superconductors (no), but the list gives a nice sense of the scope of contemporary materials science.

And yet (here it comes)... Well, for one thing, like all such lists this one is biased towards the present. It's hard to justify such emphasis on nanotechnology (still unproven as a truly disruptive technology) at the expense of, say, biomedical materials. Many immensely important materials, such as Kevlar (which Wood also mentions), synthetic zeolites and vapour-deposited diamond, fall off the podium simply because they have become so pervasive or routine to produce.

But while a discussion of what's missing can be instructive, it's perhaps more revealing to consider the trends that the list brings to light. For example, with the possible exception of carbon nanotubes, carbon-fibre composites are the sole representative of structural materials (indeed, in this regard carbon nanotubes are only an elaboration of the same thing). The majority of the innovations here are concerned with ways of storing, sending, reading and manipulating data. It appears that the past five decades have seen materials science transformed from being about 'holding things together' to managing information flows. I'm not convinced that three decades ago one could consider that transition to have been made, which is again why the list seems a little amnesiac.

Another characteristic is how extraordinarily high-value-added these innovations are. I don't think I'm quite ready to demand a place for self-compacting concrete on the list, but it seems unlikely that such things were ever given a moment's thought when pitched against the dazzle of, say, metamaterials. One might say the same of PZT and cubic boron nitride. Along with high-pressure synthetic diamond, they fall right on the edge of the chosen time frame, but that in itself reminds us both how fertile the 1950s were for new materials and how different the priorities were then for those who sought them.

May 2008

Shrouded in mystery

Radiocarbon dating has revolutionized the study of archaeological specimens, but it remains something of an art. Fluctuations in the ¹⁴C content of the atmosphere over time make calibration against other dating techniques necessary, and the spectre of contamination with recent organic matter always hovers.

There is probably no single instance in which these inherent ambiguities in the technique's precision have been more widely advertised than its application to the Shroud of Turin in 1988. That investigation, described the following year (P. E. Damon *et al.*, *Nature* **337**, 611-615; 1989) famously revealed the shroud's linen to be of medieval origin, most probably early fourteenth century, suggesting that this celebrated relic of the Catholic Church is a fake and not the true burial shroud of Jesus.

Whatever the science might say, there is now a groundswell of dissent that is finding a voice in prominent media outlets. One objection is that the dating was distorted either by recent fungal growth on the material or by smoke or scorching from a fire in 1532 that is known to have damaged the shroud, burning holes that were later patched.

These issues were in fact addressed at the time of the initial report by one of the investigators, the late Teddy Hall of Oxford University (*Archaeometry* **31**, 92-95; 1989). Hall pointed out that if the linen was truly 2000 years old, it would have to be contaminated with as much as 40 percent of modern carbon to give the date measured. Moreover, the data did not vary between samples washed to different degrees. And tests on other samples of scorched cloth gave identical dates even after extreme damage.

Another view is that the small sample removed from the shroud for dating came from a section that had been repaired in the Middle Ages with an almost invisible weave. The claim is not entirely ad hoc – circumstantial and technical arguments can be advanced in its favour (R. N. Rogers, *Thermochim. Acta* 425, 189-194; 2005). It's certainly regrettable that only one small part of the shroud was studied.

Other critics challenge the radiocarbon study with historical evidence. Hall echoed the standard view that the shroud first appears in the records in 1353. But it is now claimed that an identical shroud is depicted in a late twelfth century manuscript from Hungary, and that an alleged burial shroud imprinted with the image of Christ can be traced at least to the sixth century.

It's fair to say that, despite the seemingly definitive tests in 1988, the status of the Shroud of Turin is murkier than ever. Not least, the nature of the image and how it was fixed on the cloth remain deeply puzzling. All of this calls for further testing, but that's unlikely to be permitted any time soon. Of course, the two attributes central to the shroud's alleged religious significance – that it wrapped the body of Jesus, and is of supernatural origin – are precisely those neither science nor history can ever prove.

July 2008

Materials match-making

In the ideal equilibrium market considered by traditional economics, supply always matches demand and products always find their way to the consumers who want them. This 'market-clearing' situation is often absent in the real world, but to judge from the discussion at a recent seminar*, the materials market is particularly prone to such inefficiency.

I don't mean whether the construction industry in China can satisfy its voracious appetite for cement and steel, but rather, whether a designer in Manhattan or Milan can find the material she needs for a theatre set or a new apartment. How do the people who want to use new materials on a modest scale even begin to survey the vast and daily-expanding array of choices to find the one that meets their needs?

At present this is a haphazard process. But designers, architects and others do not have to wander alone through the maze of new materials. There are people out there who can guide them. The UK has the Materials Knowledge Transfer Network (http://www.materialsktn.net), part of which, the Institute of Materials' Materials and Design Exchange (MADE; http://www.iom3.org/MADE/) specializes in matchmaking producers and consumers. And at the seminar, Margaret Pope discussed the challenges of running her London-based consultancy to identify and source materials for clients.

It's not easy to create these marriages. MADE's Sumeet Bellara explained that people unfamiliar with materials properties don't always know quite what they want. While a request for 'something squidgy' is enough to make a start, this may not be an exhaustive or even prioritized description of what is really required – the material might also need to be tough and odourless, say. And Bellara said that some requests for problem-solving materials turn out to be motivated by factors that no material will solve.

Often the best way for consumers to get literally to grips with what is on offer is to have direct, experiential contact with materials – not just to address existing problems but to find new ideas. The Materials Research Group at King's College London maintains a materials library that provides 'a intellectual and sensual intersection between the arts and sciences' – a place where anyone can experience the astonishing fabrics now available, from aerogel to thermochromic bricks.

Yet the qualities, and thus the design potential, of a material may depend not only on bulk quantifiers of performance, but on, say, size and shape. Can one judge the architectural impact of a fabric from a postcard-sized swatch? This is a difficult issue for materials librarians.

Satisfying consumers' demands is only half the problem. Pope said that manufacturers are often conservative, wary of supplying a material for uses different from that for which it was originally conceived. 'Oh, we don't work with designers' is a common response. Overcoming this resistance may require a lot of face-to-face persuasion and reassurance, Pope explained. It's not surprising, then, that new materials are probably only finding a fraction of their potential applications.

*'New Materials, New Technologies: Innovation, Future and Society', Kings College London seminar series, 12 May 2008.

September 2008

Old gold

In 1896 the Louvre museum declared that it had bought an ancient Greek gold tiara for 200,000 French francs – roughly €1.3 million today, but considered a bargain in view of the object's antiquity. It had allegedly been given to the Scythian king Saïtapharnes around the end of the third century BC as part of a bribe to leave the Greek colony of Olbia unmolested.

But almost immediately doubts surfaced, as experts questioned both the tiara's design and its apparent lack of ageing. The Louvre defended the item's authenticity, but then one day a Russian goldsmith named Israel Rouchomovsky came knocking at the door with an incredible claim. I made the tiara, he said. He explained that two dealers had commissioned him to make a gift in the antique style for an archaeologist friend. Now news had reached Rouchomovsky of their true intent. When the goldsmith demonstrated that he could reproduce part of the tiara, the Louvre officials had no choice but to believe him. They quietly consigned the gold object to their vaults.

Were it not beyond the capabilities of fin-de-siècle science, a new technique for spotting forgeries of ancient gold objects would have saved the Louvre its embarrassment. Otto Eugster and his coworkers at the University of Bern in Switzerland say that radioisotope dating can be used to estimate the last time that gold was melted down (O. Eugster *et al.*, *Archaeometry* doi:10.1111/j.1475-4754.2008.00426.x).

Forgeries of gold artefacts are probably the most difficult to detect of all fakes. Aside from stylistic grounds, the more objective criterion of patination is unreliable because gold's noble character leaves signs of surface decay tenuous and easily removed by cleaning. And gold has no intrinsic isotopic signatures of age, because it has only one stable isotope.

Eugster and his coworkers have for over a decade been studying the signatures of radioactive trace elements such as uranium and thorium that get incorporated into gold in the Earth's crust. Alpha decay of these elements leads to the accumulation of helium-4 in the metal. So measurements of U, Th and ⁴He in gold can reveal when it was last solidified, since radiogenic helium is expelled on melting.

The researchers proposed in 1996 that this approach could be used to date ancient gold artefacts, but only now do they have the instrumentation needed to put the idea into practice. It demands an ability to detect extremely small amounts of ⁴He, both because it will have accumulated for only a relatively short time compared with geological samples and because such analyses, being destructive, must be based on very small amounts of material.

The Bern group has now used their dating method on a variety of historical gold items, ranging from gold bowls of the first or second centuries BC from Central Asia to a French gold coin minted in 1857. Although at present the method doesn't constrain the dates very tightly, the researchers found that all the ancient objects were made more than 350 years ago, while the French coin is of more recent provenance.

November 2008

A twisted tale

What do the crystal structure of strontium disilicide, liquid crystals used for electrooptics, and the wings of the Green Hairstreak butterfly have in common? All can be mathematically described with reference to a three-dimensional network structure known as srs, as Stephen Hyde and his colleagues explain in a recent paper (*Angew. Chem. Int. Ed.* doi:10.1002/anie.200801519; 2008).

The apparent unlikelihood of these connections between very different kinds of materials structured at scales ranging over at least three orders of magnitude is part of the point Hyde *et al.* seek to make. For the history of the srs structure is as tortuous as the system of interwoven passageways it can be used to describe, illustrating how understanding in one discipline could profit others if only their practitioners could find ways to talk to one another.

For crystallographers, srs is an old story: it was they, after all, who labelled the network after the strontium compound. The pioneer of crystal chemistry Alexander Frank Wells noted it in 1954, but the crystallographers Fritz Laves and Heinrich Heesch identified it 21 years previously while studying the packing of spheres. The structure, sometimes called a Laves net, is easier to look at than to describe: a periodic arrangement of linked vertices, its framework corkscrews through space, exhibiting fourfold symmetry along some axes and threefold along others. This twist makes the structure chiral, and the net of opposite chirality can be perfectly interwoven with it, as Wells recognized.

That's where the next element of the story enters. In the 1960s, NASA physicist Alan Schoen discovered a labyrinthine, curved surface that divides space into two interconnected systems of channels, whose centres turn out to correspond exactly to the entwined srs nets. Scohen's surface is a so-called periodic minimal surface, which everywhere has zero mean curvature, and is known as the gyroid or G surface. And at much the same time Vittorio Luzzati, a crystallographer working at the Centre for Molecular Genetics in France found that surfactants form ordered sponge-like phases whose structures could be rationalized with the srs net, and which in fact correspond to membranes with the gyroid structure.

Then in the 1980s, Kåre Larsson and coworkers in Sweden made this connection explicit, and went on to identify gyroid phases in the membranes of some living cells. Meanwhile, Charles Kresge and colleagues at Mobil Research in Princeton discovered that self-assembling surfactant mesostructures can be used to template ordered porous forms of silica, one of which, called MCM-48, has the gyroid structure. Block copolymers can organize themselves this way too.

Thus, crystallographers, biophysicists, chemists and materials scientists gradually revealed a remarkable natural pattern that mathematicians seem curiously to have overlooked. And Doekele Stavenga and Kristel Michielsen have recently shown that hardened cuticle structures in some butterfly wings, probably also templated by soft membranes, are based on the gyroid structure, which here may produce optical interference effects responsible for wing coloration (*J. R. Soc. Interface* **5**, 85-94; 2008). Nature always seems to get the last word.

February 2009

What's philosophy got to do with it?

'Should engineers think?' That question, at first glance mildly insulting to the profession, crops up early in a recent volume of *Interdisciplinary Science Reviews* devoted to 'Philosophy and Engineering' (**33(3)**, 2008). But as Natasha McCarthy of the UK's Royal Academy of Engineering points out in her editorial introduction, 'The stereotype tells us that engineers are 'doers' and not 'thinkers'.'

Leaving aside the flaws in the notion of sharp boundaries between scientists (the 'thinkers') and engineers, the message is clear: engineers have a job to do, and 'philosophy' is rarely seen as relevant to it. But beyond thinking about the technical aspects of the task, should engineers consider matters of cost, safety, risk, environmental, social, ethical and aesthetic impacts? If they don't, should this be seen as a form of engineering failure?

Of course, few engineering jobs don't explicitly embrace some of these concerns. Many materials, for example, are developed specifically to improve safety or to reduce harm to the environment. But even then, the issues are not always straightforward. A biodegradable product can't be assumed to be 'greener' without a life-cycle analysis that might lie beyond the expertise of the product designers. No one foresaw, or could be expected to foresee, or even now agrees on, the social impact of automobiles, computers and mobile phones.

But truly to engage with some of these matters, or even to make seemingly routine assessments of risk and safety, might require that engineers acknowledge a genuinely philosophical dimension of the profession, particularly in the sphere of epistemology, or as McCarthy puts it, what we know and how we know what we know. Partly this is a question of how one obtains reliable information. But there has been increasing recognition that it also bears on what is knowable. Some complex engineered systems show emergent phenomena that can't be predicted, even in principle, from a knowledge of the components. Dealing with that challenge is considered here by W. P. S. Dias of the University of Moratuwa in Sri Lanka, and by Darryl Farber and colleagues at Pennsylvania State University. A related difficulty tackled by the latter group is how to meaningfully forecast performance in the face of incomplete knowledge about what the system will encounter.

Epistemology aside, much of engineering philosophy might be considered to encompass ethics. Here McCarthy takes a stance: an engineer cannot be expected to reflect on aspects beyond the call of duty, which basically means getting the job done efficiently, effectively and safely. Indeed, it might be dangerous to do so without the necessary expertise. But that, she says, doesn't absolve engineers of moral obligations – for they have a duty to ensure that such broader issues have been given due thought by others suitably qualified.

This sound principle might quickly become a minefield in practice. How can engineers assure themselves that this process has been carried out, and done well? How is the

obligation enforced? (Clearly, it isn't.) In this and other ways, this volume is just the start of the discussion.

July 2009

Dream on

One of the notable but seldom noted features of late-twentieth century science is its willingness to extrapolate beyond the lab bench. The work of Maxwell, Rayleigh, Kelvin and the Braggs, say, was firmly focused on problems of the here-and-now, characterizing and explaining the world as we find it. Even in the synthetic sciences such as chemistry and metallurgy, the rudimentary understanding of basic principles meant that new materials were either minor variations of existing ones or discovered by serendipity. And the thought experiments of early quantum theory were envisaged not as blueprints for real experiments (although some became that) but as heuristic devices used to explore and challenge interpretations of the quantum-mechanical formalism.

Now, in contrast, it is routine for molecules and materials with dramatic new properties to be designed and tested purely in the virtual realm, with barely a thought for whether they could actually be made. The ultimate examples of these leaps of imagination are found in fundamental physics, with its explorations of ultra-small or higher-dimensional spaces that lie far beyond current empiricism. Sceptics dismiss some of those speculations as mere metaphysics.

The purely theoretical imagining of new substances has also been criticized as unproductive. At its best, however, these sojourns into fantasy might challenge preconceptions about what is and isn't permitted by physical law, as well as casting an existing field in a new light. The trick is to balance boldness of vision against sheer unattainability – a tightrope that physicist Michio Kaku tries to walk in his recent book *Physics of the Impossible* (Allen Lane, 2008).

A preprint by Che Ting Chan and colleagues at the Hong Kong University of Science and Technology arguably falls more towards the stimulating than the far-fetched end of this scale (http://www.arxiv.org/abs/0905.1484). It suggests that the invisibility cloaks that have captured much of the general interest in the field of optical metamaterials are just one manifestation of a more general topic, which the researchers call illusion optics. The paper demonstrates how, in principle, metamaterial 'cloaks' might be devised that allow any given object to take on the appearance of any other arbitrary object.

Invisibility shields are not exactly the same sort of illusion: they involve the bending and reshaping of light-ray trajectories, whereas the proposed illusion devices first cancel out the 'optical space' of the first object and then build up that of the disguise from scratch. This generalizes earlier work by Chan and colleagues on 'anti-cloak' shields (Y. Lai *et al., Phys. Rev. Lett.* **102**, 093901 (2009)).

In some ways the demands on the metamaterial are not so great – much of the cancelling medium is a homogeneous negative-refractive-index material, for instance. Needless to say, full implementation of the idea is still well beyond current means, although relatively simpler examples such as virtual tips for near-field optical microscopy could perhaps be entertained. And like all good what-if proposals, this one offers at least one mind-

boggling possibility: using a slab of material to open up a virtual hole in a wall and allow us to look through it.

August 2009

Cross purposes

Some stories of serendipitous discovery have the non-sequitur character of myth. People routinely recount the tale of the optical polarizer herapathite thus: a student of the Bristol toxicologist William Herapath dropped iodine into the urine of a dog fed on quinine, and precipitated green crystals that Herapath studied under the microscope. Noticing that the translucent, needle-like crystals were sometimes dark where they overlapped, Herapath realised that this was a polarizing medium. Not the first, for the silicate mineral tournaline was already used in that respect. But tournaline was rare and expensive, and that at a time when polarization effects had become central to optics.

But why was a dog being fed on quinine, and why collect its urine? Even in the midnineteenth century this seems an odd thing to do. Of course, quinine was then an important anti-malarial drug, but that hardly solves the mystery. In any event, this story is usually drawn from the account of Edwin Land, the pioneer of Polaroid photography, who made herapathite famous in the polarizing filters of his new technology. Land came across herapathite in an account of the kaleidoscope by its inventor David Brewster, who hoped to use Herapath's material in the eyepiece to make kaleidoscopic images from interference colours.

The problem with such applications was that it was tough to grow large crystals. Land took a different route, making a viscous colloidal dispersion of small needle crystals which he aligned in plastic sheets by squeezing the liquid through narrow slits. Land's initial motivation was not photography but anti-glare films for vehicle headlights. In the Second World War this application, which was never adopted for cars, improved the visibility of enemy vessels at sea by cutting out polarized reflections of sunlight on water.

It was a wartime shortage of quinine that put paid to herapathite filters. Supplies of quinine extracted from *Cinchona* trees in the Dutch East Indies were cut off, and the limited quinine available was needed as an antimalarial for troops fighting in the tropics. This forced Land to develop new filters based on aligned polyvinyl alcohol dyed with iodine. It was also what prompted his Polaroid Corporation in Cambridge, Massachusetts, to hire the dazzling young Harvard chemist Robert Woodward as a consultant, stimulating him to synthesize quinine with William von Eggers Doering in 1944.

Although herapathite did not at once fall wholly out of use, its diminished importance perhaps explains why its crystal structure has never been deduced – until now. This meant that its polarizing properties have not been fully understood. Bart Kahr and colleagues at the University of Washington in Seattle have now solved this rather complex structure (*Science* **324**, 1407 (2009)). It is lamellar, with the quinine molecules complexed to triiodine ions linked into extended chains. Delocalized excitons on these chains lie at the root of the light-absorbing properties. So herapathite now joins an illustrious list of historically important materials, including Prussian blue and Mayan blue, understood only by the grace of modern crystallography.

November 2009

Shaking hands with robots

Should robots pretend to be human? The plots of many science fiction novels and movies – most famously, Philip K. Dick's *Do Androids Dream of Electric Sheep?*, filmed by Ridley Scott as *Blade Runner* – hinge on the consequences of that deception. *Blade Runner* opens with a 'replicant' undergoing the 'Voight-Kampff' test, in which physiological functions betray human-like emotional responses to a series of questions. This is a version of the test proposed by Alan Turing in a seminal 1950 paper pondering the question of whether machines can think¹.

But human-like thought (or its appearances) is only one aspect of the issue of robotic deception. There would be no need to test *Blade Runner*'s replicants if they had been made of gleaming chrome, or exhibited the jerky motions of a puppet or the stilted diction of an old-fashioned voice synthesizer. To seem truly human, a robot has to perform accurate mimesis on many (perhaps too many) fronts².

Today we might insist on a conceptual distinction between such mimicry and the real thing. But this was precisely what Turing set out to challenge in the realm of mind: if you can't make the distinction empirically, in what sense can you say it exists? And in former times, that applied also to the other characteristics of humanoid machines. In the Cartesian world of the eighteenth century, when many considered humans to be merely elaborate mechanisms, it was not clear that the intricate automata which entertained salon society by writing and playing music and games were rigidly demarcated from humanity. Descartes himself refuted any such boundary, implying that automata were in a limited sense alive. In his *Discourse on Method* (1637) he even proposed a primitive version of the Turing test, based on the ability to use language and adapt behaviour to circumstance.

One of the most famous automata of that age was a mechanical flute player made by the virtuoso French engineer Jacques de Vaucanson, who described it to wide acclaim in 1738. Not only did it sound right but its breathing mimicked human mechanics, and its right arm was upholstered with real skin³. This feat is brought to mind by a preprint by John-John Cabibihan at the National University of Singapore and colleagues, in which the mechanical properties of candidate 'robot skin' polymers (silicone and poyurethane) are tested for their likeness to human skin⁴. Can we make a robot hand *feel* human, the researchers ask? Not yet, at least with these materials, they conclude – in the process showing what a delicate task that is (a part of the feel of human skin, for example, comes from its hysteretic response to touch).

Underlying the research is the notion that people will be socially more at ease interacting with robots that seem 'believable' – we will feel queasy shaking hands if the touch is wrong. That's supported by experience⁵, but also in itself raises challenging questions about the proper limits of such illusion⁶. Arguably there are times when we should maintain an evident boundary between robot and person.

1. Turing, A. Mind 59, 433-460 (1950).

2. Negrotti, M. Naturoids (World Scientific, Singapore, 2002).

3. Stafford, B. M. Artful Science p.191-195 (MIT Press, Cambridge, Ma., 1994).

4. Cabibihan, J.-J., Pattofatto, S., Jomâa, M., Benallal, A. & Carrozza, M. C. Preprint http://www.arxiv.org/abs/0909.3559 (2009).

5. Fong, T., Nourbakhsh, I. & Dautenhahn, K. *Robotics Autonomous Syst.* **42**, 143-166 (2003).

6. Sharkey, N. Science 322, 1800-1801 (2008).

June 2010

Magnetic botany

According to Charles Darwin, attempts to explain the mathematical patterns of phyllotaxis – the arrangements of leaves or florets on a plant stem – could 'drive the sanest man mad.' That hasn't served as a deterrent, for these regular, helical patterns present an irresistible challenge. Their generic form is famously composed of two oppositely rotating clusters of spirals in groups whose sizes are equal to adjacent numbers in the Fibonacci series, inviting a geometric interpretation that pays scant heed to the biochemical details of plant growth. Indeed, the relationship of the leaf arrangements to point lattices on a cylinder was identified in 1837 by the pioneers of crystallographic symmetry August and Louis Bravais.

What is more, phyllotactic-like spiral patterns have been seen in a variety of non-living systems, ranging from the vortices of superconductors¹ to the self-assembly of inorganic microstructures², the buckling of thin sheets³, and the interaction of magnetic droplets floating on oil⁴. In all of these cases, the structures seem to result from mutual repulsion of the pattern elements, supporting the idea that in plants a new bud is apt to appear an optimal distance from the preceding one so that the arrangement corresponds to a form of optimal packing. Such an ordering can be generated by reaction-diffusion models⁵, perhaps instigated in plants by the diffusion of a growth hormone, as Alan Turing suspected over 50 years ago⁶.

Last year, Vincent Crespi and coworkers presented a simple experimental system for studying the patterns generated by mutual repulsion of entities in cylindrical geometry. They constructed a 'magnetic cactus', composed of a stack of disks free to rotate on a central axis, to the edge of each of which are attached magnetic arms with like poles directed outwards⁷. The arms rotate to find a stable compromise position with respect to their neighbours. Crespi and colleagues saw a range of complex dynamical behaviours, such as the propagation of topological soliton-like disturbances along the lattice.

Phyllotactic-like arrangements are certainly achieved in this system, but it was not clear that these are genuine minimal-energy ground states, as earlier models of the spiral ordering have tended to assume¹. Crespi and colleagues have now found an experimental procedure to magnetically anneal their 'cactus' so that a true ground state can be attained from a disordered initial state⁸. This involves creating small random fluctuations using an external magnet and mechanical vibrations, and continuing the process until the orientation of the arms attains a stable state. They also simulated annealing with a genetic algorithm. And the researchers extended their study to the case of two arms on opposite sides of each disk – a situation known in botany as whorled phyllotaxis.

In all cases, the resulting arrangements correspond to the phyllotaxis seen in botanical specimens. Sometimes domains of different structure form along the axis, which share one type of spiral form at the boundary. This establishes Fibonacci phyllotaxis as a generic energy-minimum state of repulsive interactions in cylindrical geometry.

- 1. Levitov, L. S. Phys. Rev. Lett. 66, 224-227 (1991).
- 2. Li, C., Zhang, X. & Cao, Z. Science 309, 909-911 (2005).
- 3. Shipman, P. & Newell, A. C. Phys. Rev. Lett. 92, 168102 (2004).
- 4. Douady, S. & Couder, Y. Phys. Rev. Lett. 68, 2098-2101 (1992).
- 5. Koch, A. J. & Meinhardt, H. Rev. Mod. Phys. 66, 1481-1507 (1994).

6. Turing, A. M., in *Morphogenesis: Collected Works of A. M. Turing*, Vol. 3, ed. P. T. Saunders (North-Holland, 1992).

- 7. C. Nisoli et al., Phys. Rev. Lett. 102, 186103 (2009).
- 8. C. Nisoli et al., Phys. Rev. E 81, 046107 (2010).

January 2011

Trouble on the Silk Road

No one really knows how China (the Middle Kingdom, *Zhongguo*) came to be so-called in the West, although there is no shortage of theories: perhaps it is from *Qin*, the first dynasty of Imperial China, or maybe from *Cin*, the Persian word for the region. But Ji-Huan He of the Modern Textile Institute in Shanghai argues for another derivation: beginning with *si*, the Chinese word for silk, we get 'Sino', then 'Cina' and finally 'China'.¹

That etymology is significant because, for He, it links China's national identity with its claim to be the cradle of sericulture, the production of silk. That of course is the traditional picture; after all, the Silk Road commences at the ancient Chinese capital of Xi'an. The science and technology of silk manufacture is still afforded dedicated research institutes in China, where surely more is known about this ancient craft than anywhere else in the world. So it is not surprising that a recent suggestion by Irene Good of the Peabody Museum at Harvard and her colleagues that silk production might have begun independently in the Harappan culture of the Indus Valley (now in east Pakistan) has been greeted with some dismay in China. Good and colleagues identified the Harappan silks in an archaeological project conducted in 1999-2000 via a US-Pakistan collaboration².

The claim is challenged by He, who says that the Harappan silk fragments dated by Good *et al.* to the mid-third millennium BC far postdate evidence for Chinese sericulture from around 5000 BC¹. But that evidence is partly circumstantial: it comes from engraved drawings on ivory that have been interpreted, but hardly conclusively, as silkworms. Some samples of silk have been found in the Yangtse delta in Zhejiang province in association with a bamboo basket dated to 3500-2700 BC, but Good *et al.*³ say that the presence of items (such as peanuts) that must stem from a much later period raise questions about the silk's age. Silk from Qingtai in Henan province is associated with cultural artefacts from 4000-3500 BC, but the textile itself lacks a radiocarbon date. So Good and colleagues argue that there are no clear examples of Chinese silk before around 2500 BC.

The debate doesn't just rest with the archaeological evidence. Good *et al.* also pointed out that, on the basis of microscopic morphology of the threads, their samples of early Harappan silk were made from the silk of wild silkmoths indigenous to southeast Asia, not the domesticated silkworm *Bombyx mori* used in China¹. They now point out that nothing in their findings threatens the notion that the domestication of silkworms first happened solely in China. Domesticated silk does not start to appear outside China until around two millennia ago.

It's unlikely that this is the end of the story. Ji-Huan He may of course be right that sericulture had a unique origin in China. But because definitive proof of that is likely to be very hard to come by, it seems risky to develop too much emotional attachment to the idea.

1. He, J.-H. *Archaeometry* advance online publication doi: 10.1111/j.1475-4754.2010.00550.x (2010).

2. Good, I. L., Kenoyer, J. M. & Meadows, R. H. Archaeometry 51, 475-466 (2009).

3. Good, I. L., Kenoyer, J. M. & Meadows, R. H. Archaeometry (in press).

December 2011

A light compass?

The idea that the Vikings navigated across the Atlantic using birefringent Iceland spar (calcite) to locate the sun's position on cloudy days is surely one of the most ingenious and captivating recent hypotheses about ancient materials use. The suggestion itself is an old one¹, but has been given strong support in new experiments by Ropars *et al.*².

The claim, which has understandably enjoyed much media interest, has a lot going for it. References in Viking sagas to a 'sunstone' used in seafaring sound akin to magic, but there is now a good physical basis for thinking that Iceland spar – abundant in the Viking homelands, as the name implies – might be used in this way with sufficient accuracy.

A narrow beam of polarized light passing into the mineral is split into two by the optical anisotropy that causes birefringence. The 'ordinary' beam behaves as it would in glass; the 'extraordinary' beam is parallel but displaced from it, defying Snell's law. Light passing through a hole in a screen over a calcite crystal therefore forms two images on the far side. When the crystal is oriented to equalize their brightness, it has completely depolarized the light.

Sunlight acquires a slight polarization as it is scattered by the atmosphere. The researchers demonstrate how, with calibration on a clear day, the depolarization point at which the split images are equally bright could be used to locate a sun obscured by cloud from the light arriving from a patch of blue sky. They have constructed a wooden device containing a calcite crystal that could have been used by Viking sailors to pinpoint the sun even at twilight.

They say that this proposal is made all the more plausible by the recovery of a piece of Iceland spar from an Elizabethan ship wrecked off the coast of the Channel Island of Alderney in 1592³. It may have been carried as an alternative to the compass, they say, which was vulnerable to disturbance from the iron cannons.

The idea that birefringence of Iceland spar might have been used by navigators from the Dark Ages until at least Elizabethan times is, however, problematic. It is hard to see how this would have been common practice without it ever having been recorded or coming to the attention of natural philosophers. It is just the kind of trick Giambattista della Porta, a specialist in optics who conceived of the telescope before its invention, would have revelled in discussing in his 1558 book *Natural Magic*, had it been known. When Rasmus Bartholin wrote the first experimental account of birefringence in Iceland spar in 1669, he made no mention of such uses; neither did the eminently practical Christiaan Huygens when he offered the first explanation of birefringence 21 years later.

This is not to say that the hypothesis of Ropars *et al.* is wrong. Rather, it underscores the need for studies of historical materials usage to integrate the scientific arguments with careful consideration of historical sources and context.

1. Ramskou, T., Skalk 2, 16-17 (1967).

2. Ropars, G., Gorre, G., Le Floch, A., Enoch, J. & Lakshminarayanan, V. *Proc. R. Soc. A* http://rspa.royalsocietypublishing.org/content/early/2011/10/28/rs pa.2011.0369.full.html.

3. Bound, M. & Monaghan, J., *A ship cast away about Alderney: investigations of an Elizabethan shipwreck* (Alderney Maritime Trust, Alderney, 2001).

October 2012

Bringing crystals to life

Attempts to connect crystals to the life sciences have a long history, much of it tinged with mysticism. Kepler invoked a mysterious 'formative principle' to account for the vegetative intricacy of snowflakes; Newton attributed to something like organic growth the 'treelike' salt precipitates of silica gardens. In the mid-eighteenth century a Swedish mineralogist could write that "there are naturalists who maintain that minerals have a life like that which vegetation enjoys". The discovery of liquid crystals in the late nineteenth century was interpreted by Ernst Haeckel as the missing link between crystalline order and organic plasticity of form, and in some ways he was not wrong: liquid crystalline and other mesophases abound in living organisms, from the reflective pigmented stacks of animal 'structural colours' to the fibrous alignment of silk and the membranes that template complex biominerals.

Meanwhile, the connection between quasi-regular structures and the encoding of information was introduced with Schrödinger's famous invocation of an 'aperiodic crystal' as the material basis of genetics – an insight validated by the discovery of the structure of DNA. It is increasingly apparent that DNA in fact has a hierarchy of structural ordering in vivo, including liquid crystal phases, and that important information is encoded at higher levels than the primary sequence, for example in the condensed phases of chromatin. The possibility that inorganic crystals might enable the storage, transmission and mutation of 'genetic' information – for example in the stacking sequences clays – was introduced to prebiotic chemistry by Graham Cairns-Smith in the 1960s.

So it surprising in retrospect that a collection like that provided in a special issue of *Phil. Trans. Roy Soc. A* entitled "Beyond crystals: the dialectic of materials and information"¹ has not appeared sooner. It is in effect a Festschrift for Alan Mackay, who has thought perhaps more deeply than anyone else about the relationships between crystal structure, periodicity and information. Mackay predicted quasicrystals before their discovery in 1984, and in the introduction to his 1999 translation of Haeckel's book *Crystal Souls* he foreshadows some of the concepts in the present volume².

The *Phil. Trans.* collection, which Mackay coedits with Julyan Cartwright, shows that even the oldest themes remain relevant. 'Crystal gardens' like those that fascinated Newton remain imperfectly understood: the morphologies are varied and complex, and seem to involve the formation of membranes, compartments and chemical gradients that could indeed provide a bridge from the inorganic to the organic on the early Earth. Russell and coworkers consider whether iron sulphide chimneys at hydrothermal vents could have provided electron sources and catalytic structures that seeded the development of protein/nucleic acid biochemistry³.

The "materials/information dialectic" is perhaps most apparent today in supramolecular chemistry, described by Lehn as a science of 'informed matter'. Crystal engineering can be profitably regarded as the navigation of an energy landscape akin to that of protein folding⁴, with attendant possibilities for obtaining function from dynamical transitions

between metastable conformations⁵. And just as in biological structures the interaction of 'primary sequence' information with environment, self-assembly and defects can give rise to complex hierarchical structures and shapes such as multi-protein devices or biominerals such as nacre, so may similar considerations open opportunities at the nanoand mesoscales in synthetic materials⁶.

1. Cartwright, J. H. E. & Mackay, A. L. (eds) *Phil. Trans. R. Soc. A* **370**, 2805-3039 (2012).

2. Mackay, A. L., Forma 14(1&2) special issue, 11-29 (1999).

3. McGylnn, S. E., Kanik, I. & Russell, M. J. *Phil. Trans. R. Soc. A* **370**, 3007-3022 (2012).

4. Tothadi, S. & Desiraju, G. R. Phil. Trans. R. Soc. A 370, 2900-2915 (2012).

5. Wales, D. J. Phil. Trans. R. Soc. A 370, 2877-2899 (2012).

6. Cademartiri, L., Bishop, K. J. M., Snyder, P. W. & Ozin, G. A. *Phil. Trans. R. Soc. A* **370**, 2824-2847 (2012).

May 2013

A place for making

If you could make anything, what would it be? A materials scientist will probably come up with a long list rather easily, but most other people are likely to find themselves trapped between their imagination (which might exceed the creativity of many scientists) and their ignorance of what is possible and how it might be done. The Institute of Making (www.instituteofmaking.org.uk), which opened at University College London in March, hopes to offer a way to bridge that gap between ideas and means.

The principle is elegantly simple. Anyone at UCL (and hopefully soon a wider public) can pay a modest membership fee, which entitles them to come along to the institute – an old loading bay wedged between the Petrie Archaeological Museum and the Department of Engineering, now converted into a space both stylish and functional – and use the battery of fabrication equipment to make whatever they want. The institute houses, among other things, a state-of-the-art laser cutter, a 3D printer, and various milling, moulding, casting, calcining and cutting devices, along with some wet-chemical facilities and a cooker – for experimenting with food, not for making lunch (although a bar remains under discussion).

But as director Mark Miodownik realises, it is not enough – indeed, positively unwise – simply to make all this gear accessible to all comers. To turn an idea into a product, you need to understand the materials issues: to appreciate the virtues and limitations of different kinds of material, so as to select those that are best suited to the task in hand. This is the kind of issue on which Miodownik and the institute's creative director Zoe Laughlin regularly offered advice when they ran its previous incarnation, the Materials Library at King's College London. Much of that library – a collection of materials new and old, from pewter to aerogels and ferrofluids – is now housed in a mouth-watering display in the institute's entrance. There are no glass windows to protect the samples: visitors can pick them up and examine them, and if they desire, use them.

The Institute of Making will offer regular workshops and on-going instruction on the considerations that surround materials choices and use, from physical properties to aesthetics, ethical and environmental issues. This isn't merely a facility that allows people to make, but one that will teach people how to make.

That is really the institute's motivation: to disseminate the art and science of creating *things*. Miodownik imagines that some members will be researchers needing bespoke experimental equipment, but hopes that others will come from farther afield both geographically and intellectually: artists, musicians, textiles specialists – and, if all goes to plan, school children, for whom the Institute may offer a Saturday Club at which, under careful supervision, they can spend the day inventing and making. "It's OK if people just come in here and mend their bikes", Miodownik says.

It's not hard, on visiting the institute, to imagine every university principal saying "I want one too". But what the institute's team has understood is that this is about more than creating a gallery of tools. It is about crafting an environment that is approachable,

informative, safe (of course), unintimidating to non-scientists and most of all, inspirational.

February 2014

No substitute

Materials scientists are well accustomed to basing their materials choices on a careful balancing of performance criteria, for example trading off toughness, hardness and cost. It's less common to have to base those choices on geopolitical criteria. But such stark realities are not so unfamiliar, perhaps most notably in recent years in concerns about the Chinese near-monopoly on rare earth elements, and continuing fluctuations in the availability of tantalum for semiconductor electronics due to political instability in the Congo region. When abrupt materials shortages have occurred, substitutes have sometimes been found. The isolation of southeast Asian colonial rubber plantations during World War II prompted seminal work in Europe and the USA on synthetic rubber. And when civil war in Zaire in the 1970s impaired the supply of cobalt, an important component of magnets, cobalt-free designs were developed.

It might be tempting to suppose, then, that whenever shortages of materials components occur, alternatives will soon emerge. That would be complacent, according to a recent report by Graedel *et al.*¹ They have considered as many as possible of the major uses for 62 different metals and metalloids, and whether there are known alternatives that could substitute for them if supplies become scarce. In many cases there are, but for 12 of the elements considered, substitutes are currently either inadequate or non-existent. What's more, none of these elements have good replacements for all of their major uses.

Although scarcity of important materials is an ancient issue – one famous, though controversial, case was the British navy's wood shortage in the seventeenth and eighteenth centuries due to deforestation – it is rendered more critical today by several factors. The market for materials is more global, and so more susceptible to international affairs. And the complexity of materials usage has increased. In engineering alloys, for example, a steady enhancement of performance by an accumulation of ingredients means that the formulations of superalloys used for high-temperature applications may include a dozen or more elements. Environmental considerations now play a much bigger role in resource exploitation, even while the rapid growth of some emerging economies has increased the demand on non-renewable sources.

It's for such reasons that in 2006 the US National Research Council performed an audit of economically important materials, developing a framework for assessing their 'criticality' based on both the importance of their uses and the security of their sources². Several metals, including rhodium, manganese, platinum and niobium, were deemed by these criteria to be 'at risk'. Graedel *et al.* seek to extend that work, concurring for example with the assessment for the former two metals while offering more reassurance for the latter.

What are we to do? Simply recognizing the problem – and abandoning a naive faith in the ability of markets to produce substitutes – is a start. A systematic enumeration of the risks – which applications of 'at risk' materials would be hit first, for example? – would provide a framework for assigning priorities. But arguably this problem might compel a realignment of some of the materials community's research objectives: instead of

obsessing over improved performance, more attention might be given to maintaining current performance by other means.

1. Graedel, T., Harper, E. M., Nassar, N. T. & Reck, B. K. *Proc. Natl. Acad. Sci. USA* 10.1073/pnas.1312752110 (2013).

2. National Research Council, *Minerals, Critical Minerals, and the U.S. Economy* (National Academies Press, Washington, 2008).

July 2014

The clean air act

Most poets probably harbour a hope that their poems might change the world, but none has taken that wish quite as literally as Simon Armitage, whose "In Praise of Air" is the first 'catalytic poem'. Displayed on a 10m by 20m panel on the side of a university building overlooking a busy road in Sheffield's city centre, it is not just an ode to the vital joys of clean air but is actively producing that very stuff. The panel is coated with a layer of photocatalytic titanium dioxide nanoparticles which, when irradiated with sunlight (or indeed street lights), convert nitrogen oxides (NO_x) adsorbed on their surface to nitrate.

The project is a collaboration with Sheffield materials scientist Tony Ryan, and has been funded as part of the city's Lyric Festival of literature. As well as breaking down nitrogen oxides, the catalytic nanoparticles transform toxic volatile organic compounds into fatty acids. They are, of course, barely able to make a dent on the fumes from passing vehicles: each square metre of the display removes about 2g of NO_x a day, about as much as is produced by a single bus.

But of course the point is to make a difference in another way: to create a visible and arresting symbol of the need to tackle air pollution. Armitage's image of "days when thoughts are fuddled with smog/or civilization crosses the street/with a white handkerchief over its mouth" will be all too familiar with many urban dwellers, perhaps especially in China, where today cellphone apps tell users whether or not the PM10 index (the level of airborne particulate matter smaller than 10 micrometres across) is low enough for children to play safely outside.

That same objective motivates the technology from which this project arose: 'catalytic clothing', developed by Ryan with designer and artist Helen Storey, who specializes in art-science collaborations for fashion, design and technology. They have devised a process in which the titania nanoparticles can become attached to ordinary clothing fabric (so far cotton, but they are working on other fibres) during the laundering process, so that subsequently the wearer may combat air pollution simply by walking around. Ryan and Storey say that the effects are not insignificant: 30 people in catalytic clothing walking past a metre-width stretch of pavement every minute could effect a noticeable drop in levels of NO_x . The duo are still trying to bring the idea to the market.

"In Praise of Air" is also singing the praises of materials. The technology is nothing particularly new, but Ryan's work is a reminder that bringing a useful laboratory product to the attention of both investors and consumers is often a matter of engaging the imagination – and that this is where scientists can benefit from interactions with designers and artists. It shows too that serious problems can be tackled playfully and in ways that encourage the public to see that they can participate and not be merely the passive recipients of some cryptic and forbidding technology.

August 2014

Cutting-edge metallurgy

There can be few more mythologized ancient materials technologies than sword-making. The common view – that ancient metalsmiths had an extraordinary empirical grasp of how to manipulate alloy microstructure to make the finest-quality blades – contains a fair amount of truth. Perhaps the most remarkable example of this was discovered several years ago: the near-legendary Damascus blades used by Islamic warriors, which were flexible yet strong and hard enough to cleave the armour of Crusaders, contained carbon nanotubes¹. Formation of the nanotubes was apparently catalysed by impurities such as vanadium in the steel, and these nanostructures assisted the growth of cementite (Fe₃C) fibres that thread through the unusually high-carbon steel known as wootz, making it hard without paying the price of brittleness.

Yet it seems that the skill of the swordsmith wasn't directed purely at making swords mechanically superior. Thiele *et al.* report that the practice called pattern-welding, well established in swords from the second century AD to the early medieval period, was primarily used for decorative rather than mechanical purposes and, unless used with care, could even have compromised the quality of the blades.

Pattern-welding involved the lamination and folding of two materials – high-phosphorus iron and low-phosphorus mild steel or iron – to produce a surface that could be polished and etched to striking decorative effect. After twisting and grinding, the metal surface could acquire striped, chevron and sinuous patterns that were highly prized. A letter to a Germanic tribe in the sixth century AD, complimenting them for the swords they gave to the Ostrogothic king Theodoric, conqueror of Italy, praised the interplay of shadows and colours in the blades, comparing the pattern to tiny snakes.

But was it all about appearance? Surely what mattered most to a warrior was that his sword could be relied on to slice, stab and maim without breaking? It seems not. Thiele *et al.* commissioned an internationally renowned swordsmith to make pattern-welded rods for them using traditional techniques and re-smelted medieval iron. In these samples the high-phosphorus component was iron and not, as some earlier studies have mistakenly assumed, steel.

They subjected the samples to mechanical tests that probed the stresses typically experienced by a sword: impact, bending and buckling. In no cases did the patternwelded samples perform any better than hardened and tempered steel. This is not so surprising, given that phosphoric iron itself has rather poor toughness, no matter how it is laminated with other materials.

The prettiness of pattern welding didn't, however, have to compromise the sword's strength, since – at least in later examples – the patterned section was confined to panels in the central "fuller" of the blade, while the cutting edge was steel. All the same, here's an example of how materials use may be determined as much by social as by technical and mechanical considerations. From the Early to the High Middle Ages, swords weren't just or even primarily for killing people with. For the Frankish warrior, the spear and axe

were the main weapons; swords were largely symbols of power and status, carried by chieftains, jarls and princes but used only rarely. Judging by the modern reproductions, they looked almost too gorgeous to stain with blood.

1. Reibold, M. et al., Nature 444, 286 (2006).

2. Thiele, A., Hosek, J., Kucypera, P. & Dévényi, L. *Archaeometry* online publication doi:10.1111/arcm.12114 (2014).

February 2015

Holding Rome together

Calling it the world's earliest shopping mall is perhaps a qualified accolade, but Trajan's Market in Rome is certainly a remarkable structure. These vaulted arcades, built early in the second century AD and perhaps originally administrative offices, have withstood almost two millennia of moderate-scale earthquakes. They aren't alone in that: the Pantheon, Hadrian's Mausoleum and the Baths of Diocletian in Rome have all shown comparable longevity and resilience. What is their secret?

The structures use concrete made from the pyroclastic volcanic rock of the region: coarse rubble of tuff and brick bound with a mortar made from volcanic ash. It is this mortar that provides structural stability, but the properties that give it such durability have only now been examined. Jackson *et al.*¹ have reproduced the mortar used by Roman builders and used microdiffraction and tomography to study how it acquires its remarkable cohesion.

The Roman mortar was the result of a century or more of experimentation. It used pozzolan, an aluminosilicate volcanic pumice found in the region of the town of Pozzuoli, near Naples, which, when mixed with slaked lime (calcium hydroxide) in the presence of moisture, recrystallizes into a hydrated cementitious material. Although named for its Roman use, pozzolan has a much longer history in building and remained in use until the introduction of Portland cements in the eighteenth century.

The production of the volcanic ash–lime cement was described by the Roman engineer Vitruvius in his book an architecture from the first century BC, and Jackson *et al.* followed his recipe to make modern analogues. They found that the tensile strength and fracture energy increased steadily over several months, and used electron microscopy and synchrotron X-ray diffraction to look at the fracture surfaces and the chemical nature of the cementitious phases. Among the poorly crystalline matrix are platey crystals of a calcium aluminosilicate phase called strätinglite, crystallized *in situ*, which seem to act rather like the steel or glass microfibres added to some cements today to toughen them by providing obstacles to crack propagation. Unlike them, however, strätlingite resists corrosion.

Since the cement industry is a major producer of carbon dioxide liberated during the production of Portland cement, there is considerable interest in finding environmentally friendly alternatives. Some of these have a binding matrix of similar composition to the Roman mortar, and so Jackson *et al.* suggest that an improved understanding of what makes it so durable could point to approaches worth adopting today – such as using chemical additives that promote the intergrowth of reinforcing platelets.

Of course, the Roman engineers knew of the superior properties of their mortar only by experience. A similar combination of astute empiricism and good fortune lies behind the medieval lime mortars that, because of their slow setting, have preserved some churches and other buildings in the face of structural shifting. They tempt us to celebrate the skills of ancient artisans, but we should also remember that what we see today is selective: time has already levelled the failures.

1. Jackson, M. D. et al., Proc. Natl Acad. Sci. USA doi:10.1073/pnas.1417456111 (2014).

March 2015

A graphene explosion

If all has gone according to the plan as this piece went to press, Manchester will have been showered with meteorites. An exhibition at the University of Manchester's Whitworth art gallery by the artist Cornelia Parker is due to be opened on 13th February with a firework display in which pieces of meteoritic iron will be shot into the sky.

The pyrotechnics won't be started simply by lighting the blue touchpaper. The conflagration will be triggered by a humidity sensor, switched by the breath of physicist Kostya Novoselov, whose work on graphene at Manchester University with Andre Geim won them both the 2010 physics Nobel prize. The sensor is itself made from graphene, obtained from flakes of graphite taken from drawings by William Blake, J. M. W. Turner, John Constable and Pablo Picasso as well as from a pencil-written letter by Ernest Rutherford, whose pioneering work on atomic structure was conducted at Manchester.

That graphene (oxide) can serve as an ultra-sensitive humidity sensor was reported by Bi *et al.*¹, and has since been refined to give a very rapid response². Adsorption of water onto the graphene oxide film alters its capacitance, providing a sensing mechanism when the film acts as an insulating layer between two electrodes. These sensors are now being developed by Nokia. The devices used for Parker's show were provided by Novoselov's group after the two of them were introduced by the Whitworth's director Maria Balshaw. Novoselov extracted the graphite samples from artworks owned by the galley, using tweezers under careful supervision.

"I love the idea of working on a nano level", Parker has said. "The idea of graphene, something so small, being a catalyst." She is not simply talking figuratively: doped graphene has indeed been explored as an electrocatalyst for fuel cells^{3,4}.

Parker has a strong interest in interacting with science and scientists. In 1997 she produced a series of works for *Nature* examining unexpected objects in a quasi-scientific context⁵. Much of her work focuses on connotations of materiality, associations arising from what things are made of and the incongruity of materials repurposed or set out of place. Her installation *Thirty Pieces of Silver* (1988-9) used an assortment of silver objects such as instruments and cutlery flattened by a steamroller. She has worked with the red crepe paper left over from the manufacture of Remembrance Day poppies, with lead bullets and gold teeth extruded into wire, and with her own blood. Perhaps even her most famous work, *Cold Dark Matter: An Exploded View* (1991) – the reconvened fragments of an exploded shed – was stimulated as much by the allure of the "matter" as by the cosmological allusion.

"I like the garden shed aspect of scientists", she has said, "the way they like playing about with materials." Unusually for an artist, she seems more excited by the messy, ad hoc aspects of practical science – the kind of experimentation for which Rutherford was so renowned – than by grand, abstract ideas. The fact that Novoselov and Geim made some of their graphene samples using Scotch tape to strip away layers from graphite no doubt added to its appeal. Parker also recognizes that materials tell stories. There's a good chance that both Blake and Rutherford would have used graphite from the plumbago mines of Borrowdale in Cumbria, about 80 miles north of Manchester and the source of the Keswick pencil industry. So even Parker's graphene might be locally sourced.

- 1. Bi, H. et al., Sci. Rep. 3, 2714 (2013).
- 2. Borini, S. et al., ACS Nano 7, 11166-11173 (2013).
- 3. Geng, D. et al., Energy Environ. Sci. 4, 760-764 (2011).
- 4. Fei, H. et al., ACS Nano 8, 10837-10843 (2014).
- 5. Anon., Nature 389, 335, 548, 668 (1997).

May 2015

Concrete mixing for gorillas

Corning's Gorilla Glass must be one of the great success stories in modern materials. Pretty much everyone with a mobile phone, tablet or other touchscreen device benefits from this amazingly robust, scratch-proof glass (or one of its competitors). Provided you don't drop your phone onto a stone floor, it feels close to being an immortal material.

Chemically strengthened glass dates back to the 1960s, when it was in demand for the automotive and aerospace industries. But it was touchscreen electronics that made the difference. Famously, Corning is said to have been pushed into its breakthrough by Apple's Steve Jobs, who, searching for the right material for the iPhone concept in 2006, told the company "Get your mind around it. You can do it." With Apple on board, Gorilla Glass couldn't fail (almost literally).

In 2013 Corning introduced Gorilla Glass 3, which was still more scratch-resistant. Allegedly, the next-generation Gorilla Glass 4 will even withstand being dropped onto a hard surface. But perhaps the most remarkable thing about Gorilla Glass 3 is that it was designed at the drawing board, so to speak, rather than the lab. It is hardened by getting just the right chemical composition of elements in the alkali aluminosilicate, with some of the sodium ions being replaced with potassium. To predict that ideal composition, Corning scientists used rigidity theory, an approach first developed by the pioneer of glass microstructural physics James Phillips in the late 1970s¹.

In rigidity theory, the mechanical properties of a glass are calculated from the topology of the atomic network, which is disorderly at long range but has some structural order at short range. The network is regarded rather like a mechanical truss, and its flexibility or rigidity is deduced from the constraints on the movements of atoms – by stretching or bending of bonds – due to their links to neighbouring atoms. Loosely speaking, these constraints can give rise to networks that are floppy, locked rigid, or somewhere in between. By changing the chemical composition of the network, a glass can undergo a rigidity transition that renders it extremely hard and scratch-resistant.

This is all very useful, as Gorilla Glass testifies – which is why it would be good to know if rigidity theory (also called topological constraint theory) can be applied to a wider range of materials than glasses. Bauchy *et al.* report evidence that it can^{2,3}. They have used the same concepts of topological constraint to look at the rigidity of the calcium silicate hydrate network that forms the binding phase of concrete. Here too they see a rigidity transition as a function of the Ca/Si ratio of the composition: the first direct evidence of such a thing in a non-glassy material. The bond-stretching and bond-bending constraints play different roles in contributing to the hardness: this property depends mostly, and linearly, on the number of bending constraints (which are weak compared with stretching) per atom. While concrete is hardest for low Ca/Si, it is – like glasses – toughest for the intermediate state between rigid and flexible. With such information to hand, maybe concrete too can be designed from theory alone.

1. Phillips, J. C., J. Non-Cryst. Solids 34, 153 (1979).

- 2. Bauchy, M. et al., J. Phys. Chem. C 118, 12485 (2014).
- 3. Bauchy, M. et al., Phys. Rev. Lett. 114, 125502 (2015).

July 2015

The complex costs of faking it

Debates about distinctions between "natural" and "synthetic" materials date back to antiquity, when Plato and Aristotle wondered if human "art" can rival that of nature. Scepticism about alchemists' claims to make gold in the Middle Ages weren't so much about whether their gold was "real" but whether it could compare in quality to natural gold. Such questions persisted into the modern age, for example in painters' initial suspicions of synthetic ultramarine and in current consumer confusion over the integrity of synthesized natural products such as vitamin C.

It is all too easy for materials technologists to overlook the fact that what to them seems like a question of chemical identity is for users often as much a matter of symbolism. Luxury materials become such because of their cost, not their composition, while attitudes to the synthetic/natural distinction are hostage to changing fashions and values. The market for fake fur expanded in the 1970s as a result of a greater awareness of animal conservation and cruelty, but providing a synthetic alternative was not without complications and controversy. Some animal-rights groups argue that even fakes perpetuate an aesthetic that feeds the real-fur market, while recently there has been a rise in real fur being passed off as faux – a striking inversion of values – to capture the market of "ethical" fur fans. The moral – familiar to marketeers and economists if less so to materials scientists – is that market forces are dictated by much more than chemical composition.

These considerations resonate strongly in the current debate over plans by Seattle-based bioengineering company Pembient to use 3D printing for making fake rhinoceros horn from keratin. The company hopes to reduce rhino poaching by providing a synthetic alternative that, by some accounts, is virtually indistinguishable in composition, appearance and smell from the real thing. It claims that 45% of rhino horn traders have said they would buy the substitute. How to interpret that figure, even taken at face value, is unclear: will it help save the rhino, or does it show that over half of the buyers value something more than material identity? In the black-market Chinese and Vietnamese medicines that use the horn, it is supposed to imbue the drugs with an essence of the wild animal's vitality: it is not just an ingredient in the same sense as egg is a part of cake mix, but imparts potency and status.

The same is true of the tiger bone traded illegally for medicines and wine. Even providing the real thing in a way that purports to curb the threat to wildlife, as for example when tigers are farmed in China to supposedly relieve the pressure on wild populations, can backfire in the marketplace: some experts say that tiger farming has revitalized what was a waning demand.

Critics of Pembient's plans – the company intends to print tiger bone too – make similar complaints, saying that the objective should be to change the culture that creates a demand for these products rather than pandering to it. There's surely a risk here of unintended outcomes in manipulating markets, but also a need to remember that materials, when they enter culture, become more than what they're made of.

March 2016

The Roman melting pot

Recycling of materials is generally good for the planet, but it makes life hard for archaeologists. Analysis of ancient materials, for example by studying element or isotope compositions, can provide clues about the provenance of the raw materials and thus about the trade routes and economies of past cultures. But that business becomes complex, even indecipherable, if materials were reused and perhaps reprocessed in piecemeal fashion.

This, however, does seem to have been the way of the world. Extracting metals from ores and minerals from quarries and mines, and making glass and ceramics, were labourintensive and often costly affairs, so that a great deal of the materials inventory was repurposed. Besides, the knowledge was sometimes lacking to make a particular material from scratch *in situ*. The glorious cobalt-blue glass in the windows of medieval French churches and cathedrals is often rich in sodium, characteristic of glass from the Mediterranean region. It was probably made from shards imported from the south using techniques that the northern Europeans didn't possess, and perhaps dating back to Roman or Byzantine times. The twelfth-century monk Theophilus records that the French collected such glass and remelted it to make their windows¹.

In that instance, composition *does* say something about provenance. But if glass was recycled en masse, the chemical signature of its origin may get scrambled. It's not surprising that such reuse was very common, for making glass from scratch was hugely burdensome: by one estimate, 100 kg of wood was needed to produce the ash for making 2 kg of glass, and collecting it took a whole day².

Just how extensively glass was recycled in large batches in Roman times is made clear in a new study by Jackson and Paynter³. Their analysis of glass fragments from a Roman site in York, England, shows that a lot of it came out of "a great big melting pot": a jumble of recycled items melted together. The fragments can be broadly divided into classes differentiated by their antimony and manganese compositions. Both of these metals were typically added purposely during the Roman glass-making process because they could remove the colour (typically a blue-green tint) imparted by the impurities, such as iron, in the sand or ash⁴. Manganese was known in medieval Europe as "glassmaker's soap".

It's the difficulty of making it that meant colourless glass was highly prized – and so particularly likely to be recycled. The results of Jackson and Paynter confirm how common this was. The largest category of glass samples that they analysed – around 40 percent of the total – contained high levels of both Sb and Mn, implying that glass rendered colourless by either additive would be separated from the rest and then recycled by melting.

But most of those samples *aren't* colourless. That's because remelting tends to incorporate other impurities, such as aluminium, titanium and iron, from the crucibles, furnaces or blowing irons. The recycled glass may then end up as tinted and undistinguished as that made with only low amounts of Mn. As a result, while it is

derived from once highly prized, colourless glass reserved for fine tableware, this high Sb-Mn glass becomes devalued and used for mundane, material-intensive items such as windows and bottles. Eventually it just disappears into the melting pot.

1. Theophilus, *On Divers Arts*, transl. Hawthorne, J. G. & Smith, C. S. (Dover, New York, 1979).

2. Smedley, J. W., Jackson, C. M. & Booth, C. A., in *Ceramics and Civilisation* Vol. 8, eds McCray, P. & Kingery, W. D. (American Ceramic Society, 1998).

3. Jackson, C. M. & Paynter, S., *Archaeometry* **58**, 68-95 (2016). Doi:10.1111/arcm.12158

May 2016

None more black

It turns out that black is the new black. Specifically, Vantablack, a coating made by the British company Surrey Nanosystems from carbon nanotubes. The nanotubes, tens of micrometres long, are aligned normal to the surface like the threads of a carpet. They absorb 99% of the incident light, giving Vantablack an other-worldly appearance of absolute void. When you look at a surface coated in this material, it seems to have no topography at all: it's as if a small black hole has opened up in the prosaic fabric of the world.

Surrey Nanosystems say that their material might find uses in optical or microwave technologies, for example to improve optical isolation in mirror telescopes or in stealth technology. But the strangeness of its appearance lends itself to artistic uses too. The British-Indian artist Anish Kapoor, who has long experimented with intense colour and disorientating illusionism – for example in large sculptures with highly reflective surfaces – has been captivated by the possibilities of Vantablack. Because the coating is not only so thin but also defies perceptions of shape, he considers it almost a "non-material": it "rests on the liminal edge between an imagined thing and an actual one" he says. Kapoor imagines coating the walls of a room with this black substance to confuse any sensations of space or confinement.

In this regard, Vantablack approaches the realm of invisibility. It is of course the opposite of transparent, but by denying three-dimensional shape it conjures an odd illusion of nonpresence. A material that absorbs light perfectly is the means by which a chemist in Jack London's 1903 short story "The Shadow and the Flash" turns himself invisible (it couldn't really do that, of course, but to London it felt as though it should.) Such dematerialization – what Kapoor calls "the non-space, or the non-object" – has long fascinated artists. The French artist Yves Klein, who shared Kapoor's fascination with the spiritual possibilities of colour and materiality, began work in the 1960s on an "invisible architecture" in which walls would be made of powerful jets of air.

Yet there's something else Klein shares with Kapoor: a proprietorial attitude to special materials. When, in collaboration with a Parisian paint manufacturer, Klein devised a coating that preserved the magical lustre of dry powdered ultramarine pigment, he patented it as International Klein Blue to preserve what he saw as the purity of the concept. Kapoor has no patent on Vantablack, but he does have a monopoly – for, to the dismay of some other artists, he has secured exclusive rights with Surrey Nanosystems to use their material artistically.

Is that proper? Modern pigment technology has made art much more egalitarian than in the days when you could use the finest materials, such as natural ultramarine and gold, only if you had a wealthy patron. Klein's ultramarine was industrially produced by the ton, not extracted painstakingly from rare lapis lazuli. Kapoor's coup seems to take matters in the other direction, conferring privilege on those with access to the best materials.

Regardless of how you feel about that, there's probably no one better than Kapoor to reveal the creative potential of Vantablack. And its makers themselves have no monopoly on carbon-nanotube-derived blackness. The Belgian artist Frederick De Wilde created works such as his metre-wide black square *NanoBlck-Sqr#1* (2014) after a collaboration in 2010 with nanotube researchers at Rice University in Houston, and he has also used black nanotube coatings developed by NASA. There's plenty of black at the bottom, it seems.

November 2016

Searching the web

"No one", wrote the great ethologist Karl von Frisch, "would call spiders dim-witted."¹ Were they not, after all, the descendants of the skilled but boastful human weaver Arachne, who was transformed into a spider for unwisely provoking the goddess Athena into a weaving contest – and then, worse, making superior work?

The legend shows how the architectural genius of the spider's web has always drawn admiration. Scientific study has only enhanced that response. What is less often recognized is that the web is not just an intricately wrought trap for prey, but a sensing mechanism that enables the spider to locate it. The spider's eyes are of little use there; it is her sense of touch that does the job. Vibration sensors in her feet enable the spider to deduce the whereabouts of the victim from the vibrations of the threads.

If the prey is still, she plucks the converging radial threads to betray its location. The spider then picks her way delicately along those threads, avoiding the connecting "capture" threads laden with glue.

This suggests that the web might be engineered to optimize its sensing properties, permitting effective vibrational communication between the periphery and the central locus where the spider sits and waits. Mortimer *et al.* have examined that idea by measuring the vibrational characteristics of the web of the garden cross spider *Araneus diadematus.*² They have used a combination of laser vibrometry and finite-element modeling to test whether there is evidence for active tuning of the silk-thread properties to transmit vibrations.

It's the radial threads that are crucial here. As the capture threads are under no tension, they cannot sustain transverse (side to side) waves. However, those bridging threads do affect damping of radial-thread transverse waves. The spiders seem to introduce "prestress" into the radial threads, which are the ones constructed first. But if (and only if) the capture threads are present, these pre-stresses can vary along the radial threads – such stress gradients can amplify a transverse vibration as it travels from a region of high to low stress. In other words, the web architecture might include a built-in vibration amplifier.

The capture threads also couple radial threads and so induce dispersion of both transverse and longitudinal (along-axis) waves. The latter, however, are dispersed less, and so they are likely to transmit more precise directional information about the prey's location. What's more, longitudinal waves are more sensitive to the size of the impact causing them, and so can provide more information about prey size and might help to distinguish genuine prey capture from, say, wind gusts.

Mortimer *et al.* say that another way the spider might tune the vibrational features of the web, beyond active control of tension, is via supercontraction of the radial threads: a dramatic shrinkage at high humidity levels.³ This significantly lower the silk modulus, and thus, via changes the propagation speeds of both transverse and longitudinal waves, alters the frequency filtering of the web.

There are probably tradeoffs here between vibrational (sensing) and mechanical (capture and robustness) performance of the web. But there are always tradeoffs in life. The wonder of silk is that it is multifunctional enough to accommodate them.

1. Von Frisch, K., Animal Architecture, 30 (Hutchinson, London, 1975).

2. Mortimer, B., Soler, A., Siviour, C. R., Zaera, R. & Vollrath, F., *J. R. Soc. Interface* 201670341 (2016). http://rsif.royalsocietypublishing.org/content/13/122/20160341

3. Liu, Y., Shao, Z. & Vollrath, F., *Nat. Mater.* **4**, 901-905 (2005). [http://www.nature.com/nmat/journal/v4/n12/abs/nmat1534.html]

February 2017

Old gold - or new?

It seemed like the kind of discovery amateur archaeologists dream of making. In 1998 two of them declared that they had found objects made from gold sheet, apparently from a crown, a belt and other ornaments, in the soil under uprooted trees at the hamlet of Bernstorf in Bavaria, Germany. The site had been known since the early twentieth century as the location of a Bronze Age settlement, but much of it had been destroyed by gravel mining. Here, though, were precious artefacts disclosed by that very ground clearance.

Or were they? An analysis in 1999 using X-ray fluorescence, led by Rupert Gebhard of the State Archaeological Collection in Munich, showed that the gold was unusually pure. Natural gold typically contains significant amounts – up to fully 40% - of silver, as well as other trace elements such as copper. But the XRF measurements revealed less than 0.2% silver¹. Subsequent, more precise studies by Ernst Pernicka at Mannheim using mass spectrometry² showed that the gold was at least 99.99% pure – an astonishing degree of refinement hitherto known only in modern samples.

So are the Bernstorf artefacts fakes? Pernicka thought so. But it's hard to see how amateur archaeologists could achieve so sophisticated an act of deception, and there are no other features of the objects that make them suspicious in the context of Middle Bronze Age culture. Then how could they be so pure?

Maybe the measurements were wrong. After all, the mass-spectrometry results showed some trace-element discrepancies with other earlier studies³. But now a new XRF analysis using intense synchrotron radiation from the BESSY source in Berlin, led by Martin Radtke in collaboration with Gebhard has confirmed that the Bernstorf gold indeed has a purity of more than 99.9%, comparable to a modern sample produced by the Degussa chemicals company⁴.

Bronze-Age gold purer than that in nature is not in itself a complete mystery. A technique for stripping silver impurities from gold, which involves heating foils of the metal with salt at around 800 °C for several hours, was known at least in the sixth century BC, when the earliest archaeological evidence of it appears. Known as cementation, it is described by Pliny in his *Natural History* from the first century AD. It's not impossible that it was known in the Late Bronze Age.

But would it do the job this well? Roman gold coins purified by cementation – it was the introduction of gold currency that made the process necessary – are no more than 99.8% pure. It seems possible that greater purity could have been attained by several repeated rounds of cementation. But there is no obvious motivation for that. Most silver is removed in the first go (it is volatilized as silver chloride), after which there is no discernible further change in the colour of the gold – the general means of assessing its purity in the ancient world. So why would Bronze Age metalworkers have bothered?

At this stage, then, the Bernstorf gold is still a puzzle – and a reminder that sometimes not even state-of-the-art science can definitively answer questions about the past.

1. Gebhard, R., Bayerische Vorgeschichtsblätter 64, 1-8 (1999).

2. Pernicka, E., in *Jahresschrift für mitteldeutsche Vorgeschichte* Band 94, 517-526. (Landesmuseum für Vorgeschichte, Halle, 2014).

3. Bähr, V., Krause, R. & Gebhard, R., Bayerische Vorgeschichtsblätter 77, 5-41 (2012).

4. Radtke, M., Reinholz, U. & Gebhard, R., Archaeometry doi: 10.1111/arcm.12294 (2016).

September 2017

A symphony of materials

"It is remarkable to me how materials that were developed by people to make tools and buildings end up being used to make musical instruments." This remark by composer Molly Herron might as well speak for artistic endeavour in general through the ages: from Egyptian pigments derived from experiments in glassmaking to Naum Gabo's nylon-filament webs, materials innovation driven by other priorities has always been quickly embraced by artists.

Often, however, advances in materials have been used simply to substitute traditional fabrics for new ones, while keeping the design or the function unchanged. Chrome yellow could replace arsenic-laden orpiment, carbon fibre might supplant pernambuco, but still the new materials were used to paint sunsets or make violin bows. For her composition *Assembly*, on the other hand, commissioned by the Hopkins Center for the Arts at Dartmouth College in New Hampshire and premiered in May, Herron explored how materials both old and new could be used in entirely novel types of instrument to create a non-traditional sonic landscape.

Since 2016, Herron has worked with students at the Thayer School of Engineering at Dartmouth to design instruments from scratch, in collaboration with materials scientist Ulrike Wegst and engineer and educational specialist Vicki May. *Assembly* was, Herron says, much indebted to Wegst's research on the acoustic and mechanical properties of woods used for musical instruments¹⁻³.

Assembly was structured according to what is in effect a chronology of materials for musical use. The first movement drew on the acoustic repertoire of the most ancient instrument materials: bone, grass and skin, mindful in particular of the bone flutes discovered in Germany and dated to over 40,000 years ago. The second movement used instruments of wood, particularly dense woods like those of Central and South America that European colonists began to import after the discovery of the New World.

Metals have of course an old provenance in music too: bronze trumpets were used in Greece and Rome. But it was during the Renaissance that brass instruments related to the trumpets and trombones today began to appear. *Assembly*'s third movement took in not only more recent metallurgical innovations such as aluminium and titanium but also twentieth-century synthetics such as nylon and carbon fibre.

"We were really focusing on the materials themselves", Herron says. "What does this material want to do? What is its true nature?" Musicians and engineers have in common, she adds, that "we both think of things that don't yet exist, and make them exist."

What does it all sound like? The piece was performed by singers along with instrumentalists from the percussion ensemble Tigue, "one-half new music ensemble, one-half art-rock band". One description might be medieval plainchant meets Javanese gamelan – which, perhaps unsurprisingly, then ends up not far from the sonic palette of Steve Reich. The only text for the singers was the names of the materials used "tungstensilver-zinc-carbon-fibre-nylon...", moving Wegst to comment that "I have never [before]

heard a composition that was truly dedicated to the materials used in the making of the music". Let's hope it's not the last.

1. Wegst, U.G.K., Am. J. Bot. 93, 1439–1448 (2006). doi:10.3732/ajb.93.10.1439

2. Wegst, U.G.K., *Annu. Rev. Mat. Res.* **38**, 323-349 (2008). doi:10.1146/annurev.matsci.38.060407.132459

3. Wegst, U.G.K., Oberhoff, S., Weller, M. & Ashby, M. F., *Int. J. Mat. Res.* **98**, 1230–1237 (2007). doi:10.3139/146.101580

December 2017

Who made the first glass?

No other material continually exceeds itself as silica glass does. Whether it is in the stained glass of Gothic churches, the airy Crystal Palace of the Victorians or the modern skyscrapers that mirror the sky they reach towards, glass has been constantly refined to redefine its architectural possibilities. Meanwhile, in fibre composites and optical cables it challenges preconceptions about its properties and limits.

So who could not wonder when this substance first entered the palette of human-made materials? It starts to appear in archaeological remains in significant quantities in the Late Bronze Age, around 1500 BC, and consensus has long located the geographical origins in the Middle East. But that still leaves options open. Ancient Egypt used to be the obvious and default assumption, but Mesopotamia – the region mostly overlapping with present-day Iraq, with a distinct culture – has been a contender too for at least a century.

Opinion in recent decades has shifted in that direction, thanks especially to the finding of extensive glass remains in the city of Nuzi, near Kirkuk in northern Iraq, which was excavated in the 1920s and 30s. The material culture of Nuzi is currently being reexamined in an international project [1]. A new study of the Nuzi glass artefacts housed at the Harvard Semitic Museum now argues for another reconsideration of the origins of glass-making, indicating that there is after all no compelling reason to prefer this region over Egypt [2].

Shortland *et al.* have conducted scanning electron microscope-wavelength dispersive spectroscopy (SEM-WDS) analysis to deduce the elemental compositions of the samples (which include raw glass ingots, beads and fragments of worked objects), along with measurements of strontium and neodymium isotope ratios that help to distinguish different sources of the parent silica. The results reveal that some of the artefacts are modern: introduced, presumably, by local workers during the excavation because they were paid to hand over their finds. Most of the genuine Nuzi glass is tinted blue by traces of copper; in contrast, Egyptian glass from this period shows a wider range of colorants, suggesting a more mature glassmaking technology.

The latest dating of the strata at Nuzi where most of the glass was found [3] puts it pretty much contemporaneous with extensive glass remains in Egypt, in the middle of the second millennium BC – undermining some of the rationale for thinking the Nuzi glassmaking industry came first. True, there are also texts on glassmaking from Nineveh, the Assyrian capital in Mesopotamia from the first millennium, which maybe copies of older documents, while no Egyptian records from this period have been found. But that doesn't mean Egyptians weren't making the material.

The only real reason still to prefer Nuzi over Egypt, then, would be if the former technology looked more sophisticated than the latter. But the results of Shortland *et al.* seem to offer no evidence of that. The Egyptian artefacts seem to be of higher quality, and moreover have a wider colour range. That too doesn't clinch the matter, but it leaves

open the question of where humankind first mastered this most useful and beautiful of materials.

1. Shortland, A., Eremin, K., Kirk, S. & Armstrong, J., in Materials Issues in Art and Archaeology VIII, November 26–28, 2007 (eds Vandiver, P. B., McCarthy, B., Tykot, R. H., Ruvalcaba-Sil, J. L. & Casadio, F.), 217–32 (Materials Research Society, Warrendale, PA, 2008).

2. Shortland, A. J., Kirk, S., Eremin, K., Degryse, P. & Walton, M., *Archaeometry* online publication doi:10.1111/arcm.12332 (2017).

3. Stein, D. L., Z. Assyriologie und Vorderasiatische Archäologie 79, 36–60 (1989).

June 2018

Zombie materials

As it becomes increasingly immersive, virtual reality will demand virtual materials. Users, such as doctors performing operations remotely via a robotic interface, might need not only to see their artificial reality but to feel it too. The interface will therefore need to be haptic: to create a sensation of touch, a simulacrum of the mechanical properties of materials that the user is supposedly manipulating.

Haptic interfaces have existed for many years, but touch is still challenging to emulate. There is still plenty to be understood about how the mind develops a tactile sense of materials – their softness, compliance, texture and so forth – from the delicate feedback between skin and brain. It's not clear, for example, what the relevant coordinates are for tactile space: how we categorize such sensual characteristics.

A new study of haptic sensation in virtual reality (VR) supplies a demonstration of how touch is acutely sensitive to other sensory cues, especially vision. Berger *et al.* tested users of a VR system that generates an illusion of material objects from small vibrations delivered to handheld controllers in each hand [1]. When the vibrations are suitably synchronized, the user experiences the sense of there being a single, material source located in the empty space between the hands. In the experiments this source could be rendered visually in the VR headset as a vibrating white marble.

It seems natural to assume that the more intense the haptic sensation, the more realistic and immersive the VR environment will be. But it's not as simple as that. Participants reported a good sense of localization for the source of vibration, yet making this sensation increasingly realistic (by control of the synchrony and amplitude of the vibration) didn't enhance, but rather diminished, a sense of immersion unless the visual cues were similarly enhanced.

This diminution of the illusion could be avoided, however, if the VR headset showed an animated cloud that 'obscured' the marble, or if the haptic stimulation occurred only in response to user movements – in both cases offering a plausible "reason" for the mismatch of stimuli.

Berger *et al.* interpret their findings in the context of the well-known 'uncanny valley' of robotics. Robots that closely approach but do not quite attain fully human appearance elicit more unease – a greater cognitive dissonance – than ones with lower realism. They argue that there is a haptic uncanny valley too.

On the one hand these results can be regarded as a cautionary note for designing haptic interfaces: it benefits you little to enhance the tactile experience if other stimuli are not similarly improved. But one can also see here an indication of the subtlety of how the human mind creates our reality by integrating sensations and judging them against prior knowledge. Put simply, that process is not easily fooled.

Or perhaps one should say, the brain demands causal consistency. We will believe what we experience only if we can construct reasons -a narrative - for it, a creative act that

enlists all available sensory input. A key factor here is agency: I sense *this* because *that* caused it, or indeed because *I* caused it. It's in this respect that the haptic experiments truly connect with notions of the uncanny in robotics and AI more generally. Robin Murphy suggests that the uncanny valley exists only when we suspect a humanoid robot of being a zombie-like automaton emulating a conscious agent (so-called weak AI) [2]. If, in contrast, we have reason to suspect the robot is a genuine thinking entity (strong AI), our sympathy is engaged and the creepiness disappears. This distinction, says Murphy, is apparent in the robots from the original 1973 movie of *Westworld* (weak AI) and those of the new HBO series (strong AI). By the same token, it seems, we will not be misled by zombie materials.

1. Berger, C. C., Gonzalez-Franco, M., Ofek, E. & Hinckley, K. Sci. Robot. 3, eaar7010 (2018).

2. Murphy, R. R., Sci. Robot. 3, eeat8447 (2018).

October 2018

Moonage daydreams of space rock

The moon landing by Apollo 11, which will be widely celebrated on its 50th anniversary next year, seemed at least to settle that hoary old question of what material the moon is made of. In all, the Apollo astronauts brought back around 380 kg of the satellite – rocks and regolith – for chemical and mineralogical analysis: one of the few (literally) tangible scientific benefits of the Apollo program. (NASA, however, had to admit several years ago that many 'astromaterials' had been lost from its collection, including many of the Apollo lunar rock samples, mostly misplaced following loans to researchers and educators.)

Surprisingly, though, these materials have still not produced a consensus about the composition of the moon. Even now, half a century later, studies of physical samples and remote measurements from spacecraft are yielding conflicting conclusions about the lunar fabric. Just last year, Milliken and Li reported that spectra of lunar pyroclastic (volcanic-derived) deposits, widespread on the lunar surface, taken by the Indian Space Research Organisation's Chandrayaan-1 lunar probe suggest that these materials, which originated deep within the moon's interior, have a high water content¹. That was consistent with water-rich volcanic glassy grains found in Apollo samples², and implied that those materials weren't anomalies but may reflect the general composition of the lunar interior. This in turn cast doubt on the common view that the moon's geological fabric is depleted in volatile substances such as water.

The implications of water-rich moon rocks are profound. Media reports spoke excitedly of potential sources of water for future moon bases, but the more immediate issue concerns the moon's formation. If, as was widely suspected, it was created from material torn off the young Earth in a collision with a planet-sized object dubbed Theia in the early solar system, then the violence of that event might have been expected to deplete the debris of volatiles. So whence the water? Did it somehow remain with the terrestrial material that formed to moon? Or was it delivered soon after by comets? Or is the impact hypothesis wrong?

Modern analyses of moon rocks, benefitting from the precision of today's techniques, are still informing and changing this story. Wang and Jacobsen, for example, recently showed³ that the lunar samples are enriched in heavy isotopes of potassium relative to the Earth, which they explain by invoking a much more catastrophic impact than previously considered, more or less vaporizing the colliding bodies.

As for that water: the jury is not in yet. A new analysis⁴ of one of the Apollo 16 samples brought back in 1972 – which has plenty of volatiles – shows that its zinc-isotope composition is what one would expect from a material that had been boiled dry by volcanism. The authors suggest that the interior of the moon thus is dry after all, while surface materials like the Apollo volcanic glasses became hydrated by condensation of expelled volatiles.

It seems unlikely that we have heard the last word. The stories we tell about the moon seem acutely dependent on how sensitively we can probe the materials that, nearly 50 years ago, we began to bring back from it.

1. Milliken, R. E. & Li, S., Nat. Geosci. 10, 561-565 (2017). doi: 10.1038/ngeo2993.

2. Saal, A. E. et al., Nature 454, 192-195 (2008). doi: 10.1038/nature07047.

3. Wang, K. & Jacobsen, S. B., Nature 538, 487-490 (2016). doi:10.1038/nature19341.

4. Day. J. M. D., Moynier, F. & Shearer, C. K., *Proc. Natl Acad. Sci. USA* **114**, 9547-9551 (2017). doi: 10.1073/pnas.1708236114.

June 2019

Small change

The "dematerialization" of SI units so that they are defined in terms of fundamental constants is predicated on the eminently reasonable idea that this frees standards and measures from the contingent fluctuations that can occur in a reference object like the platinum-iridium standard kilogram. But what if the constants themselves are susceptible to variation? A new proposal [1] turns the tables by showing how extremely sensitive measurements on a material system could reveal such changes.

Of course, any such variation in a "constant" of nature would have to be extremely small, or it would have been seen already. (And even if it occurs, it would not undermine a definition of units in these terms – simply, the scale would shift accordingly.) All the same, there are reasons why such inconstancy might be possible. Some theories that seek to unify the forces of nature invoke extra spatial dimensions, so that there is nothing "fundamental" about the projection of higher-dimensional constants onto our own three dimensions: like shifting shadows, they might change both in space and over time. What is more, some theories of dark matter predict couplings to ordinary matter that can alter these constants, perhaps in an oscillatory way. Such variations might therefore offer hints about physics beyond the Standard Model, making them worth seeking.

One way in which they could become manifest is through a change in the sheer size of a material system. For example, this size should change with any change in the fine-structure constant α , which is a measure of the strength of the interaction between charged particles. The reason is subtle, arising from relativistic effects on atomic radii: the way these depend on the change of an electron's mass when it moves at an appreciable fraction of the speed of light. Another change in atomic (and thus material) dimensions could arise from variations in the ratio of the electron mass to the nuclear mass as a result of an inconstant electron/proton mass ratio μ .

Pašteka *et al.* [1] have calculated how sensitively such variations in these two constants might be probed. Ultimately the change in material dimensions arises from a shift of interatomic bond lengths (sensitive to both α and μ). In principle this could be seen by looking at the dimensions of diatomic molecules, but it might be more readily studied by seeking changes in the lattice constants of inorganic crystals – in particular, using laser interferometery. If the materials are used to make optical cavities, say, then changes in dimensions would very slightly shift the resonant frequencies. For two different materials, a variation in α due to relativistic effects would show up as a (unit-independent) change in the ratio of these resonant frequencies. In fact, the authors say, the ratio of resonator frequency to that of an atomic clock would depend on α even without relativistic corrections.

Shifts in the lattice constants of elemental crystals such as copper, silicon, aluminum, niobium and titanium, say Pašteka *et al.*, could typically be of the order of a few thousandths of an angstrom for a change in α of around 25%. That's certainly detectable, but any plausible variability of α would have to be a great deal smaller than that: variations in α have been excluded above a limit of one part in 10¹⁷ per year [2].

According to the new calculations, a rate of change at this limit would cause shrinkage of a gold bar by a factor of 10^{-18} per year. Seeing such contraction by monitoring over a few years would be a tremendous challenge – but the extreme sensitivity of laser interferometry as demonstrated by gravitational-wave detectors should make one hesitant to rule it out.

1. Pašteka, L. F., Hao, Y., Borschevsky, A., Flambaum, V. V. & Schwerdtfeger, P. *Phys. Rev. Lett.* **122**, 160801 (2019). https://doi.org/10.1103/PhysRevLett.122.160801

2. Srianand, R., Chand, H., Petitjean, P. & Aracil, B. *Phys Rev. Lett.* **92**, 121302 (2004). https://doi.org/10.1103/PhysRevLett.92.121302

July 2019

New dating agency for artists

As the arguments over the painting *Salvator mundi* demonstrate – is it the work of Leonardo da Vinci himself? – there is a lot riding on the authentication of art. The painting sold for a record-breaking \$450 million on the strength of its attribution to Leonardo, but some say it was made only by his studio, and it has now been excluded from a Leonardo exhibition in the Louvre because of its uncertain status.

Verifying authenticity is sometimes no easier for outright fakes. One of the most successful art fakers of all time, the Dutch painter Han van Meegeren, went to great lengths to disguise the deception, for example by scraping old canvases clean so that they looked suitably aged. Van Meegeren copied the styles of Dutch Old Masters such as Frans Hals and Jan Vermeer so skillfully that some critics hail his work in its own right, and he became a national hero when it emerged after World War II that he had sold a fake to Hermann Göring during the German occupation of the Netherlands.

Spotting faked paintings usually involves a close inspection of the materials. Sometimes they come to light because of the anachronistic use of pigments: a "modern" pigment such as chrome yellow could not possibly feature in a genuine Rembrandt. But the canny forger will use period-appropriate paints. Another option is to use radiocarbon dating, but this has traditionally involved destructive testing of a significant amount of material – perhaps a few grams. Those might be taken from the frame or a hidden part of the canvas – but this would be of no avail against a smart practitioner like Van Meegeren.

A more exacting test would carry out dating on the paints themselves, looking at the organic components in individual paint layers – in particular the liquid binder, which until the advent of modern acrylic resins was typically a drying oil such as linseed oil, perhaps mixed with natural resins. This level of inspection has not previously been possible, however, because the tests required too much material. Recent developments in accelerator mass spectrometry (AMS) radiocarbon dating, such as the "gas ion source" method, have however reduced the necessary sample size down to mere micrograms.

This has now enabled Hendricks *et al.* to identify a modern faked painting by radiocarbon microanalysis of the materials in the paint [1]. Their sample was purposely chosen to be a known forgery: made by the American artist Robert Trotter, who was convicted in 1990 of producing and selling faked American folk art. His *Village Scene with Horse and Honn & Company Factory*, signed "1866" by the "artist" Sarah Honn, isn't a very sophisticated deception – conventional spectroscopic pigment analyses have already revealed telltale anachronisms, such as the total absence of lead white [2].

But Trotter did use an old canvas, and radiocarbon dating of that is inconclusive, spanning from the late 17^{th} century to the mid- 20^{th} century. Dating of a tiny amount of the binder (yielding just 19 µg carbon) has, however, proved more exacting: the oil appears to have come from seeds harvested either between 1958-61 or 1983-89. (The double date comes from the confounding influence of nuclear-bomb radiocarbon in the 1950s and 60s.) If we didn't know already that this was a fake, we would now.

Trotter, incidentally, is still painting in a faux nineteenth-century style after leaving prison – but openly so, selling to buyers of modern folk art. Making a living as an artist was, it seems, all he had really wanted.

1. Hendriks, L., et al., Proc. Natl Acad. Sci. USA doi: 10.1073/pnas.1901540116 (2019).

2. Smith, G. D., Hamm, J. F., Kushel, D. A. & Rogge, C. E., in Lang, P. L. & Armitage, R. A. (eds), *Collaborative Endeavors in the Chemical Analysis of Art and Cultural Heritage Materials*, ACS Symp. Ser. **1103**, 1-21 (Am. Chem. Soc., Washington DC, 2012). doi: 10.1021/bk-2012-1103

March 2020

Living robots

The original "robots", described in the 1921 play *R*. *U*. *R*. by the Czech writer Karel Čapek (the word is Czech for "labourer") were not made from steel and controlled by electronics, but were fleshy and autonomous. Čapek's manufacturing process, in which organs and other parts were made from vats of flesh-like dough and assembled into bodies, took inspiration from the emerging technology of *in vivo* tissue culture. It blurred the boundaries between engineering and biotechnology in a way that seemed far beyond the technologies of the time.

The results now reported by Kriegman *et al.* make this vision seem almost unnervingly prescient [1]. They describe "reconfigurable organisms" made from living cells assembled into conglomerates about a millimetre across with arbitrary shapes, which are designed *in silico* for particular functions such as locomotion. These structures have been dubbed "xenobots" – which might be given the literal and apt interpretation of "strange robots", although here "xeno" comes from the use of embryonic stem cells of the African clawed frog *Xenopus laevis* as the construction material.

The cells are harvested from embryos at the blastula stage, when they mostly retain pluripotency: the ability to grow into any tissue type of the body. But particular functions can be engineered into the design by using cell types that have begun to differentiate towards a target tissue. For example, passive tissue may come from the progenitors of epithelial cells, which line the surfaces of organs, blood vessels and skin. Motile tissues for movement, meanwhile, can be constructed from cardiac progenitor cells, the precursors to heart muscle, which contracts by supporting waves of electrical activity.

The researchers cultured these cells types separately and then pooled them in the desired numbers so that they could aggregate into a single mass. The specific arrangement of cells was decided by using an evolutionary algorithm in simulations that seek the geometries that performed best at the target task. It was then engineered by hand with a combination of microsurgery forceps to manipulate cells and a fine cautery electrode to remove cells at certain locations. The resulting cellular structures are necessary rather crude approximations of the original design, but Kriegman *et al.* show that they can work as intended. For example, a "two-legged xenobot" with contractile cells on its lower half was able to show non-random, directional movement over a surface.

The designs can be optimized by iteration, using the best performing structures as the input for further rounds of *in silico* evolution: there will surely be an empirical element to the process. The motile structures also showed emergent behaviours, both *in silico* and *in vivo*, for example temporarily attaching to or orbiting one another when they collide. Some evolved designs included unexpected features that the researchers say could be opportunistically "exapted" for new uses. One "walker" evolved a hole in the design stage to reduce hydrodynamic drag, which might function instead as a cavity for storing and transporting objects.

Kriegman *et al.* speculate that "living" structures like these might provide biocompatible devices for *in vivo* drug delivery or tissue repair. The limitations are yet to be fully explored. Cells in natural tissues, for example, tend to fill in concavities spontaneously, restricting the stable geometries. And stem cells have their own agendas: their fates are governed by the signals received from surrounding cells, and some are themselves mobile in developing tissues, so that these "xenobots" might begin to subvert the original designs. Maybe this spontaneous development could itself become an empirically guided design element.

Such autonomy raises a more profound question. Kriegman *et al.* call their structures, perhaps controversially, "organisms". But when does engineered tissue become organism? At present, they lack the reproductive capacity that might be deemed an essential feature of a real organism (though some are of course by their nature sterile). It's by no means obvious that they could not be given that ability – with attendant biosafety and ethical considerations. They might even be equipped with simple cognition too. We would then need to ask: are multicelled aggregates plastic enough to support totally different yet wholly viable life forms from the ones their genomes have evolved to create?

1. Kriegman, S., Blackiston, D., Levin, M. & Bongard, J., Proc. Natl Acad. Sci. USA doi: 10.1073/pnas.1910837117 (2020).

September 2020

The plastic legacy

The Carboniferous period around 350-300 million years ago left its geological mark in the form of rich deposits of coal and oil worldwide. It seems possible that the stratigraphic legacy of the Anthropocene will see some of that carbonaceous material reappear within a much narrower time window in synthetic form: as a preserved sedimentary layer of plastics [1].

The raw figures are sobering. By 2017, around 8,300 million tonnes of plastic had been manufactured, mostly over the preceding half-century or so [2]. Around 30 percent of it was still in use; the rest has become waste, of which around four-fifths ended up as landfill. Plastic waste is found in most natural environments, including all the major ocean basins – where it can pose a serious threat to organisms and ecosystems, potentially (through ingestion of microplastic particles) including humans [3].

At face value, it's puzzling how we could have reached this alarming juncture. The very features that made plastics so alluring in the days when they seemed a utopian wonder material – recall the famous line from *The Graduate* (1967): "One word. Plastics" – was always going to cause difficulties for disposal: their durability. As Lau *et al.* [4] put it with devastating understatement, the problem was that waste featured in conventional economic models only as an "externality", meaning that it could be conveniently shunted outside of cost-profit analyses. That, of course, has been true for the environment as a whole, which is in many ways why we have unthinkingly created the Anthropocene in the first place.

But can we undo or avert the worst of the damage? Lau *et al.* have explored some scenarios for that – in effect, charting possible strategies towards zero plastic pollution in much the same way as we must now attempt to do for carbon emissions to avoid catastrophic global heating. The irony is that the two issues are almost complementary: turning fossil fuels into carbon dioxide damages the environment, but so does converting oil instead into carbon that may remain fixed in plastics for centuries or millennia.

The solutions, meanwhile, echo one another. Plastic waste, like carbon dioxide, needs to be captured rather than dumped into the environment; ideally it will be reused and recycled. It should be possible to produce some plastics, like fuels, from sustainable natural sources. But perhaps most of all, we need to find ways to simply reduce our profligate use of geological carbon resources.

To sharpen these ideals, Lau *et al.* use a model of global production, use and disposal of both macro- and microplastics to look at the effects and economic costs of several mitigation strategies over the period 2016-2040. In particular they examine the relative effectiveness of reducing use, substituting plastics for other materials (for example in packaging), recycling, and altering collection and disposal practices.

For a business-as-usual strategy, plastic pollution will increase 2.8-fold in terrestrial systems and 2.6-fold in aquatic systems over this period. Even a portfolio approach that implements all of these solutions to a degree currently foreseeable doesn't eliminate

plastic pollution, although it is reduced by 78 percent by 2040 relative to business-asusual – which is a 40 percent reduction on today's level. Using the full suite of possible interventions also produced the lowest waste-management costs.

None of this would be easy to implement, and neither would it be a complete solution. Even the most optimistic scenario considered here still results in massive accumulation of plastic pollution, and further problems would come from mismanaged or poor disposal practices, especially open burning – which is common in emerging economies, and carries hazards for human health as well as producing greenhouse gases. But pressing needs can also be opportunities for technological innovation: to find ways of making greener plastics, whether from more efficient use of resources, cleaner and more sustainable feedstocks, or with better recyclability. As ever, though, technology cannot be a sticking plaster for problems that have socioeconomic root causes.

1. Zalasiewicz, J. *et al.*, *Anthropocene* **13**, 4-17 (2016). Doi:10.1016/j.ancene.2016.01.002

2. Geyer, R., Jambeck, J. R. & Law, K. L. *Science Adv.* **3**, e1700782 (2017). Doi: 10.1126/sciadv.1700782

3. Barboza, L. G. A. *et al.*, *Mar. Pollut. Bull.* **133**, 336-348 (2018). Doi:10.1016/j.marpolbul.2018.05.047

4. Lau, W. W. Y. *et al.*, *Science* advance online publication (2020). Doi:10.1126/science.aba9475

December 2020

Waking up old instruments

Wolfgang Amadeus Mozart was a piano prodigy from early childhood, but he was also an accomplished violinist. The instrument that his father bought him still exists, kept by the Mozarteum Foundation in Salzburg. It's a fine instrument, made by the Klotz family of Bavarian violin-makers. But when Christoph Koncz, violinist with the Vienna Philharmonic, was granted permission recently to perform with it, he found that after such a long time of disuse "its sound had fallen asleep."

"At first its wood was stiff and it lacked resonance", says Koncz. "Each time I played it, its sound opened up and the wood was in harmony again." By the time Koncz was playing it in public and using it to record Mozart's violin concertos, it had attained "a focused, very silky, silvery tone."

But how? Koncz attributes the change of tone to the instrument's material: the wood needed "loosening" somehow to make it sing. Yet although the need for a "playing in" period for any violin new to the musician is well attested, no one seems to know what it entails.

"As yet no one has been able to explain what is involved in such a process", says physicist Colin Gough of the University of Birmingham, an expert in violin acoustics. It's likely to be at least partly a perceptual issue. "Top players often say that it can take them as long as a year to coax the kinds of sound they want out of instrument. Almost certainly this involves the brain becoming familiar with the sound of the instrument, and the development of the very subtle skills used by top performers in achieving the optimum sound."

"The phenomenon is well-known in the sense of folklore among players and makers", says Jim Woodhouse, a mechanical engineer at the University of Cambridge. "Whether it is a physical phenomenon is more tricky: evidence is divided."

"Until now, there have never been any convincing physical measurements on instruments as they are being played in", says Gough. Some violin-makers and restorers use mechanical shaking devices that claim to induce this playing-in effect artificially. Woodhouse says he and a student once made acoustic measurements with such a device – with mixed results. "We saw something change the first time we used it on our test instrument. But then we deliberately induced the kind of changes that are claimed to produce a need for further playing-in, and we never say any change on subsequent occasions."

There seems no doubt that the tone of an instrument improves as the player gets to know it – but is any of that due to changes in the acoustic properties of the materials? One study found decreased internal damping after mechanical excitation in samples of violin wood (spruce) [1]. But while some investigations of prolonged mechanical vibration produced improvements in violin tone as judged by listeners and players [2, 3] and measurable changes in vibro-acoustic properties [2, 4], others found no measurable mechanical change in violin wood after such treatment [5]. One particularly careful study looked at

two instruments made from the same wood (with a spruce top-plate), conducting expert blind listening tests after one had been played regularly for three years and the other hardly at all [6]. No significant differences in tone were identified.

By what mechanism could playing cause material changes in the instrument anyway? That's been little studied, but Woodhouse thinks it is possible that vigorous vibrations could relax residual stresses around important contact points that rely on friction: string notches, bridge feet, and the ends of the soundpost. Or – just possibly – traditional gelatine glue may creep a little to relieve stresses.

Chemist Hwan-Ching Tai of the National Taiwan University has another suggestion: that stress-induced deformations will redistribute water molecules in the wood. "Although precise measurements are difficult, it is not far-fetched to attribute the awakening of old instruments to these factors", he says.

He believes there could also be age-related changes in the wood cellulose, which would be seen also in ancient Chinese stringed instruments called *guqin*. His team's preliminary data show cellulose rearrangements in such instruments, probed by small-angle X-ray scattering with synchrotron radiation, caused either by age or by artificial treatment during manufacture.

Vibration-induced redistribution of water was proposed to explain earlier observations of a change in damping after vibration [1] – interestingly, this seems to make the wood stiffer with playing, *contra* Koncz's subjective impressions. Tai hopes it might be possible to use techniques such as neutron scattering to probe stress-induced microscopic redistribution of water explicitly.

That would be a worthy project. Whether anyone would consent to placing Mozart's priceless instrument in a neutron beam is another matter.

- 1. Hunt, D. G. & Balsan, E., Nature 379, 681 (1996).
- 2. Hutchins, C. M. & Rodgers, O. E., Catgut Acoust. Soc. J. 2 (1), 13-19 (1992).
- 3. Ling, D. & Killion, M. Catgut Acoust. Soc. J. 3 (3), 42-44 (1997).
- 4. Hutchins, C. M., Catgut Acoust. Soc. J. 1 (4), 10-19 (1989).
- 5. Grogan, J., Braunstein M. & Piacsek, A., J. Acoust. Soc. Am. 113, 2315-2316 (2003).
- 6. Inta, R., Smith, J. & Wolfe, J. Acoustics Australia 33, 25-29 (2005).

March 2021

Coming alive

Materials scientists have been singing the praises of biomaterials for decades – and exploiting them forever. The strength of silk, the toughness of nacre, the resilience of wood: all have long been advertised as examples of how control of micro- and nanostructure, and typically a hierarchy of structural features, can lead to superior bulk properties. But the virtues of nature's materials are barely done credit by focusing solely on their structural aspects. Arguably the key feature of a material like wood, for instance, is not that it performs well mechanically but that it is, in its natural environment, genuinely a living substance: created and degraded sustainably from its own energy source, adaptive to changing circumstances (for example, being responsive to changes in stress), and autonomous in its life cycle. It is not merely a smart material but an *animate* one.

In February, the Royal Society in London launched a research initiative on what it calls animate materials [1] – meaning synthetic materials systems that capture at least some of these characteristics of natural ones. The concept brings together several recent strands of materials research, ranging from work on smart materials and composites to self-healing materials and tissue engineering. The over-arching vision is not to make better materials but to create better ways of making materials: with longer lifespans and an ability to selfrepair, made from sustainable feedstocks and that are biodegradable, and which can harvest materials and energy from their environment. In short, they don't impose themselves on an ecosystem but become part of it. The applications of such substances are as wide as our imaginations: from self-healing roads and buildings to better, safer biomedical implants and functional textiles.

Defining "animate" is as fraught as defining "life". But the working group behind the Royal Society initiative proposes three general principles underpinning the term. These materials will be *active*: able to change their properties or perform some action, in the manner of gels or alloys that change shape in response to stimuli. They will be *adaptive*, responding to changes in the environment in a way that benefits function. And they will be *autonomous*, not requiring separate and elaborate control or power systems to function. Many existing artificial materials show some degree of one or more of these properties. But none exhibits them all to the extent that, say, a tree, a biofilm or a lab-grown organoid does. This "3A" framework for understanding animate materials might need refining or even replacing as the field develops, but it offers a serviceable scheme for locating existing materials systems both synthetic and natural in a "space of possibilities", and discerning objectives and directions of travel.

While materials science has always been a paradigm of interdisciplinary research, animate materials would place unprecedented demands on the ability of diverse fields of research to find a common cause and language. Much of the work done on self-healing materials, for example, has come from applications either in civil engineering – long-established materials such as asphalt [2] and mortars [3] show some of that capacity – and in polymers and coatings for the automotive and construction industry [4]. Self-actuating materials, meanwhile, have typically featured in robotics [5]. Both are a long way either

from the kind of embodied computation performed by cell aggregates in tissue engineering [6], or efforts to incorporate a degree of computational ability at the molecular scale in DNA-based extended assemblies [7] and those that use other types of molecular machines and logic circuits. Creating materials with energy autonomy, meanwhile, might benefit from research on systems that can harvest ambient energy from wi-fi signals, mechanical vibrations or even the human body's metabolic processes – from biomedical devices to portable electronics.

Ultimately, developing these properties in materials systems might demand a recapitulation of life itself: the development of materials systems that show some of the defining properties of living ones [8], from replication to adaptation. It will be a challenging goal, but the benefits – from greener production and disposal methods to a reduction in the financial and social costs of maintenance and repair (erosion of pipes, tanks and other components of industrial infrastructure is estimated to cost about \$2.5 trillion annually [9]). In the end the objective is a qualitative shift in the art of making: from designing and building to growing and sustaining.

1. Royal Society, <u>https://royalsociety.org/topics-policy/projects/animate-materials/</u> (2021)

2. Sun, D. *et al.*, *J. Coll. Interface Sci.* **256**, 65-93 (2018). <u>https://doi.org/10.1016/j.cis.2018.05.003</u>

3. Lubelli, B., Nijland, T. G. & Van Hees, R. P. J., *Heron* **56(1/2)**, 5 (2011). <u>http://resolver.tudelft.nl/uuid:ff226ad0-ffb2-4b4c-bdb6-9881961bc7f1</u>

4. Zhang, F. *et al.*, *Corrosion Sci.* **144**, 74-88 (2018). <u>https://doi.org/10.1016/j.corsci.2018.08.005</u>

5. McEvoy, M. A. & Correll, N., *Science* **347**, 1261689 (2018). http://dx.doi.org/10.1126/science.1261689

6. Ramos, T. & Moroni, L., *Tissue Eng. C Meth.* **26**, 91-106 (2020). <u>http://doi.org/10.1089/ten.tec.2019.0344</u>

7. Seeman, N. & Sleiman H., *Nat. Rev. Mater.* **3**, 17068 (2018). https://doi.org/10.1038/natrevmats.2017.68

8. Gobbo, P., *et al.*, *Nat Mater*. **17**, 1145-1153 (2018). <u>https://doi:10.1038/s41563-018-0183-5</u>

9. NACE International, International Measures of Prevention, Application and Economics of Corrosion Technology (2016). <u>http://impact.nace.org/documents/Nace-International-Report.pdf</u>