Stone conservation – statues and antiquities

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Introduction

This material has been compiled by Ted Lister with the help of the British Museum Department of Conservation.

Acknowledgements

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Susan Bradley, Head of the Conservation Research Group, British Museum
Vincent Daniels, Principal Scientific Officer of the Conservation Research Group at the British Museum.

The resource

This resource consists of two pieces of material suitable for 14–16 year old students and accompanying Teachers' notes. The first section, *Conserving stone objects – a case study*, discusses some of the issues involved with the museum conservation of objects made of stone and looks at a research project to investigate methods of removing salts from porous stone objects. The second, *Practical work on stone*, follows on from the first and, as well as questions, has some experimental work on identifying types of stone, measuring porosity of stone and investigating fillers or glues. There is a mixture of class practical exercises, planning exercises and suggestions for open-ended investigations.

The *Teachers' notes* contain further details for the teacher, especially about ethical debates about how to conserve objects in museums. It also includes lists of requirements for the practical work and answers to all the questions.

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Teachers' notes

How and why we conserve things – ethical debates about how to conserve objects in museums

This section was written by Susan Bradley, Head of the Conservation Research Group at the British Museum. It is presented for the information of teachers who may wish to use it in discussion with their students.

What is conservation?

Museums store and display objects, conserving them to prevent deterioration. To do this work they employ conservators who have been trained in the conservation of collections. A small number of museums employ scientists to carry out scientific investigations on the deterioration and conservation of their collections. These scientists are called conservation scientists, and their work underpins the work of the conservators.

Conservation is about keeping things. In a museum like the British Museum it is about keeping archaeological and historic objects in good condition, and in good repair, so that they can be studied and displayed to provide information and enjoyment for the millions of people who visit the Museum every year, and for future generations. Because archaeological objects, objects that have been dug up from the ground, have often been in wet or salty conditions for a very long time, a lot of damage has occurred. This means that relatively few whole objects are dug up and it also means objects can break down even more when they come into contact with the air. Conservation involves stopping this breakdown and repairing the objects so that they are recognisable.

Conservation is different to restoration. In conservation the conservator reveals the object as it exists, and does not add to it to make it look as it did when it was made. Thus new arms have not been made for the Venus de Milo statue. The conservator is always looking for evidence of how the object was made, or what happened to it when it was in use. This evidence is extremely helpful to the archaeologist, and to those who study the development of ancient technologies.

In restoration an attempt is made to return the object to the way it looked when made. For instance, on a statue lost body parts will be replaced with modern copies. The problem with this is that the copies will be based on studies of other similar statues, and they are not necessarily correct for the individual object. Similarly if a substantial repair is made to a painted and glazed pottery vessel the repair will be painted with a continuation of the design and coated with a resin to give the appearance of the painted, glazed and fired original. This may lead some people to think that the vessel is an intact original, which it is not.

What are the basic principles of conservation?

Conservation scientists, who investigate deterioration and the methods of conservation, and conservators who carry out the conservation of the objects adhere to some agreed principles. These are:

- that the work they do on the objects does not alter the chemistry and physical structure of the material the object is made from;

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- that the chemicals, resins and adhesives used in conservation do not increase the rate at which the object decays; and
- that the chemicals, resins and adhesives are themselves stable.

If restoration or repair is to be carried out, it is usual to try to ensure that they are easily removable. So if a chipped porcelain vase is repaired with filler or adhesive, materials should be used that can later be removed without damage to the rest of the piece – ones that are easily soluble, for example. This is sometimes called 'the principle of reversibility'. Here it is vital to understand the chemistry of the materials used – both of the original material and of the filler or adhesive.

How do objects deteriorate?

There are many different materials in museum collections and many different deterioration processes. Many deterioration processes are not fully understood, and new processes are being identified. However there are some ways in which deterioration occurs which are well researched, and materials can be grouped according to these. A few of these are discussed below.

Metal objects corrode in the air through oxidation. The rate of corrosion increases when the air is humid, and when the temperature is high. Metals also react with gases that are present in small quantities such as sulfur dioxide, forming sulfates on the surface. This is the reason that copper alloy statues in the open air are often green.

Some types of stone and pottery objects are porous, that is, water can pass through them. They can often contain soluble salts, such as sodium chloride, which, in the case of pottery, moved into the object during burial, and in the case of stone are either present naturally, or have moved into the stone from ground water. When the humidity in the air changes, the amount of moisture within the pores of the object changes, and the soluble salts start to move. If there is enough moisture present they are in solution in the pores. If the water dries out they crystallise, both within the pores and at the surface of the object, causing damage, particularly at the surface.

Objects made from natural organic polymers such as wood, leather, ivory, bone, paper, cotton, linen and wool react to changes in the moisture in the air, expanding and contracting. If they expand and contract too much, or the changes in dimensions are very large, the objects can be physically damaged with cracks and tears appearing. The polymers also react with water and acids or alkalis in the air, or present within the object, causing hydrolysis (breaking) of the polymer chain. The polymers can also undergo oxidation, again causing breakdown. These reactions cause the polymers to become more brittle and to change colour.

Paints and dyes used to colour objects can fade, or undergo a colour change on exposure to light. Ultraviolet light is particularly damaging, but exposure to visible light alone can also cause fading.

What are the main activities of conservation?

The conservation of an object can involve several different processes:

- examination;
- cleaning;
- repair; and
- stabilisation.

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Examination

Objects are carefully examined before conservation begins to ensure that the conservators know exactly what they are dealing with. This may be a visual examination, by eye or under a microscope; or it may involve radiography, analysis on the surface of the object, or analysis of a sample taken from the object. As the conservation process proceeds more examination may be necessary.

Cleaning

Objects may be cleaned because they have become covered with dust over years of storage or display. This type of cleaning is not controversial. Objects may also be cleaned to remove thick layers of corrosion, or deposits that have built up during burial. Some conservators think that such layers should not be removed, or that minimal removal only should be carried out. However for an object to be viewed by the public it must be visible and so this type of cleaning is important in museums. For metal objects cleaning is normally preceded by radiography to identify the shape of the object and provide a guide to the conservator as to what they are likely to find. Removal of corrosion and deposits is called investigative cleaning, and it is normally carried out under a microscope so that any material that may be part of the object, or be evidence of its use, is not discarded with the unwanted layers.

Repair

Objects may need to be repaired for a variety of reasons. They may have been excavated in pieces, or have suffered damage following excavation, or have been previously repaired using an adhesive that has failed. Adhesives of several different types are used to stick together pieces of objects. In selecting an adhesive the conservator will take into account the strength of the material the object is made of, the weight of the object, and the ease of removal of the adhesive.

Another type of repair is consolidation and this is used on materials that are powdering and flaking. This type of deterioration is caused by soluble salts in porous objects, by corrosion of metals, and can be caused by dimensional changes on organic objects. Consolidation involves applying a dilute solution of a resin to the surface of the object to stick the powered or flaking particles to the sound body of the object.

Stabilisation

Many objects in museum collections are stable in the museum environment. For those that are not, stabilisation can be approached in two ways – through a treatment applied to the object, or through treatment of the environment in which the object is stored or displayed (preventive conservation). Treating an object to stop deterioration can involve applying a chemical that reacts with the material the object is made from, chemically altering it. This happens when copper alloy objects are treated with benzotriazole to stop a reaction called bronze disease from occurring. Benzotriazole is the material that is applied to copper roofs to protect them. It makes the roof turn green when it reacts with the copper. On the other hand, silver objects are sometimes coated with a lacquer to reduce the rate at which they tarnish. The lacquer does not react with the silver and can be removed.

Preventive conservation is appropriate when the method by which an object deteriorates is fully understood. It is common to keep metal objects that are prone to corrosion at a low humidity, thus preventing the corrosion reaction from occurring; or to remove pollutant gases, (such as the gases that cause silver to tarnish) from the air by filtration in air conditioning systems. This prevents reaction at the surface of objects. Keeping objects at low temperatures will also slow down deterioration reactions, but this can only be used in storage, not display, because visitors would object to very cold galleries.

In order to reduce the deterioration of objects in museum collections conservation scientists conduct research into the materials that objects are made from, and their reactions with the museum environment. It is also important that the materials used in the conservation treatments are fully researched to avoid damaging reactions between the materials the objects are made from and the conservation material. To do their job conservators have to understand the chemistry of the materials they work with.

Conserving stone objects – a case study – Answers

1. Water expands when it freezes; most other liquids contract.
2. Igneous rocks are those formed by the solidification of molten rock. Sedimentary rocks are those laid down by the settling and binding together of particles eroded from other rocks. Metamorphic rocks are those that have been changed by heat and/or pressure.
3. The simplest suggestion is to find the mass of a sample of dry rock, immerse it in water and periodically re-weigh it until there is no further increase in weight (taking suitable precautions to remove surface water).
4. After each poultice is removed, squeeze out some of the water and test for ions present using standard tests such as the formation of a precipitate with silver nitrate to show the presence of chloride ions. Continue until the tests show no ions in the water samples. One source of information about these tests is K. Hutchings, *Classic Chemistry Experiments*, London: Royal Society of Chemistry, 2000, pp 203–207.
5. To ensure that all the soluble salts had dissolved completely.
6. The powder would have a greater total surface area than a lump – this would speed up dissolution of the salts.
7. We need to know the amount of salts in a known mass of the dust in order to make fair comparisons between the samples.
8. EA646. This suggests that the previous treatment of EA1332 had been at least partially successful in removing salts.
9. Calcium ions could have come from the limestone itself (mainly calcium carbonate). Ammonium ions could have come from fertilisers (such as ammonium nitrate) applied to the soil. Other suggestions are possible.
10. Ethanoic acid.
11. See Figure 1 overleaf.

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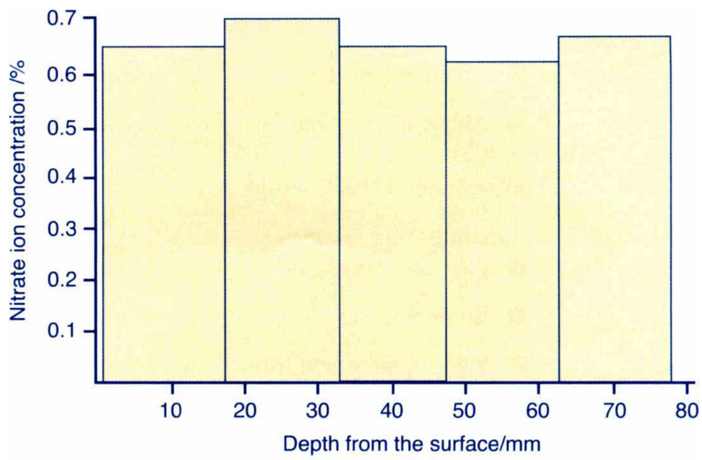

Figure 1

The concentration of ions is almost constant throughout the stela. In particular, there is not a high concentration near the surface and lower ones inside the object.

12. See Figure 2

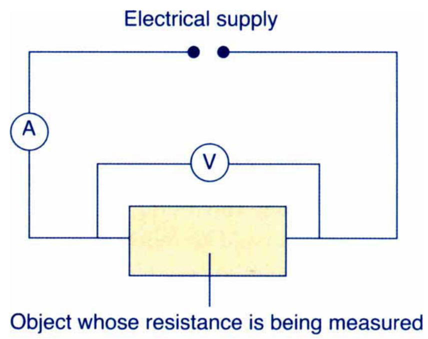

Figure 2

Strictly, the electrical supply should be alternating current to prevent electrolysis of the solution but this is probably too subtle a point for most students at this level. Note that the ammeter must be in series and the voltmeter in parallel.

13. Experiments to measure the water content directly and the resistance of stone samples to produce a calibration curve.

Practical work on stone – notes on the specific experiments

It is the responsibility of teachers to carry out an appropriate risk assessment for all practical work.

Experiment 1 Testing for a carbonate

Apparatus (per group)

- One test tube
- Test tube rack
- Glass rod

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Chemicals (per group)

- One small lump of calcium carbonate (a marble chip)
- About 10 cm^3 1 mol dm^{-3} hydrochloric acid (irritant)
- About 10 cm^3 limewater (calcium hydroxide solution)

Experiment 2 Flame testing

Apparatus (per group)

- One cork (any size)
- Bunsen burner
- Piece of nichrome wire about 6 cm long (spares will be needed)
- Mortar and pestle

Chemicals (per group)

- One small lump of calcium carbonate (a marble chip)
- About 10 cm^3 1 mol dm^{-3} hydrochloric acid (irritant)

Another type of mineral that could be tested is malachite. This contains copper carbonate and therefore will fizz with acid and give a blue-green flame colour. Many types of sandstone will also contain calcium carbonate.

Experiment 3 Insoluble material

This activity could be used simply as a planning exercise. If it is to be carried out, a sample of sandstone that is soft enough to be easily crushed will be required. The sandstone would need to be crushed in a mortar and pestle and a weighed sample left in hydrochloric acid, possibly with gentle heating, for some time to dissolve any carbonates. The residue is filtered off, washed, dried and reweighed. Strictly, the process should be repeated until there is no further weight change in the residue but lack of bubbles could be taken as a simpler indication that the reaction is complete.

Since the available samples will vary from area to area, teachers are advised to try the experiment beforehand to determine the sort of results to be expected.

Exact requirements for apparatus and chemicals will depend on the plans proposed by the students.

Experiment 4 The reactions of marble with acids

Apparatus (per group)

- One 100 cm^3 conical flask with a bung and flexible delivery tube
- One 100 cm^3 beaker

Chemicals (per group)

- About 20 cm^3 1 mol dm^{-3} hydrochloric acid (irritant)
- About 20 cm^3 1 mol dm^{-3} sulfuric acid (irritant)
- About 20 cm^3 1 mol dm^{-3} nitric acid (irritant)
- Small lumps of calcium carbonate (marble chips)

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Experiment 5 The porosity of stone

This activity could be used simply as a planning exercise. If it is to be carried out, small samples of different types of stone will be needed along with access to a top pan balance (reading to at least 0.01 g) and an oven set at about 100 °C.

The principle of the ink soaking into stone can easily be demonstrated by using a stick of suitable blackboard chalk instead of the stone. Different brands of chalk vary; in general, cheaper brands seem to work better than the chalk provided in most schools.

Exact requirements for apparatus and chemicals will depend on the plans proposed by the students.

Since the available samples will vary from area to area, teachers are advised to try the experiment beforehand to determine the sort of results to be expected.

Experiment 6 Investigating fillers

This activity could be used simply as a planning exercise. If it is to be carried out, a variety of different brands of filler will be required (from a DIY store) along with containers and stirrers for mixing (disposable containers and stirrers such as old yoghurt pots and lollipop sticks are a good idea). Samples of types of stone will be needed to test adhesion.

Exact requirements for apparatus and chemicals will depend on the plans proposed by the students.

Since the available samples will vary from area to area, teachers are advised to try the experiment beforehand to determine the sort of results to be expected.

Experiment 7 Investigating glues

This activity could be used simply as a planning exercise. If it is to be carried out, a variety of different brands of adhesive will be required (from a DIY store). Samples of types of stone will be needed to test adhesion.

Exact requirements for apparatus and chemicals will depend on the plans proposed by the students.

Since different glues will vary considerably in their properties, teachers are advised to try the experiment beforehand to determine the sort of results to be expected.

Care should be taken with solvent-based adhesives as the solvent vapours may be flammable and, in any case, should not be inhaled.

Answers to questions

1. Some possibilities include: dropping it; exposure to light; exposure to moisture in the atmosphere; exposure to acidic gases in the atmosphere; exposure to gases given off by other exhibits (especially if both are in the same display case); people touching it; expansion and contraction caused by changes in temperature.

2. (i)
   calcium carbonate + hydrochloric acid → calcium chloride + carbon dioxide + water

   (ii) $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

3. The limewater goes milky. (This is due to the formation of a precipitate of insoluble calcium carbonate, addition of further carbon dioxide will dissolve the precipitate as soluble calcium hydrogencarbonate.)

4. (a) Sodium chloride (common salt) among others.
   (b) This will colour the flame orange as a result of the presence of sodium ions.

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5. (a) It checks that there is no contamination of the hydrochloric acid solution with ions that might colour the flame.
   (b) If a flame colour does appear, discard the acid and use a fresh supply.

6. They should do.

7. (a) Approximately 10 cm^3.
   (b) 10/24 000 = 1/2400 mol
   (c) 1/2400 mol
   (d) 100 g
   (e) 100 /2400 = 0.04 g
   (f) Probably.

   Note: the other answers will, of course, vary depending on the estimate of the volume of a test tube.

8. See Figure 3.

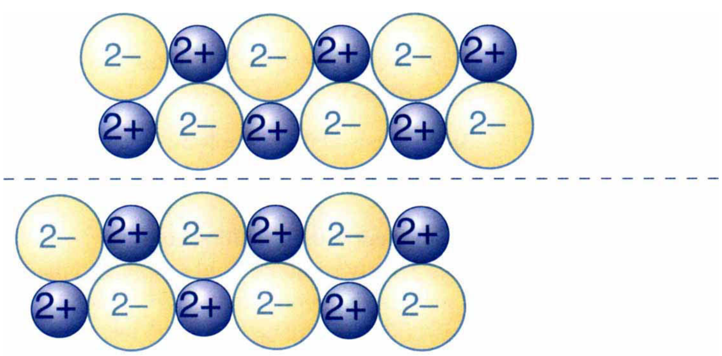

Figure 3

   (b) Ions of the same charge.
   (c) The structure will break apart due to the repulsion of ions of like charge that are touching.

9. $S(s) + O_2(g) \rightarrow SO_2(g)$

   $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

   $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

10. (a) Sulfuric acid
   (b) (i) calcium nitrate (ii) calcium sulfate (iii) calcium chloride
   (c) (i) calcium nitrate: approximately 1000 g dm^{-3} (ii) calcium sulfate: approximately 6 g dm^{-3} (iii) calcium chloride: approximately 600 g dm^{-3}. Calcium sulfate is the least soluble. These figures will vary a little according to source but their relative magnitudes should be clear.
   (d) The reaction will slow down and eventually stop.

11. Water expands when it freezes. If the water were to freeze, this expansion could cause the statue to crack. If a bottle of milk freezes, the water expands and will push off the top.

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12. Suggestions might include: adhesion to statue; non-porous; similar colour to original material; able to be removed easily (with a suitable solvent, for example); expansion and contraction similar to the original material.

13. Suggestions might include: adhesion to statue; non-porous; similar colour to original material (or colourless); able to be removed easily (with a suitable solvent, for example); expansion and contraction similar to the original material.

Further notes

Marble, limestone and calcium carbonate

These three terms are used throughout the resource and it may be worth ensuring the students understand the differences between them. Both limestone and marble are largely calcium carbonate. Marble is a form of limestone that has been metamorphosed – that is, its structure has been changed by heat and pressure. It is harder than limestone.

The brittleness of stone

The explanation of the brittleness of stone given in is probably an oversimplification for many types of stone. The explanation in terms of layers of ions sliding over one another is probably accurate for pure ionic materials such as marble but in most types of stone, the situation is more complex. Typically the stone may consist of small crystals of one material cemented together by other materials and breakage will probably occur between these crystals, Figure 4.

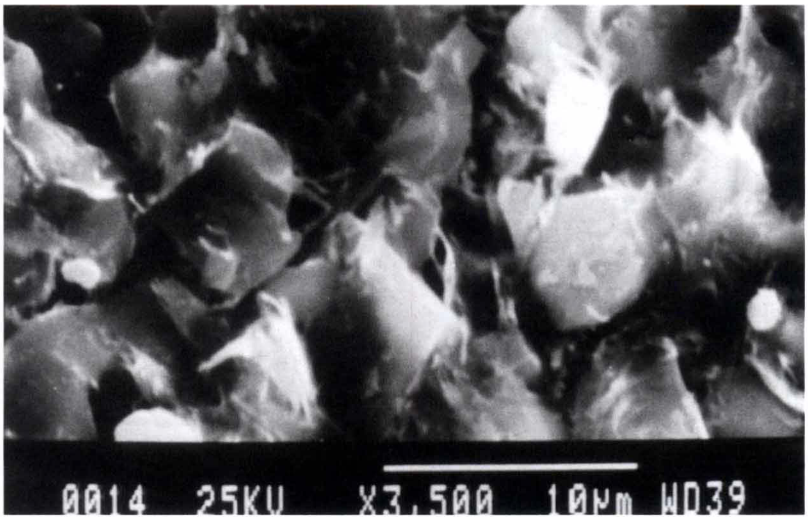

Figure 4 Limestone – 'large' calcite crystals in a 'cement' of calcite and clay material

Sulfur oxides in the atmosphere

Care should be taken not to give the impression that all the oxides of sulfur in the atmosphere result from the actions of mankind. Volcanic gases are a significant source of sulfur dioxide in the atmosphere – this gas typically forms 8% of volcanic gases.

Many fuels, such as petrol and diesel, are treated during the refining process to remove sulfur compounds and many power stations have a flue gas desulfurisation plant fitted.

Adhesives

Adhesives work in a number different ways. The essential principle of many of them is that the two materials being joined are held together by intermolecular forces. The

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relative weakness of these forces is compensated for by the large number of them that operate when significant areas of the two surfaces approach very closely. Adhesives wet both surfaces and then set hard by either solvent evaporation or a polymerisation reaction. This leaves both surfaces in very close contact with the now solid adhesive allowing the intermolecular forces to hold them together.

Some other types of adhesive form actual covalent bonds between the two surfaces being joined.

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Conserving stone objects – a case study

We all know that museums store and display historical objects. This is so that the public can see them and also so that historians and others can use them for research. Museums need to preserve these objects in the best possible condition to prevent them deteriorating. This is the job of the conservation scientist, who needs to understand how different materials decay, and devise methods to slow down deterioration.

Many objects in museums are made of stone, Figure 1. Most types of stone seem to be strong and chemically fairly unreactive – you would probably not think that a stone object would need action to conserve it. However, a stone object can be damaged in a number of ways, Figure 2. These include, for example:

- it could be dropped which might chip or shatter it;
- it could be attacked by acidic gases; or
- it could soak up water which could freeze and shatter it.

Figure 1 Statue of the Three Graces by Canova on display at the Victoria and Albert Museum
(Picture reproduced with permission from the V&A Picture Library.)

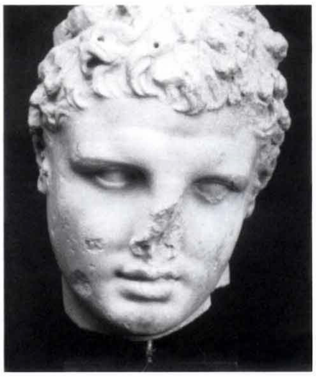

Figure 2 The Aberdeen Head, a Greek statue dating from about 325–280 BC
(Reproduced by courtesy of the British Museum.)

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Q1. What unusual property of water is illustrated by the fact that when water freezes it can shatter stone?

Salts in stone

Water soaking into stone can damage it in another, less obvious, way. Water can carry soluble salts into the pores of the stone. These salts can crystallise in the pores and, as the crystals form, they may exert pressure and crack the stone. If a stone object such as a statue has been buried for some time, salts are often carried into the stone from the soil. This case study looks at the problem of salts in stone and how to remove them. It describes a research project into how to remove these salts that was carried out by conservation scientists at the British Museum in London.

Types of stone

Stone can be classified into one of three types – igneous, metamorphic and sedimentary. These differ in how porous they are (that is how much water they can soak up). Igneous rock is generally non-porous and does not present problems due to water soaking into it. Most types of metamorphic rock are slightly porous, typically absorbing about 5% of their own volume of water. Sedimentary rocks are generally more porous and may absorb between 15 and 30% of their own volume of water.

Q 2. Explain briefly the terms igneous, metamorphic and sedimentary.

Q 3. Devise an experiment to measure the porosity of a sample of rock. Explain what you would do and what measurements you would make.

What is a salt?

Salts are compounds in which a metal has replaced the hydrogen of an acid. For example zinc sulfate ($ZnSO_4$) contains the metal zinc that has replaced the hydrogen in sulfuric acid (H_2SO_4). The metal is obvious from the name of the salt, and the acid usually is too – nitrates are related to nitric acid, sulfates to sulfuric acid and so on. Common exceptions, however, are chloride salts such as sodium chloride (NaCl). Their parent acid is hydrochloric acid. The difference in the names is because the ending '–ate' means 'containing oxygen' while '-ide' means 'and nothing else'. Sulfate and nitrate ions contain oxygen but chloride ions do not.

Salts are all ionic compounds. The metal forms a positive ion, and the negative ion comes from the acid. Some common negative ions found in salts are:

Sulfate, SO_4^{2-};

Nitrate, NO_3^-; and

Chloride, Cl^-.

The only common positive ion found in salts that is not derived from a metal is the ammonium ion, NH_4^+.

Removing salts from stone objects

Crystallised salts can often be seen on the outside of stone objects – you can sometimes see them on bricks, for example, see Figure 3.

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Figure 3 Efflorescence (salt deposits) showing up as white patches on a house and a wall
(Pictures reproduced by courtesy of the Brick Development Association www.brick.org.uk)

Salts on the outside can damage the surfaces of objects, but they are not the major problem for conservation scientists. This is because salts on the outside can usually be removed by brushing. It is also easy to see when they have been removed. However, in order to prevent damage to a stone object, conservation scientists may need to remove any salts that have been absorbed inside it. This can be more difficult. One method of doing this is to surround the object with filter paper soaked in pure water. This is called poulticing, and the water-soaked filter paper is called a poultice. Water from the poultice soaks into the object and dissolves any soluble salts. The poultice is then dried, and this draws the water (now containing dissolved salts) back into the poultice. This is removed (along with the salts it contains) and replaced with a fresh poultice soaked in pure water. The process is repeated many times.

Q4. One problem with poulticing is how to know when all the salt has been removed. Suggest how this could be done. Hint. There are a number of simple tests for different salts such as chlorides, sulfates, nitrates *etc*. You could look these up in a chemistry textbook or database.

Researching the process

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. They also wanted to know how far salts penetrated into stone objects and how far the water from the poultice got. This information would help conservation scientists using this process in the future.

To do this they investigated two Egyptian carvings made from limestone (a type of sedimentary rock). These are called stelae (the singular of this word is stela). They look rather like the ones in Figure 4.

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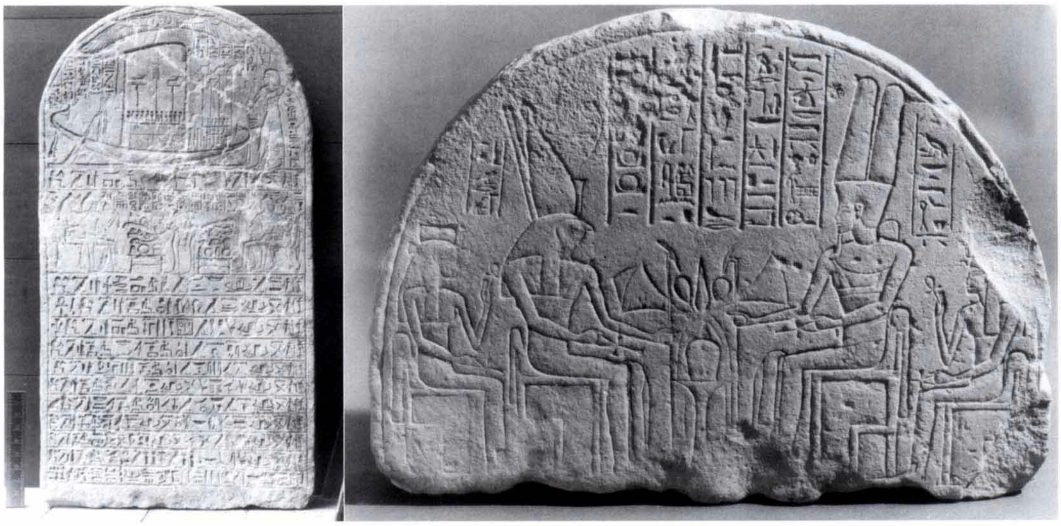

Figure 4 Stela EA1332 (left) and EA646 (right)

These were identified by the museum identification numbers EA1332 and EA646. 'EA' stands for Egyptian Antiquity. EA1332 had been previously treated by conservation scientists because of problems with salts, EA646 had not. Egyptian carvings with high salt contents were already known to deteriorate more rapidly than those containing less salt.

Samples of the stone from the stelae were obtained by drilling into them (from the back so as not to damage the carving). The dust from the drilling was collected at different depths into the stelae – firstly from the surface to a depth of 2 mm and then every 15 mm until the drill bit almost reached the front, carved surface. A weighed sample of the dust at each depth was taken, shaken with 10 cm^3 of pure water and left for 16 hours to dissolve any soluble salts.

Q5. Why was the sample left in water for so long?

Q6. Why was it helpful that the sample was in the form of dust rather than lumps?

Q7. Why was it important to weigh the samples of dust?

The samples were then filtered and the concentrations of various ions in them were measured by a method called ion chromatography. The results for the first 2 mm are shown in Table 1. These results represent the layer of stone closest to the surface.

Negative ions	**Ion concentration/%**		**Positive ions**	**Ion concentration/%**	
	EA1332	**EA646**		**EA1332**	**EA646**
Chloride	1.076	8.588	Sodium	0.673	5.565
Nitrate	0.591	0.528	Potassium	0.098	0.638
Sulfate	0.420	2.721	Ammonium	0.002	0.210
Methanoate	0.046	0.629	Magnesium	0.081	0.125
Ethanoate	0.042	0.392	Calcium	0.644	3.746

Table 1 Concentration of ions found in the two stelae from the surface to a depth of 2 mm/%
(*ie* (mass of ion / mass of stone) x 100)

Most of the above ions may be found in soil, but methanoate and ethanoate are not. The conservation scientists are sure that they have come from the wood of the museum cases in which the stelae had been displayed.

Q8. Which *stela* contained most ions? What does this suggest about the treatment of *stela* EA1332?

Q9. Suggest where (a) the calcium ions and (b) the ammonium ions might have come from.

Q10. What is the name of the acid to which ethanoate ions are related?

Table 2 gives the concentrations of nitrate ions at different depths from the surface of stela EA1332.

Depth from surface/mm	Nitrate ion concentration/%
2–17	0.66
18–32	0.71
33–47	0.66
48–62	0.65
63–77	0.67

Table 2 The concentrations of nitrate ions at different depths from the surface of stela EA1332

Q11. a) Plot a graph of nitrate ion concentration (vertically) against depth from surface (horizontally).

b) What pattern do you see?

The water used in poulticing can only remove salts if it can reach them. So the conservation scientists wanted to know how far the water soaked into limestone. They did this by measuring the electrical resistance of the limestone – the more water the stone contains, the less its resistance.

Q12. Draw an electrical circuit, including an ammeter and a voltmeter, which could be used to measure electrical resistance.

For this experiment they used blocks of limestone rather than the stelae, to avoid damage to the carvings. This was because two holes had to be drilled into the limestone 1 cm apart, each taking a wire placed in contact with the stone at a certain depth from the surface (see Figure 5). An electrical circuit was used to measure the resistance of the stone between the two wire probes.

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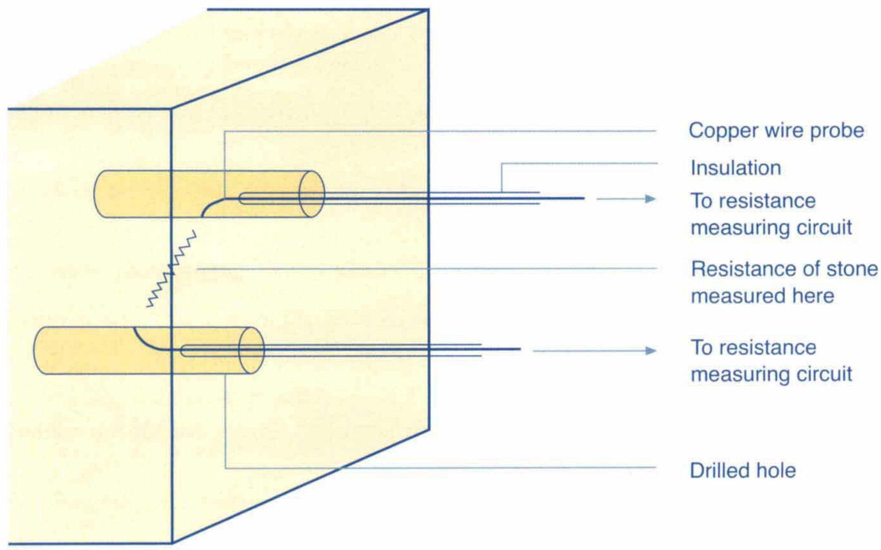

Figure 5 The experimental set-up to measure the resistance of the stone

Three blocks of limestone were tested – one was untreated and the other two had been treated with different silicone-based sealants somewhat like those used to make a waterproof seal round the edges of baths and sinks in the home. A poultice was applied to each block as described above. The resistance of the stone was measured at different depths into the stone over a period of three days. The resistance was then used to calculate the water content of the stone.

Q13. What extra experiments would the conservation scientists have had to do to allow them to convert the resistance figures into percentage water content of the stone?

The results indicated that water penetrated up to 40 mm into the untreated stone but less than 20 mm into the treated stone.

Three significant pieces of information resulted from these experiments:

1. Water from the poultice does not penetrate all the way into stone objects, so there is a limitation on how useful the poultice method of salt removal can be.
2. There is a fairly even distribution of salts throughout the stone – salts are not just confined to a layer close to the surface.
3. The previous treatment had reduced water penetration into the stone.

In the future, conservation scientists will be able to use these conclusions to help them plan the treatment of other stone objects.

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Practical work on stone

Museums store and display historical objects. Part of the job of a conservations scientist in a museum is to slow down the deterioration of such objects. Imagine you have a statue made of marble that is going to be displayed to the public in a museum.

Q1. Make a list of all the possible ways in which the statue could be damaged or begin to deteriorate if it were exhibited in a museum. Hint. What sort of things is the statue exposed to? What could happen to it? What sort of changes will occur around it during the day and night?

Before we can think about how to conserve the statue, we will need to know what type of stone it is made from. One of the most common types of stone for making statues is marble. Others include sandstone and granite, see Figure 1. We can use the appearance of the stone and chemical tests to help us decide if the statue could be made of marble.

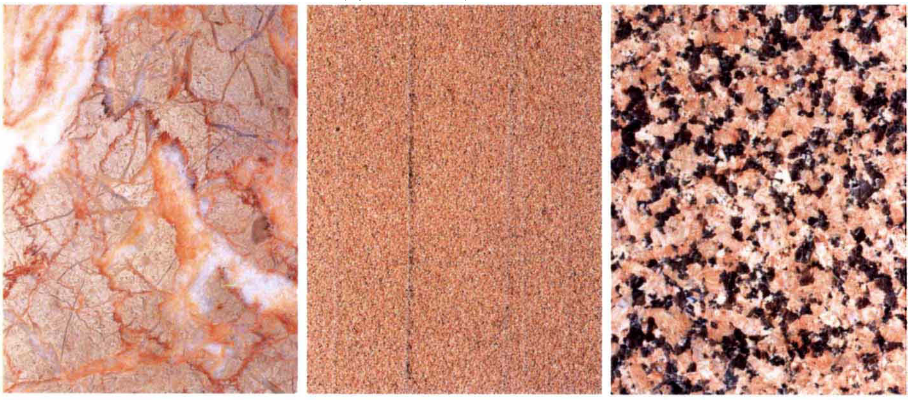

Figure 1 left to right: marble, sandstone & granite
(Reproduced with permission from Science Photo Library. Photographer George Bernard.)

Testing for marble

Marble is hard and is usually white, but impurities can give it a variety of colours, including black. Marble is made of calcium carbonate, $CaCO_3$. All carbonates react with acid to give off the gas carbon dioxide so this can be used as a test for calcium carbonate.

Q2. Write (i) a word and (ii) a balanced symbol equation for the reaction of calcium carbonate with hydrochloric acid.

Q3. We can test for carbon dioxide by using limewater (calcium hydroxide solution). Describe the result of this test.

Experiment 1 Testing for a carbonate

You can try the test for a carbonate on a small chip of marble. Place a marble chip in a test tube and add about 1/3 test tube of 1 mol dm^{-3} hydrochloric acid. You should see bubbles of gas. Test the gas by holding a drop of limewater on a glass rod in the mouth of the test tube, see Figure 2. After a few moments, look closely at the drop. What do you see?

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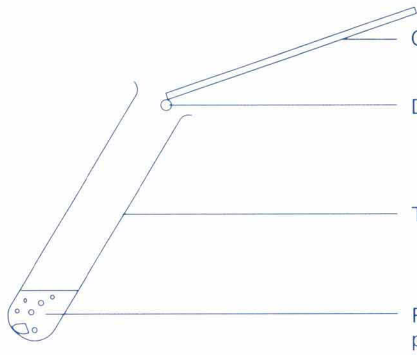


Figure 2 The limewater test

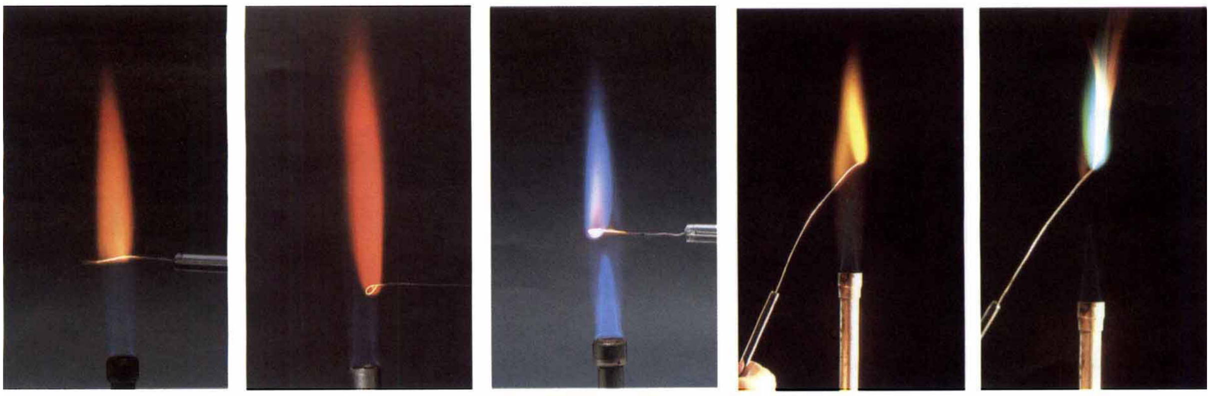
Bear in mind that this test shows only that the stone sample contains a carbonate – marble is almost pure calcium carbonate but some sandstones contain small percentages of calcium carbonate along with other substances such as silicon dioxide.

Experiment 2 Flame testing

We can find out what metal is in a carbonate by using a flame test. When heated in a Bunsen flame, certain metals give particular colours to the flame as shown in Table 1 and Figure 3.

Metal	Flame colour
Calcium	Brick red
Copper	Green-blue
Sodium	Orange-yellow
Potassium	Lilac
Lithium	Scarlet

Table 1 Some examples of flame colours



Calcium Lithium Potassium Sodium Copper

Figure 3 Flame test colours
(Reproduced with permission from Science Photo Library.)

Take a clean piece of nichrome wire about 6 cm long. Push one end into a cork to act as a handle. Hold the wire in the hottest part of a Bunsen flame (just above the blue cone, see Figure 4).

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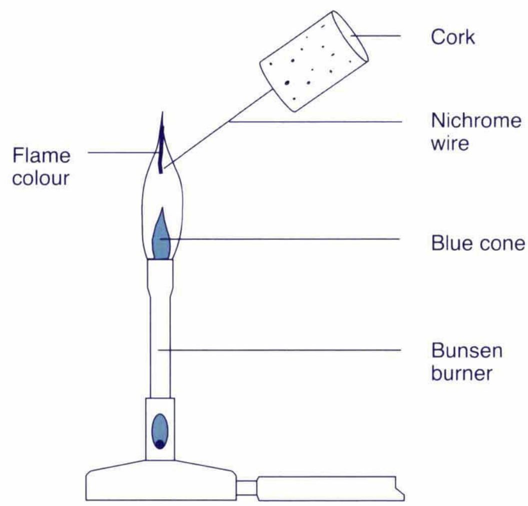

Figure 4 Flame test

If it is clean, the wire should barely colour the flame. If there is a strong colour from the wire, discard it and get a new piece. Avoid handling the wire as it will be hot and when cold it will pick up traces of sweat from your fingers.

Q4. **a)** What salt is present in sweat?

b) What colour will this turn the flame?

Now dip the wire into a little 1 mol dm^{-3} hydrochloric acid and again place it in the flame. There should still be no colour in the flame.

Q5. **a)** What is the point of this part of the test?

b) What should you do if the flame becomes coloured when the acid-dipped wire is placed in it?

Grind a small marble chip to powder in a mortar and pestle. Dip one end of the wire into hydrochloric acid and then immediately place the wetted end into the powdered marble. Now place the wire in the flame. What colour does it produce?

Q6. Do the results of your tests indicate that marble contains calcium carbonate?

Q7. (Harder) If a conservation scientist has to test a statue to find out what it is made of, he or she will want to use as little of the stone as possible to avoid damaging the statue. You will probably agree that the limewater test needs more marble than the flame test. This exercise shows you how to estimate how much stone is needed for the limewater test. Note that this is an exercise in estimation. Use round numbers, so that an estimate of the volume of a test tube to the nearest 10 cm^3 would be sensible, for example.

a) Estimate the volume of a test tube. (This is roughly the volume of carbon dioxide that is made for the test.)

b) How many moles of carbon dioxide is this (1 mole of any gas has a volume of about 24 000 cm^3 at room temperature and pressure)?

c) The equation for the reaction of calcium carbonate with acid tells us that one mole of calcium carbonate produces one mole of carbon dioxide. How many moles of calcium carbonate is required for the test?

d) What is the mass of a mole of calcium carbonate, $CaCO_3$, (A_rs: C = 12, O = 16, Ca = 40)?

e) How many grams of calcium carbonate is needed for the test?

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f) Do you think that this could be taken from a small statue without leaving an obvious mark?

It is worth bearing in mind that more advanced methods of analysis need much smaller amounts of material to test, and that some may be completely non-destructive, that is they can be done on the complete object without having to remove a sample at all.

Experiment 3

Insoluble material

Another test used to find out about stone is to measure the percentage of material that does not dissolve in acid. Plan an experiment to measure this – say what you would do and what measurements you would make.

One problem with stone objects is that they are brittle – a force such as a small tap can make them shatter. This means that a statue could break into many small pieces or that a part could break off – the Venus de Milo is a famous example, see Figure 5. Either way, the conservation scientist is left with the problem of whether to repair the object or not and, if so, how to do it.

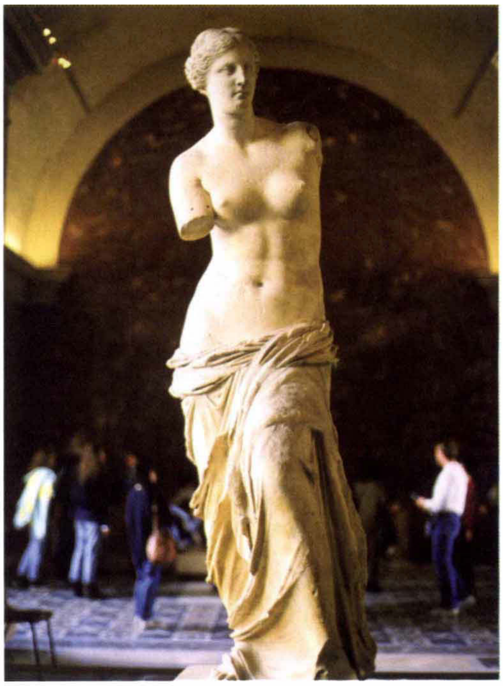

Figure 5 The Venus de Milo statue

(Picture reproduced with permission from Corbis photo library.)

Q8. This question helps you explore why most types of stone are brittle. This is to do with the fact that most types of stone are made of ionic compounds. Take marble (calcium carbonate, $CaCO_3$) as an example; calcium carbonate consists of a giant structure made up of alternating Ca^{2+} and CO_3^{2-} ions, see Figure 6. Notice that positive ions are always surrounded by negative ions and vice versa. The structure is held together by the attraction of these oppositely charged ions with each other.

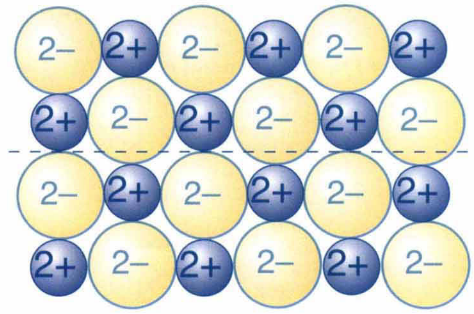

Figure 6 A giant ionic structure

a) A small force can make one layer of ions slide past the next layer. Redraw Figure 6 to show the ions above the dotted line each moving one ion to the right while the ones below the line stay in the same position.

b) What sorts of ions are touching now?

c) What will happen to the structure?

The effect of acids on limestone

You might think that objects made of stone would last forever, but this is far from being true as is shown by the gargoyle in Figure 7.

Figure 7 Badly eroded gargoyle at Whitby Abbey
(Picture reproduced with permission from English Heritage.)

This gargoyle, made from limestone (which is also a form of calcium carbonate), has been eroded by acid rain. Rainwater is naturally acidic because of the reaction of carbon dioxide in the atmosphere with water to form carbonic acid, H_2CO_3.

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

So rainwater will dissolve calcium carbonate. As well as erosion of gargoyles, this process is responsible for the formation of caves in areas where the rock is limestone.

Nitric and sulfuric acids are also found in the atmosphere partly because of the burning of fossil fuels. Most fossil fuels contain a little sulfur and, when this is burned, it combines with oxygen to form first sulfur dioxide and then sulfur trioxide. Sulfur

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trioxide reacts with water in the air to form sulfuric acid. Many power stations now have systems in place to remove sulfur dioxide from their emissions.

Q9. Write word and symbol equations for the reactions by which sulfur in fuel becomes sulfuric acid. You will need the following formulae:

sulfur dioxide; SO_2

sulfur trioxide; SO_3

water; H_2O

sulfuric acid; H_2SO_4

When fuels burn at high temperatures, some of the nitrogen and oxygen in the air combine to produce a mixture of nitrogen oxides. These too combine with water in the atmosphere, to form nitric acid in this case.

Experiment 4 The reactions of marble with acids

Investigate the reactions of marble with nitric acid, sulfuric acid and hydrochloric acid. What gas is produced in each case? Do a test to confirm this. Can you compare by eye the rates of the reactions? Do they all seem to go at the same rate? What factors will you have to keep constant to make this a fair comparison? To confirm your visual comparison of the reaction rates, try the following experiment. Set up the apparatus shown in Figure 8.

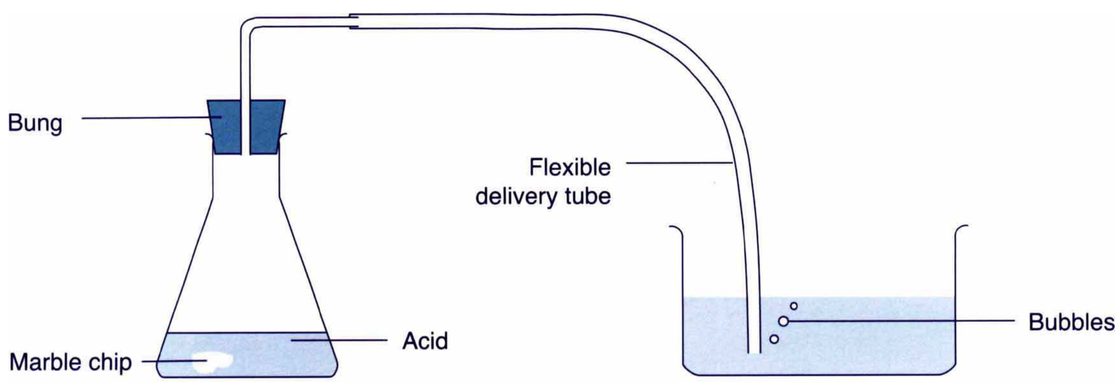

Figure 8 Bubble counting

Add a marble chip and quickly replace the bung and delivery tube. Count the bubbles produced each minute for five minutes. Repeat with a different acid, keeping all other factors as nearly the same as possible. You could plot graphs (possibly using a spreadsheet computer program) of your results. How could you modify the apparatus so that you could measure the volume of gas produced rather than just counting bubbles?

Q10. **a)** You should find that one of the acids reacts more slowly than the others – which one? Try to explain your results by answering the following questions.

b) What salt is produced by the reaction of calcium carbonate with (i) nitric acid, (ii) sulfuric acid and (iii) hydrochloric acid?

c) Look up in a data book or database the solubilities in water of each of these salts – which is the least soluble?

d) What is likely to happen to the reaction of marble with acid if the marble becomes coated with an insoluble salt?

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The porosity of stone

Some types of stone are relatively porous, that is they soak up water. This is because they have a network of microscopic cavities, called pores, in their structures.

Q11. How could water soaking into a statue cause it damage? Hint. Think about what happens to a bottle of milk (mostly water) when it is left on the doorstep in freezing weather.

Experiment 5 The porosity of stone

You can compare the porosity of different types of stone in a number of ways. You could immerse a sample of stone in water for different lengths of time and weigh it to find out how much water it has absorbed. You could stand a sample of stone in a beaker of water that has been coloured by adding a little ink and measure how far up the sample the ink has travelled after different time intervals.

Plan an experiment to compare the porosity of different stone samples by one of the above methods. You will need to think carefully about what factors you will keep the same to make the experiment a fair test, what measurements you will take and how to record them. You may need to do preliminary experiments first to test your ideas.

Use of fillers

There is a debate in the world of museums about whether it is right to repair broken objects or not. Some think that this allows the public to see objects as they were originally made, others believe that any damage is part of the history of the object and should be left. Either way, there is agreement that any repair or restoration should be done so that it can be removed at a later date without further damage to the object. This is sometimes called the principle of reversibility.

A simple way to repair chips or cracks in a stone object would be to use a filler like the fillers used to repair cracks in plaster when decorating at home.

Q12. Make a list of the properties that a filler would need to make it suitable for repairing a statue. Think about how this might affect the appearance of the object and about the principle of reversibility.

Experiment 6 Investigating fillers

Plan an investigation to compare the properties of different brands of filler.

Some of the properties you could investigate might include:

- How porous are they? (How much water does a sample of dry filler soak up when it is placed in water?)
- How well do they stick to the material of the statue? (Remember they will need to stick quite well to be any use at all but should not stick so well that they cannot be removed without damage to the object.)
- What is the easiest way to remove them?
- Do they expand or shrink in different conditions such as when wet or when the temperature changes?
- How long do they take to set?

But you may be able to think of other relevant properties.

Use of glues

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A simple way to repair a broken stone object would be to use some type of glue to stick back any parts that have broken off.

Q13. Make a list of the properties that a glue would need to make it suitable for repairing a statue. Think about how this might affect the appearance of the object and about the principle of reversibility.

Experiment 7 Investigating glues

Plan an investigation to compare the properties of different brands of glue.

Some of the properties you could investigate might include:

- How strong are they? (What load is required to pull apart two pieces of material that have been glued?)
- How effective are they in different conditions? (Is the strength of the bond affected by temperature or moisture, for example?)
- How well do they stick to the material of the statue? (Remember they will need to stick quite well to be any use at all but should not stick so well that they cannot be removed without damage to the object.)
- What is the easiest way to remove them?
- Is the join visible?
- How long do they take to set?

But you may be able to think of other relevant properties.