

MUSEUM CLIMATOLOGY AND THE CONSERVATION OF PALAEOONTOLOGICAL MATERIAL

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ABSTRACT. Variations in the environment within museums can cause significant damage to palaeontological material. The deterioration of sub-fossil bone occurs within a short time of exposure to air at relative humidities below 45%. Fossil specimens containing predominantly framboidal and microcrystalline pyrite are susceptible to deterioration when stored at relative humidities of 60% and above, and observation shows that the oxidation of pyrite in air is more consistent with electrochemical rather than bacterial causation. Small pyritic specimens can be safely stored in silicone fluid but the conservation of larger specimens requires rigid control of relative humidity in storage or exhibition environment. The failure of conventional consolidants in the protection of moisture-sensitive material can be explained by the high permeability of plastic films to water vapour. Deterioration of calcareous specimens through the efflorescent growth of calclacite (and related compounds) may be caused by storage in oak cases.

AN international survey of major museums and galleries carried out by the International Council of Museums during the late 1950s (Plenderleith and Philippot 1960) revealed that constancy of environmental variables, notably temperature and relative humidity, was generally considered to be synonymous with good conservation. Of the 32 museums, galleries, and archival institutions included in the survey, few gave specific ranges of storage conditions for particular types of susceptible material, and it was evident that considerable over-all variations were tolerated (relative humidities ranged from 30% to 80%, whilst temperatures ranged between 12 and 24 °C.). Stollow (1976) called for a more detailed study covering a wider range of institutions, in which the permissible environmental ranges for the safe storage of various classes of museum objects and specimens be specified.

Wagstaffe and Fidler (1968) and others have described techniques developed for the preservation of the soft parts and skins or organisms (e.g. storage in alcohol, formalin, or phenoxytol, and the use of freeze-drying and taxidermal techniques), but little research has been carried out into the requirements for the storage and exhibition of other natural history material. It is generally considered that recent bone, rocks, and fossils, being of a mineral nature, are either inherently stable in air or, if not, are relatively easily replaceable.

In palaeontological collections certain categories of material have suffered considerable damage or even destruction because much reliance has been placed on the use of resins and lacquers for specimen coating and impregnation. A closer examination and understanding of both the factors affecting the stability of palaeontological material and the responses of certain (unstable) types of specimen to variations in the environment are clearly necessary before effective conservation treatments can be prescribed with any degree of confidence.

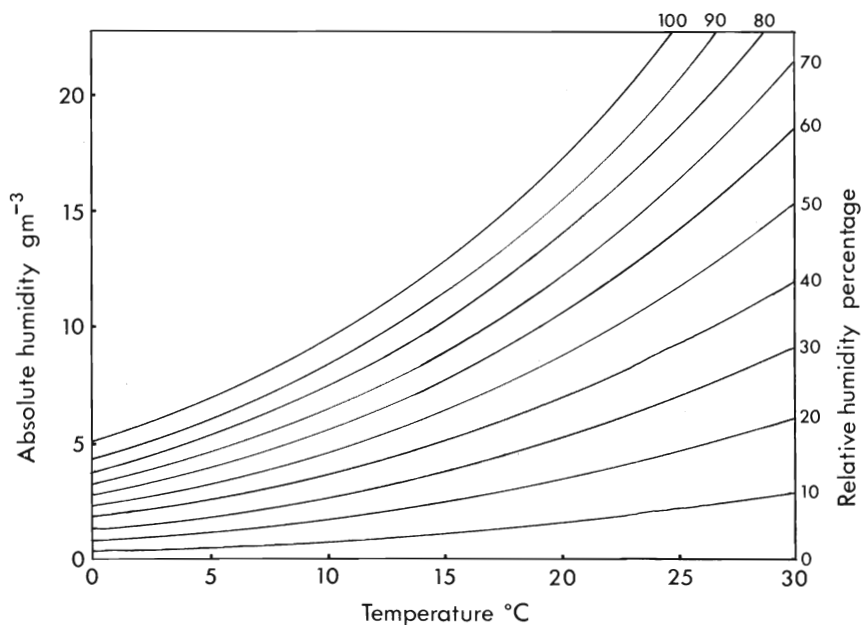
ENVIRONMENTAL VARIABLES

The majority of museum specimens are susceptible to change brought about by variations in temperature, humidity, and light, and many are affected by atmospheric pollutants and vibration. Palaeontological material is most sensitive to temperature and humidity variations but, to a lesser extent, the other factors must be considered.

Temperature and humidity. Within the museum environment it is unlikely that significant physico-chemical changes are brought about in fossil material by variations in temperature alone. Of greater importance is the relationship between temperature and atmospheric humidity. The moisture content of air can be expressed in several ways, the most useful and well known being absolute and relative humidity. Absolute humidity is defined simply as the ratio of the mass of water vapour in a sample of air to the total sample volume (expressed as g m^{-3}). Relative humidity (r.h.) is the ratio of the mass of water vapour in a sample of air to the mass that would saturate that sample volume at the same temperature, expressed as a percentage.

The relationship between the absolute and relative humidity of air is determined by temperature (see text-fig. 1). Hygroscopic materials will respond to increases or decreases in the r.h. of surrounding air by absorbing or losing moisture but are not much affected by changes in absolute humidity at constant r.h. (Rawlins 1942). Changes in air temperature will, however, vary the moisture content of hygroscopic materials where r.h. does not remain constant, and this is of fundamental importance to the conservation of many museum specimens.

Atmospheric pollutants. The major pollutants found in air in urban districts are sulphur dioxide, carbon monoxide, ammonia, and traces of mineral acids. These impurities have not been reported as causing damage to fossil specimens in museums. Problems can arise, however, in the storage environment where timbers or adhesives emitting organic acid vapours are used in cabinet construction. These acid vapours react in damp storage conditions with areas on the surface of calcareous specimens contaminated with minute traces of inorganic salts such as chlorides, nitrates, and sulphates, sometimes causing considerable deterioration. The occurrence and treatment of this problem is described here in a later section.



TEXT-FIG. 1. Simplified hygrometric chart showing relationship between atmospheric humidity, relative humidity, and temperature for air at atmospheric pressure.

Vibration. All specimens are susceptible to damage by inadvertent shock or by sustained exposure to vibrations due to, for example, road or rail traffic, air-conditioning plant, or building operations. The use of metal-constructed storage units, where sonic resonance readily develops, can cause problems in this respect. The use of timber constructed storage cabinets coupled with the cushioning of especially fragile specimens on lint-free tissue, polyether foam, or expanded polystyrene supports, will considerably lessen the occurrence of damage.

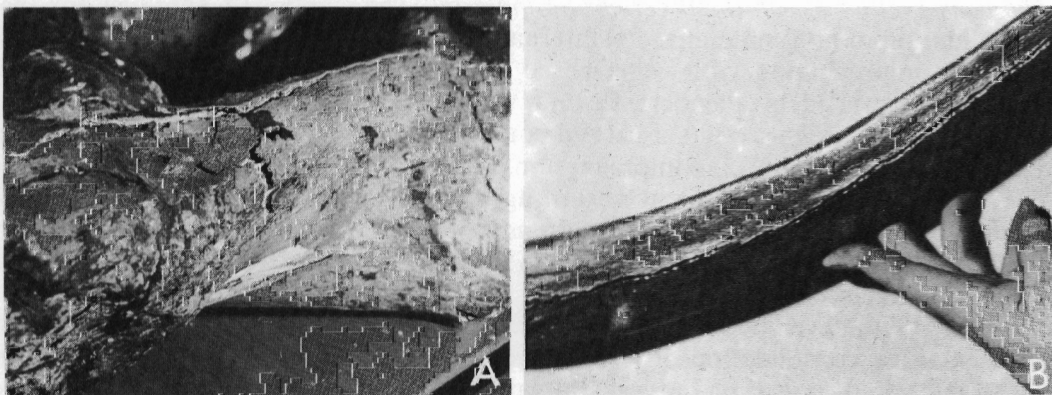
Lighting. Few fossil materials are directly affected by exposure to light. Ultra-violet radiation of wavelength 290–400 nm will, however, slowly destabilize many synthetic polymers (von Fraunhofer and Boxall 1976) used in conservation, and it would appear sensible, wherever possible, to store treated material away from direct natural light and unfiltered artificial light.

This paper describes the major problems encountered with the storage and conservation of sub-fossil bone and pyritic material, and gives some practical advice on monitoring and modifying storage environments.

SUB-FOSSIL BONE—DETERIORATION AND CONSERVATION

Large numbers of mainly Quaternary vertebrate specimens in several museum collections are extremely susceptible to damage by warping, splitting, and exfoliation of surface layers of bone. Well-known examples are the long bones, teeth, and tusks of proboscideans, cervine antlers, and non-mineralized bone from certain cave deposits (e.g. Kent's Cavern, Devon). The extent of deterioration is illustrated (text-fig. 2A) by a humerus of *Mastodon americanus* from the Pleistocene of Missouri; this particular specimen had been conserved, probably during the latter part of the last century, by coating with shellac or animal glue and infilling with plaster. Attempts at mitigating this problem by thoroughly impregnating affected bone with consolidants such as emulsified polyvinyl acetates and the use of gap-filling adhesives do not confer a high degree of stability if the treated specimens are returned to the same uncontrolled environment (see text-fig. 2B).

Possible causes for the deterioration of fossil bone. The changes occurring in buried bone have been investigated by Rogers (1924), Doberenz and Matter (1965), and



TEXT-FIG. 2. A, humerus of *Mastodon americanus* showing deterioration caused by storage in dry environment, $\times 0.1$. B, Mastodon rib showing deterioration after impregnation with polyvinyl acetate, $\times 0.3$.

others, and it is now widely accepted that in certain non-oxidizing deposits bone can retain significant quantities of fibrous collagen and related compounds for long periods. The proportion of collagen in bone generally decreases rapidly with increasing antiquity, but Isaacs *et al.* (1963) identified collagen-like material in bovid bone of Miocene age. Collagen is responsible for the mechanical strength of fresh bone, and its removal, either chemically (Brothwell 1966) or by natural leaching and oxidation processes, leaves a brittle framework composed of hydroxy-apatite or a closely related phosphate. Partial removal of collagen will undoubtedly result in considerable loss of bone strength.

Dense bone, as found in the shafts of mammalian or avian limb-bones, probably retains a higher proportion of leachable and oxidizable constituents than porous cancellous distal or proximal bone and it is commonly observed that the shafts of such bones are more susceptible to distortion. Preliminary investigations at the British Museum (Natural History) have involved empirically measuring the relaxation of distorted bone in an untreated *Mastodon* scapula (Pleistocene, North America). By using a John Bull dial test indicator with the stylus in direct contact with the distorted bone surface, it was demonstrated that when the r.h. in the vicinity of the specimen was raised from 38% to 50% relaxation was apparent within six hours. Raising the r.h. above 50% however, did not result in further significant dimensional change.

The results of this simple experiment tended to confirm subjective observations of the behaviour of sub-fossil bone in stored collections, i.e. that such specimens show little distortion if kept in fairly humid environments. As very damp conditions cause archaeological bone and ivories to swell (Plenderleith and Werner 1972), it appears that critical levels of relative humidity are in operation, and the lower level is fixed, tentatively at this stage, in the range 45–50% r.h.

The distortion of sub-fossil bone is undoubtedly related to the hygroscopicity of remnant collagen, and further experimental work is required before more definite storage limits can be established. It is significant to note (Stolow 1977) that the range 50–60% r.h. is conducive to the safe storage of modern ivories and bone carvings.

The conservation of sub-fossil vertebrate material. The standard techniques for the consolidation of non-mineralized Quaternary and archaeological bone, enamel, and antler by impregnation with water-based emulsions of plastics such as polyvinyl acetate are detailed by Plenderleith and Werner (1972) and Rixon (1976). These methods give excellent results if careful consideration is given to the fragility of the material prior to and during impregnation, and to the post-treatment drying stage. The major difficulty inherent in saturating dry bone with an aqueous-based consolidant is that unless adequate support is given the bone may swell, and further damage occur. In most cases impregnation is only really effective when the specimen is totally immersed in the consolidant.

Rixon (1976) developed a technique for pre-treating dry, shattered, and powdery bone entailing consolidation of all exposed surfaces with several applications of a dilute solution of polyvinyl butyral (Butvar B98) in isopropanol (5% approx.). This is followed by impregnation with diluted polyvinyl acetate emulsion, in the ratio 1 (emulsion) to 2 or 3 (water), carried out, wherever possible, by total immersion over

a 24 to 48 hour period. If immersion is impractical then several applications of the diluted emulsion by brush or pipette are required, allowing partial drying between each coat. Warped or partly detached bone can, when thoroughly wetted, be clamped gradually back into place using bandages, wooden clamps, or copper wire. The final stage is to run undiluted emulsion into any remaining cracks and allow the specimen to dry gradually in a polythene tent with shallow trays of water containing sponges to aid evaporation. Reduction of the humidity is effected by allowing increasingly longer periods between refilling the trays with water, and inclusion of thymol crystals in the tent is necessary to prevent mould growth. As further clamping and adhesives may be required during the drying stage the clamps and bandages should not be removed until the specimen is almost dry. The drying process should be prolonged and several weeks may be required for larger specimens. With freshly collected bone the normal practice is to keep the material wet until it reaches the laboratory. Here impregnation with diluted emulsion is normally carried out without the need for pre-treatment using an organic solvent-based resin. Specimen drying should, as for the salvage treatment described above, be slow and, ideally, discontinued when 50% r.h. (approx.) is reached.

Treated material should be stored or exhibited in locations that are not subject to rapid temperature fluctuations of more than about 5 °C., and r.h. should be in the range 45–60% at all times. In this respect it is significant to note that several hundred sub-fossil (mainly) bovid bones excavated in the Banwell Bone Cave (owned by Goughs Caves Limited, Cheddar, Somerset) have been stored without deterioration stacked around the walls of the cave for 100 years or more (pers. comm. from Mr. A. Carrant, BM(NH)). This is undoubtedly due to the stable high humidities maintained naturally in cave environments (Wigley and Brown 1976). Methods of locally altering unsuitable storage or exhibition areas are discussed further below.

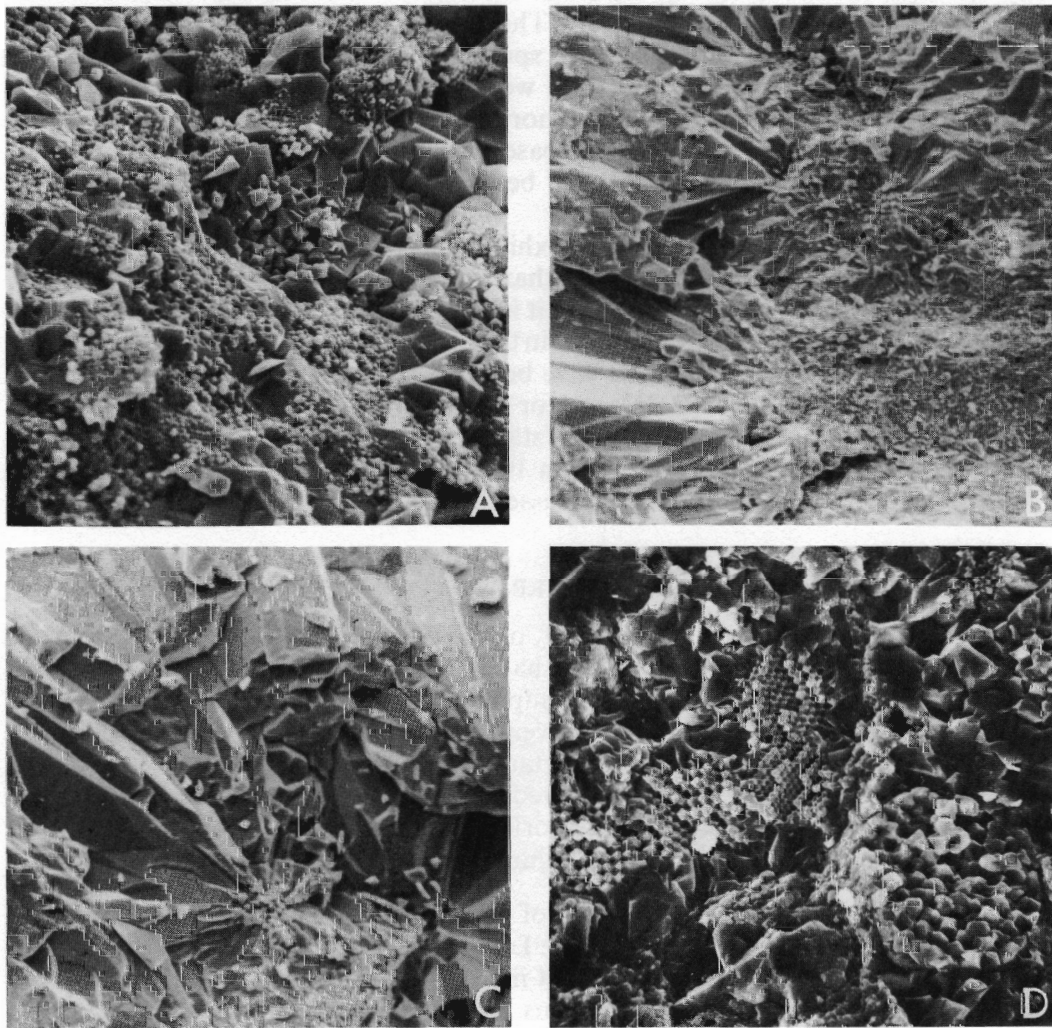
PYRITIC FOSSIL MATERIAL—DETERIORATION AND CONSERVATION

It is estimated that between 5% and 10% of the palaeontological collections in the BM(NH) are pyritic, and it is probable that several other museums contain similar or even greater quantities. The apparent impossibility of predicting deterioration and the failure of various treatments in preventing pyrite oxidation (Howie 1977a, b) have led to significant damage to important collections. The extent of such losses are rarely recorded but Phillips (1977) noted that evacuation of ammonite collections from the BM(NH) during the Second World War to unsuitable outstations resulted in the destruction of some 45 type and figured specimens.

Pyrite and fossilization. The pyritization of fossil material has been a comparatively neglected field of study until recently (see Love 1970). This is surprising since fossils containing pyrite are extremely abundant in sediments formed in reducing environments. Much of the pyrite in argillaceous sediments is syngenetic (Rickard 1973), probably of colloidal origin (Kříbec 1975), and generally characterized by a tendency to occur as disseminated framboids and microcrystals (Love and Amstutz 1966). Rickard (1970) suggested that pyrite framboids formed where blobs of iron sulphide gel infilling voids, such as gas bubbles entrapped in sediments, recrystallized. The

formation of pyrite within cavities in organic remains appears to be a related phenomenon, and observations by Fabricius *et al.* (1971), Sweeney and Kaplan (1973), and others show that framboidal pyrite textures are commonly developed in the tests of microfossils.

Howie (1977b), in a scanning electron microscope (SEM) study of pyrite in common Mesozoic and Tertiary fossils, showed that a range of pyrite textural types were developed. Freshly fractured samples of specimens were mounted on aluminium stubs, gold coated, and examined in a Cambridge 600 SEM. Text-figs. 3 and 4 illustrate some of the range of pyrite textures found.



TEXT-FIG. 3. A, microcrystalline and framboidal pyrite in outer zone of a Gault hoplitid ammonite infilling, $\times 1400$. B, peripheral microcrystalline and underlying compact radiating pyrite in London Clay gastropod infilling, $\times 500$. C, enlarged detail from B, showing relationship between framboidal and radiating pyrite, $\times 1000$. D, framboidal texture of pyrite replacing a *Nipa burtini* endocarp, $\times 1400$.

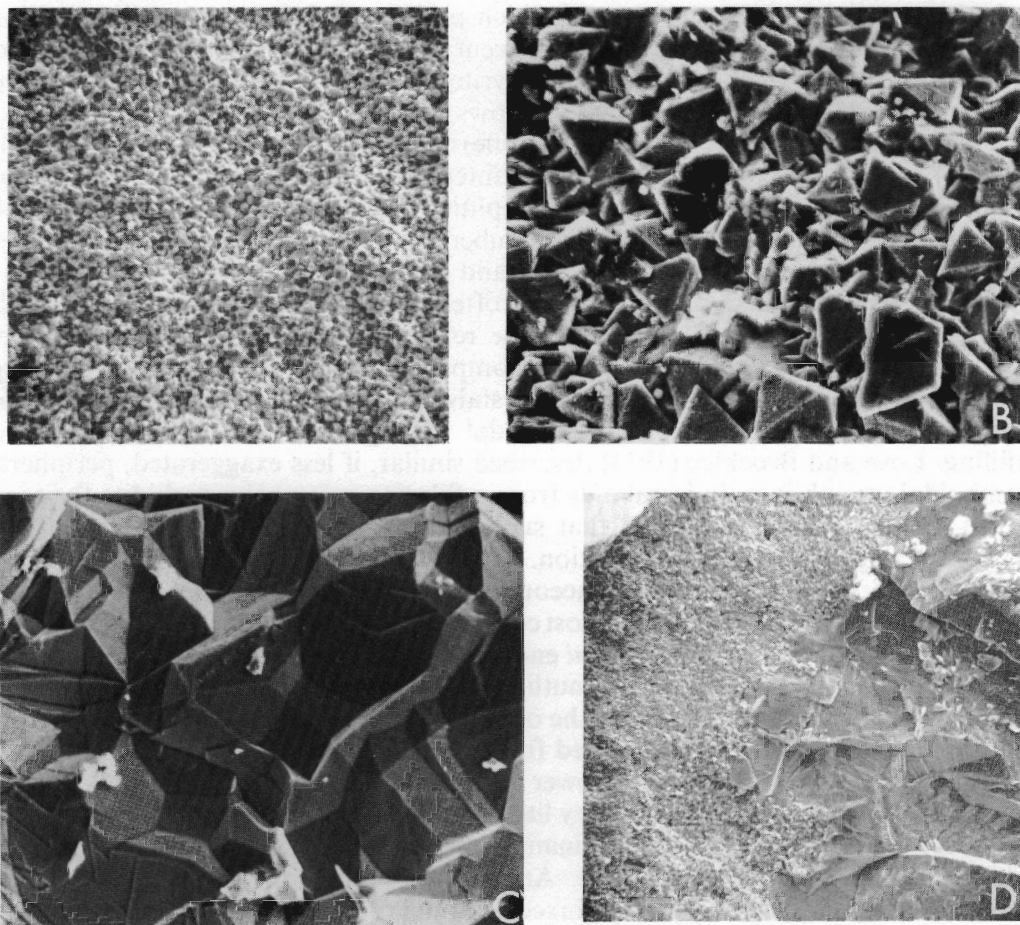
Pyritic infillings of invertebrates in which peripheral shell remains often exhibit similar internal features. Immediately adjacent to and below the periphery is a zone, often up to 200 μm thick, of framboidal pyrite in a groundmass of microcrystalline and more compact pyrite. Text-fig. 3A shows such pyrite lining the chamber of a hoplitid ammonite (Gault Clay, Folkestone). This zone gives way, usually fairly abruptly, to a thicker zone of euhedral intergrown pyrite crystals with average diameters of about 100 μm which, in the hoplitid, terminate in well-developed crystal faces growing towards the centre of the chamber. In other Gault ammonites, nukulids, and ammonites from the Oxford Clay, and gastropods from the London Clay (Sheppey), the euhedral pyrite crystals have often continued to grow until all available cavities are infilled. Text-fig. 3B shows the relationship between the outer microcrystalline pyrite zone and the inner, more compact pyrite in a London Clay gastropod infilling. Here elongate radiating pyrite crystals (text-fig. 3C) have as their origin the peripheral microcrystals in poly-framboidal aggregates near the surface of the infilling. Love and Brockley (1973) described similar, if less exaggerated, peripheral framboidal growth in poly-framboids from a Silurian greywacke-turbidite facies of North Wales, and demonstrated that such textures developed during the earliest diagenetic stages of sediment formation.

The pyrite contained in carbonaceous plant remains from the London Clay (Sheppey) is generally found to be almost completely framboidal; text-fig. 3D illustrates a representative area in a *Nipa burtini* endocarp. In other specimens, e.g. *Stizocarya* sp., pyritization has preserved the outline of individual cells and it is frequently found, especially in elongate cells of the outer part of the carpal wall, that each pyrite infilled cell contains a centrally placed framboid.

Ammonite infillings from the Lower Liassic of Dorset contain mainly microcrystalline or compact pyrite, and very little framboidal pyrite appears to be present. Text-fig. 4A illustrates the predominantly microcrystalline texture of the pyrite infilling an eoderoceratid ammonite. Another specimen contained partially intergrown octahedral pyrite crystals admixed with microcrystalline pyrite (text-fig. 4B). Those containing mainly well-crystallized euhedral pyrite (text-fig. 4C), the pyrite infilling a hemimicroceratid ammonite) have microcrystalline pyrite replacing shell or concentrated in occasional thin-surface lenses (text-fig. 4D).

The pyrite infilling bone canals and medulla in fossil vertebrate material may be compact or microcrystalline. Encrusting pyrite usually has a well-crystallized outer surface but, where in contact with the bone, framboidal and microcrystalline textures are developed.

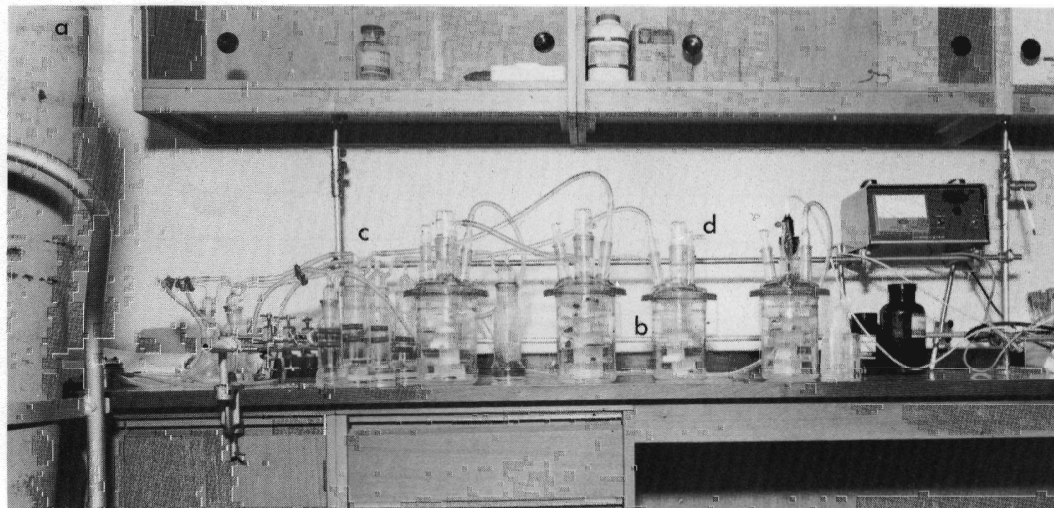
Pyrite oxidation as a function of its texture and storage r.h. Initial experimental results reported by Howie (1977b, 1978) showed that the oxidation of pyrite (reactivity) was a consequence of texture and directly related to the r.h. of the surrounding air. More detailed results are presented here from experiments carried out in ventilated reaction vessels. The apparatus used (text-fig. 5) consisted of a source of compressed air, cylinder (a), feeding one-litre-capacity reaction vessels (b) via gas-washing bottles (c) containing super-saturated solutions of salts giving approximately the r.h. required to the air bubbled through them. The outlet tube (d) and low rate of air flow used (100–200 ml of air per hour) ensured that pressure within the vessel was near to



TEXT-FIG. 4. A, microcrystalline pyrite in Lower Liassic eoderoceratid ammonite infilling, $\times 1000$. B, octahedral and microcrystalline pyrite in Lower Liassic ammonite infilling, $\times 750$. C, compact euhedral pyrite in Lower Liassic hemimicroceratid ammonite infilling, $\times 200$. D, peripheral microcrystalline pyrite in Lower Liassic hemimicroceratid ammonite infilling, $\times 500$.

atmospheric. The experiments were carried out in a laboratory where temperature variations were minimal (21 ± 2 °C.). The r.h. within the vessels was monitored using a Shaw Moisture Meter fitted with a Normal Sensor probe, and once gas flow was regulated it was found that r.h. drift within the vessels could be kept to $\pm 3\%$ for indefinite periods.

Samples of pyrite (1–4 g approx.) of known textural type were pre-treated by washing in dilute sulphuric acid (0.01 molar) followed by intensive water washes to remove soluble oxidation products. Drying was effected by immersion in anhydrous acetone and finally the samples were dried to constant weight over silica gel. Samples were placed in weighed trays, transferred to the reaction vessels and weight changes recorded at regular intervals. At the end of (approx.) 100 days the samples were



TEXT-FIG. 5. Apparatus used for determining the dependence of moisture absorption and oxidation of pyrite on variations in r.h. The moisture sensor is in position, in the reaction vessel at extreme right, connected to the meter above, right (see text for details).

removed from the reaction vessels, weighed, transferred to a silica gel desiccator, and dried to constant weight. Selected samples were analysed, along with controls stored over silica gel, for the extent of iron oxidation. The results are summarized in Table 1.

The specimens containing compact pyrite showed little tendency to absorb moisture and oxidize even at high r.h. during the test period. This behaviour is in accordance with the (subjectively) known stability of such specimens in storage. Those specimens containing microcrystalline and framboidal pyrite showed wide variation in both their capacities for moisture absorption and concurrent oxidation; they all, however, exhibited a considerable acceleration in both at about 60% r.h. The carbonaceous pyritic specimens showed a tendency for some oxidation to occur below 50% r.h., and intensified moisture absorption and oxidation above 60% r.h. In no case were visible signs of deterioration observed below 60% r.h.

Products of the oxidation of pyrite in air. The major products of the oxidation of pyrite in air are sulphuric acid and various hydrated iron sulphates, which in fossil material react with and destroy associated shell, bone, and clay minerals forming, for example, gypsum, vivianite, and potassium and iron alums. In relatively completely pyritized fossils the growth of hydrated iron sulphates within open-textured microcrystalline and framboidal varieties will, unless checked, continue until the reactive pyrite is consumed. In certain specimens, notably those containing carbonaceous pyrite or wholly composed of microcrystalline pyrite, cracking will often occur after a few days exposure in r.h. in excess of 75%. This cracking is indiscriminate (i.e. does not follow any planes of weakness due to fossil structures) and occurs well before there is significant growth of iron sulphates. The cause of this behaviour is not clear, but

SAMPLE DETAILS EXPERIMENTAL DETAILS	ORIGIN	Mt. Isa Shales Precambrian	Concretion Lower Chalk	Hemimicroceratid Lower Liassic	Eoderoceratid Lower Liassic	Hoplitid Gault	Nipa endocarp Lower Eocene
	PYRITE TYPE	cubic, compact	radiating prismatic, porous	pyritohedral, compact	microcrystalline, porous	framboidal and microcrystalline	framboidal (carbonaceous)
	GRAIN SIZE	15mm edge length	n.d.	50-100µm	1-15µm	0.1-5µm	0.1-5µm
34±3% RELATIVE HUMIDITY (MgCl ₂ ·6H ₂ O: super-saturated solution)	% WEIGHT GAIN	0.01	0.06	0.10	0.05	n.d.	0.44*
	% PYRITE OXIDATION	0.01	n.d.	n.d.	0.18	-	0.46*
	VISIBLE CHANGE	none	none	none	none	-	none
47±3% RELATIVE HUMIDITY (K ₂ CO ₃ ·2H ₂ O: super-saturated solution)	% WEIGHT GAIN	0.01	0.10*	0.05	0.10*	n.d.	1.20*
	% PYRITE OXIDATION	n.d.	n.d.	n.d.	n.d.	-	n.d.
	VISIBLE CHANGE	none	none	none	none	-	none
59±3% RELATIVE HUMIDITY (MgNO ₃ ·6H ₂ O: super-saturated solution)	% WEIGHT GAIN	0.02	0.41	n.d.	0.77	0.25 ^(a)	2.58*
	% PYRITE OXIDATION	n.d.	n.d.	-	n.d.	n.d.	n.d.
	VISIBLE CHANGE	none	none	-	none	none	slight growth of products
65±3% RELATIVE HUMIDITY (NaBr·2H ₂ O: super-saturated solution)	% WEIGHT GAIN	0.03	0.19	0.16*	0.92*	1.15*(a)	2.60*
	% PYRITE OXIDATION	n.d.	0.44	n.d.	0.42*	n.d.	1.34*
	VISIBLE CHANGE	none	none	none	slight growth of products	slight growth of products	destroyed, moist
76±3% RELATIVE HUMIDITY (NaCl: super-saturated solution)	% WEIGHT GAIN	0.05*	0.43*	0.45*	1.40*	7.30*(a)	8.70*
	% PYRITE OXIDATION	0.01	0.86	0.18	0.76*	n.d.	4.68*
	VISIBLE CHANGE	none	slight tarnish	none	cracked, slight growth of products	extensive product growth	destroyed, moist
86±3% RELATIVE HUMIDITY (KCl: super-saturated solution)	% WEIGHT GAIN	0.05	1.13	n.d.	1.65*	n.d.	13.52*
	% PYRITE OXIDATION	n.d.	n.d.	-	n.d.	-	n.d.
	VISIBLE CHANGE	none	tarnished, cracked, moist	-	extensive growth of products, cracked	-	destroyed, very moist
CONTROL SPECIMENS STORED OVER SILICA GEL	% PYRITE OXIDATION	less than 0.01	0.10	0.10*	0.20*	n.d.	0.20*

n.d. not determined.

^(a) after 30 days' exposure.

* average of two or more determinations.

TABLE 1. Weight gains and oxidation shown by pyrite samples of differing textural type exposed to various relative humidities for 105 days.

one explanation is that wetting of porous pyrite by moisture absorption causes a rapid reduction in the surface forces that aggregate the microcrystals resulting in brittle fracture of the structure.

The growth of iron sulphates on actively oxidizing pyrite specimens was monitored by SEM (Howie 1977b) and by analyses of fresh and old oxidation products using XRD or chemical methods. The initial products, visually identified as szmolnokite (FeSO₄·H₂O) by SEM, grew at contacts between microcrystals after a few days' exposure to 75% r.h. Continued exposure to humid conditions resulted, after about

six weeks, in destruction of the samples, and chemical tests showed that much of the product consisted of ferrous sulphates. XRD of separated fresh crystalline products confirmed the presence of szmolnokite, melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and other hydrated ferrous sulphates. Chemical analyses of old desiccated products showed that these had been oxidized to mainly ferric sulphates. Such sequential formation of iron sulphates has been reported as occurring in the oxidation zones around sulphide ore bodies (Bandy 1938) and from laboratory investigations (Buurman 1975).

Mechanisms for pyrite oxidation. Investigations into the chemistry of pyrite under aqueous conditions have shown the existence of three possible oxidation pathways. At the high temperatures and oxygen pressures used in the commercial leaching of pyritic ores, two oxidation mechanisms have been proposed. The first and older mechanism suggested that oxygen is adsorbed on to the surface of pyrite in water, and oxidation proceeds by a series of molecular reactions (Burkin 1966). Bailey and Peters (1976) demonstrated, by isotope exchange experiments with O^{18} , an electrochemical pathway where the oxygen in the sulphate actually originates in the water rather than the gas phase. The third pathway, oxidation of pyrite by bacterial activity, especially *Thiobacillus ferrooxidans*, occurs at temperatures of up to 40 °C. in fully aqueous environments where the acidity of the reaction medium remains above about pH 1 (Zajic 1969).

Although the mechanisms responsible for the oxidation of pyrite in air have received little investigation, bacterial activity has been suggested in several articles on the conservation of pyritic museum material (e.g. Booth and Sefton 1970; Oddy 1977). Howie (1977*a, b*) reviewed the situation and concluded that thiobacteria were not involved in the oxidation of pyrite in the museum environment for the following reasons:

(a) The methods based on bactericides advocated by Booth and Sefton (1970) and Broadhurst and Duffy (1970) failed to protect pyritic specimens.

(b) The high concentrations of sulphuric acid present in actively oxidizing pyrite would preclude the activity of iron-oxidizing bacteria such as *Thiobacillus ferrooxidans* (Silverman 1967).

(c) Other thiobacteria, e.g. the sulphur oxidizers such as *T. thiooxidans*, will not oxidize metallic sulphides, although they could possibly tolerate the high acidities present (Zajic 1969).

(d) *T. ferrooxidans* will not oxidize iron at sulphate concentrations above about 0.2 molar (Steiner and Lazaroff 1974); sulphate concentrations reaching saturation levels, i.e. about 1.0 molar, are probably present at oxidation product growth sites in unstable pyrite textures.

(e) The material tested experimentally had been effectively sterilized by acetone washing before oxidation occurred.

Further support for purely chemical causation came from the results of a series of microbiological screening tests carried out at Warren Spring Laboratory. Samples of several actively oxidizing pyritic fossils were put on culture in various thiobacilli media for one month. The results indicated that *T. ferrooxidans* was not present in any sample, and that, possibly *T. thiooxidans* might have been present in one sample, but in quantities too small to be significant (pers. comm. from Mr. P. Dacey, Warren Spring Laboratory, 1976). Steger and Desjardins (1978) have investigated the oxidation of crushed pyrite samples in air and suggest a purely chemical mechanism whereby pyrite initially oxidizes to unstable ferrous thiosulphates which, on exposure to air, yield ferric sulphates. They did not, however, take into account the possible

activity of water in their experiments and their findings are at variance with those reported earlier in this paper.

An electrochemical mechanism for the oxidation of pyritic material in air is suggested by the following observations:

(a) Moisture absorption and concomitant oxidation in reactive pyrite samples do not occur substantially until a critical relative humidity (approx. 60%) is exceeded (text-fig. 6A). This suggests that a film of moisture on the surface of the pyrite is required for electrolyte formation, i.e. an acid/sulphate aqueous phase. Evans and Taylor (1972) showed that iron rusting in air containing sulphur dioxide is mainly due to electrochemical reactions involving such a phase, and a critical relative humidity similar to that shown by pyrite was found (text-fig. 6B).

(b) The presence of soluble chloride contaminants in pyritic fossil material accelerates deterioration (Rixon 1976). Aqueous solutions of chlorides are good electrolytic conductors.

(c) The enhanced oxidation of pyritic specimens associated with carbonaceous material (see Table 1), also reported by Schopf (1965), suggests that pyrite is in galvanic contact with carbon. Semi-quantitative measurements using platinum electrodes showed that a potential difference of about 200 μ v developed between the inner, pyritic, part of a fractured pyritized *Nipa* endocarp (London Clay, Sheppey) and the outer highly carbonaceous integumen after a short period of exposure to 75% r.h.

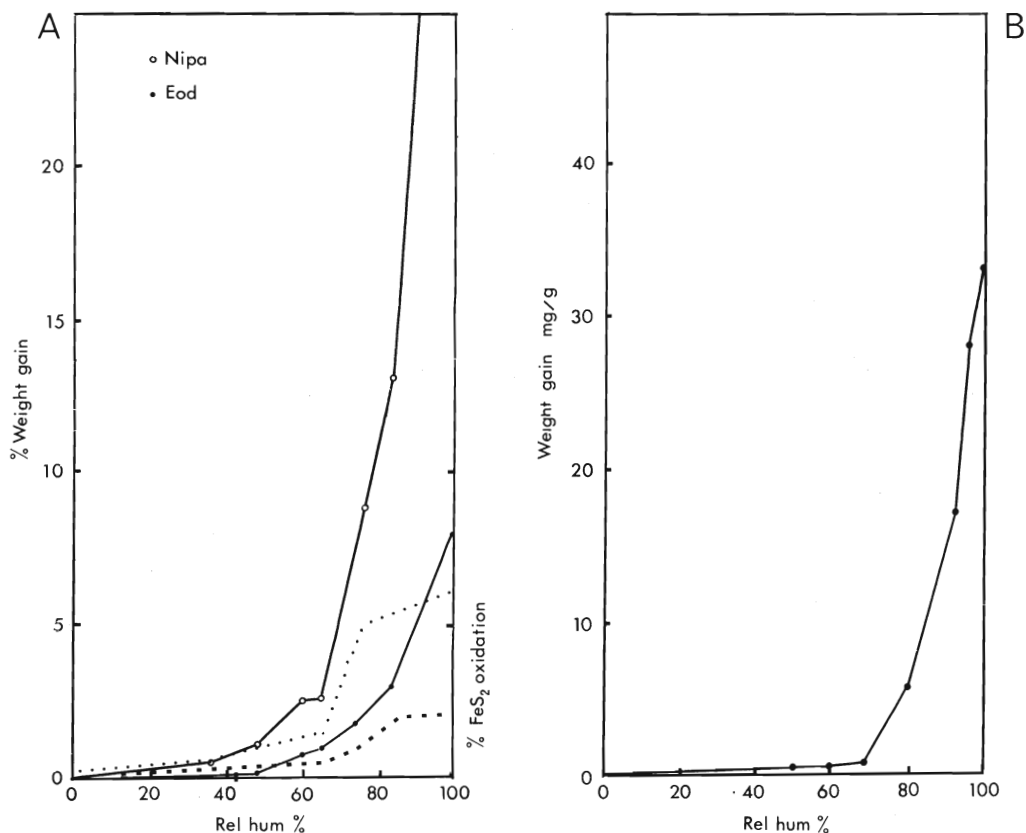
(d) Peters and Majima (1968) demonstrated electrochemical mechanisms for the aqueous corrosion of pyrite at atmospheric pressure and 25 °C.

The nature of possible cathodic and anodic reactions involved in the oxidation of pyrite in air await empirical investigation. If their existence is shown, there is the possibility of interfering with the reactions by using vapour phase inhibitors in storage or exhibition cases, or inhibitors in the plastics used to consolidate pyritic specimens.

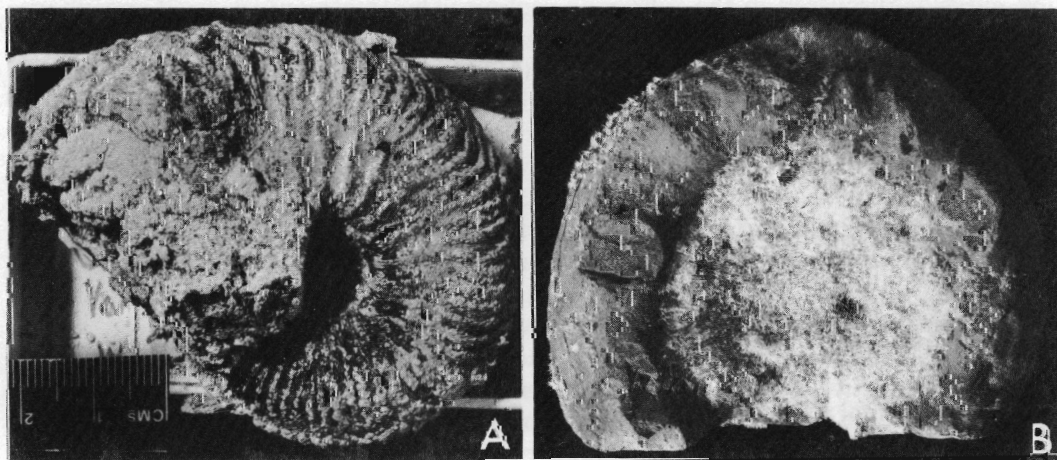
Treatment and storage of pyritic fossil material. The methods recommended for treating pyritic fossils based on impregnation with plastics give very little protection to specimens exposed to environments where r.h. exceeds 60% (Howie 1977b, 1978). The failure of a thick surface coating of Bedacryl 122X in preventing deterioration is illustrated by text-fig. 7A. To test the efficiency of surface coating plastics, sets of selected unstable pyritized seed cases (London Clay, Sheppey) were impregnated with 5–10% solutions of Bedacryl 122X (in ethyl acetate) or Vinylite YHH (in ethyl methyl ketone), either by vacuum impregnation or by brush application. Another set was brush treated using 5% Butvar B98 (in isopropanol). Specimens were weighed before and after impregnation, and it was found that the Butvar had failed to adhere. Sets representing each treatment and untreated control specimens were exposed to $58 \pm 3\%$ r.h. and $85 \pm 3\%$ r.h. in the apparatus described earlier, and weight gains determined for each specimen over a 63-day period. The results are shown in Table 2.

Moisture absorption by the treated specimens differed little from that shown by the untreated controls. Cracking and growth of oxidation products occurred in all specimens exposed to 85% r.h. The permeabilities of thin films of polymers used in surface coating applications have received considerable investigation (Von Fraunhofer and Boxall 1976) and the great majority are permeable to water, both liquid and vapour. Permeabilities of up to $300 \text{ mg.cm}^{-2} \cdot 24\text{h}^{-1}$ water (as vapour) through plastic films of 0.1 mm thickness have been reported, indicating that their failure in the protection of moisture sensitive fossil materials is to be expected and, as such, their use should be restricted purely to consolidation treatments.

The rescue or salvage of actively deteriorating specimens should be approached



TEXT-FIG. 6. A, moisture absorption (solid lines) and concomitant pyrite oxidation for pyrite in samples of eoderoceratid ammonites (Eod, dashed line) and Nipa (dotted line) after 65 days' exposure to r.h.s between 30% and 100% at 20 °C. (approx.). B, weight change for iron samples exposed to air at various r.h.s containing sulphur dioxide. (Adapted from Evans and Taylor 1972.)



TEXT-FIG. 7. A, pyritic kosmoceratid ammonite (Oxford Clay) showing extensive deterioration after impregnation with Bedacryl 122X, $\times 1$. B, growth of efflorescent calcilicite on a Jurassic reineckiid ammonite (Iquique, Chile) stored in case containing oak.

EXPOSURE PERIOD (DAYS)	% WEIGHT GAINS AT $58 \pm 3\%$ RELATIVE HUMIDITY FOR NIPA TREATED THUS:					% WEIGHT GAINS AT $86 \pm 3\%$ RELATIVE HUMIDITY FOR NIPA TREATED THUS:				
	CONTROL, UNTREATED	BUTVAR COATED	BEDACRYL COATED	VINYLLITE COATED	BEDACRYL VACUUM COATED	CONTROL, UNTREATED	BUTVAR TREATED	BEDACRYL COATED	VINYLLITE COATED	BEDACRYL VACUUM COATED
7	0.46	0.96	0.94	1.31	1.11	3.12	0.54	1.67	2.73	1.07
14	0.69	1.26	1.13	1.56	1.44	4.78	0.90	3.52	4.94	2.00
22	1.08	1.56	1.31	1.95	1.81	6.65	1.57	4.97	7.58	2.51
35	1.46	1.86	1.48	2.18	2.08	9.70	2.36	6.73	9.65	3.32
63	2.55	2.73	1.99	3.05	3.31	11.13	3.36	9.64	13.13	4.97
EXPOSURE PERIOD (DAYS)	% WEIGHT GAINS AT $58 \pm 3\%$ RELATIVE HUMIDITY FOR STIZOCARYA TREATED THUS:					% WEIGHT GAINS AT $86 \pm 3\%$ RELATIVE HUMIDITY FOR STIZOCARYA TREATED THUS:				
	CONTROL, UNTREATED	BUTVAR COATED	BEDACRYL COATED	VINYLLITE COATED	BEDACRYL VACUUM COATED	CONTROL, UNTREATED	BUTVAR TREATED	BEDACRYL COATED	VINYLLITE COATED	BEDACRYL VACUUM COATED
7	0.40	0.50	0.95	0.82	0.49	3.18	1.25	3.16	2.73	2.51
14	0.65	0.76	1.22	0.92	0.57	5.72	2.49	5.26	5.24	4.45
22	1.09	1.22	1.68	1.16	0.61	9.00	2.94	8.23	10.47	7.53
35	1.54	1.86	2.17	1.41	0.60	12.92	9.84	11.89	15.87	12.02
63	3.15	2.73	3.71	2.48	0.72	19.61	18.02	17.57	28.01	21.42

TABLE 2. Weight gains shown by treated pyrite samples exposed to $58 \pm 3\%$ r.h. and $86 \pm 3\%$ r.h. over 63 days.

from an environmental standpoint. Affected material must be immediately transferred to a dry storage or treatment area. Small specimens can be satisfactorily dried by desiccation over silica gel, but large specimens in shale or clay should not be dried to below 45% r.h. (lessening the possibility of matrix splitting by dehydration), and this can be carried out by placing bags of conditioned silica gel in cabinets or exhibition cases as discussed in the following section. The treatment of dried specimens, i.e. removal of oxidation products, neutralization of sulphuric acid, and consolidation or restoration has been detailed by Rixon (1976) and Howie (1977b).

Where pyritic specimens are deeply oxidized, exposure to moist ammonia vapour for several days or weeks usually results in superficial neutralization only. The experimental use of dry ammonia gas on such specimens results in rapid and complete neutralization (this operation is hazardous and should only be attempted in an efficient fume cupboard). The removal of acidic oxidation products in large specimens using ammonia vapour is not normally a practical possibility and Rixon (1961) suggested the repeated application of dilute (5% approx.) alcoholic solutions of morpholine to affected areas until neutralization was achieved. However, where deterioration has penetrated to a depth of more than about a centimetre this technique is often not effective. (There is a health hazard associated with using morpholine as it is extremely toxic by both skin absorption and inhalation; its use therefore necessitates a well-ventilated treatment area, preferably a fume cupboard, and the use of protective clothing.)

Ammonia or morpholine neutralization results in the formation of red or brown basic ferric sulphates and hydrated iron oxides which, although quite stable, are usually extremely friable. Removal of extensive neutralized oxidation products may be accomplished mechanically by Airbrasive equipment or vibropeen, although this usually necessitates subsequent restoration using a non-aqueous filler (e.g. North Hill Plastic cold-setting acrylic mounting plastics). Removal of superficial products can be effected by immersing specimens in a dilute (5% approx.) solution of ammonium thioglycollate in ethanol. This compound chelates iron from insoluble ferric compounds (Howie 1974) and specimens thus treated should be thoroughly washed by several immersions in clean dry ethanol before further treatment. After neutralization friable specimens require consolidation using an organic solvent based resin (e.g. Bedacryl 122X or Vinylite YHH).

Freshly collected pyritic specimens from coastal localities should be thoroughly soaked in several changes of deionized or distilled water to remove soluble chlorides. Short-term contact between unoxidised pyritic material and water does little harm so long as specimens are transferred immediately after soaking to water-free acetone, ethanol, or isopropanol and subsequently dried over silica gel. Further treatment, where necessary, is restricted to consolidation of friable or fragile areas using a suitable synthetic resin as before. Water-based fillers and adhesives (e.g. plaster of paris and polyvinyl acetate emulsions) are not recommended for the treatment of pyritic material.

Pyritic specimens, whether treated or not, require storage in areas where, ideally, 55% r.h. is not exceeded. Although experiment has shown that the oxidation of reactive pyrite will occur within a few days of exposure to 60% r.h. or above, deterioration does not generally become visibly manifest for some weeks. Continuous monitoring of the storage environment (discussed below) will give early warning of expected problems, allowing steps to be taken to reduce the r.h. before serious damage occurs. Certain types of specimens, notably Lower Tertiary pyritized plant remains, will, however, deteriorate within a matter of days when exposed to high r.h., and these require storage in very dry conditions.

Small collections of such specimens may be stored over silica gel in desiccators but for large collections the only practical alternative is storage under an inert liquid. Several liquids, including linseed oil, carbon tetrachloride, paraffin, and glycerol have been tried unsuccessfully. The experimental use of silicone fluids, commenced at the BM(NH) during the early 1960s, was extended to the storage of type and figured pyritic London Clay material and complete transfer mainly from glycerol was completed in 1972. Removal of glycerol from porous pyritized seeds posed a serious problem. Washing by Soxhlet extraction using water resulted in further damage to specimens and, as Rixon (1976) pointed out, did not totally remove glycerol. The method finally adopted consisted of several prolonged immersions of specimens, supported on fine-mesh brass sieves, in a mixture of nine parts of dry ethyl methyl ketone and one part of anhydrous isopropanol. Four or five 24-48 hour immersions in fresh ketone-alcohol mixtures were found to remove most of the glycerol without damaging specimens. After washing, the specimens were dried over silica gel, fully immersed in Silicone Fluid DC 200/350 cs, and any air remaining within specimens removed under vacuum.

Several thousand pyritized plant specimens have been stored in Silicone Fluid DC 200/350 cs for up to 18 years and very few have shown signs of deterioration. Removal of silicone fluids from treated specimens for examination can be simply effected by a brief wash in toluene, the high volatility of this solvent giving a perfectly dry specimen within a few seconds. After examination, specimens should be immediately returned to silicone fluid and vacuum treated for the removal of air.

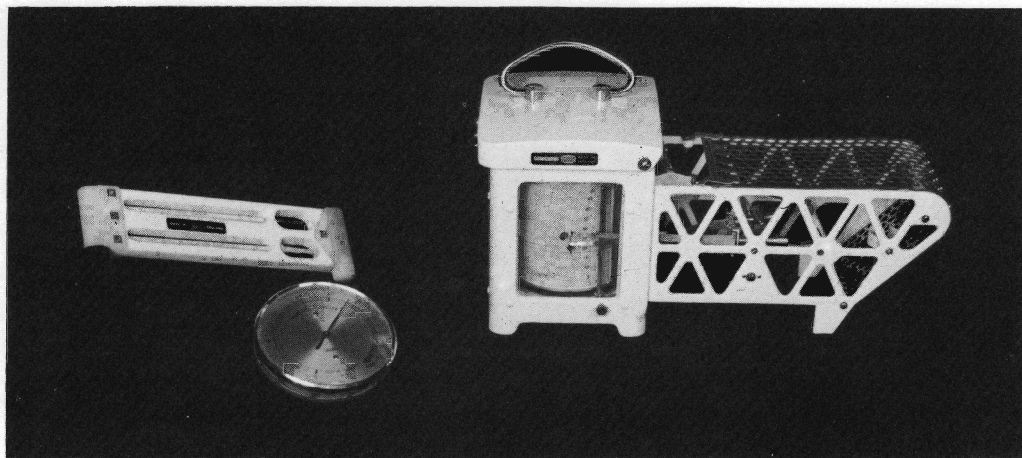
Silicone fluids are extremely inert materials which have a very low permeability to water and oxygen, and extension of their use to the storage of other small pyritic specimens is suggested. The evidence available suggests that long-term contact between pyrite and silicone fluids is favourable, but compatibility with other minerals present in pyritic fossil material, e.g. calcite, gypsum, and silica, has not been ascertained. A further important consideration is that specimens must be free of water (and its dissolved oxygen) prior to immersion. Desiccation over silica gel may not be effective in all cases and specimen drying in a vacuum oven (at 10–20 °C. above ambient temperature) or by critical-point (freeze-) drying techniques might be appropriate. A problem with 'total' drying methods is that exposure of water-free specimens to air, i.e. during transfer processes, results in rapid and enhanced moisture absorption. Freeze-dried pyritized seeds exposed to air, even at fairly low r.h. (40–45%), deteriorate extremely rapidly.

MONITORING AND MODIFYING THE ENVIRONMENT FOR UNSTABLE FOSSIL MATERIAL

The importance of being able to ascertain variations in temperature and, more importantly, relative humidity in the vicinity of unstable fossil material cannot be overstressed. Information on annual cycles of relative humidity in museums and areas in buildings which, used to store and exhibit unstable fossils, are prone to rapid or seasonal environmental variation, will give early warning of expected conservation problems and dictate possible remedial action. Such data should be prerequisite to the planning of storage and exhibition of fossil material.

Monitoring storage and exhibition environments. The temperatures and r.h. within museums reflect, in modified form, the external climatic conditions of their geographical location (Plenderleith and Philippot 1960), with those in temperate northern latitudes having annual cycles exhibiting winter troughs (10–30% r.h.) and summer peaks (65–70% r.h.) (Thomson 1977).

Storage area and gallery r.h. can be monitored using a variety of instruments, and three in use at the BM(NH) are shown in text-fig. 8. The sling or whirling hygrometer is the most accurate instrument shown, but its use necessitates several readings in any one location and the results obtained are subject to operator error. The dial-type hair hygrometer is relatively inexpensive and can be used to monitor areas of limited volume such as exhibition cases or storage drawers. The pen recording thermohygrograph is undoubtedly the most convenient instrument for long-term monitoring but, as with the dial-type hair hygrometer, it is not particularly accurate ($\pm 3\%$ r.h. is quoted by manufacturers) and requires re-calibration at approximately two monthly



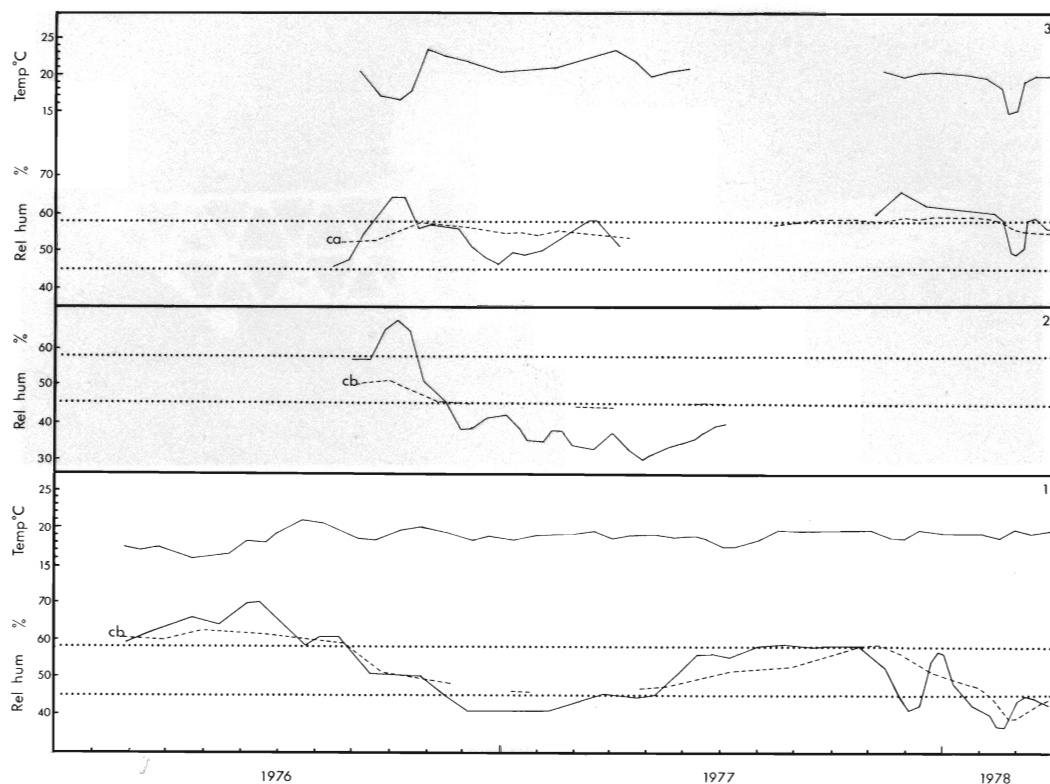
TEXT-FIG. 8. Instruments used to monitor relative humidity. Whirling or sling hygrometer (*left*), dial-type hair hygrometer (*centre*), and recording thermohygrograph (*right*).

intervals. Measurements using these instruments in storage and gallery areas should be obtained away from windows, doors, radiators, and air-conditioning vents.

The annual cycles of r.h. and temperature in three areas at the BM(NH) are illustrated in text-fig. 9 (solid lines). The r.h. cycle for an exhibition gallery, with glazed roof, shows limited seasonal variation, major short-term fluctuations, and a tendency towards high values. This is undoubtedly due to the high heat gains and losses through the roof and the (almost) continual influx of visitors. The open exhibition of pyritic material in this gallery would be expected to, and indeed does, cause conservational problems, but open exhibition of sub-fossil vertebrates causes few problems. The cycle for a basement storeroom, with windows facing an enclosed courtyard, shows a more typical seasonal pattern with r.h. during winter of less than 30%, and during summer of about 60%. The open storage of sub-fossil bone in such storerooms has generally been found to lead to deterioration, whereas pyritic specimens have survived relatively well.

The annual cycles for temperature and r.h. in an air-conditioned East Wing, BM(NH), storage area show certain characteristics found in newly constructed buildings. The high r.h. (over 60%) during the summer of 1976 (one year after construction was completed) was due to a number of factors, including imbalance of the various air-conditioning plants installed, the drying-out of structural and decorative elements, and the large volume of fresh timber used in the construction of storage units. The winter and summer cycles for 1977 and winter cycle for 1978 gave more generally acceptable storage conditions, except for a period early in 1978 when winter humidification equipment failed.

Modification of storage and exhibition environments. The majority of palaeontological specimens are stored or exhibited in some form of closed case or cabinet. Where such units are constructed of well-seasoned dry timber it is generally found that a fairly stable r.h. is generated internally. This is due to the capacity of wood to exchange



TEXT-FIG. 9. Graphical representation of annual cycles of relative humidity and temperature. 1. Air-conditioned storage area; 2. Non-air-conditioned basement storage area (r.h. plot only). 3. Gallery area. Solid lines represent exterior conditions, dashed lines represent exhibition case (ca) interior and cabinet (cb) interiors. The dotted lines at 58% r.h. and 45% r.h. represent approximate upper and lower limits for pyrite and sub-fossil bone storage respectively.

water with air. A volume of wood at equilibrium with air in a closed case at median r.h. and temperature (e.g. 50% r.h. and 20 °C.) will contain several hundred times as much water as the same volume of air. Upward (or downward) variations in the r.h. of the air in the case at constant temperature are caused by relatively small increases (or decreases) in absolute humidity (see text-fig. 1); any wood present will respond by rapidly taking up much of this excess water vapour (or giving up water to air) and the resulting r.h. will remain virtually unchanged. Water-vapour exchange between the air inside and outside a closed case takes place by leakage via door or sash seals and by diffusion through the timber used in construction. Increase or decrease in ambient temperature will cause slight rise or fall of internal r.h. Thomson (1964) and Padfield (1966) discuss the mathematical and mechanical aspects of r.h. buffering in cases containing wood, and such coverage is outside the scope of this paper.

The effect of timber buffering on the seasonal r.h. cycle will not substantially alter the cycle within the case, but it will effectively smooth out short-term fluctuations and cause delay between internal r.h. catching up with external r.h. The effect of timber

constructed units in modifying the annual r.h. cycles of storage and gallery areas is shown in text-fig. 9 (dashed lines). The well-seasoned timber and tight seals used in old cases and cabinets monitored in the gallery and basement areas have considerable buffering capacity, with the r.h. cycles established within the units approaching an average condition. The new units in the East Wing also exhibited good buffering characteristics (except during summer 1976, as discussed previously) but their capacity is not as high as for the older cabinets, mainly because the door seals are poor. These new units, however, clearly demonstrate the delayed response of internal r.h. to external changes, i.e. during the summer of 1977 the delay period was between two and four months, and the unit interior r.h. only marginally exceeded the upper storage limit. A slightly shorter lag occurred during the winter (1978) which resulted in the lower limit being transgressed, and this resulted in some damage to sub-fossil vertebrate material.

For the emergency treatment of deteriorating pyritic material in humid exhibition cases or storage cabinets the use of conditioned silica gel is recommended. This material behaves similarly to timber but its buffering capacity for r.h. below 50% is greater. Thomson (1977) describes the theory and practice of the use of conditioned silica gel and recommends that approximately 20 kg will effectively buffer one cubic metre of case volume against short-term fluctuations and even cut longer-term seasonal variations in r.h.

This method has recently been employed at the BM(NH) to lower and stabilize the relative humidity in a glazed case containing a deteriorating pyritic Liassic ichthyosaur. The monitored r.h. within the case was initially fluctuating daily between 60% and 64% (due to variations in gallery temperature), and gallery r.h. varied daily between 60% and 70%. The case volume was 0.6 m³ and a relatively large volume of wood was present. For the latter reason approximately 4 kg of dry silica gel was conditioned to air at 35% r.h. by exposure to water vapour in a closed perspex box. The length of time taken to condition this weight of silica gel was seven days. The appropriate conditioning level was ascertained by reference to the moisture absorption (weight gain) versus r.h. curves for silica gel and confirmed by hygrometer readings. The conditioned silica gel was then placed in the case and the r.h. fell rapidly to 40%. Subsequently a slight rise occurred and after three months the r.h. within the case had stabilized at $47 \pm 1\%$. During that period gallery r.h. had fluctuated between 40% and 70% and no further deterioration in the state of the specimen was observed.

The reverse procedure, i.e. raising the relative humidity in a dry case, may be effected using silica gel conditioned to between 50% and 60% r.h. (Stolow 1966). An alternative method that could be of use in small storerooms or large storage units is air humidification by portable atomizer-humidifiers. These instruments are electrically operated and, by the use of time switches, short periods of humidification will quickly give acceptable levels in storage where large volumes of wood are present. The use of conditioned silica gel for the long-term stabilization of r.h. in well-sealed cases and cabinets offers considerable advantages to the smaller museums where air-conditioning may not be feasible. Its use will remove the low winter troughs and high summer peaks more efficiently than wood, and this alone will undoubtedly result in enhanced stability of both sub-fossil bone and pyritic material in buildings where the annual r.h. cycle is between 30% (winter) and 70% (summer).

Cabinets and cases in buildings or parts of buildings where r.h. is either above 60% or below 45% throughout the year will not be buffered to acceptable levels using conditioned silica gel. The only option available is to move unstable specimens to areas where acceptable conditions prevail. A situation to avoid is the use of cases and cabinets in contact with external walls. Units in such locations often suffer from internal condensation at night during winter months due to rapid heat loss through adjacent walls. The situation can be relieved by allowing free circulation of air behind the case or cabinet.

Conservation problems caused by storage in wooden units. Timber generally has many advantages over glass, metal, or plastic when used in case and cabinet construction. The choice of timber, however, is important as the use of certain woods may result in damage to material. Text-fig. 7B illustrates a fairly common problem encountered with specimens stored in cabinets partly constructed of oak. The specimen appeared to be covered with typical efflorescent salt growths, as commonly occur where unwashed specimens contaminated with soluble chlorides and carbonates are exposed to alternating dry and damp conditions (Howie 1978). Chemical analyses revealed that the efflorescences were composed of calclacite (a series of hydrated calcium chloride-acetates, sometimes containing nitrate and sulphate).

The formation and occurrence of calclacites and associated compounds on a wide variety of stored and exhibited museum specimens are discussed by Fitzhugh and Gettens (1971). The source of the problem is the minute traces of acetic acid vapour continuously emitted by timbers such as oak and birch. This vapour reacts, in humid storage conditions, with traces of deliquescent salts on or near the surface of specimens, and damage of fossil material, mainly surface pitting, is caused during the growth of efflorescences by the acid etching of underlying calcareous minerals. Treatment consists of mechanically removing the efflorescence by brush or airbrasive, followed by the consolidation of friable areas using a suitable organic solvent-based plastic, and subsequent storage in dry conditions away from oak.

CONCLUSIONS

The environmental aspects of the storage and exhibition of palaeontological material have been severely neglected in the past and this has resulted in considerable deterioration and loss of important specimens in collections both large and small. Very little published information is available on the state of palaeontological collections, but it appears that two major problems are encountered; both have variations in relative humidity as their main cause.

The first is with sub-fossil vertebrate material, where storage in dry environments often leads to permanent damage. Very little is known about the physico-chemical state of sub-fossil bone, and research into this field is required before limiting storage conditions can be stipulated. Subjective observations of stored specimens and preliminary experimental work suggest that the lower limit of r.h. is in the range 45–50%. Damage to sub-fossil bone in dry areas can occur extremely rapidly, i.e. within a few hours or days.

The second and undoubtedly most serious problem is the conservation of pyritic

material. Lack of research into pyritization and reliance on subjective assessment of conservational treatments (e.g. bactericides) have hindered the establishment of clear criteria for preservation. Pyrite in sediments occurs in two characteristic forms. Compact crystalline varieties (stable types) are fairly resistant to oxidation in air. Microcrystalline and framboidal varieties (reactive or unstable types) are extremely susceptible to deterioration. Reactive and stable types are often found associated in fossil material. Reactive pyritic material tends to deteriorate when exposed to air at r.h. above 55–60% at normal temperatures. The complicity of thiobacteria in the deterioration of pyritic specimens in museum collections is not considered to be an adequate explanation of the phenomenon; the mechanisms appear to be electrochemical in nature, but objective testing of this hypothesis is required. Carbonaceous pyritic specimens require storage under very dry conditions. Silicone fluids, used successfully for the storage of London Clay endocarps for several years, are recommended, and extension of this technique to other small specimens is suggested.

The use of conventional consolidants does not confer stability to either sub-fossil vertebrate or pyritic material stored in environments where relative humidity is uncontrolled. Recurring conservational problems are probably related to the annual cycles of relative humidity pertaining to the interior environment of museums and other buildings used to store palaeontological material. In museums of northern latitude winter troughs and summer peaks of relative humidity occur. Specimens in wood-constructed storage and exhibition units are protected to some extent from seasonal variations by the moisture buffering characteristics of seasoned timber. Conditioned silica gel, both in salvage or rescue operations and in cases or cabinets where long-term stable humidities are required, is a potentially useful technique.

There are certain situations where sensitive palaeontological material cannot be stored satisfactorily. In such cases there can be no compromise but to move affected material to a more suitable environment.

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DISCUSSION

S. A. Baldwin. Have viruses been completely ruled out as a cause of pyrite decay?

F. M. P. Howie. No, although I know of no reported work showing that viruses affect minerals. I would rather pursue the question of known biological effects on minerals—in this case thiobacteria and pyrite. The idea of bacterial complicity in the breakdown of museum specimens was convenient, both as an explanation of causation, i.e. the apparent spread of 'decay' from specimen to specimen in storage, and also attractive in terms of treatment through the simple use of antiseptics as douches or as vapour phase inhibitors. The former effect can be explained quite simply, I believe, when one considers that reactive specimens, i.e. those containing microcrystalline pyrite, often occur together in particular types of sediment and may be stored together; changes in storage relative humidity would tend to result in deterioration affecting these specimens simultaneously. The latter requires little clarification, as such antiseptics do not in fact work at all.

I have other support for the non-complicity of thiobacteria from Professor Rolfe (Australia) who has informed me that the examination of some dry cores of oxidizing pyritic sediment showed the absence of micro-organisms. Bacteria only influence pyrite oxidation when sufficient (liquid) water is present to hold the pH of the system above about one. Dry, oxidizing pyrite has a pH far below this value.

C. D. Waterston. On what is perhaps a provocative note, it seems to me that the installation of elaborate air-conditioning systems may create more harm than good; for example, specimens may be subjected to traumatic conditions should the system go awry, with the result that perhaps a critical relative humidity might be reached at a very rapid rate. I have often considered whether this is worse than the specimens just mouldering slowly.

F. M. P. Howie. The problem is that material does not just moulder slowly—it either moulders or is not affected at all. I think that air conditioning has advantages, especially in a modern building which is like a glasshouse. Without air conditioning the extremes would probably be much greater; with old buildings, such as the one we had previously at the BM(NH), the large volume of masonry and old timber acted as buffers for fluctuation in relative humidity. And, I am sure that curators intuitively segregate their material with, for example, the unstable pyritic specimens finding their way to the drier areas. The need for air conditioning to be strictly controlled when used in museums has been recognized by UNESCO for some time now.

C. D. Waterston. It may have been recognized by UNESCO but it is important for us to make sure that our requirements are recognized by the air-conditioning engineer.

F. M. P. Howie. What is really needed is research into aspects of the stability of various types of fossil material. It would be useful if such topics could form bases for research work for Ph.D. students in either palaeontology or museum training courses.