

effective at diverting other asteroids.

The ejected material was observed by LICIAcube, the Hubble Space Telescope and a network of ground-based telescopes. Li and colleagues<sup>4</sup> (page 452) used 3D numerical modelling and the Hubble data to characterize the ejecta over the course of the 18 days during which Hubble observed it. Gravity and solar-radiation pressure sorted the material naturally by particle size during this period, enabling the authors to identify micrometre- to centimetre-sized dust populations. They estimated the ejecta cone to be wider than that produced by impacts performed in laboratory experiments, but found its dust tail to be consistent with the shape of asteroid tails that are thought to have been produced by natural impacts<sup>8,9</sup>. Several days after impact, a secondary tail appeared, pointing 4° off-axis from the original tail, but the mechanisms underlying this tail remain to be explored.

A network of citizen scientists observed the Didymos system during the days before and after the impact event to help set limits on the mass, velocity and kinetic energy of the ejecta plume and tail. Their efforts are reported by Graykowski and colleagues<sup>3</sup> (page 461), who estimate that the fast-moving plume carried away 3–30% of the kinetic energy, with a total mass of hundreds to thousands of kilograms. The slower-moving tail material moved 150–250 kilometres towards the Sun before solar-radiation pressure imparted enough force to turn the plume around. The authors found that the mass of this material was around 13 million kilograms, with an average particle size of around 2 millimetres.

The team also report the detection of a brief but pronounced reddening of the light emitted by the binary system at the time of impact. This reddening phenomenon was observed previously when NASA's OSIRIS-REx mission made contact with an asteroid called Bennu<sup>10</sup>. Many interpretations of the possible cause remain<sup>3</sup>.

One limitation of the experiment is that Dimorphos's mass could not be measured directly by DART, leading to large uncertainties in the densities of the binary parent and satellite. Density and porosity are key to understanding the impact dynamics, as well as how the properties of this binary system relate to those of the meteorites catalogued so far<sup>11</sup>. The European Space Agency's Hera mission is planning a close-up reconnaissance of Didymos and Dimorphos by 2027 that promises valuable context and refined understanding of the DART experiment. Likewise, the sample returning this September from asteroid Bennu will provide more insight into how the properties of asteroid material relate to the contact dynamics measured by OSIRIS-REx<sup>12</sup>.

NASA's Near-Earth Object Surveyor mission is also expected to come online by the end of

this decade. The mission will detect and track the remaining population of potentially hazardous asteroids that are larger than Dimorphos. This will give scientists a more complete view of any would-be threats to our planet that could require follow-up characterization or possibly a controlled deflection. The DART mission was a crucial first test of how such a deflection might be carried out, and the data reported in these five papers will inform our understanding of other asteroid impact events that have been observed previously<sup>13</sup>, as well as those still to be detected.

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## Inorganic chemistry

# Metal-oxide cage traps radioactive element

May Nyman & Gauthier Deblonde

The ability to separate the radioactive element americium from spent nuclear fuel would lower the long-term hazards of nuclear waste. An inorganic molecular cage that selectively binds to americium opens up a separation strategy. **See p.482**

On page 482, Zhang *et al.*<sup>1</sup> provide a rare atomic-level glimpse of a notoriously dangerous radioactive element, americium (Am), in its highest oxidation state. The authors used a water-soluble metal-oxide cage, known as a polyoxometalate (POM), to facilitate the isolation of americium from chemically similar elements found in nuclear waste. Such a POM-mediated separation could solve a long-standing problem in reprocessing spent fuel from civilian nuclear reactors, thereby enhancing the efficiency and safety of the nuclear industry.

Lowering the greenhouse-gas emissions generated by energy production is one of the most urgent challenges of the twenty-first century, and nuclear energy has a key role in achieving this goal. A considerable hurdle to the widespread use of civilian nuclear reactors is finding a way to deal with radioactive waste, which currently requires long-term storage. Spent fuel rods can be processed to recycle uranium (U) and plutonium (Pu), but other elements in the waste remain radioactive for thousands of years and need to be managed accordingly.

Fission reactions in nuclear reactors split uranium atoms to release energy, but also generate various products consisting of lighter elements from across most of the periodic

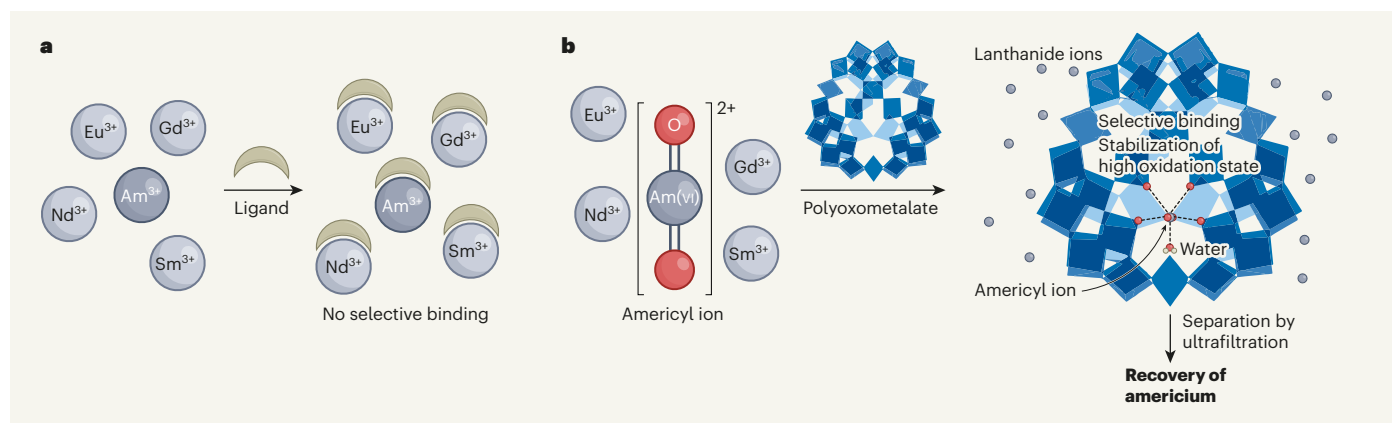
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table. Among them, a family of 15 elements – the lanthanides – must not be recycled into new fuel because they hinder energy-producing nuclear reactions by capturing neutrons. A fraction of the uranium atoms in nuclear fuels also absorbs neutrons and produces heavier radioactive elements, including americium. Several isotopes of americium are particularly problematic because of their toxicity and long-lived radioisotopes, and because their decay contributes substantially to the residual heat produced by nuclear waste.

Typical civilian nuclear fuel yields about 10–20 kilograms of lanthanides and 0.5–2.0 kg of americium per tonne of uranium<sup>2</sup>. Americium separated from these complex waste mixtures could be used in next-generation reactors, thereby greatly decreasing the long-term toxicity of nuclear waste and facilitating its storage. However, lanthanides and americium are chemically very similar, having the same predominant oxidation state (+III) and similarly sized ions. Organic ligand molecules designed to bind to trivalent americium ions (Am<sup>3+</sup>) therefore typically also bind to the analogous lanthanide ions (Fig. 1a).

Since the 1960s, scientists have researched various processes to separate americium from lanthanide fission products<sup>3</sup>. Most are based on solvent extraction (the selective



**Figure 1 | Separation of americium from lanthanide elements. a**, Spent nuclear fuel contains ions of radioactive americium in the +III oxidation state ( $\text{Am}^{3+}$ ) and analogous ions of the lanthanide series of elements, such as europium ( $\text{Eu}^{3+}$ ), gadolinium ( $\text{Gd}^{3+}$ ), neodymium ( $\text{Nd}^{3+}$ ) and samarium ( $\text{Sm}^{3+}$ ). Separation of  $\text{Am}^{3+}$  from lanthanide ions would lower the long-term toxicity of nuclear waste, but is challenging because these ions all have similar sizes and chemistries. Organic ligand molecules have been developed that bind to

$\text{Am}^{3+}$  ions in such mixtures, but the selectivity is too low for use in industrial separations. **b**, Americium in the +VI oxidation state forms americium ions ( $\text{AmO}_2^{2+}$ ), the size, geometry and chemistry of which differ from those of the lanthanide ions. Zhang *et al.*<sup>1</sup> report an inorganic molecular cage, known as a polyoxometalate, that binds selectively to and stabilizes the otherwise highly reactive americium ions. The resulting complex could be separated by the ultrafiltration technique to recover americium.

transfer of components of nuclear waste from acidic solution into a suitable solvent), and take advantage of minute differences in the chemical affinities of aqueous ligands or solvent components for trivalent americium and lanthanides. However, because these separations are relatively inefficient, none of them is currently implemented at the industrial scale. Alternative methods for performing this crucial task have therefore been sought for decades.

One underused trick for separating americium from lanthanides is to change its oxidation state. A tantalizing option would be to oxidize americium to the +VI oxidation state. This state is not accessible to lanthanides, but can be reached by certain elements in the actinide series, including uranium, neptunium, plutonium and americium. The +VI oxidation state of actinides is stabilized by the formation of complexes in which the metals form double or triple bonds with two oxygen atoms; such compounds are collectively known as actinyl ions, and have the general formula  $\text{AnO}_2^{2+}$ , where An represents the actinide. The americium ion ( $\text{AmO}_2^{2+}$ ) is chemically very different from trivalent lanthanide ions, a feature that could be used as the basis of a separation technique.

The challenges in this approach are how to access the +VI oxidation state for americium, and how to stabilize the highly reactive americium ion so that it doesn't return to the more stable +III state during the separation process. To make the challenge even greater, the recycling of nuclear fuel requires conditions that are not conducive to the persistence of such unstable, high oxidation states. The instability of the americium ion makes it capable of oxidizing almost anything, including water or any of the organic solvents used in the previously reported separation processes.

Zhang and colleagues overcame some of

these challenges by using a type of POM known as a selenotungstate to selectively bind to the americium ion, while ignoring the trivalent lanthanides (Fig. 1b); this POM contains nothing organic that could convert  $\text{AmO}_2^{2+}$  back to  $\text{Am}^{3+}$ . Other POMs have previously been shown<sup>4</sup> to stabilize the actinyl ion of plutonium ( $\text{PuO}_2^{2+}$ ), and even  $\text{Am}^{4+}$  (the ion corresponding to the unstable +IV oxidation state of americium)<sup>5</sup>, but the formation of a POM complex that confers long-term stability on the americium ion in aqueous solution is unprecedented. Moreover, the authors were able to obtain an X-ray crystal structure of the  $\text{AmO}_2^{2+}$ -POM complex. Indeed, the fact that this crystal structure could be acquired speaks to the stability of the  $\text{AmO}_2^{2+}$ -POM complex: only two crystal structures featuring  $\text{AmO}_2^{2+}$  had been published before this study<sup>6,7</sup>.

The POM used by Zhang *et al.* has the formula  $[\text{Se}_6\text{W}_{45}\text{O}_{159}]^{24-}$  (Se, selenium; W, tungsten) and the structure of a doughnut-shaped cage with an outer diameter of about 2 nanometres. The atoms that line the hole of the doughnut exhibit crystallographic disorder – that is, these atoms are mobile, which leads to uncertainty in their locations in the X-ray crystal structure. The structure therefore resembles a spider's web when visualized, which is unsatisfactory for understanding how an americium ion fits into the doughnut hole. However, when the authors added the americium ion to a solution containing the POM and characterized the resulting complex, the X-ray data revealed that the tungsten and oxygen atoms around the hole of the POM cage organize to form a pocket that has the perfect geometry to capture the ion (Fig. 1b). Moreover, the doughnut structure remains rigid.

Zhang *et al.* also report that, once the americium ion has become locked into the POM cage, the resulting complex can potentially

be separated physically from lanthanide ions in aqueous solution using an ultrafiltration technique. That is, the authors show that the large POM complex cannot pass through the pores of the filter membrane, whereas the lanthanide ions – which do not get trapped by the POM – can do so.

Other POM cages have recently been used to lock away trivalent curium<sup>8</sup>, americium's heavier radioactive neighbour in the periodic table. In that case, physical separation was achieved by adding caesium ions ( $\text{Cs}^+$ ), which causes rapid precipitation of the solid curium-POM complex from solution. Zhang and colleagues' method could, in principle, be used to separate americium ions from trivalent curium – another separation long sought by the nuclear industry.

Interestingly, but perhaps unsurprisingly, Zhang and colleagues' experiments and modelling efforts show that their POM can also capture the actinyl ions of uranium, neptunium and plutonium about as effectively as (if not slightly more effectively than) the americium ion. The high stability of the  $\text{UO}_2^{2+}$ -POM complex was useful to the authors, because the uranium-238 isotope is much less radioactive and much cheaper than the americium isotopes used for research, Am-241 and Am-243. The  $^{238}\text{UO}_2^{2+}$ -POM complex could therefore be studied in depth as a substitute for the americium complex, without the regulatory, safety, time and cost constraints associated with using americium compounds.

For example, the authors used high-resolution transmission electron microscopy (HRTEM) to produce atom-scale images of individual uranium complexes, which clearly show how actinyl ions bind within the POM cage. This is particularly satisfying because it confirms the binding geometry of the americium ion using a method that overcomes the

problem of crystallographic disorder: X-ray crystal structures represent the average positions of all the atoms in a crystal, which complicates the interpretation of structures if any of the atoms are mobile, whereas HRTEM does not have this problem because it simply produces ‘snapshots’ of single POM complexes. It should be noted that the early steps of nuclear-fuel recycling remove most actinyl ions, minimizing the possibility that such ions will compete with the americium ion for binding to the POM, should Zhang and colleagues’ separation process be implemented by the nuclear industry.

The reported POM does not yet separate americium from lanthanides as well as does another method<sup>9</sup> described last year by researchers from the same group as Zhang *et al.*, in which an organic system was used to oxidize americium to the +V oxidation state. Nevertheless, the new findings are important for several reasons. They demonstrate that POMs have great promise for the selective binding of various radioactive metals in different oxidation states, and offer flexibility in how they can be used for physical separations. They show that the separations could be done in the absence of organic ligands or solvents that can degrade in the presence of these highly radioactive elements, simplifying and increasing the safety of the processes. And finally, the X-ray structure of the AmO<sub>2</sub><sup>2+</sup>-POM complex provides useful information to aid the design of POMs that are even more selective for binding to the americium ion.

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## Evolution

# Genome reveals how the skate got its wings

Chris Amemiya

Genome sequencing, combined with methods for deducing how genomic regions interact, have now provided insight into how the wings that give skates and rays their characteristic shapes evolved more than 200 million years ago. **See p.495**

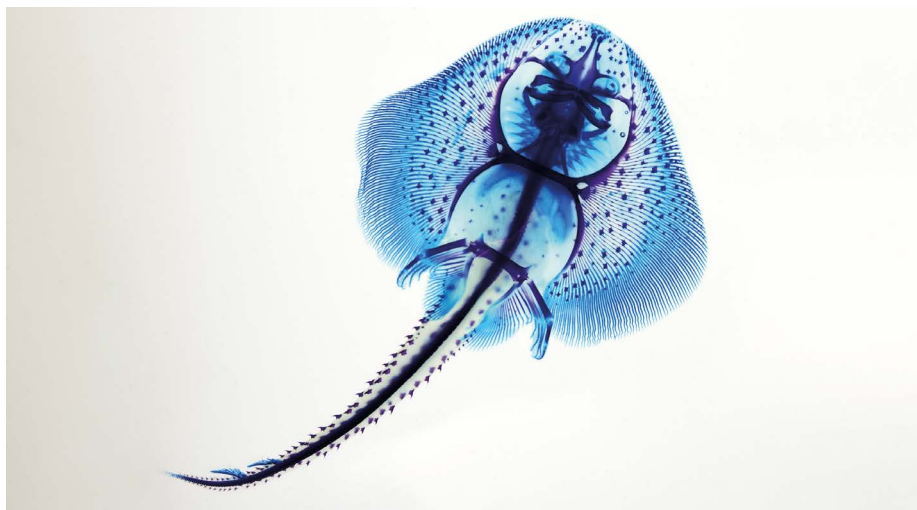
Evolution involves the selection of particular traits, and these frequently arise during embryonic development. This interplay between evolution and development (known as evo-devo) was first recognized by Charles Darwin<sup>1</sup>, but, in the past few years, evolutionary research has been buoyed by remarkable advances in molecular biology and genomics. On page 495, Marlétaz *et al.*<sup>2</sup> report the genome sequence of a fish known as the little skate (*Leucoraja erinacea*). The authors used an armamentarium of sequencing and developmental-biology tools to analyse how skates diverged from their closest relatives, sharks, and how their unusual pectoral fins evolved.

Skates and rays together make up the batoids – cartilaginous fishes characterized by wing-like pectoral fins that extend from their heads, resulting in a flattened body shape (Fig. 1). The evolution of these modified fins gave batoids different locomotor abilities from those of sharks, and enabled them to adapt to life on the sea floor. It has not been known how expanded pectoral fins emerged, although there is some evidence<sup>3</sup> for the

involvement of a rapidly expanding ‘growth zone’ in the anterior part of the pectoral fin (the section closest to the head), which produces the unique fin shape during embryonic development.

Marlétaz and colleagues chose the little skate for their investigation into the evolution of batoid wings because it is one of the few batoid species for which embryos can be readily obtained. The team sequenced the fish’s genome using a bevy of methods. One of these, Hi-C, can reveal regions of the chromosome that do not lie adjacent to one another, but that interact through the formation of chromosome loops. The authors used Hi-C to analyse DNA from developing pectoral fins, capturing fragments of chromosomes that were in close proximity. These fragments then served as anchors that enabled the researchers to produce assemblies (in which individual stretches of sequence are arranged in the correct order) that were the length of entire chromosomes.

The authors also used their Hi-C data set to identify topologically associating domains



**Figure 1 | The little skate skeleton.** Marlétaz *et al.*<sup>2</sup> sequenced the genome of the little skate (*Leucoraja erinacea*), and analysed the genetic changes that led to the evolution of the unusual wing-shaped pectoral fins that extend from either side of its head.

DUNCAN LEITCH