

Van Gogh's darkening legacy

The brilliant yellows of van Gogh's paintings are turning a nasty brown. **Andrew Brown** reveals how sophisticated X-ray techniques courtesy of the European Synchrotron Radiation Facility in Grenoble, France, can explain why.

Along with his expansive brush strokes, Vincent van Gogh's (1853-1890) choice of vibrant and often unrealistic colours to convey mood and emotion were central to his unique style, one which had a powerful influence on the development of modern painting. The new-generation pigments of the 19th century made it possible for van Gogh to create, for example, the rich yellows used in his celebrated *Sunflowers*. These striking shades, used in many of his works, contained

one of these new pigments, called chrome yellow. Unfortunately, more than 100 years after it left van Gogh's brush, chrome yellow has in some cases darkened visibly to a less than striking brown, a phenomenon that recently caught the interest of a group of scientists.

Vincent van Gogh

An international team led by Koen Janssens of the University of Antwerp, Belgium, believes that chemical changes to chrome yellow

Image courtesy of the Van Gogh Museum, Amsterdam

($\text{PbCrO}_4 \cdot x\text{PbO}$), brought about by exposure to ultraviolet (UV) light, are responsible for its colour transformation (Monico et al., 2011). The darkening of the pigment in sunlight has been known since its invention. Studies in the 1950s demonstrated that it is caused by the reduction of chromium from Cr(VI) to Cr(III) (see Figure 1 on page 20).

Until now, however, the precise mechanism was unknown, and the degradation products were uncharacterised.



1853

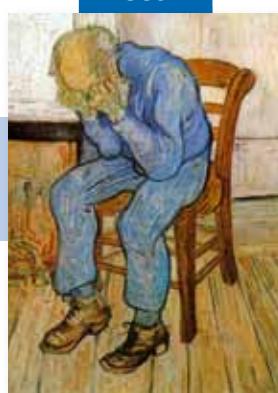
Image courtesy of the Van Gogh Museum, Amsterdam



1888

Image courtesy of the Van Gogh Museum, Amsterdam

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1889

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1890

Image courtesy of the Van Gogh Museum, Amsterdam

Van Gogh, aged 13.
Vincent van Gogh was born in 1853 in the town of Zundert, the Netherlands. Although only active as an artist for 10 years, in this short period he produced more than 800 paintings and 1000 drawings, of which he sold only one in his lifetime

Self-portrait with Bandaged Ear. In October 1888, van Gogh was joined in France, where he was living, by French painter Paul Gauguin. Relations between the two men were fraught, and following an argument with Gauguin on Christmas Eve, van Gogh cut off half of his left ear; a graphic indicator of the fragility of his mental health

Old Man in Sorrow (On the Threshold of Eternity). Van Gogh admitted himself voluntarily to a psychiatric hospital in Saint-Rémy, France. In the 12 months he was there, he produced many of his greatest masterpieces. This painting, completed in Spring 1890, of an old man in despair, provides a further insight into van Gogh's mental state

Wheatfield with Crows. In July 1890, only three months after leaving the hospital and in the middle of a period when his artistic vision was still developing, van Gogh walked into a wheat field and shot himself in the chest. Of all van Gogh's paintings, *Wheatfield with Crows* is probably subject to most speculation. Many believe it to be his last work, interpreting the dramatic sky filled with crows and the cut-off path as portents of his coming death

Historic paint tubes

To address these unknowns, Janssens's team began by collecting samples from paint tubes belonging to van Gogh's contemporary, Flemish painter Rik Wouters (1882–1913). Some tubes contained unmixed chrome yellow paint, whereas others contained paint of a lighter shade of yellow, formed by mixing chrome yellow with a white substance. The researchers artificially aged the samples under UV light, expecting to observe a colour change after several months. To their surprise, in only three weeks, a thin surface layer of the lighter yellow paint had darkened significantly to a chocolate brown. The unmixed samples changed either comparatively little or not at all. "We were amazed," says Janssens.

Having identified the sample most likely to be undergoing the fatal chemical reaction, the team subjected it to sophisticated analyses based on X-rays. Much of the work was carried out at the European Synchrotron Ra-

diation Facility (ESRF)^{w1} in Grenoble, France, where two techniques, XRF and XANES, were used to detect, with extreme sensitivity, the spatial distribution and oxidation state of selected elements in the paint samples (see box on page 22).

Analyses revealed that the darkening of the thin surface layer of pigment was linked to a reduction of the chromium in chrome yellow from Cr(VI) to Cr(III); this fits with what has been observed for industrial paints based on lead chromate. In addition, the Cr(III)-containing degradation product was identified for the first time as $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, better known as the pigment viridian green. But how can a green pigment's presence explain the brown colouration observed in the researcher's experiments? The scientists suspect that the reduced chromium in viridian green is formed during the oxidation of the oil component of the paint. It is this oxidised form of the oil, together with the mixture of green and any remain-

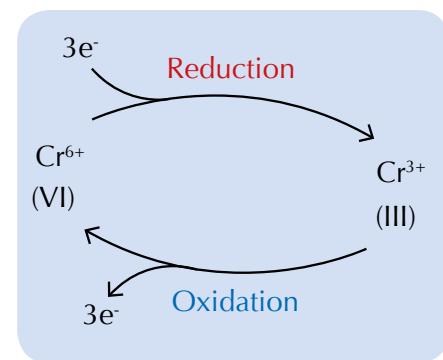


Figure 1: Oxidation state. In chemistry, for reactions that involve electron transfer, oxidation is defined as the loss of electrons, whereas reduction is defined as the gain of electrons. We can describe these oxidation-reduction (redox) processes in terms of the oxidation state of the reactants: oxidation is a reaction involving an increase in oxidation state, whereas reduction involves a decrease. For example, two of chromium's most common oxidation states are III and VI, corresponding to Cr^{3+} and Cr^{6+} species, respectively. We can say that Cr^{6+} is reduced when it gains three electrons to form Cr^{3+} because its oxidation state decreases from VI to III



Chemistry

Physics

Science and conservation

Deterioration by chemical processes

Ages 15–18

This article nicely links science with art and conservation studies. The sophisticated techniques used by the scientists reveal chemical changes in the pigments, which occur many decades after van Gogh's paintings were finished.

The article is a useful way of demonstrating to students that there is always a scientific explanation for why artefacts change with time. It would be best used as a teaching aid in chemistry lessons and for students aged 16–18. The article could also be used to teach selected chemistry topics, such as oxidation and reduction.

To develop the students' understanding of the chemistry behind the research, you could ask the following questions:

1. The work of the scientists described in this article shows that sulphide ions may be the chemical species responsible for the reduction of chromium. Write down separate equations for the reduction of lead chromate (PbCrO_4) by the sulphide-ion-containing compounds H_2S and PbS . Hint: Cr(VI) compounds are oxidising agents.
2. The scientists suggest that sulphate-containing compounds in the paint used by van Gogh may be a source of sulphide ions. Try to think of other ways in which paintings could be exposed to sulphide ions.
3. Silver jewellery darkens over time when in contact with air. Write down the equation for the reaction responsible for this. Note that this is not a simple displacement reaction.

To show that lead chromate darkens when exposed to sulphide ions, you can demonstrate the following experiment in class:

1. Synthesise lead chromate in a beaker by adding any water-soluble lead salt, such as lead(II) acetate, $\text{Pb}(\text{CH}_3\text{COO})_2$, or lead(II) nitrate, $\text{Pb}(\text{NO}_3)_2$, to an equal volume of potassium chromate solution, K_2CrO_4 . Dilute solutions (~ 0.03 M) will be sufficient.

REVIEW

ing yellow pigment, that may be the root of the brown colouration.

Using the X-ray techniques, the researchers were also able to show that the mixed, lighter-coloured paint contained sulphur compounds. They

concluded that these compounds were somehow involved in the reduction of chromium, explaining why there was comparatively little darkening in the unmixed paint samples.

2. A yellow precipitate of lead chromate will form instantly. Filter off the residual liquid using a funnel and filter paper. In a fume hood, gently dry the precipitate with a blow dryer, ensuring that it does not dry completely.
3. Prepare a dilute aqueous solution of hydrogen sulphide (H_2S), by dissolving 50 mg sodium sulphide (Na_2S), in 90 ml water. Add the resulting solution to 10 ml hydrochloric acid (HCl , 0.1 M). Stir the mixture.
4. Fill a rubber balloon with air and connect it to a small glass Drechsel's bottle containing a few millilitres of the dilute hydrogen sulphide solution (see image below). Aim the resulting stream of hydrogen-sulphide-gas-containing air onto the surface of the lead chromate precipitate.
5. The precipitate will instantly turn brown. You have simulated and accelerated the darkening process observed in van Gogh's paintings by many orders of magnitude.



Safety note: All soluble lead salts are toxic, and soluble chromates are toxic (above 0.003 M) and suspected to be carcinogenic. Potassium chromate may cause sensitisation and / or ulcers after contact with the skin. There is limited evidence that lead chromate is carcinogenic. It may also cause harm to unborn children, so should not be used if the teacher or any of the students are, or may be, pregnant. Hydrogen sulphide is a toxic gas with a very unpleasant odour.

Perform the above experiment in a fume hood and wear safety goggles and gloves. Dispose of all chemicals according to your local safety regulations. See also the general safety note on the *Science in School* website (www.scienceinschool.org/safety) and on page 73. You may find it helpful to consult the CLEAPSS student safety sheets on chromium and lead^{w5}.

Vladimir Petruševski, Republic of Macedonia

Shining the X-ray beam on van Gogh

Having uncovered the chemistry of the reaction in isolated paint samples, the scientists sought to ask whether the darkening of the surface layer of



Studying art with a synchrotron

The chemical characterisation of precious works of art can be problematic. It is only possible to take a few very small samples for analysis, and these often consist of a diverse mixture of complex compounds in heterogeneous states of matter. To overcome these challenges, scientists use techniques based on X-rays. The more powerful and precise the X-rays are, the better the quality of the analysis. The most potent X-rays available are produced by a synchrotron source^{w2} (see Figure 2). In this study, two spectroscopic techniques at ESRF were used on the paint samples: XRF and XANES.

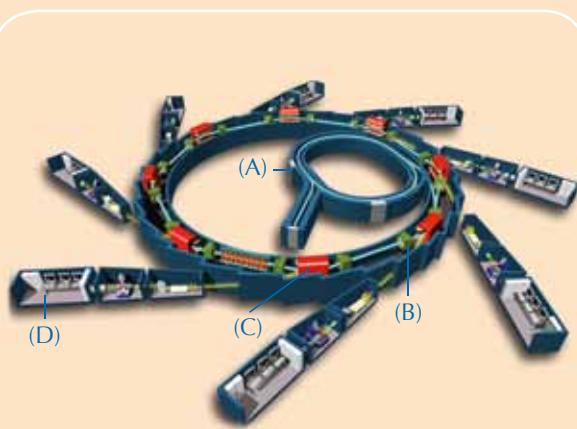


Image courtesy of EPSIM 3D / JF Santarelli; Synchrotron Soleil; image source: Wikimedia Commons

BACKGROUND

Figure 2: Synchrotrons. There are currently about 50 synchrotrons in the world, of which ESRF is the most powerful in Europe. The X-ray beams produced by ESRF are a thousand billion (10^{12}) times brighter than those produced by a hospital X-ray machine. Their high intensity and narrow diameter (100 µm to <1 µm) permit the detection of minute concentrations of elements at sub-micro-scale resolution and from the smallest of samples. The production of X-ray beams in a synchrotron begins with electrons (A), which are accelerated to a very high energy (six billion electron-volt, 6 GeV, at ESRF) before being injected into a storage ring (B) where they circulate in a vacuum at close to the speed of light. Strong magnetic fields (C) cause the electrons to change direction, resulting in the emission of the X-ray beams, which are directed towards the experimental stations (D) that surround the storage ring

XANES

XANES spectroscopy relies on the physics of X-ray absorption. Atoms of a particular element absorb X-rays in a characteristic way. By looking at the X-ray absorption spectrum, which is the pattern of X-ray absorptions of a particular sample (Y axis) against the energy range of the X-rays (X axis), it is therefore possible to identify the sample's constituent elements. High-resolution X-ray absorption spectra are usually collected in particular energy regions (called XANES) that are close to an *absorption edge* of an element of interest (see Figures 3 and 4). Such detailed spectra can show what oxidation state the element of interest is in. This information was of great interest to the researchers.

Figure 3: X-ray absorption

(A) X-ray absorption spectrum. Let us take a pure sample of an element. If X-rays directed at the sample are scanned through a range of energies, at certain energies the rays will be strongly absorbed, giving rise to a series of *absorption edges*. Each edge corresponds to the specific energy required to eject an electron occupying a particular energy level in the element's atoms (see Figure 4). Thus, a 'pattern' of absorption edges emerges that is specific to atoms of that element, a sort of atomic hallmark. In a sample that consists of multiple unidentified elements, it is possible to deduce the identity of those elements by observing the pattern of absorption edges (the X-ray absorption spectrum). The purple, green and red arrows correspond to the ejection of electrons from the first ($n=1$), second ($n=2$) and third ($n=3$) energy levels, respectively

(B) An absorption edge in detail. When we zoom in on a seemingly smooth absorption edge, we can find that it is decorated with a number of smaller impressions relating to correspondingly smaller absorptions. The region at the leading edge of the absorption edge (shaded in blue) is referred to as an X-ray Absorption Near-Edge Structure (XANES, the dark blue box) and it corresponds to electrons making transitions to unoccupied energy levels close to those that they left. The XANES region was used by the scientists analysing the van Gogh paintings, because it can provide information on the oxidation state of the atoms in a sample: atoms that have different oxidation states contain different numbers of electrons (see Figure 1, on page 20). This alters the value of their energy levels and therefore their XANES spectra

Image courtesy of Nicola Graf

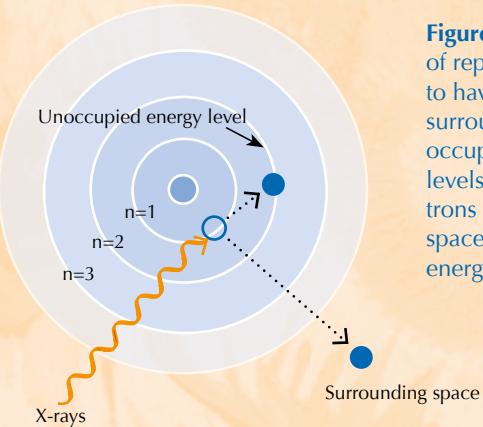
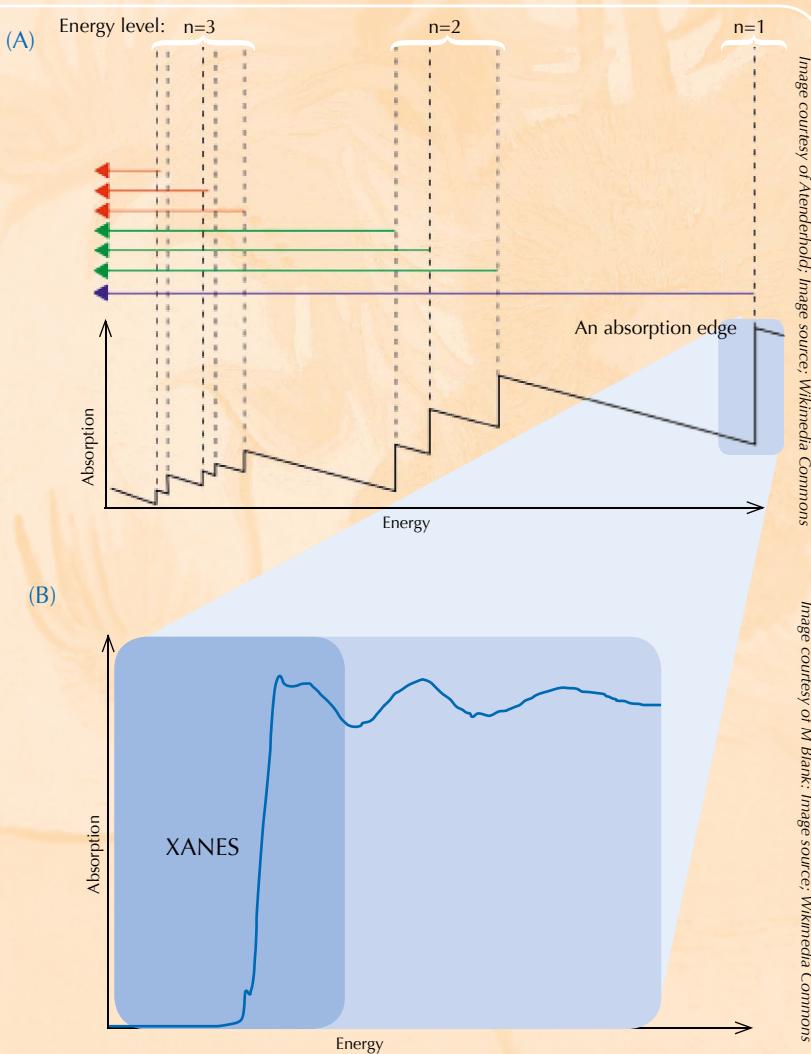
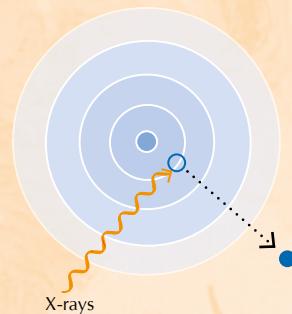


Figure 4: A common way of representing an atom is to have a central nucleus surrounded by electrons occupying distinct energy levels. X-rays can eject electrons either into surrounding space or into an unoccupied energy level

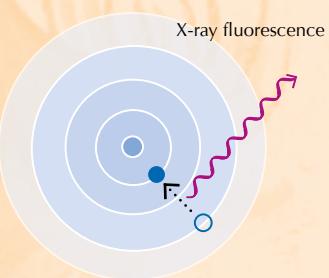


XRF

When they absorb X-rays, atoms enter an unstable excited state. When they then return to a more stable state, they emit secondary X-rays in a process called X-ray fluorescence (see Figure 5). The pattern of X-ray fluorescence (XRF) produced by a particular sample, called the XRF spectrum, can be used to map the distribution of elements across a given area. In contrast, XANES can only be performed on an isolated point in the sample. By combining the information obtained with both XRF and XANES, the authors were able to form a detailed picture of the chemistry of the paint samples.



(A)



(B)

Image courtesy of Nicola Graf

Figure 5: X-ray fluorescence. The ejection of an electron following X-ray absorption leaves an atom in an unstable excited state (A). The most important way in which the atom relaxes back to a stable state (B) is by the emission of secondary X-rays, or XRF signals. This is a consequence of electrons filling the vacancy left behind by the ejected electron

Image courtesy of the Van Gogh Museum, Amsterdam



View of Arles with Irises

yellow paint in samples taken from two of van Gogh's paintings, *View of Arles with Irises* (1888) and *Bank of the Seine* (1887), could be attributed to the same phenomenon.

XRF spectroscopy was used to map the chemistry of the region encompassing the interface between the dark surface layer and the underlying unaltered yellow layer of paint. XANES spectra were collected at specific points within these regions. The findings mirrored those of the previous experiment: the reduced form of chromium, Cr(III), was found in the darker surface layer, suggesting that its presence here was responsible for the brown colouration. Furthermore, Cr(III) was not distributed uniformly, but occurred in loci that also featured sulphate- and barium-containing compounds. Chemically, these regions resembled the lighter yellow paint samples from the previous experiment, further supporting the researchers' conclusion that sulphur compounds were involved in reducing chromium (see equation to the right). Because of their white colour, van Gogh blended powders containing such compounds

with chrome yellow to create the lighter shades that were vital in creating the brightly lit scenes characteristic of a certain period of his life.

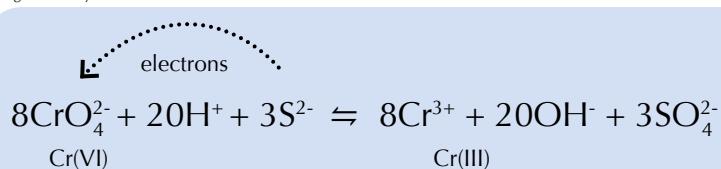
One important question remained: how does the supposed trigger for the reaction, UV light, actually work? Quite simply, it supplies the reactants with the energy needed to overcome the activation energy barrier, allowing the reaction to proceed (see Figure 6 on page 25).

What can be done?

Janssens's team has exposed the chemistry that underlies the darken-

ing of van Gogh's paintings. But can we use this knowledge to rescue the artist's work? Ella Hendriks of the Van Gogh Museum^{w3} in Amsterdam, the Netherlands, has her doubts: "Ultraviolet light...is already filtered out in modern museums. We display the paintings in a controlled environment to maintain them in the best possible condition." Part of what constitutes a controlled environment is the maintenance of a low temperature in the museum. As a general rule, an increase of 10 °C increases the rate of a reaction by a factor of 2-4, and reduction of chromium is no exception to this.

Image courtesy of Nicola Graf



The role of sulphur. Janssens's team believe that sulphide ions (S^{2-}) may be the chemical species responsible for the reduction of chromium. Sulphide ions are an electron-rich form of sulphur, which can readily donate electrons to and thereby reduce Cr(VI) to Cr(III), by the above redox reaction.

Barium was also associated with areas containing reduced chromium, possibly because compounds containing this element were a source of sulphide ions

Image courtesy of Nicola Graf

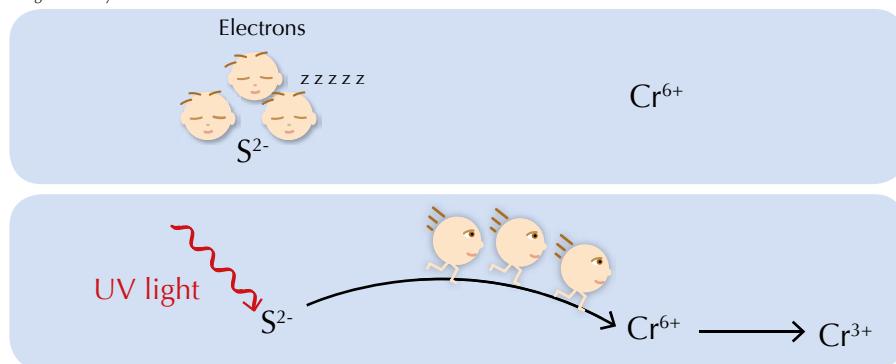


Figure 6: Electrons involved in a redox reaction cannot move spontaneously from one reactant to another. UV light supplies the electrons belonging to sulphide ions (the form of sulphur thought to be involved in the darkening reaction) with sufficient energy for them to become mobile enough to be transferred to Cr(VI)

So if both UV levels and temperature are already controlled, what more can be done for van Gogh's paintings? There is a more radical alternative: rather than slow the degradation process, attempt to reverse it altogether. "Our next experiments are already in the pipeline," says Janssens. "Obviously, we want to understand which conditions favour the reduction of chromium, and whether there is any hope of reverting pigments to their original state in paintings."^{w4}

Although turning back the hands of time in this way would be the supreme solution, Janssens admits that the prospect of reverting the altered pigment to its original colour is at present rather unlikely. Nevertheless, the scientists' work offers us reassurance that we are doing everything we can to preserve van Gogh's paintings, and hope that future generations can appreciate what this great artist achieved.

Reference

- Monico L et al. (2011) Degradation process of lead chromate in paintings by Vincent van Gogh studied by means of synchrotron X-ray spectromicroscopy and related methods. 2. Original paint layer samples. *Analytical Chemistry* **83**: 1224-1231. doi: 10.1021/ac1025122

w5 – CLEAPSS is a UK advisory service providing support in science and technology teaching, on the subjects of health and safety; risk assessment; sources and use of chemicals; and living organisms and equipment. For more information, see: www.cleapss.org.uk

For safety advice on using lead, chromium and their compounds, see the student safety sheets, which can be downloaded for free here: www.cleapss.org.uk/free-publications

Resources

Images and an animation of the investigation of the historic paint samples can be found at: www.vangogh.ua.ac.be

To learn more about the science of preserving art, see:

Leigh V (2009) The science of preserving art. *Science in School* **12**: 70-75. www.scienceinschool.org/2009/issue12/katylithgow

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To read all other *Science in School* articles about research at ESRF, see: www.scienceinschool.org/esrf

Andrew Brown recently graduated from the University of Bath, UK, with a degree in molecular and cellular biology. During his course, he took a year out to work for the agrochemical company Syngenta where he specialised in light and electron microscopy. He now works as an intern for *Science in School*, based at the European Molecular Biology Laboratory in Heidelberg, Germany.



To learn how to use this code, see page 1.

