Wood conservation – the Mary Rose

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Teacher's notes

Acknowledgements

The Royal Society of Chemistry thanks Dr Mark Jones and colleagues at The Mary Rose Trust and Dr Des Barker, formerly of Portsmouth University for their help in producing this resource.

The resource

Overview

The Mary Rose is a wooden Tudor warship that sank off Portsmouth in 1545, during the reign of Henry VIII (1509–1547). Most of her hull became covered in silt, which effectively sealed it and the artefacts it contained in anaerobic conditions and preserved them from decay. In 1982, the hull was raised and since then the hull has been undergoing conservation treatment in a former dry dock at Portsmouth. Over 19 000 artefacts were recovered from in and around the ship and these are also being preserved. Many of them are on display in a museum next to the hull. The ship and the objects give historians and the general public a rare insight into life at sea in Tudor times.

The material presented here looks at the chemistry of the decay processes and the methods used to conserve the wood of the Mary Rose's hull and some of the other materials involved. It provides teaching and learning materials that deal with familiar chemistry in an unfamiliar context. It also helps to show how the chemical sciences play a part in many unexpected areas of life.

As well as these Teacher's notes, there are five pieces of material:

The Mary Rose – a historical introduction. This is a brief introduction to the historical context of the Mary Rose, her sinking, preservation on the sea bed, subsequent raising and conservation. It does not deal with chemistry in any detail and there are no questions. It can be used by teachers as a background to work on the Mary Rose (found in the materials below) and is suitable for independent reading by students between the ages of 11–19. Students could read it before tackling any of the other sections of the material. Students and teachers could also visit **http://www.maryrose.org** (accessed May 2004) to see more material on the context of the Mary Rose.

Why does the Mary Rose need to be conserved? This material is suitable for 11–16 year-old students. It deals with some of the different materials found in the Mary Rose and how they decay. It is set out as reading material interspersed with questions that relate the chemistry that the students know to the decay (and preservation) of materials found in the Mary Rose.

Preserving the wood from the Mary Rose (1). This is also suitable for 11–16 year-old students. It looks at the chemistry of the preservation of the wood of the Mary Rose and is similar in style to Why does the Mary Rose need to be conserved?, consisting of reading material interspersed with questions.

Preserving the wood from the Mary Rose (2). This material is aimed at post-16 chemistry students and looks at the decay and preservation of the wood in the Mary Rose with reading matter interspersed with questions. The main topics covered are intermolecular forces and polymers.

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Metals from the Mary Rose. This is another example of reading matter with questions for post-16 students. It deals with the decay of various metals and the way in which metal objects can be preserved. The main chemical topics are redox reactions and electrochemical cells. http://www.chemsoc.org/learnnet/.

Some material linked to the Mary Rose and suitable for primary students is available separately at

Sample material presented is not directly related to the curriculum, it could be used for revision, homework or in case of teacher absence (planned or unplanned). The material can be tackled by students without teacher input provided that students read *The Mary Rose – a historical introduction* first to set the scene.

All the material presented here is available for free download as Word documents from http://www.chemsoc.org/learnnet/conservation.htm. This means that teachers may edit them to tailor them to their own requirements. Some teachers may prefer to re-present the reading material as comprehension exercises with all the questions at the end rather than interspersed throughout the material.

The material is also available at the same URL as pdf files that can be read using Adobe Acrobat Reader, available to download from

http://www.adobe.com/products/acrobat/readstep2.html.

Notes for the teacher on the material

Why does the Mary Rose need to be conserved

At this level, it was not thought necessary or desirable to distinguish between hemicelluloses and celluloses. For the information of the teacher, celluloses are polysaccharides made up of several thousand glucose (sugar) molecules linked together via oxygen atoms (see Figure 1). Hydrogen bonding between the chains lines up the molecules to form bundles called fibrils.

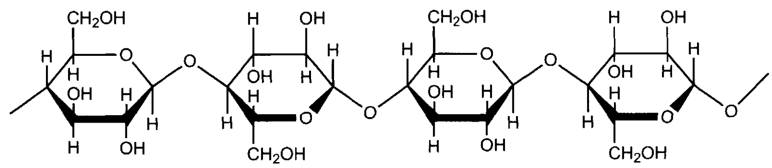

Figure 1 Part of a cellulose molecule

Hemicellulose is also a polysaccharide but has shorter chain than cellulose (between 100 and 200 sugar units) and the chains are branched. In contrast to cellulose, a number of different sugars are found in hemicellulose.

Preserving the wood from the Mary Rose (1)

The point made in the student's material about the chosen conservation method having to allow public viewing was important for financial reasons. The Mary Rose is a major tourist attraction and visits by the public raise a good deal of money which can be spent on conservation. Teachers may wish to stress this economic dimension in the decision-making as well as scientific and purely conservation considerations.

There are ethical debates within the world of museum conservation between conservation (literally 'stopping the rot', but going no further) and restoration (returning an object to how it might have looked originally). Conservators generally try to make sure that any treatment they carry out can be reversed if necessary. There is more material about these issues in the accompanying material on conservation of stone and of plastics.

Preserving the wood from the Mary Rose (2)

It may sound odd to say that in order to preserve the wood from the Mary Rose, it had to be sprayed with water for several years! The long term aim is to have the wood dry but in order to achieve this, spraying with first water, then PEG 200, then PEG 2000 is required so that the drying process is extremely gradual.

Metals from the Mary Rose

Some of the considerations as to which conservation method to use for which metal and in which situation are quite technical. More detail can be found in Mark Jones (ed) *For Future Generations conservation of a Tudor maritime collection*, Portsmouth: The Mary Rose Trust, 2003. This is available from The Mary Rose Trust.

Answers to questions

Answers for Why does the Mary Rose need to be conserved

1. Salt (mostly sodium chloride).

2. (a) Possible answers include precious metals (*eg* gold), some types of stone, glass *etc.*

   (b) Possible answers include more reactive metals, some types of fabrics, paper *etc.*

3. (a) It prevents water coming into contact with the rope.

   (b) Synthetic materials are not attacked by bacteria and other microorganisms.

4. Fish are able to breathe underwater (using their gills to extract the dissolved oxygen).

5. Organic: wood, leather, wool, silk, bone, hemp, horn, flesh
   Inorganic: bone, bronze, copper, cast iron, lead, pewter, gold, glass, stone, pottery, brick, silver, steel.

NB Bones could be placed in either list – organic because it was once-living, inorganic because it is not (mainly) carbon-based. This could be discussed with a suitable group of students.

6. Mainly synthetic (man-made materials, especially synthetic polymers including poly(ethene) (polythene), Nylon™, polyesters such as Terylene™. A significant amount of aluminium would also be expected. Aluminium was not isolated until much later than Tudor times (1827).

7. Temperature, concentration of reactants (pressure of gaseous reactants), surface area of solid reactants, catalysts and (in some cases) light.

8. Metals vary in their intrinsic reactivities (essentially the ease with which they lose electrons). Some metals (aluminium is the classic example) form a protective oxide layer on their surface that prevents further oxidation.

9. The tar prevented water, air and microorganisms coming into contact with the ropes.

10. It already has a high percentage of oxygen in its structure.

11. (a) The (pure) metals known in Tudor times were: iron, copper, zinc, silver, gold, mercury, tin and lead. These are all relatively unreactive metals which means that they could be found uncombined (*eg* gold) or could be fairly easily

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extracted from their compounds (*eg* by reduction of the oxide with carbon, as in the case of iron).

(b) Gold, it is the least reactive.

12. Gold is an extremely unreactive metal – it is almost unaffected by water or air.

13. Iron rusts quite rapidly on exposure to air and water (especially salt water).

Answers for Preserving the wood from the Mary Rose (1)

1. **(a)** 6

(b) A glucose molecule contains six carbon atoms and these all end up as carbon dioxide.

2. **(a)** Respiration, *ie* the arrow from 'carbon in green plants' to 'carbon dioxide in the

atmosphere'.

(b) Photosynthesis, *ie* the arrow from 'carbon dioxide in the atmosphere' to 'carbon in green plants'.

3. As carbon dioxide.

4. Photosynthesis.

5. It would be difficult for the public to view. An enormous tank would be required holding a huge volume of water. It would be impossible for researchers to work under water.

6. The metabolisms of living things slow down at low temperatures.

7. It is less dense than steel (4.5 g cm^{-3} compared with 7.9 g cm^{-3}) and also stronger than steel. This means that smaller and therefore less visually-intrusive supports can be used. It is also less readily corroded than many types of steel.

8. **(a)** 44

(b) **(i)** 194

(ii) 1998

(c) The are the approximate relative molecular masses of the two polymers to the nearest round number.

9. See Figure 8. The monomer units are marked with ovals.

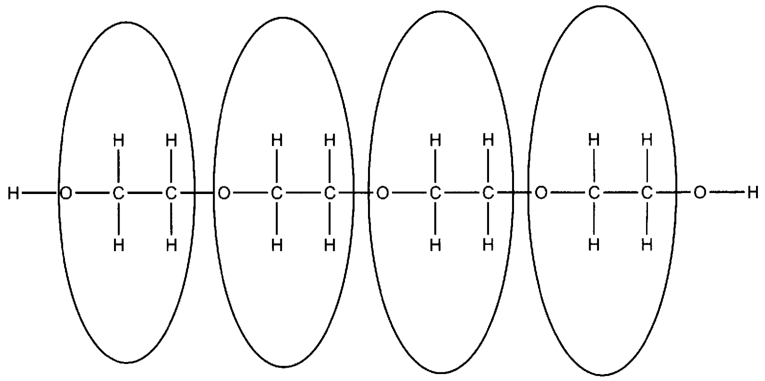

Figure 8

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Answers for Preserving the wood from the Mary Rose (2)

1. There are many types of wood from different types of tree and even wood from two different trees of the same type will be different due to conditions of growth *etc.*

2. **(a)**–OH (alcohol) and R–O–R (ether)

(b) –OH (alcohol) and R–O–R (ether)

(c) –OH (alcohol), $-OCH_3$ (ether), –CHO (aldehyde), aromatic rings.

3. It would be difficult for visitors to view it, it would be difficult to work on, a vast mass of water would be required.

4. It is less dense than steel (4.5 g cm^{-3} compared with 7.9 g cm^{-3}) and also stronger. This means that smaller and therefore less visually-intrusive supports can be used. It is less readily corroded than steel.

5. Their metabolisms will slow down at low temperatures.

6. **(a)** M_r = 200. M_r of the end groups (H and OH) totals 18 which means that the M_r of the repeat unit $(OCH_2CH_2)_n$ must total 200 – 18 = 182. M_r of each repeat unit is 44 and 182/44 = 4.13. So n = 4 to the nearest whole number. It is

not exactly 4 because the bulk polymer will consist of a mixture of chain lengths and also because the value of 200 has been rounded off to a round number

(b) M_r = 2000. M_r of the end groups (H and OH) totals 18 which means that the M_r of the repeat unit $(OCH_2CH_2)_n$ must total 4000 - 18 = 1982. M_r of each repeat unit is 44 and 1982/44 = 45.04. So n = 45 to the nearest whole number. It is not exactly 45 because the bulk polymer will consist of a mixture of chain lengths and also because the figure of 2000 has been rounded to the nearest round number.

7. **(a)** 60°

(b) The C–O and C–C bond lengths are approximately the same so the ring is an equilateral triangle.

(c) Approx. 109.5°.

(d) The four pairs of electrons in the outer shell of the carbon atom mutually repel so they site themselves as far away from each other as possible. This gives an angle of 109.5°.

(e) The shape of the ring forces the O–C–C angle to be much smaller than the ideal angle. Thus the ring tends to 'spring apart'.

8. Between an electronegative atom (N, O, F) and a hydrogen atom covalently bonded to an electronegative atom.

9. The oxygen atom.

10. See Figure 9

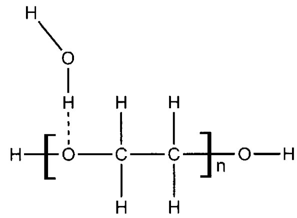

Figure 9 A hydrogen bond between water and PEG

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11. (i) –OH

(ii) –OH, $-OCH_3$, –CHO.

12. (a) There are many possibilities for hydrogen bonding between the polymer and water molecules.

(b) Larger molecules have higher melting points due to there being stronger intermolecular forces between the molecules.

13. Water.

14. $4OCH_2CH_2 + H_2O \rightarrow H[OCH_2CH_2]_4OH$

Answers for Metals from the Mary Rose

1. About 90, depending on which of the semi-metals are counted.

2. (a) Various answers are possible and should be given credit. Among the most likely responses are aluminium, titanium, cobalt, nickel, tungsten, chromium and vanadium. Some will be found in alloys rather than as pure metals.

(b) Reasons will depend on the metals suggested and any sensible suggestions should be given credit. Aluminium is used because of its low density, for example.

3. Mercury – it is a liquid at room temperature.

4. $Zn^{+2}O^{-2}(s) + C^{0}(s) \rightarrow Zn^{0}(l) + C^{+2}O^{-2}(g)$

5. $Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(l) + 3CO(g)$
(an alternative equation with carbon dioxide as the product would be acceptable).

6. Charcoal.

7. The upper equation must be multiplied by 2. This gives the overall equation as

$2Fe(s) + O_2(aq) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^{-}(aq)$

8. $H^{+}(aq)$ ions from the dissociation of water would be attracted to the cathode and discharged:
$2\,H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$

9. Cl^{-} ions will be leached into the water and will form (along with positive ions) a conducting solution that will promote further corrosion.

10. Test a sample of the water with silver nitrate solution. If Cl^{-} ions are present, a white precipitate of silver chloride will be formed:
$AgNO_3(aq) + Cl^{-}(aq) \rightarrow AgCl(s) + NO_3^{-}(aq)$

11. Chlorine

$2Cl^{-}(aq)\ \text{-}2e^{-} \rightarrow Cl_2(g)$

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12. See Figure 4.

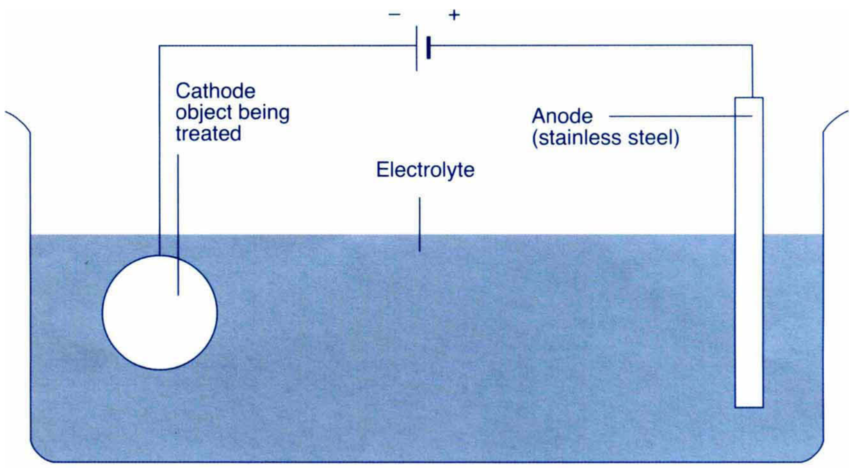

Figure 4 A possible set up for the electrolytic removal of chloride ions from a metal object

13. (a) The Haber process.

(b) It is unreactive.

(c) Hydrogen reacts explosively with oxygen in the air.

14. It takes place a high temperature and involves a gas.

15. Some or all of it would be reduced back to iron:
$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$

More information

If you have access to the internet, you can visit **http://www.maryrose.org**accessed August 2004) for a variety of extra information about the Mary Rose.

This site also gives contact details for The Mary Rose Trust from which a number of publications can be obtained. One particularly useful one is *The Mary Rose Museum and Ship Hall*, Portsmouth: The Mary Rose Trust, 2002. It costs just £2.50 and is suitable for all age groups.

There is an article 'The Mary Rose' in *Catalyst* magazine: Chris Young, *Catalyst*, 1998, 8 (3), 1. This is written for 14–16 year old students but could be used with both older and younger children.

A wealth of technical information about the conservation of the Mary Rose can be found in Mark Jones (ed) *For Future Generations conservation of a Tudor maritime collection*, Portsmouth: The Mary Rose Trust, 2003. This is an academic book giving a good deal of technical detail.

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The Mary Rose – a historical introduction

The Mary Rose is an almost 500 year-old Tudor warship. She was sunk off Portsmouth in a battle with the French in 1545. After spending over 400 years on the sea bed protected from decay by a deposit of silt, her hull was raised in 1982 and is now being preserved in a former dry dock in Portsmouth. Over 19 000 objects were found in and around the ship and these form a sort of 'time capsule' giving historians a unique insight into life in Tudor times. Many scientists, including chemists, are involved in devising and carrying out methods for preserving the ship and her contents from further deterioration so that historians can carry out research and the general public can view this Tudor marvel.

Figure 1 The Mary Rose as she looked in her prime

The Mary Rose was built in Portsmouth and launched in 1511. She was the pride of the Navy in the time of Henry VIII, who ruled from 1509 to 1547. In July 1545 she was sunk during a battle with a French fleet that was attempting to invade England. She went down only about two kilometres (just over a mile) from Portsmouth. We know this because the loss of the ship was recorded at the time – it was watched by a large crowd including the king himself. Nobody is quite sure of the reason she sank. The English version was that the ship was overloaded and mishandled. The French version is that she was hit by French cannon fire, though no French cannon balls have been found inside the wreck.

There was a heavy loss of life when the ship sank. Although the ship was close to shore, nets had been placed over the deck to prevent the enemy boarding her and these stopped many of the crew from escaping as the ship went down.

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Why is the Mary Rose so important?

The working lives of wooden Tudor ships were only a few tens of years. Their hulls were attacked by a variety of wood-boring organisms and after this length of time they became uneconomic to repair. So, there are very few existing examples of ships from this era. The Mary Rose is very special because she was a working ship when she sank. Studying the Mary Rose and the objects found with her gives historians a sort of 'snapshot' of life in the mid-1500s because as well as items connected with seafaring and naval warfare, many of these objects relate to normal everyday life at the time. These range from medical instruments to a backgammon set and carpenter's tools to clothing – a small selection is shown in Figure 2.

Figure 2 A small selection of objects found in and around the Mary Rose

How did the Mary Rose survive over 400 years on the sea bed?

What is so unusual about the Mary Rose is that she did not completely rot away during her over 400 years on the sea bed. This was because much of the wreck became covered in silt which protected it (Figure 3).

- She sank onto a bed of silt (a fine mud), and tipped over to the right (starboard).
- A lot of her contents fell into the lowest part of the ship.
- She was anchored to where she fell partly by the weight of her cannons.
- The strong tide washed the silt into the hull where it was trapped and the bottom half of the hull with all its contents was buried there.

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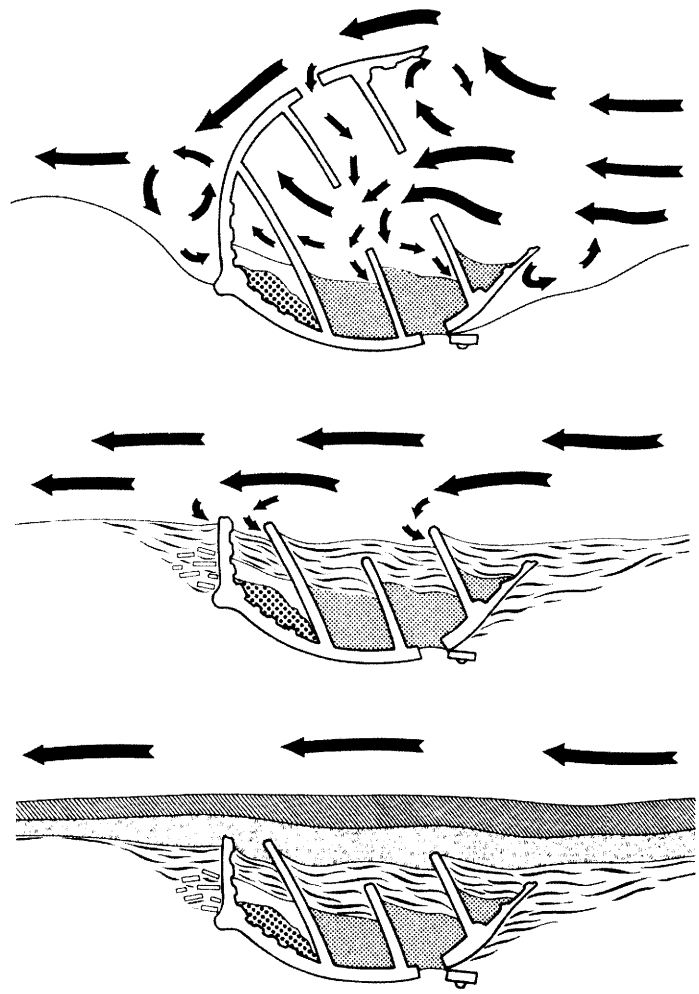

Figure 3 Why the Mary Rose did not rot away
Top: After she sank, the lower part of the Mary Rose's hull filled with silt. This protected the lower timbers but the exposed upper ones were eroded and attacked by a variety of organisms.
Middle: After some time the weakened upper timbers collapsed.
Bottom: Much later a hard layer of clay and crushed shells sealed away the ship and its contents.

The silt acted to protect the part of the ship that was covered by it. It kept the oxygen that is dissolved in seawater away from the ship. In the parts of the ship that were covered, microorganisms, such as fungi and bacteria and larger organisms such as worms could not attack the wood because these all need oxygen. The part of the ship sticking out of the silt rotted away, but the buried section lay preserved under a layer of silt, clay and crushed shells 12 metres (40 feet) below the surface of the sea. Many of the contents of the ship that had fallen into the hull were also preserved in the airless conditions under the silt. As well as the cannons and other weapons you would expect in a fighting ship there were many everyday objects.

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Raising the Mary Rose

Raising the Mary Rose was a major engineering task because the hull was deep under the water. It was also more than 400 years old and likely to be quite fragile especially once it was out of the water that helped to support its weight.

The problem was tackled by building a steel lifting frame and suspending the hull of the boat from this. Steel cables were used to attach the wood to the lifting frame. Then, the hull was moved (still under water) to a steel support cradle, lined with air bags. The cradle and hull were then lifted to the surface and out of the water. This whole operation took over nine months. It is shown in Figures 4 and 5

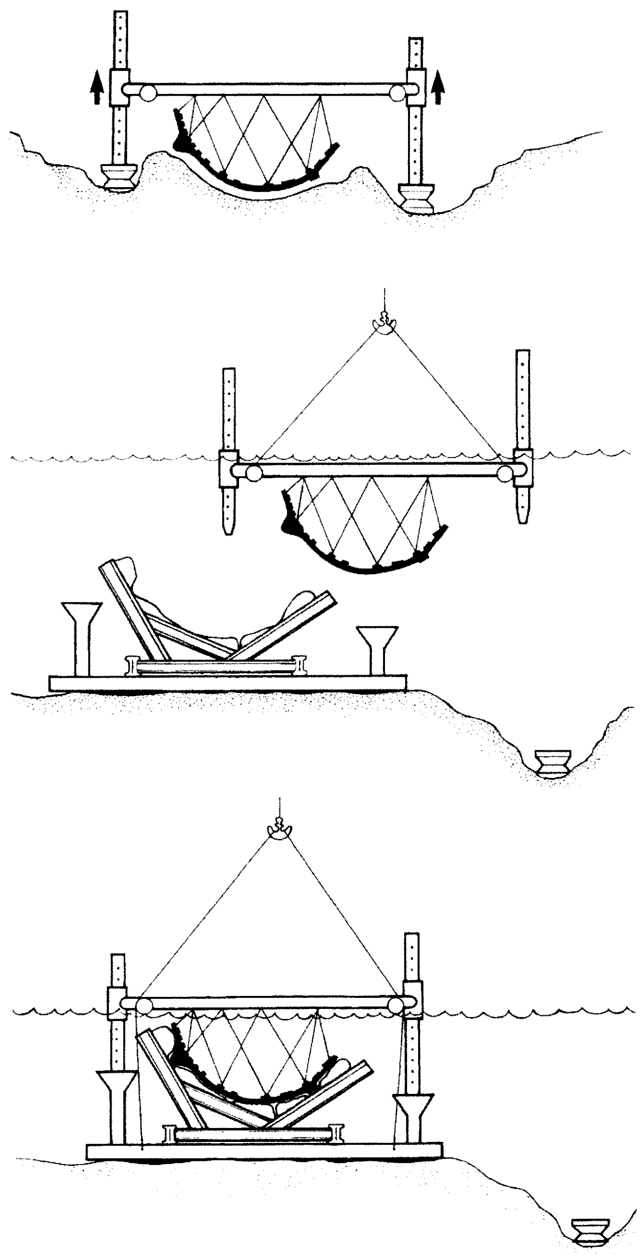

Figure 4 How the Mary Rose was raised
Top The Hull was attached by cables to a steel lifting frame.
Middle Still underwater, the frame and hull were lifted by crane onto a support cradle. The water helped to support the weight of the hull.
Bottom The support cradle holding the hull was lifted out of the water.

Figure 5 The Mary Rose sees the light of day after 437 years

Why does the Mary Rose need to be conserved?

The Mary Rose was rediscovered in 1836 and divers brought to the surface some objects including guns. In the 1960s divers carried out surveys of the wreck site and in the 1970s it was decided to try to raise the remains of the ship. In 1982 she was raised and transported to a former dry dock in Portsmouth.

The remains of the Mary Rose and many of the thousands of objects found in and around her are now in the course of being preserved so that historians can find out about life in Tudor times and so that the general public can visit and marvel at her (Figure 6). However, a great deal of effort has to be put in to ensure that, having survived over 400 years on the sea bed, the remains of the Mary Rose and the objects found in and around her can be preserved for posterity. This effort involves many scientists, including chemists, who need to understand the processes that cause decay and devise ways to control them.

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Figure 6 The Mary Rose as she is today (2004), being sprayed with a waxy solution as part of the preservation process

As well as the ship itself, over 19 000 objects were recovered from the wreck. These range from guns to medical instruments and clothing to coins and include a large range of materials – metals, cloth, rope, leather and many others. During their over 400 years on the seabed, each material decayed in a different way and at a different rate. Now they have been recovered they require different methods of conservation to prevent further decay now they are exposed to air and higher temperatures and to enable them to be studied and/or put on display.

More information

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As well as the ship itself, over 19 000 objects were recovered from the wreck of the Mary Rose. These range from guns to medical instruments and from clothing to coins and include a large range of materials – metals, cloth, rope, leather and many others. During its over 400 years on the seabed, each material decayed in a different way and at a different rate. Now they have been recovered they require different methods of conservation to prevent further decay and to enable them to be studied and/or put on display.

The objects are made from a variety of materials but the main one in terms of sheer bulk is wood. Wood does not last for ever in contact with water and the air that is dissolved in it; it is attacked by bacteria, fungi and wood-boring animals and slowly rots away. Because there are many organisms that attack wood and other similar materials, most archaeological finds are ceramics (*eg* pottery), stoneware or precious metals, like gold. These are not attacked chemically by the oxygen in air, and bacteria and fungi are not able to digest them.

Q1. What is present in seawater as well as water and dissolved air?

Q2. **(a)** Suggest three materials that you could put in seawater that might last 500 years or more.

(b) Suggest three materials that you could put in seawater that would rot within a year.

Stopping the rot

Materials that would otherwise rot in water can be preserved for longer if their surfaces are coated with a waterproof protective film. In Tudor times, shipbuilders used to use tar or pitch. This is a sticky, waterproof material that is obtained by making cuts in a pine tree and collecting the sticky substance that the tree produces to seal the cuts. It can be melted down (an oven was found on the Mary Rose for this purpose) and the liquefied pitch applied to sails, ropes etc. The ropes aboard the Mary Rose were made from a plant-based material called hemp. They still smell tarry.

Q3. **(a)** Suggest how applying tar might help to preserve a rope made from hemp.

(b) Modern rope is made from synthetic materials such as Nylon or poly(propene) (polypropylene). Suggest why there is no need to protect these ropes with tar.

Because wood rots relatively easily we might have expected the Mary Rose to have quietly rotted on the seabed. But, something different happened to her.

- She fell onto a bed of silt (a fine mud), and tipped over to the right (starboard).
- A lot of her contents fell into the lowest part of the ship.
- She was anchored to where she fell partly by the weight of her cannons.
- The strong tide washed the silt into the hull where it was trapped and the bottom half of the hull with all its contents was buried there.

Figure 1 shows what is thought to have happened.

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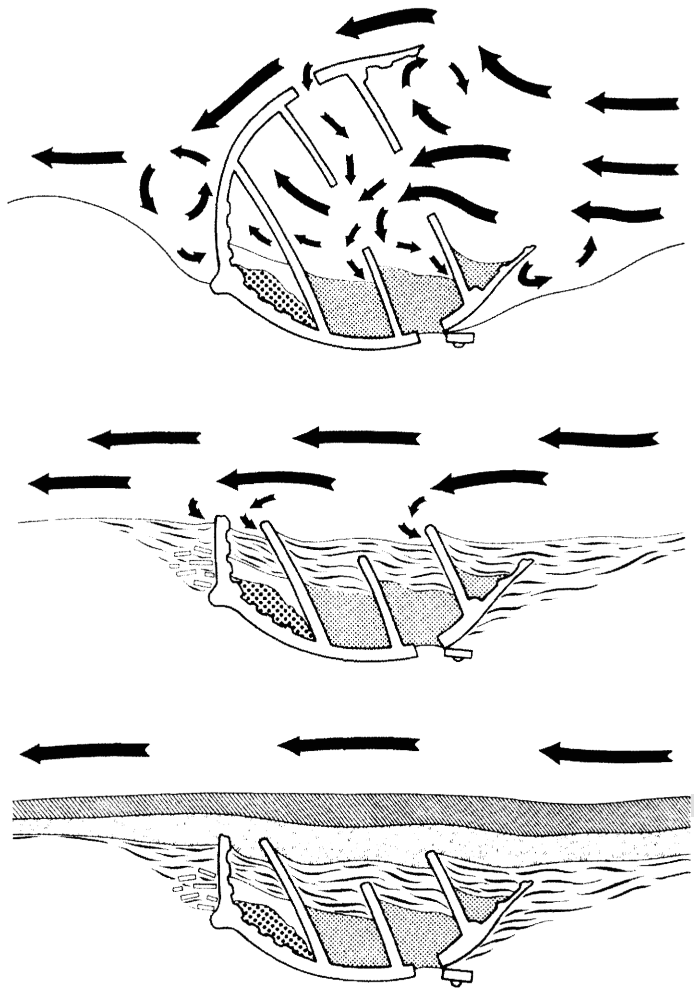

Figure 1 Why the Mary Rose did not rot away

Top After she sank, the lower part of the Mary Rose's hull filled with silt. This protected the lower timbers but the exposed upper ones were eroded and attacked by a variety of organisms.
Middle After some time the weakened upper timbers collapsed.
Bottom Much later a hard layer of clay and crushed shells sealed away the ship and its contents.

The silt acted to protect the part of the ship that was covered by it. It kept the oxygen that is dissolved in seawater away from the ship. In the parts of the ship that were covered, microorganisms, such as fungi and aerobic bacteria and larger organisms such as wood-boring animals (all of which require oxygen) could not attack the wood. The part of the ship sticking out of the silt rotted away, but the buried section lay preserved under a layer of silt, clay and crushed shells 12 metres (40 feet) below the surface of the sea. Many of the contents of the ship that had fallen into the hull were

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also preserved. As well as the cannons and other weapons you would expect in a fighting ship there were many everyday objects. More than 19 000 separate items were found in the hull. Some are shown in Figure 2.

Q4. Suggest an observation that shows us that seawater contains dissolved oxygen.

Figure 2 Just a few of the items found in and around the Mary Rose

How do different materials decay?

Decay means rotting away. It is a series of chemical reactions. The rates of decay of different materials vary enormously. If we look at the some of the things that survived on the Mary Rose we can divide them into organic (or carbon-based) objects and inorganic ones. Organic materials are generally made from things that were once alive and include wood, leather, and silk.

- Organic materials tend to be attacked biologically by algae, microorganisms (organisms that can only be seen under a microscope) and macroorganisms (larger organisms).
- Inorganic materials tend to be oxidised by oxygen (dissolved in seawater in this case).
- Metals, too, tend to be oxidised.

Table 1 lists some of the material used in Tudor times.

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Found in large quantities in the Mary Rose	Not found in the Mary Rose or found only in very small quantities
Wood	Hemp sails
Leather	Horn
Wool and silk	Flesh
Bones	Steel
Bronze / copper	
Cast iron	
Lead	
Pewter	
Gold	
Glass	
Stone	
Pottery	
Brick	

Table 1 Materials used in Tudor times

Q5. Classify each of the materials in the Table into organic or inorganic.

Q6. What types of materials would you expect to find in a modern ship that were not found on the Mary Rose?

What happened over time with either of these groups depended on the conditions that control all rates of reaction. But some things deteriorated more than others, although they were all under the same chemical conditions. Whether they lasted depended to a large extent on their structure and reactivity.

Q7. What are the factors that control the rate of chemical reactions in general?

Q8. Why do some substances of a similar type (*eg* metals) become oxidised at different rates?

How do different materials decay?

Wood

Wood has a complicated structure. Like all once-living materials it is made up of cells. The cells in wood have walls that are made up of a mixture of polymers, mainly celluloses, and lignin. These are present in different proportions depending on the age and type of wood. This makes wood a composite – a material made up of two (or more) other materials, see Figure 3.

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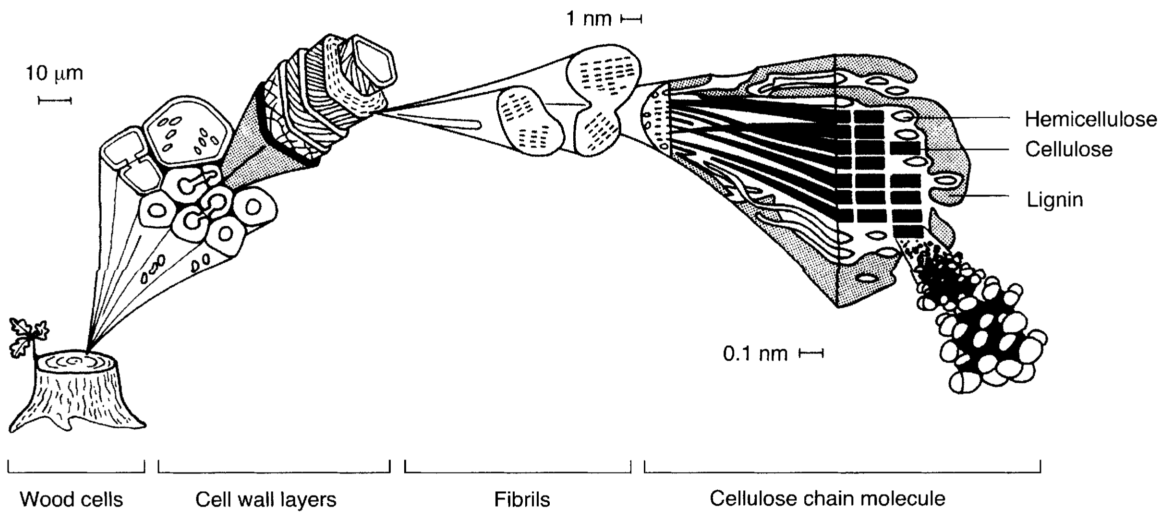

Figure 3 The microscopic structure of wood showing where cellulose and lignin are found. 1 μm is 1 millionth of a metre and 1 nm is 1 thousand-millionth of a metre.

Celluloses (and hemicelluloses) are polysaccharides made up of several thousand sugar molecules linked together. They absorb water, so that the material swells and weakens. After the Mary Rose sank, those materials with a high cellulose content were at first attacked by aerobic bacteria. These will only survive in the presence of oxygen.

Lignin is a polymer with cross-links. This cements the cellulose polymers together. It is a tough material, which does not absorb water and is not easily digested by microorganisms.

Bacteria, fungi and animals such as shipworms all attack wood, see Figure 4.

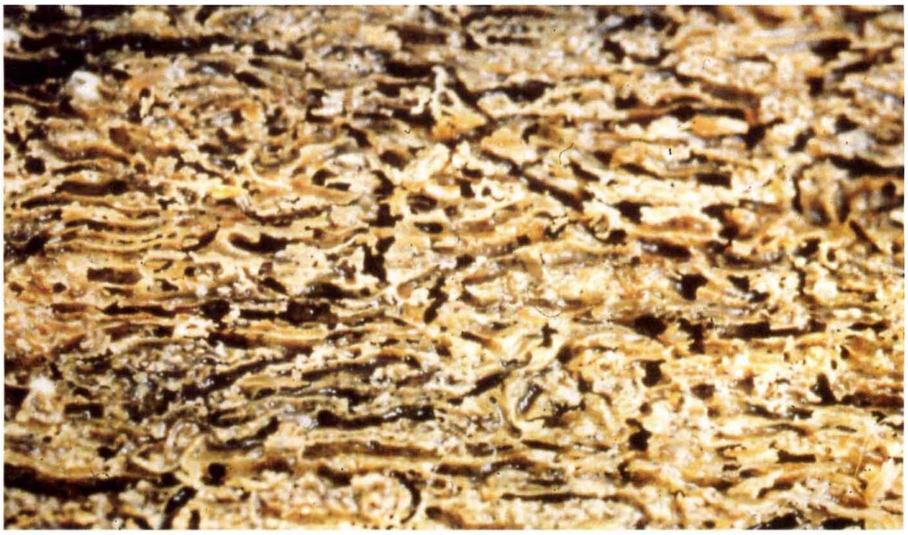

Figure 4 Wood damaged by the wood-boring organism *Limnoria*

Hemp

When the Mary Rose was found, the sails, made of hemp, had almost disappeared. Some of the ropes, also made of hemp, but covered in a tarry, waterproof pitch, were in good condition.

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Hemp is a plant with a cell structure mostly made of cellulose, with little lignin.

Q9. Explain why most of the sails had disappeared, but the ropes had not.

Ceramics and glass

Ceramics (for example pottery and brick) are heat resistant materials – they will neither melt nor react chemically even at high temperatures. In Tudor times, ceramics would have been moulded from clay and then 'fired' in a hot kiln.

Glasses are usually transparent. Like ceramics they are chemically unreactive but they do soften on heating so that they can be moulded and re-moulded.

Both glass and ceramic materials were in use in Tudor times. They decay very slowly on exposure to oxygen and water and many objects made of these materials have been found in and around the wreck. Chemically, both ceramics and glasses are based on silicon dioxide, SiO_2. Figure 5 shows the arrangement of atoms in a typical glass.

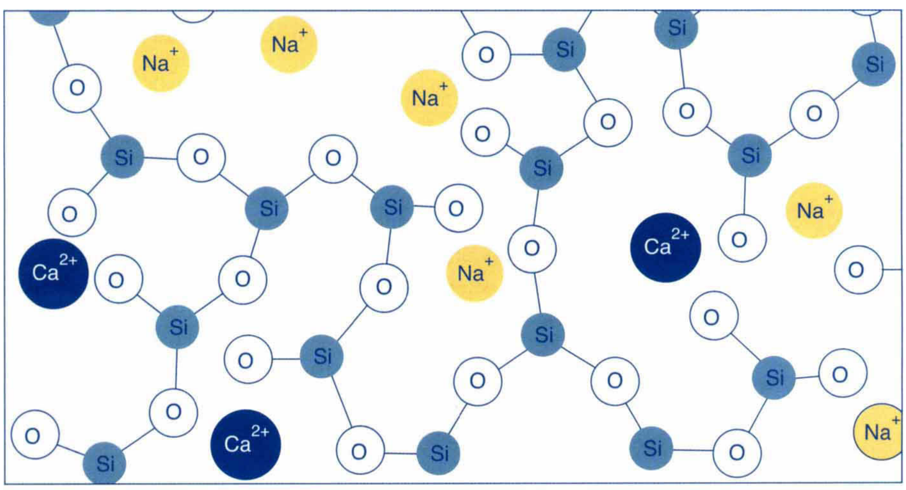

Figure 5 The structure of glass

Q10. Look at the structure of glass. Explain why glass cannot be oxidised.

Metals

Relatively few metals were known and used in Tudor times. Different metals vary widely in how rapidly they react with water and with oxygen. Their reactivities vary from metals like sodium, that react violently when placed in water and tarnish immediately when exposed to air, to gold which will react only with a mixture of concentrated strong acids called aqua regia ('royal water').The list of metals below, is in order of their reactivity, with the most reactive at the top.

Potassium
Sodium
Calcium
Magnesium
Aluminium
Zinc
Iron
Tin
Lead
Copper
Silver
Gold

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Q11. (a) Not all the metals in the list above were known in Tudor times (around 1500). Suggest which ones were known and try to explain. If you have internet access you could use the interactive Periodic Table on the Royal Society of Chemistry website to help you find the elements known at that time (go to **http://www.chemsoc.org/networks/learnnet/periodictable/**, accessed August 2004).

(b) Which of the metals known in Tudor times would be expected to last longest? Explain your answer.

Q12. A gold coin from the Mary Rose can be worth up to £60 000 today. Explain why gold coins were preserved.

Surprisingly, many objects made of iron, such as guns, have survived. Some of them were quickly covered with mussels and other shellfish. When the silt slowly crept over them, the mixture of shells and silt formed a sort of concrete, (called a concretion) which protected the iron. When these objects were brought to the surface, they had to be carefully chipped from the concretion. Under the concretion, the guns were in good condition, see Figure 6.

Figure 6 Chipping concretion from one of the Mary Rose's guns

This method of preservation has not occurred for objects made of other metals – copper, for example. This is because copper compounds are poisonous to most organisms, so the shellfish that formed the basis of the concretion died and did not stick to the object.

Q13. Why is it surprising for objects made of iron to last for over 400 years under the sea?

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Preserving the wood from the Mary Rose (1)

Although objects recovered from the Mary Rose are made of a wide range of materials (leather, horn, metals, ceramics, glass *etc*), see Figure 1, the most important in terms of sheer quantity is wood.

Figure 1 A selection of articles found in the Mary Rose

How wood decays

Wet wood is attacked by a variety of organisms including wood-boring beetles and worms (collectively called macroorganisms), and bacteria and fungi (collectively called microorganisms). Both these groups of organisms need oxygen from the air – they are called aerobic. These organisms, just like us, produce energy by respiration. The chemical equation for respiration is:

glucose + oxygen → carbon dioxide + water (energy given out)

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow XCO_2(g) + 6H_2O(l) \quad \Delta H = -2800\ kJ/mol$

Q1. The symbol equation for respiration (above) is not completely balanced.

(a) What number does X represent?

(b) Explain your answer.

The organisms obtain glucose from one of the constituents of wood – cellulose – which is a polymer made up of many thousands of glucose molecules linked together.

The main reason that the wood of the Mary Rose had been preserved while it was under the sea was that the silt that covered her had kept out oxygen, producing anaerobic conditions. But once the wet wood was lifted on to dry land and into the air it would become a sitting target for the various organisms to attack. The wood also had to be dried. The scientists were worried that if they left it to dry out in the air, the wood

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would shrink, become brittle and destroy the hull. There were several conditions that had to be met:

- The wood had to be kept wet because water was needed to prevent shrinkage.
- The wood had to be protected from attack by microorganisms and macroorganisms.
- The method used had to be cheap and safe.
- There had to be access to the hull so that researchers and those people who were looking after the process could work.
- The ship had to be able to be viewed by the public, in order to raise funds needed for research.

Over the ten years or so before the whole ship was lifted, large numbers of timbers had been brought to the surface (about 3000) – some of the timbers that make up the ship are shown in Figure 2.

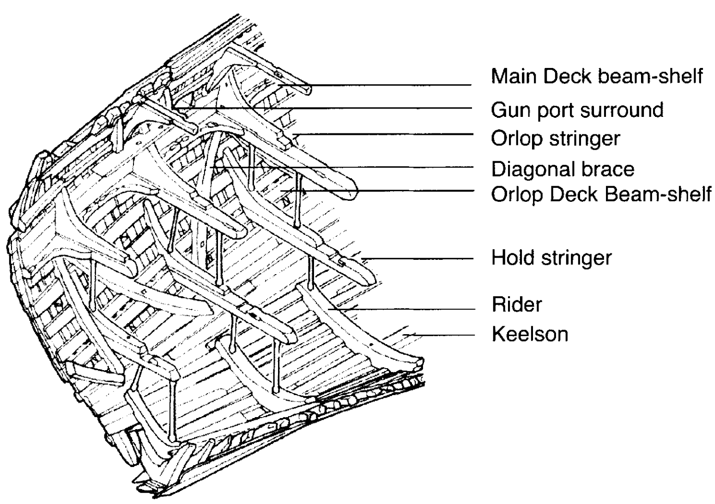

Figure 2 Some of the timber structures that make up the Mary Rose

These timbers, which were made of different types of wood, were studied carefully to learn what needed to be done to stop the wood from decaying fast once it was back on the surface. They were stored underground in the dockyard and the temperature ranged from 9 °C in the winter to 23 °C in the summer. They were studied for attack by organisms at periods.

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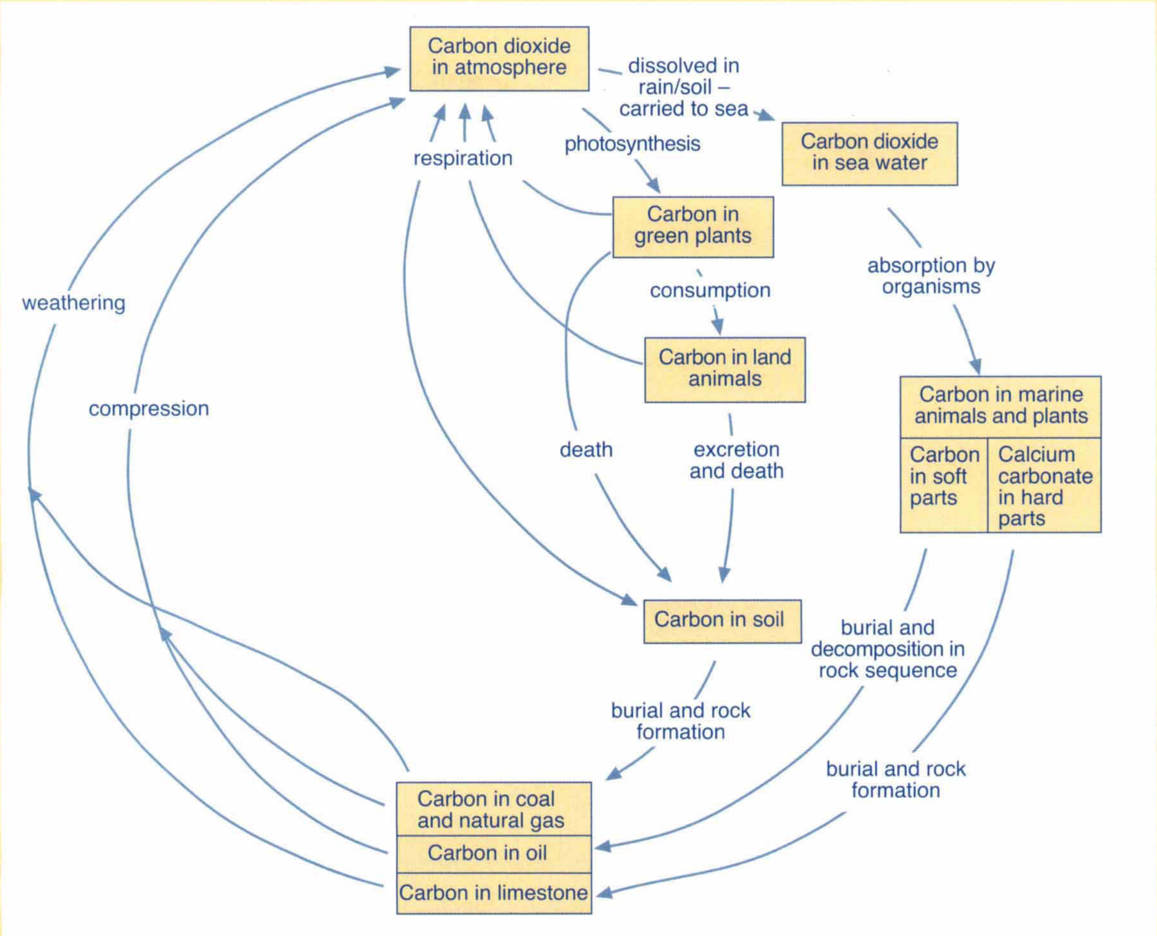
The carbon cycle

Bacteria and fungi use wood as a food (energy) source. This is important part of the carbon cycle. They release the carbon that is locked up in dead wood, and the wood gradually decays away.



Q2. Identify the parts of the carbon cycle that correspond to

(a) the decay of wood

(b) the formation of wood in the first place.

Q3. In what form is the carbon 'locked up' in the wood recycled to the atmosphere?

Q4. Eventually, the carbon that is recycled to the atmosphere will be 'locked up' again in plant material. What is the name of the process by which this happens?

Bacterial and fungal decay started as soon as the timbers were exposed to the air. A beetle called the wharf-borer (Figure 3) was also found to cause extensive damage. This lays its eggs in old timber and when the eggs hatch out, the larvae burrow through the wood. The scientists found that the greater the attack by fungi, the greater the attack by the wood-borers. They concluded that the beetle larvae were eating the microorganisms.

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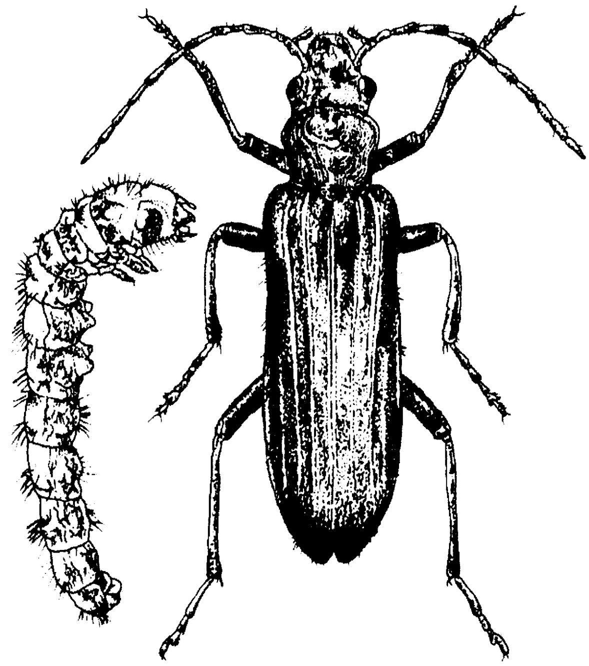

Figure 3 The wharf-borer beetle and larva

They also found that the wharf-borer could get through polythene. So, the scientists now had some information about how to approach the storage of the Mary Rose, once they had brought her out of the water.

The scientists tried some experiments to find out which methods of treatment would work to halt the wood's decay. They found that if they sprayed wood with very cold water, this both kept it wet (stopping shrinkage) and slowed down the growth of the microorganisms and the macroorganisms. They found that they needed a film of water about 1 mm thick on the wood surface.

Q5. Many pieces of wood are preserved by keeping them in a water storage tank. Explain why this was not suitable for the Mary Rose.

Q6. Suggest why low temperatures would slow down the decay caused by living organisms.

The scientists decided on a two-stage process to conserve the hull. The first stage is called a passive stage and involves spraying the wood with cold water. Its function is to give the timber the time it needs to adjust to the conditions of being out of the sea. It is a long process, taking about twelve years. The second stage, called the active stage, involves replacing the water in the wood with a waxy substance to support and strengthen it.

The first stage

Once on the surface, the hull of the Mary Rose was moved to a building once used as a dry dock at Portsmouth. Titanium struts were used to support it. You can see these struts in Figure 4.

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Figure 4 The Mary Rose being sprayed

Q7. Titanium is a much more expensive metal than steel. Suggest why titanium was used rather than steel for the support struts. You may need to look up some of the properties of the two metals to justify your suggestions.

The old dry dock at Portsmouth was made into a huge refrigerator so that the temperature of the hall could be kept between 2°C and 5°C. The wood was then sprayed with chilled tap water so that the surface of the wood was always covered with a film of water that was 1 mm thick. The water was continually recycled. The water was only turned off for a maximum of four times a day, for an hour each time, so that the boat could be examined, worked on and research carried out. A viewing gallery with glass windows allows the public to see the ship even while the spraying continues, Figure 5. This is important because the admission fees help to fund the conservation work.

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Figure 5 The viewing gallery

This process continued for 12 years – from 1982 to 1994.

The state of the timber was continually assessed to see how well the method was working.

The second stage

The second stage is called the active stage. It began in 1994 and will come to an end in 2004.The general idea is to very gradually replace the water in the wood with a wax, which will both preserve the wood and support its structure.

This can be done by soaking the wood in a bath of a suitable chemical or by spraying it. Spraying was again chosen for the Mary Rose, because this meant the ship could continue to be seen by visitors, and scientists could still do research.

Polyethylene glycols

The chemical used is called polyethylene glycol 200 or PEG 200. It is a colourless liquid that mixes with water, Figure 6. The ship is sprayed with a mixture of PEG 200 and water; the PEG 200 is gradually absorbed by the wet wood and the water in the wood is slowly replaced by PEG 200.

This will continue until the water in the wood is almost completely gone.

From 2004 a different grade of PEG will be used with a more waxy property, called PEG 2000, Figure 6. This is a solid that dissolves in water. The mixture of PEG 2000 will be sprayed onto the wood until enough of it is absorbed to support and protect the wood. The changeover from PEG 200 to PEG 2000 is due to place during 2004. The reason for using two different grades of PEG is that PEG 200 is more quickly absorbed than PEG 2000 but gives the wood a somewhat tacky feel.

Figure 6 PEG 200 (left) and PEG 2000 (right)

When the wood has absorbed the wax, the boat will be dried out very gradually in the air.

The chemistry of PEG

Polyethylene glycol is a polymer. Polymers are made up of many smaller molecules called monomers. Monomers join together (polymerise) to make a polymer.

$$\text{monomers} \xrightarrow{\text{polymerisation}} \text{polymer}$$

The monomer for both polyethylene glycol 200 and polyethylene glycol 2000 is epoxyethane, whose formula is OCH_2CH_2. The general formula for polyethylene glycol is $H(OCH_2CH_2)_nOH$. Polyethylene glycol 200 has four monomer units in its chain (plus a H atom at one end and an -OH group at the other) so n = 4, see Figure 7. Polyethylene glycol 2000 has 45 monomer units in its chain (plus end groups) so n = 45.

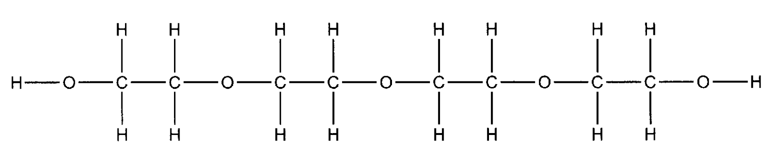

Figure 7 The PEG 200 molecule

Q8. **(a)** What is the relative molecular mass of epoxyethane, OCH_2CH_2? (A_rs: C = 12, O = 16, H= 1)

(b) Use this to help you work out the relative molecular mass of

(i) polyethylene glycol 200

(ii) polyethylene glycol 2000.

(c) Suggest the significance of the 200 and the 2000 in the names PEG 200 and PEG 2000.

Q9. On a copy of the formula of PEG 200, Figure 7, mark the four monomer units.

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Preserving the wood from the Mary Rose (2)

There were around 19 000 artefacts found in and around the Mary Rose. These were made from a large range of materials – metals, ceramics, glasses, horn, hemp, linen *etc etc*. However, in terms of sheer bulk, the main material that required preservation was wood.

The structure of wood

Wood has a complex structure. Like all once-living materials it is made up of cells. The cells in wood have walls that are made up of a mixture of polymers, mainly celluloses (40–50%), hemicelluloses (20–30%) and lignin (20–30%). These are present in different proportions depending on the age and type of wood. This makes wood a composite – a material made up of two (or more) other materials, see Figure 1.

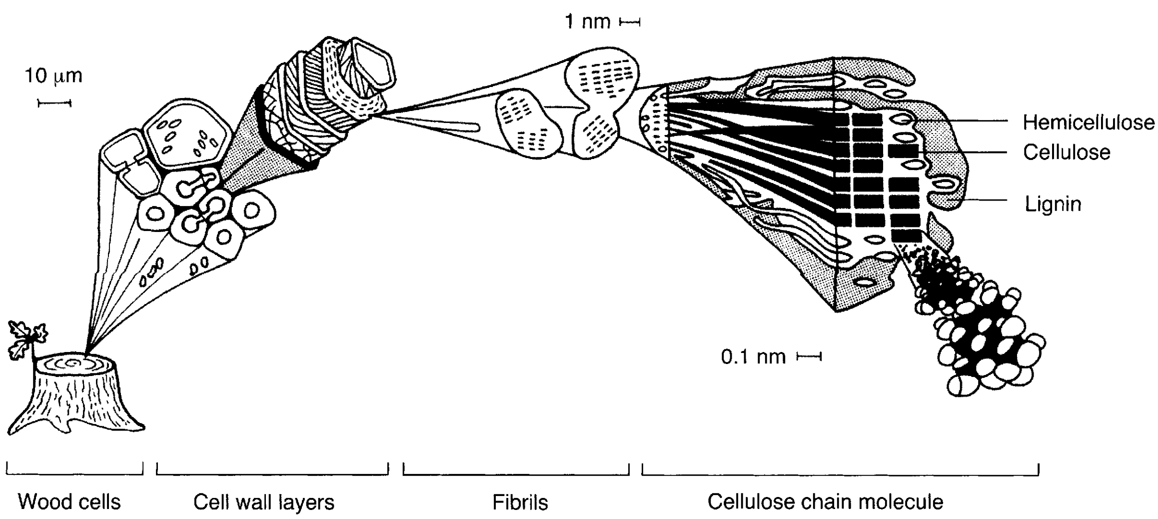

Figure 1 The structure of wood.
1μm is 1 millionth of a metre, 1 nm is one thousand-millionth of a metre

Q1. Why is it an oversimplification to talk about wood as a single material?

Celluloses are polysaccharides made up of several thousand glucose (sugar) molecules linked together via oxygen atoms, see Figure 2. Hydrogen bonding between the chains lines up the molecules to form bundles called fibrils.

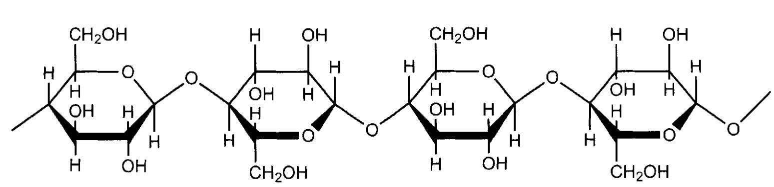

Figure 2 Part of a cellulose molecule

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Hemicellulose is also a polysaccharide but has shorter chains than cellulose (between 100 and 200 sugar units) and the chains are branched. In contrast to cellulose, a number of different sugars are found in hemicellulose.

Lignin is a polymer with cross-links, see Figure 3. This cements the cellulose polymers together. It is a tough material, which does not absorb water and is not easily digested by microorganisms.

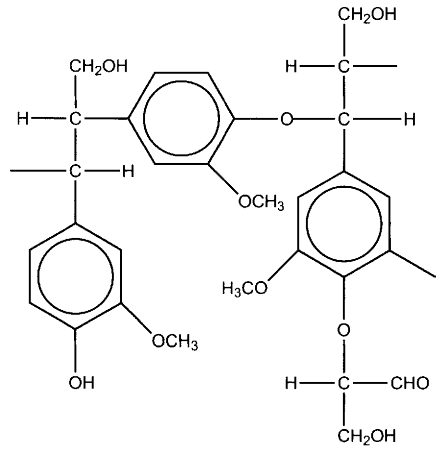

Figure 3 Part of a lignin molecule

Q2. What functional groups are present in a molecule of

(a) cellulose

(b) hemicellulose

(c) lignin?

The decay of wood

When wood is immersed in water, the cellulose and hemicellulose molecules absorb water, so that the wood swells and weakens. They absorb water because hydrogen bonds form between water molecules and the –OH groups of the glucose molecules that make up cellulose and hemicellulose, see below.

Other causes of decay are beetles such as wharf-borers, see Figure 4, and bacteria and fungi. Most of these organisms require oxygen to live and are called aerobic. The reason that the wood of the Mary Rose's hull that was protected by silt rotted very little is that the silt protected it from air, producing an anaerobic environment. The worms and other larger organisms are collectively called macroorganisms while the bacteria and fungi are called microorganisms.

Figure 4 Damage to an oak beam caused by the larva of a wharf-borer

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Most of the bacteria and fungi that attack wood need oxygen to survive. Organisms that need oxygen are called aerobic. These organisms, just like us, produce energy by respiration. The chemical equation for respiration is:

glucose + oxygen → carbon dioxide + water (energy given out)

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)\ \Delta H = -2800\ kJ\ mol^{-1}$

The only organisms that are found living in oxygen-free silts such as the one that covered Mary Rose are anaerobic bacteria. The rates of decay caused by these organisms are very slow.

Preserving the wood of the Mary Rose

Once the wet wood of the Mary Rose's hull was lifted onto dry land and into the relatively warm air it became a sitting target for both microorganisms and macroorganisms to attack. To preserve it, the wood had to be dried in the long term. The scientists were worried that if it left to dry out in the air, the wood would shrink and destroy the hull. There were several conditions that had to be met:

- The wood had to be kept wet to prevent shrinkage.
- The wood had to be protected from attack by microorganisms and macroorganisms.
- The method used had to be relatively cheap and safe.
- There had to be access to the hull so that researchers and those people who were looking after the process could work.
- The ship had to be able to be viewed by the public, in order to raise funds needed for research.

Before the Mary Rose was lifted from the sea bed, the scientists tried some experiments on smaller pieces of timber to find out what would work. They also consulted the work of other conservators who had tackled similar problems, in particular the Swedish ship the Vasa. They concluded that if they sprayed wood with very cold water, this would keep it wet and slow down the growth of both the microorganisms and the macroorganisms. They found that they needed a film of water about 1 mm thick on the wood surface.

Q3. Many pieces of archaeologically important wood are preserved by keeping them in a water storage tank. Use the list above to say why this was not suitable for the Mary Rose.

It would not be practical to spray the ship with water for ever. So, the conservators decided on a two-stage process. The first stage, spraying with water, is called the passive stage. Its function is to give the timber the time it needs to adjust to the conditions of being off the sea bed. It is a long process, taking about twelve years. The second stage, the active stage, involves displacing the water in the timbers with a waxy substance called polyethylene glycol (PEG for short).

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Problems with conservation

One of the problems with the conservation of archaeological relics is that conservators have to be careful about making changes that they cannot reverse. The following (true) story illustrates this.

One of the first objects to be raised to the surface from the wreck of the Swedish ship Vasa was a slab of butter. After 300 years under the sea in cold temperatures it was hard and solid but as soon as it was exposed to everyday temperatures it began to melt and was soon gone.

Conservators need to avoid problems of this sort on a larger scale. In the case of the Mary Rose, any damage caused by drying the hull too quickly would have been impossible to reverse.

The passive stage

Once on the surface, the hull was moved to a former dry dock at Portsmouth. Titanium struts were used to help support it, see Figure 5.

Figure 5 The Mary Rose with the sprayers in action. The titanium struts can be seen clearly

Q4. Titanium is a much more expensive metal than steel. Suggest why titanium was used rather than steel to support the Mary Rose's hull. You will need to look up some of the properties of the two metals to justify your answer.

The dry dock at Portsmouth was made into a huge refrigerator so that the temperature of the hall could be kept between 2° and 5°C.

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The wood was then sprayed with chilled tap water so that the surface of the wood was always covered with a film of water that was 1 mm thick. The water was continually recycled. The water was only turned off for a maximum of four times a day, for an hour each time, so that the boat could be examined, worked on and research carried out.

This process continued for 12 years – from 1982 to 1994.

The state of the timber was continually assessed to see how well the method was working.

Q5. Why would very cold water slow down the growth of microorganisms and macroorganisms?

The active stage

This began in 1994 and is still going on today (2004). The general idea is to very gradually replace the water in the wood with a type of wax, which will both preserve the wood and support its structure.

This can be done by soaking the wood in a bath of a suitable chemical or spraying it. Spraying was again chosen for the Mary Rose, because this meant that the ship could continue to be seen by visitors and that sprays could be turned off from time to time to allow scientists to continue their research.

Polyethylene glycols

The chemical chosen is called polyethylene glycol or PEG for short, see Figure 6. PEG is not a single substance – it refers to a range of compounds all of which are polymers of the monomer epoxyethane, see Figure 7.

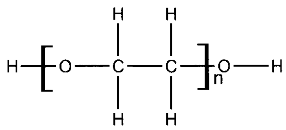

Figure 6 PEG

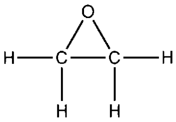

Figure 7 Epoxyethane

Two grades of PEG are used – PEG 200 and PEG 2000, see Figure 8.

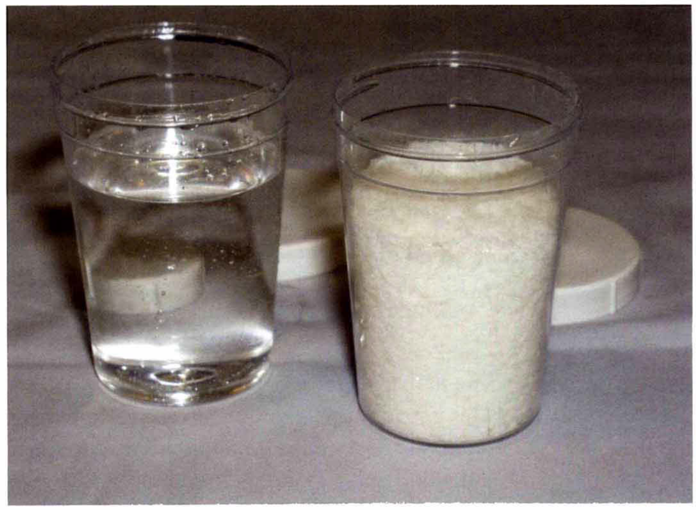

Figure 8 PEG 200 (left) and PEG 2000 (right)

The numbers refer to the relative molecular masses of the two polymers and therefore are a measure of the number of monomers in each polymer – called the chain length. That is, the two polymers have different values of n. The ship was first sprayed with a solution of PEG 200 in water. This will take place for several years, during which the PEG 200 will displace water from the timbers. This will be followed by spraying for several more years with a solution of PEG 2000, which will eventually displace the PEG 200. The changeover is about to take place at the time of writing (May 2004). When this process is complete, the solid PEG 2000 will support and strengthen the decayed timbers. The reason for using two different grades of PEG is that PEG 200 is more quickly absorbed that PEG 2000 but gives the wood a somewhat tacky feel.

Q6. The general formula of PEG is $H[OCH_2CH_2]_nOH$. Work out the number of monomer units in

(a) polyethylene glycol 200

(b) polyethylene glycol 2000.

Remember to take account of the end groups (the groups outside the brackets) in your calculation.

Hydrogen bonding

PEG mixes with water because hydrogen bonds form between the PEG molecules and water molecules.

Both water and PEG will also form hydrogen bonds with the lignin, hemicellulose and cellulose molecules in wood. This is why they are both absorbed by wood.

PEG 200 is a colourless liquid that mixes with water. The mixture of PEG and water is gradually absorbed by the wet wood and the water is slowly replaced by PEG 200.

Q8. Between what sorts of atoms do hydrogen bonds form?

Q9. What atom in the main chain of a PEG molecule will form a hydrogen bond with a water molecule?

Q10. Draw a diagram to show this hydrogen bond.

Q11. Which groups in (i) cellulose and (ii) lignin will form hydrogen bonds with PEG and with water.

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Epoxyethane

Epoxyethane is an important industrial chemical. It has no uses as an end product but is an intermediate used for making a range of other chemicals including anti-freeze (ethane-1,2-diol), detergents, polymers and lubricants. 11 million tonnes are made each year world-wide.

It is made from ethene, which itself is made by cracking long chain alkanes obtained from the distillation of crude oil. Ethene is then heated along with oxygen from the air under pressure and using a silver catalyst to produce epoxyethane:

$CH_2{=}CH_2 + {}^1/_2 O_2 \rightarrow CH_2OCH_2$

Note that epoxyethane actually exists as a ring, see Figure 7.

To make ethane-1,2-diol (ethylene glycol) anti-freeze, epoxyethane is reacted with water:

$CH_2OCH_2 + H_2O \rightarrow CH_2OHCH_2OH$

Epoxyethane is highly reactive, due largely to so-called ring strain in its three-membered ring, see Figure 7.

Q7. **(a)** Look at Figure 6. What is the approximate O–C–C bond angle in epoxyethane?

(b) What assumption are you making in your answer?

(c) What is the normal O–C–C angle in, say, ethanol?

(d) Explain your answer.

(e) Suggest how your answers to (a) and (c) help to explain the reactivity of epoxyethane.

The second phase

The second phase of PEG treatment has just begun (2004). The solution of PEG 200 used to spray the hull has been replaced with one of PEG 2000. PEG 2000 is a waxy solid that dissolves in water. The mixture will be sprayed onto the wood and will displace the PEG 2000 until enough of it is absorbed to support and protect the wood. This process, too, will take several years.

When the wood has absorbed the wax, the boat will be dried out very gradually in the air. Any cavities in the wood that originally contained cellulose will then contain solid PEG 2000.

Q12. Explain why PEG 2000

(a) dissolves in water

(b) is a solid whereas PEG 200 is a liquid.

The chemistry of PEG

Polyethylene glycol is an addition polymer. Polymers are made up of many smaller molecules called monomers. Monomers join together (polymerise) to make a polymer.

$$\text{monomers} \xrightarrow{\text{polymerisation}} \text{polymer}$$

Q13. Look at the end groups (those outside the square brackets in the formula of PEG, Figure 6). The word equation above is a slight oversimplification. What molecule other than epoxyethane is required to form the end groups in the polymerisation process?

Q14. Complete the equation below for the polymerisation of epoxyethane to form PEG 200:

$?\,OCH_2CH_2 + ? \rightarrow H[OCH_2CH_2]_4OH$

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Metals from the Mary Rose

Around 3000 metal objects were found in and around the Mary Rose. These include a wide selection of items including cannon and shot (*ie* cannon balls), utensils and cutlery, coins, navigational instruments, medical instruments and the ship's bell, see Figure 1. There was also a variety of metals, although not as many as would be found in a modern ship. This is because far fewer metal were known in the early 1500s than today. In fact the only metallic elements known at the time were iron, copper, zinc, silver, tin, gold, mercury and lead.

Figure 1 A selection of objects found in and around the Mary Rose

Q1. Use a Periodic Table to help you find out how many metals are known today.

Q2. **(a)** Suggest metals that would be found in a modern ship that were not known in the time of the Mary Rose.

(b) Suggest reasons for the use of these metals.

Q3. Which of the metals known in Tudor times would not be found in the Mary Rose? Explain your answer.

The metals found in the Mary Rose can be divided into ferrous (wrought iron, cast iron and steels) and non-ferrous (copper and its alloys, lead and its alloys, tin and its alloys, silver and gold).

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Extraction of metals

Apart from gold, almost no metals are found uncombined. They are usually found in compounds combined with oxygen, or sometimes sulfur, in which the metal exists as positive ions. Metals are often extracted from their compounds by heating with a reducing agent such as carbon. This removes the oxygen as carbon monoxide. For example

$ZnO(s) + C(s) \rightarrow Zn(l) + CO(g)$

or ionically

$Zn^{2+}O^{2-}(s) + C(s) \rightarrow Zn(l) + CO(g)$

Q4. Put in the oxidation numbers of all the elements in the equation for the extraction of zinc.

Note that this is a reduction process as it involves the gain of electrons by the metal.

This method will only work for relatively unreactive metals, which helps to explain why so few metals were known in Tudor times.

Q5. Write an equation to show the extraction of iron from iron ore (Fe_2O_3) by carbon.

Q6. Suggest a source of carbon that was available in Tudor times.

Corrosion of metals

Corrosion of metals involves metals losing electrons to form positive ions. In this sense it is the opposite of the extraction process described in the box. These electrons must be given to some other species such as another metal. In aqueous conditions such as below the sea, an electrochemical cell is formed between two metals that are in contact, such as iron and copper. The more reactive metal, iron (called the anode), loses its electrons more readily and transfers them to the copper (called the cathode) as a flow of electric current. At the copper cathode the electrons react with oxygen dissolved in the water to form hydroxide ions:

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

$O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

The copper does not corrode.

Q7. Write an overall equation for the corrosion process by adding the two half equations together. You will need to multiply one of the half equations by a suitable factor so that both half equations involve the same number of electrons.

The electrical circuit is completed by the seawater (called the electrolyte) via the movement of sodium and chloride ions.

In the laboratory we could mimic what happens with the setup in Figure 2 which shows the iron and copper as separate strips connected by a wire. It also shows the movement of ions and electrons.

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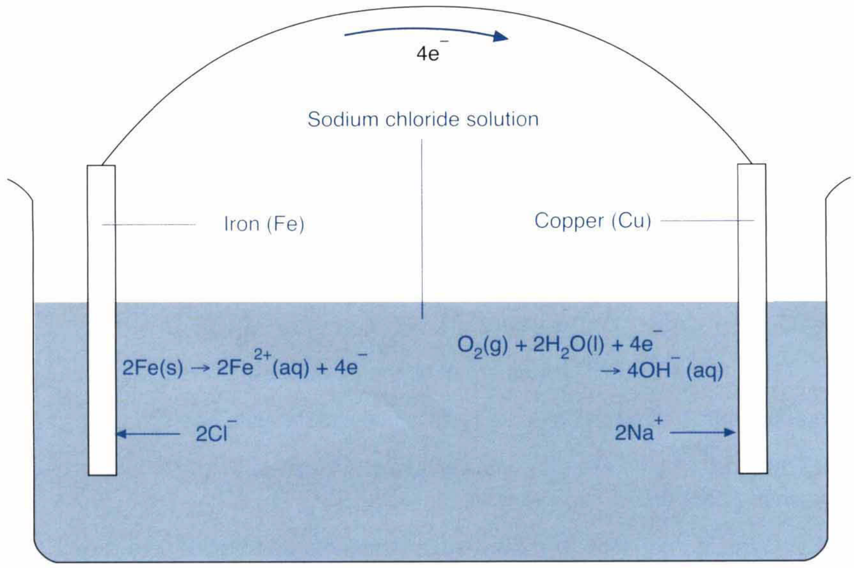

Figure 2 The electrochemical corrosion of iron in the laboratory

At first sight it is difficult to see how a single metal corrodes in this way, but in fact there are always impurities in metals (especially in metals extracted in Tudor times) and cells are set up at the points of contact between the metal and its impurities.

So electrochemical corrosion requires five conditions:

- An anode – the metal that is corroding.
- A cathode – a less-reactive metal that does not corrode.
- Contact between the anode and cathode so that electrons can flow from anode to cathode.
- An electrolyte – this is a solution containing ions that completes the electrical circuit.
- A reactant, such as dissolved oxygen, at the cathode that 'mops up' the electrons released by the anode.

If any one of these is missing, corrosion will not take place. This explains why all the metal objects on the Mary Rose did not completely corrode away during their 400 years under the sea; the silt that covered the ship sealed it away from oxygen. Once the oxygen originally in the sea water was used up no more corrosion could occur.

Concretion

Many of the metal objects from the Mary Rose were found encased in a layer of calcium carbonate – this is called concretion, see Figure 3. Concretion further protected the metal from corrosion.

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Figure 3 A cannon ball removed from its protective concretion

Concretion is caused by the OH^- ions arising from the initial electrochemical corrosion of the metal (see above). These react with calcium hydrogencarbonate that is dissolved in sea water forming a layer of insoluble calcium carbonate (this is like limestone) around the metal object which seals it off from further oxygen and stops the corrosion.

$$Ca(HCO_3)_2(aq) + 2OH^-(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$$

Once the initial layer of calcium carbonate is established, marine organisms (such as mussels, limpets and oysters) can colonise the object and their shells, also made of calcium carbonate, can add to the concretion. However, this did not happen with all metals - copper, for example, is toxic to marine organisms.

Conserving metal objects from the Mary Rose

The conditions around the Mary Rose prevented or slowed down corrosion of metal objects in many cases. However, once objects were recovered and exposed to oxygen again, corrosion could resume. Conservators wished to prevent this happening. Their aims were threefold:

- To stop the corrosion process.
- To leave the shape of the object unchanged.
- To leave the metallic structure of the object unchanged.

To do this they had to tackle a problem caused by the long immersion of the artefacts in sea water. This was that during this immersion the surface layers of metal objects had absorbed chloride ions from the sea water. This could cause two main problems.

Firstly, any water that condensed on the surface of an object would tend to dissolve these ions and form an electrically-conducting solution that would form the electrolyte for electrochemical corrosion. This, together with oxygen from the air could form the ideal conditions for corrosion. To avoid this problem, objects would have to be stored and displayed in extremely dry air – difficult to achieve in a museum, for example, where visitors are continually breathing out moist air.

Secondly, under some conditions, the chloride ions could react to form hydrochloric acid which would itself corrode the metal.

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For both these reasons it was necessary to remove the chloride ions.

Three methods were considered:

1. Washing the objects with water to dissolve the chloride ions out of the surface layer.
2. An electrolytic method in which the artefact is made the cathode (negative electrode). The negative chloride ions would be attracted to the positive electrode and drawn out of the metal.
3. Heating the object in an atmosphere of hydrogen. The chloride ions react with the hydrogen to form hydrogen chloride gas which is then sucked out of the furnace.

Experience suggested that method 1 could take up to five years to remove all the chloride ions. During this time, the object would be immersed in a solution containing chloride ions and would therefore be corroding.

Method 2 would be quicker, but could still take two years. There were two disadvantages. Firstly an electrical connection would have to be made to the object and this might damage it. Secondly, there is a possibility of hydrogen gas being produced at the cathode. If this were too vigorous, it could cause damage to corrosion already present on the cathode. As with method 1, during treatment the object would be immersed in a solution containing chloride ions and would therefore be corroding.

Q8. Explain with suitable equations how hydrogen could be produced at the cathode.

Q9. If method 1 is used, it is necessary to change the water regularly. Explain why this is needed.

Q10. If method 1 is used, it is necessary to test the water from time to time for chloride ions to confirm when all the chloride had been leached out. Suggest how this test might be done and give any relevant equation(s).

Q11. If method 2 is used, what gas will be formed when the chloride ions reach the anode. Give an equation for the formation of this gas.

Q12. Draw a diagram to show a possible setup for method 2.

For iron objects, heating with hydrogen to 850 °C was the method actually chosen – even this had to be done for a week. A special furnace had to be built to hold objects as big as cannon. The reaction that is taking place may be represented as

$2FeCl_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 6HCl(g)$

For safety reasons, the gas used in the furnace was actually a mixture of hydrogen and nitrogen. It turned out to be cheap and convenient to make this gas mixture by decomposing liquid ammonia using a catalyst:

$2NH_3(l) \rightarrow N_2(g) + 3H_2(g)$

Q13. **(a)** What industrial process is this the reverse of?

(b) Why does the presence of nitrogen not affect the chemical reactions taking place in the furnace?

(c) Why might pure hydrogen pose a safety risk?

Q14. Give reasons why the reaction with hydrogen was the fastest process.

Q15. A simplified formula for rust is Fe_2O_3. Suggest what would happen to rust when heated with hydrogen. Write an equation for this reaction.

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Question 15 highlights one problem with the hydrogen furnace method of treatment – it can actually change the metal and its corrosion products rather than simply preventing further corrosion. For this reason samples of the corroded metal were taken and stored before objects were treated in this way. Conservators are keen that objects are changed as little as possible by the methods they use.

For different metals, one of the other methods of conservation was normally chosen. In general, which metal was treated with which method is shown in the Table. Sometimes the method chosen depend on the particular object as well as the metal it was made from. For example very fragile objects might be damaged by making an electrical connection and this could rule out the electrolysis method.

Metal	**Method of conservation**	**Notes**
Iron	Hydrogen furnace	
Copper	Washing with water	Hot water was used as this contains less dissolved oxygen which might have caused more corrosion. This outweighed the increased rate of corrosion caused by the temperature of the water.
Bronze (an alloy of copper and tin)	Electrolysis	
Brass (an alloy of copper and zinc)	Washing in water containing a corrosion inhibitor	Objects were coated with lacquer after soaking
Lead	Washing with hydrochloric acid	The acid dissolved away any concretion and left a film of insoluble lead(II) chloride on the metal surface which protected against further corrosion
Pewter (an alloy of tin and lead)	Electrolysis	Except where the objects were too fragile for an electrical connection to be made.
Silver	Washing or hydrogen reduction	
Gold	None required	Gold is too unreactive to corrode

Your notes

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Your notes

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Your notes

Conservation chemistry – an introduction

This book is divided into three sections, dealing with the conservation of plastics, stone and wood. It provides teaching and learning materials that deal with familiar chemistry in an unfamiliar context. It also helps to show how the chemical sciences play a part in many unexpected areas of life.

Many people think of objects made of plastic as 'throwaway' and do not consider them as collectable items or ones that might be found in museums. In fact there are increasing numbers of plastic objects in museums as well as in private collections and many are increasing in value. To give just one example, some Barbie™ dolls can change hands for thousands of pounds. It is also a misconception that plastics do not decay easily – many of them do, and this raises issues about how best to preserve them. This section is set in a context of the collection, care, identification and display of objects in museums and by private collectors.

The section on stone focuses on a case study. In order to prevent damage to a stone object, conservation scientists sometimes surround the object with filter paper soaked in pure water. This is called poulticing. Conservation scientists at the British Museum wanted to investigate the poulticing process to see how effective it was at removing salts and to find out whether previous treatment of the stone affected the efficiency of the removal process.

The section on wood focuses on the Mary Rose, a wooden Tudor warship that sank off Portsmouth in 1545. In 1982, the hull was raised and since then has been undergoing conservation treatment in a former dry dock at Portsmouth. Over 19 000 artefacts were recovered. The material presented here looks at the chemistry of the decay processes and the methods used to conserve the wood of the Mary Rose's hull and some of the other materials involved.

This book was produced as part of the Royal Society of Chemistry's programme for the support of education in the field of the chemical sciences.

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