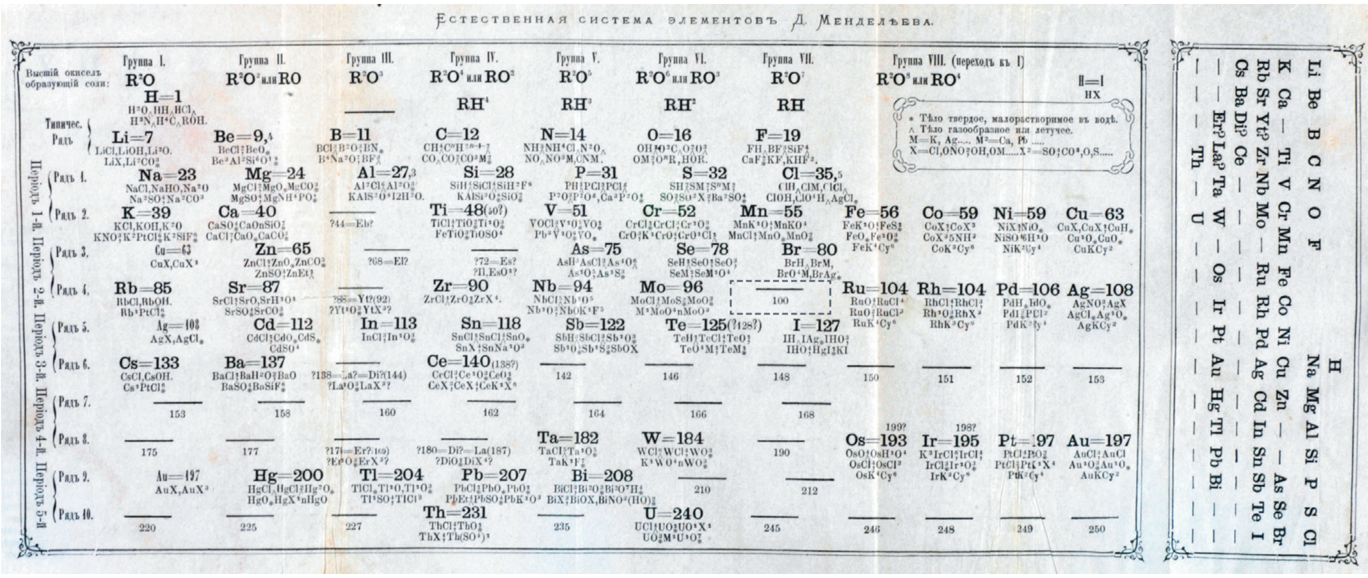

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Figure 1 | Mendeleev's periodic table. When Mendeleev devised his periodic table 150 years ago, he left spaces for elements that he thought were missing. The gap indicated by the dashed box is for element 43. Carlo Perrier and Emilio Segrè[3] discovered this element, now known as technetium, in 1937.

In Retrospect

The first synthetic element

When Mendeleev proposed his periodic table in 1869, element 43 was unknown. In 1937, it became the first element to be discovered by synthesis in a laboratory — paving the way to the atomic age.

KIT CHAPMAN

In 1937, a piece of molybdenum plate arrived at the University of Palermo in Sicily. It had been shipped from the University of California, Berkeley, where it had been part of Ernest Lawrence's 'atom smasher' — one of the first particle accelerators, known as the 37-inch cyclotron. The plate contained the most important missing piece of the chemical world.

Element 43 — provisionally named 'eka-manganese' before its discovery — was a hole in the periodic table set out by Dmitri Mendeleev in 1869. Although there had been earlier attempts to order the chemical elements, Mendeleev arranged his table according to the atomic mass and properties of elements, and left gaps where he felt particular ones were missing (Fig. 1). Most of the spaces were gradually filled, validating Mendeleev's ideas. By the 1930s, the most notable of the still-absent building blocks was eka-manganese. Researchers had long sought this elusive element, but each of the claims had been proved wrong. Now, in Palermo, it was Italian physicist Emilio Segrè's turn to try.

Aged only 32, Segrè already had a reputation for element discovery. A Sephardic Jew and son of a paper-mill owner from Tivoli, Segrè had trained as a physicist under Enrico Fermi before leaving to become an anti-aircraft officer in the Italian army. By 1929, he had rejoined Fermi as one of his 'Via Panisperna Boys', a group of impoverished scientists with a shoestring budget and no modern equipment; the scientists' younger brothers were recruited to lift apparatus, tools were made by hand and the researchers had to hide at the end of the corridor to shield themselves from radiation[1]. Yet despite their hardships, in 1934, Fermi's team had extended the limits of Mendeleev's table.

In France, Frédéric and Irène Joliot-Curie had shown that one element could be turned into another using artificially induced radiation. Fermi, Segrè and the rest of the Boys took the idea one step further by bombarding a sample of uranium — element 92, the heaviest known element at that time — with an improvised neutron beam. In doing so, Fermi seemed[2] to have synthesized elements 93 and 94.

Segrè hoped that Lawrence had unknowingly created another element as a result of using molybdenum in his cyclotron. Molybdenum is element 42; if heavy hydrogen isotopes (deuterons) had accelerated through Lawrence's cyclotron and irradiated a molybdenum plate, it could contain a few specks of eka-manganese. Segrè asked Lawrence to send him any spare parts that had become radioactive. Lawrence, having no use for the discarded metal, happily obliged.

Enlisting the help of his colleague Carlo Perrier, Segrè carried out a chemical analysis of the plate, extracting an unknown element by boiling a sample with sodium hydroxide and hydrogen peroxide[3,4]. It was the first sighting of element 43. With it, the mystery of why this element hadn't been found was solved: eka-manganese was unstable, with a radioactive half-life of a few million years. Any sample that existed naturally when Earth formed would have decayed aeons ago.

The story of the new element was only just beginning. In June 1938, Segrè headed to Berkeley to continue his research. While he was en route, Mussolini's fascist government passed laws barring Jewish people from holding university positions in Italy. Segrè, trapped in California, sent for his family and took up permanent residence. There, he worked with a young chemist, Glenn Seaborg, to isolate an unusual, metastable isotope of his new element[5].

Two pieces of news arrived soon after. In November, Fermi won the Nobel prize for his discovery of elements beyond uranium. Fermi, whose wife was Jewish, used the prize as a pretext by which to escape Italy, too. Then, two months later, word came from Germany that Fermi's 'elements' were a mistake: a group led by Otto Hahn and Lise Meitner had shown that Fermi's discoveries were the result of an atom breaking apart, and were probably barium, krypton and fragments of other elements[6]. This revelation would eventually lead to the development of nuclear weapons — and meant that Segrè and Perrier's eka-manganese was the first true synthetic element. In 1947, ten years after its discovery, they named it technetium, after 'technetos', the Greek word for 'artificial'[7]. By then, all the other empty spaces in Mendeleev's table had been filled, with Segrè also contributing to the creation of element 85, astatine.

The lab-created elements opened up a search for elements heavier than uranium (transuranium elements). In 1939, Berkeley researcher Edwin McMillan approached Segrè about an unusual atom that he'd discovered in the cyclotron, which he believed to be a new element. Segrè dismissed the finding, even going so far as to write a paper[8]: 'An unsuccessful search for transuranic elements'. In fact, McMillan had discovered element 93, which he called neptunium. Then, in February 1941, taking over McMillan's work, Seaborg discovered element 94. With Segrè's help, Seaborg soon proved that his creation — plutonium — could be used in an atomic bomb. It was the first of ten synthetic elements that he would go on to discover; another, seaborgium (element 106), was named in his honour.

Technetium proved that the exploration of the periodic table was not limited to the elements found on Earth. Today, we have extended the table as far as the superheavy element 118, oganesson. With the new elements have come applications few could have imagined: smoke detectors, power for space probes and the most devastating weapons known.

But arguably the greatest discovery remains technetium, and the metastable isotope of the element that Segrè discovered with Seaborg. With its short, six-hour half-life, it is an ideal radioactive tracer. Today, technetium is the most commonly used medical radioisotope in the world (go.nature.com/2t4iqq8), accounting for 80% of procedures in nuclear medicine, and helping to save millions of lives every year. Not bad for something first seen in a discarded piece of metal plate. ■

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1. Fermi, L. *Atoms in the Family: My Life with Enrico Fermi* (Univ. Chicago Press, 1954).
2. Fermi, E. *et al. Nature* **133**, 898–899 (1934).
3. Perrier, C. & Segrè, E. *Nature* **140**, 193–194 (1937).
4. Scerri, E. *A Tale of Seven Elements* (Oxford Univ. Press, 2013).
5. Segrè, E. & Seaborg, G. T. *Phys. Rev.* **54**, 772 (1938).
6. Hahn, O. & Strassmann, F. *Naturwissenschaften* **27**, 11–15 (1939).
7. Perrier, C. & Segrè, E. *Nature* **159**, 24 (1947).
8. Segrè, E. *Phys. Rev.* **55**, 1104 (1939).

PALAEOANTHROPOLOGY

Dating of hominin discoveries at Denisova

Denisova Cave sheltered hominins at least 200,000 years ago, and excavations there have illuminated our understanding of early hominins in Asia. New dating analyses now refine this knowledge. See Article p.594 & Letter p.640

ROBIN DENNELL

Denisova Cave lies in a valley in the Altai Mountains of southern Siberia. Excavations began there 40 years ago, focusing on layers of material from the Middle Palaeolithic period (about 340,000 to 45,000 years ago) and the Initial Upper Palaeolithic (which is defined by the identification of types of stone tool, and often by the presence of items such as ornaments, and which corresponds to 45,000 to 40,000 years ago at this site). The excavations have provided many key insights into the lives of hominins belonging to branches of the evolutionary tree close to that of our own species, *Homo sapiens*. Douka *et al.*[1] (page 640) and Jacobs *et al.*[2] (page 594) now report their use of the latest dating techniques, which lead to a revised timeline of hominin-associated material in this cave.

Previous excavations had uncovered types of ancient ornamental artefact that are often associated with early *H. sapiens*, such as bones shaped into pendants (Fig. 1) and decorative items made of mammoth ivory. However, the cave hit the news headlines in 2010 when analysis of ancient DNA[3] from a bone in a Middle Palaeolithic layer indicated that the specimen was a previously unknown type of hominin from a branch of the evolutionary tree near *H. sapiens*. Such hominins were named Denisovans, and, on the basis of DNA analysis[4], they are probably a sister taxon of Neanderthals.

Analyses of ancient DNA from the site[4–6] indicated the presence of Neanderthals and Denisovans there during the Middle Palaeolithic. However, no signs of *H. sapiens* being present during that time have been found. Neanderthals and Denisovans existed there at too early a time for radiocarbon dating of the specimens, which is usually effective only for dates up to about 50,000 years ago. Other dating techniques, such as thermoluminesence and optical stimulated luminescence, have been the main approaches used to date such remains, although each of these methods has its own drawbacks.

Knowing accurate timings of occupation at the cave would help to shed light on the presence and activities of early hominins, and might address whether the different species overlapped there. However, analysing ancient deposits is tricky. Layers can be disturbed by animal burrowing, subsidence or freeze–thawing cycles. Small items, such as fossil bones or stone tools, might be displaced from their original positions and not be the same age as that of the layer of deposits in which they were found. Douka *et al.* report their dating of Neanderthal and Denisovan fossils of hominin specimens, as well as artefacts fashioned from bones. Jacobs and colleagues report dating information for the cave sediment deposits, obtained using optically stimulated luminescence, and presenting the most comprehensive dating work yet attempted for the deposits at Denisova Cave.

Jacobs and colleagues present 103 dates for sediment deposits that range from more than 300,000 years ago to 20,000 years ago, and that extend across glacial and interglacial episodes spanning timescale stages termed marine isotope stage 9 (MIS 9) to MIS 2. Deposition of sediments at the site was episodic, with numerous gaps indicating periods when either there was no sedimentation or sediments were removed. There is some evidence of post-depositional disturbance, but the crucial late Middle Palaeolithic and Initial Upper Palaeolithic layers show relatively little sign of disturbance. This is the time frame that might mark the appearance at Denisova of our own species. However, when *H. sapiens* first appeared at the site is unknown.

The authors analysed the remains of 27 species of large vertebrate, 100 species of small vertebrate (such as mammals and fishes) and 72 species of plant to make a reconstruction