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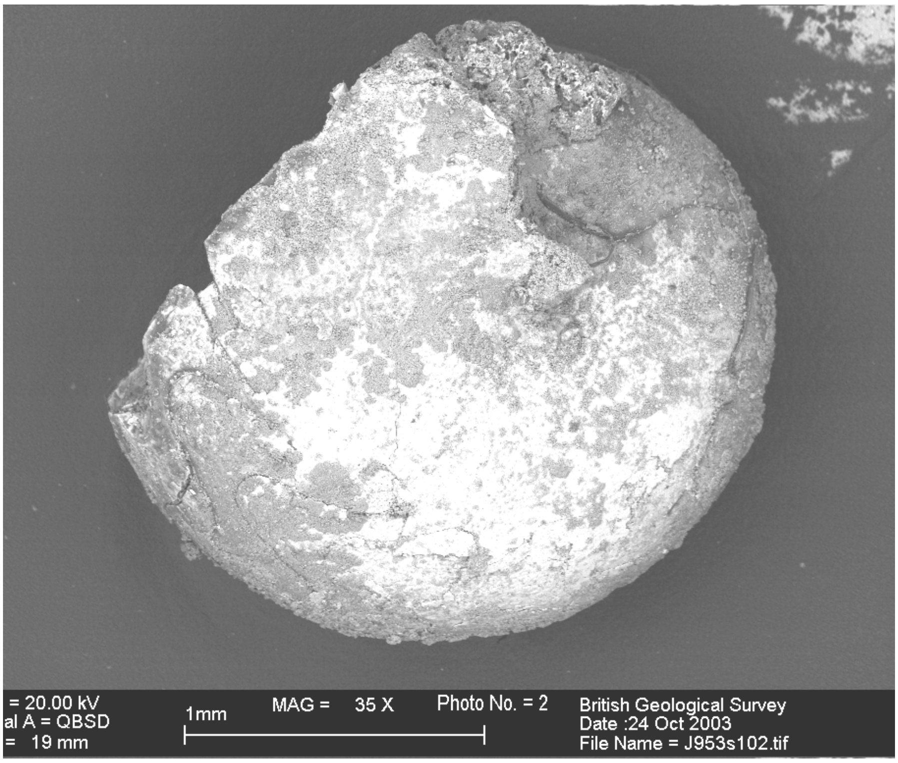
Curation history and mineralisation of highly degraded pyrite fossil collection

Information Management Programme

Internal Report IR/04/037



BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/04/037

History and mineralisation of highly degraded pyrite fossil collection

E S Hodgkinson and S Martin

Key words

Curation, pyrite, fossil, decay, Westphalian Coal Measures, relative humidity, melanterite, coquimbite, römerite.

Front cover

Goniatite specimen from Alton marine band of Westphalian Coal Measures, undergoing pyrite oxidation.

Bibliographical reference

HODGKINSON, E S AND MARTIN, S. 2004. History and mineralisation of highly degraded pyrite fossil collection. *British Geological Survey Internal Report*, IR/04/037. 34pp.

Keyworth, Nottingham British Geological Survey 2004

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Acknowledgements

Paul Shepherd is thanked for carrying out environmental monitoring measurements of relative humidity and temperature and for producing this data in an accessible format.

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Summary

A collection of fossil specimens in a wooden tray in the palaeontological collections at Keyworth was found in a catastrophically degraded state due to suspected pyrite decay. 56 of the 65 specimens had undergone total destruction and had been replaced by a large volume of grey dusts. The remaining nine specimens were extensively damaged.

The specimens (mainly goniatites) were collected from the Westphaliam Coal Measures at Stubben Edge Hall in the 1940s. They were stored at the Leeds Kippax store until 1985 when they were tensferred to Keyworth. Most of the damage appears to have occurred since the specimens were transferred. However, pyrite oxidation may have been initiated much earlier than this and once begun can be self sustaining.

Samples of the grey dust, and some of the surviving specimens, were examined by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) in order to characterise the nature of the reactions and the mineralogy of the reaction products. These observations confirmed that the pyrite had been oxidised and larger volume hydrated Fe sulphates had subsequently formed. The main reaction product is römerite ($Fe^{2+}Fe^{3+}{}_2(SO_4)_4.14H_2O$) with lesser amounts of coquimbite ($Fe^{3+}{}_2(SO_4)_3.9H_2O$). Occasional cyrstals of elemental sulphur and possible jarosite (ideal formula $KFe^{3+}{}_3(SO_4)_2(OH)_6$) are also present. Elemental sulphur has not previously been recorded as a pyrite decay product in museum specimens. It is indicative of extremely acidic, oxygen-poor conditions.

Previous work suggests that pyrite oxidation can generally be prevented or inhibited by storing samples at relative humidities of less than 60%. If specimens contain large amounts of organic carbon it may be necessary to store them at less than 30% to inhibit pyrite decay.

Environmental monitoring of temperature and relative humidity was carried out in the area where the tray was stored, and inside an adjacent tray, for a week in each location. The relative humidity inside the tray was generally close to 40% even though extremes of 25% to 75% were recorded elsewhere in the store. This implies that catastrophic damage can happen to pyite specimens even when the %RH can be kept close to 40%. However, as the monitoring was only carried out for one week in each location; a full annual record should ideally be made to assess the long term conditions of storage.

The main reaction products identified by SEM and XRD are probably stable at relative humidities of less than 60%, and so could have formed in the environmental conditions that seem to be present in the Keyworth store.

A comparison with similar material from similar geological units was made. No other material was as badly damaged as the Stubben Edge Hall specimens and the possible factors contributing to their more extreme damage could include: exact geological horizon (potentially affecting amount of pyrite and organic carbon present); weathering conditions at the collection site; storage conditions immediately after sampling and prior to final storage in the BGS collection; and fossil specimen Genus (potentially affecting pyrite microstructure).

Any correlation between fossil Genus and degree of damage was not investigated and it is recommended that this be carried out for both the Stubben Edge Hall specimens and all the comparator specimens.

The nine surviving specimens will be treated with ammonia vapour to prevent further deterioration, and monitored at 6 monthly intervals.

1 Introduction

In the BGS palaeontological collections at Keyworth, an unusual case of catastrophically degraded specimens was recently discovered. The degree of damage was far greater than for any other material accessed in recent years and most specimens were completely destroyed, leaving only powdery reaction products. The degraded specimens were from rock which is highly pyritic, while specimens from less pyrite-rich units, stored close by, had not degraded. None of the specimens had been given previous conservation treatment.

It was decided to carry out a study to investigate why these specimens, in particular, had undergone such extreme degradation. The geology and curation history of the specimens were researched and further specimens with similar geologies and storage histories were sought for comparison. The degradation products and some partially degraded specimens were examined using mineralogical and petrographic techniques, to try to characterise the mechanisms of degradation. Lastly, measurements were made of current environmental conditions (relative humidity and temperature) in the storage environment in order to try and evaluate the conditions which brought about the disintegration.

2 Background

The degradation of pyrite fossils in museum collections is a well-known hazard for curators (Howie, 1992). Different treatments have been attempted throughout the last century as new treatment products have become available and in reponse to different theories being put forward for the cause of decay. Previous work has addressed the chemical mechanisms of degradation, possible factors affecting the rate of decay, and the effectiveness of different conservation treatments. Helpful review articles include those by Howie (*op. cit.*), Newman (1998) and Waller (1987).

2.1 MECHANISMS

The oxidation of pyrite (FeS_2) is a chemical reaction which involves atmospheric oxygen and water and produces aqueous sulphuric acid (H_2SO_4) and various hydrated iron sulphates (Waller, 1987). These appear as light-coloured crystal growths on specimens. The reaction entails a large solid volume increase and specimens can be destroyed by the stresses that this produces. The reaction products are hygroscopic and so under conditions of high relative humidity they can adsorb water and thereby facilitate further reaction (Newman, 1998).

In the 1950's it was thought that a bacteria, *Thiobacillus ferroxidans,* was the cause of pyrite decay. If suitable the specimens were immersed in Savlon antiseptic solution to arrest deterioration (Buttler, 1994). Unfortunately this method was catastrophically unsuccessful and it is now known that bacterial pyrite decay only takes place in conditions of very high relative humidity, above 95%.

The alternative theory was that museum pyrite decay is a purely chemical reaction (Howie, 1992). The rate of reaction has been shown to depend on many factors, both inherent in the specimen (grain size, presence of trace elements) and environmental, namely relative humidity, temperature, pH and oxygen concentration (Newman, 1998, and references therein). In the museum environment oxygen levels and temperatures tend to be restricted in range and so humidity has emerged as the most critical factor in pyrite fossil degradation. Howie (1977; 1978) showed that pyrite oxidation in collections generally occurs only at RH of at least 60%, and only if pyrite is microcrystalline or framboidal. This is still generally accepted as a reliable guideline. Morth & Smith (1966) calculated that pyrite oxidation above 31% RH rate doubles for every 26% increase in RH. Waller (1989) found oxidation rates to increase exponentially as RH rises from 10 to 60%. More significantly, Fe sulphates can hydrate at RHs of above 60%, leading to large volume increases (Waller, 1987).

However, an electrochemical reaction mechnism has also been proposed (Bang, 1994) which may account for observations that specimens rich in organic carbon can be susceptible to pyrite oxidation even at RHs of less than 50% (e.g. Howie 1997). Plasma-ashing treatments to remove organic carbon have accordingly been proposed (Bang, *op. cit.*) and it has been suggested that carbon-rich specimens be kept at relative humidities of less than 30% (Newman, *op. cit.*).

2.2 MODERN CONSERVATION TREATMENTS

Many treatments proposed and tried over the last century. These include chemicals to neutralise acid, removal of reaction products (which would otherwise adsorb water and induce further reaction), and lacquers and oils to isolate the specimens from exposure to air. These techniques have been reviewed by Howie (1977, 1992), Waller (1987) and Newman (1998).

One of the most popular treatments to neutralise the reaction products has been exposure to ammonia vapour. Many methods of isolating the specimens from air have been tried since the 1900s, including films or coatings made of waxes, soluble plastics and lacquer. These have since mostly been shown not to work (e.g. Howie, 1979) and some specimens which had been coated with lacquers were even observed to ‘explode’ suddenly following the slow build up of pressure as pyrite oxidation products built up under the ‘protective’ solvent skin (Janssen 2003). Immersion in silicone oils has also been tried, with highly variable results: the Natural History Museum of London has successfully stabilised fossils in this way over a period of 37 years (Newman, *op. cit.*) but similar treatments at the Nationaal Natuurhistorisch Museum of Leiden in 1980s did not halt the progress of pyrite oxidation and led to complete disintegration of many specimens (Janssen, *op. cit.*). It was suggested that the time spent between collection and immersion in oil was critical.

2.3 CONSERVATION TREATMENT OF THE BGS COLLECTIONS

The collections at BGS have many specimens which have been treated in a variety of ways to arrest further deterioration from pyrite decay. These methods are known (from records on specimens) to have included Titanine, Savlon and PVA. In the BGS collections, all these methods seem to have been effective in delaying further deterioration, in that the specimens show no signs of active pyrite decay. Unfortunately there are no detailed records of the treatments documenting, for example, the length of time a specimen was soaked in a chemical.

In the 1940’s Titanine, a matt lacquer, was used as a transparent dope to coat the specimens to prevent oxidation of the iron sulphide. No written records exist as to the method of using Titanine, or to it’s reversibility.

From the late 1940’s to the late 1970’s PVA (Polyvinyl acetate) was used for the treatment of pyrite decay (Howie, 1984). The PVA powder was mixed with toluene to produce a solution, which could be made in variety of strengths depending on the required conservation methods. The specimens could be dried in an oven at 65^{o} for 24 hours. Reversibility from this method is poor (SPNHC, 1997) but PVA remains stable over the long term.

2.4 CHARACTERISATION OF REACTION PRODUCTS

Most studies of the reaction products of pyrite oxidation have looked at material from fully aqueous environments, such as in acid mine drainage (e.g. Merwin and Posnjac). Howie (1992) has observed that pyrite oxidation in fossil collections tends to produce the sulphate melanterite

($Fe^{2+}SO_4.7H_2O$) initially, which further oxidises to copiapite ($Fe^{2+},Fe^{3+}{}_4(SO_4)_6(OH)_2$), fibroferrite and other hydrates. However, a wide range of reaction products can form depending on the primary mineral assemblage (Buurman, 1975; Sclar, 1961). Buurman (1970) noted the formation of goethite and jarosite amongst pyrite reaction products.

3 Geology of specimens.

The specimens are part of a collection of marine fossils from the Westphalian Coal Measures in Derbyshire, North England. They were all collected from Stubben Edge Hall Open cast site (Grid Reference SK36SE), 300 yards northeast of Stubben Edge Hall, Derbyshire. In particular, the specimens which were found to be degraded or destroyed by pyrite oxidation were from a single unit, 10 feet above the ‘Alton’ marine band. This is a dark grey shale containing goniatites (Gastrioceras and Anthracoceras) and bivalves (Dunbarella). Notably, specimens (of fish) from 15 feet above the Alton band were unaffected by pyrite decay (see Table 1).

4 Collection and curation history

The specimens were collected by a single collector between January and April 1946. They were originally stored in a tray in the Kippax store in Leeds (a former railway premises), in conditions of fluctuating temperature and humidity. The tray was packaged for a move to Keyworth c. May 1985 as evidenced from newspaper packaging found inside the tray. It has since been stored in the tray section of the Keyworth core store, where relative humidity and temperature fluctuate but are more stable within actual sealed trays.

5 Current state of specimens

Tray 13344 was brought to the Conservators attention because of dark brown staining on the lid which was thought to be caused by water. The tray was secured with brown packaging tape and this was also stained. The Conservator identified these stains as scorching, indicating severe pyrite decay within the tray. On opening the tray, a layer of newspaper was found, dated 7th May 1985, which had been used as internal packaging. This was also scorched and in a state of disintegration. The newspaper was carefully removed to reveal the extent of damage. Approximately 80% of the contents had oxidised to a pale grey dust (Plate 1). The tray had originally held 65 specimens from a single geological unit 10 feet above the Alton Marine Band (specimen numbers Sy 1506 - 1570) Only nine specimens from the original 65 were intact. This was due to them having been stored within glass phials with cork stoppers. These nine specimens also suffered some damage from pyrite decay. They will be conserved to arrest further deterioration.. Plates 1 and 2 show photographs of the tray and its contents on initial opening.

The tray contained some additional specimens from 15 feet above the AMB (Sy 1624 - 1626) which were all unaffected by pyrite decay (Plate 2). Also present in the tray were a few specimens also from the Coal Measures but from a different collection site (We 3011 - 3062). These were also unaffected by pyrite decay.

An assessment was made of the degree of damage experienced by each individual specimen due to pyrite oxidation, and this is summarised in Table 1. A brief inventory was also made of specimens from the same locality and/or same geological horizon, stored in different trays at Keyworth. The degree of damage to each specimen was assessed by assigning it a number according to the following rough categories: *Unaffected* (0); *Early Stages* (1); *Extensive*

Damage (2); *Specimen decomposed* (3). In Table 1, the number of specimens falling under each category is shown and the mean numerical degree of damage is calculated for each sub-set of specimens to give a means of comparing different groups of specimens. The Table shows that the most damaged set of specimens are from 10 feet above the Alton Marine Band in tray 13344, while specimens[*] from a different depth (15 feet above AMB) have been preserved. Damaged specimens occur mainly in the tray in question (13344), but a certain amount of damage has occurred in specimens in other trays too, some of which were collected from different sites, i.e. Marsh Brook and Woolley Moor. The Woolley Moor borehole specimens are from the Alton Marine Band. Unfortunately the geological horizon of the Marsh Brook specimens was not recorded. Thus it appears that the geological horizon is a significant factor in determining the degree of damage, but that other factors may also play a part, such as specimen type, precise locality, collection and storage history, storage with other decaying specimens.

The pH of the grey 'dust' found in the tray was tested as follows. A small amount (one spatula) of the dust was put into a petri dish and mixed with a similar volume of water. Indicator paper was used to assess the pH to within one unit, and found to be about pH 1.

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[*] Note that the specimens from 15 feet above AMB are fish rather than goniatites and bivalves and so their preservation microtextures may be different. These specimens have not been examined but the question of the influence of fossil type is discussed further in Section 9.

Table 1 Inventory of pyrite decay-induced damage of fossil specimens from above the Alton Marine Band of the Westphalian Coal Measures, BGS Corporate Palaeontological Collection, Keyworth.

							Extent of damage caused by pyrite decay:				
Tray no.	*Date collected*	*Site*	*Collector code*	*Specimen number*	*Geological horizon (within Coal Measures)*	*Total specimens*	*Specimen decomposed (3)*	*Extensive damage (2)*	*Early stages (1)*	*Unaffected (0)*	*Mean extent of damage (0-3)*
13344	1946	Stubben Edge Hall	Sy	1506 - 1570	10' above Alton	65	56	5	4	0	2.8
		Stubben Edge Hall	Sy	1624-1626	15' above Alton					3	0.0
		Sutton Rock open cast site	We	3011-3062	“1st ELL” (Coal Survey Lab)	3				3	0.0
13398	1946	Stubben Edge Hall	Sy	1357 - 1366	10' above Alton	10	4	2	0	4	1.6
	1948	Knowlee Adit	Sy	1608 - 1610	10' above Alton	3				3	0.0
	1946-8	Marsh Brook	Sy	1647 - 1649	Not recorded	3		3			2.0
12241	1947-9	Marsh Brook	Sy	1646	Not recorded	1		1			2.0
13333	1944	Dog Lane	Sy	597-600	Alton Marine Band	4				4	0.0
13334	1944	Dog Lane	Sy	601-615	Alton Marine Band	15				15	0.0
13362	1958	Woolley Moor borehole	Bu	1623-1630	Alton Marine Band	8		6		2	1.5
						104					

6 Relative humidity and temperature measurements

The environmental conditions under which the specimens have been stored are clearly a key factor influencing the degradation process. No records are available detailing environmental conditions at the Leeds Kippax store where the specimens were initially kept, but anecdotal information suggests that it may have had high levels of relative humidity. The specimens did undergo some initial decay at Leeds, but they did not experience total destruction until transferred to Keyworth.

Relative humidity and temperature in the tray store area in Keyworth have been continuously monitored since 2002 (Shepherd and Tulloch, 2004). Data from 2002 and 2003 so far suggests that over an annual cycle the relative humidity in the tray store area varies between about 25 and 75%, with the lowest values in late Winter/early Spring and the high values in Summer. The relative humidity inside a typical tray has also been monitored and was found to be much more stable than outside it: Over a week, the RH inside the tray varied between ~47-49%, while outside the tray RH varied between ~40-58%. Thus the trays probably exert a strong buffering effect on RH. Unfortunately however, a compete annual cycle of data has not yet been recorded inside a storage tray and so it is hard to estimate the actual range of RHs that might be experienced inside a tray over a full year.

In order to obtain more information about the environmental conditions in which the specimens had been held since transferral to Keyworth, relative humidity and temperature measurements were made in two locations. Firstly a monitor was placed in the empty storage space where tray 13344 had been kept in the store[*], and left for a week. The monitor was then removed and placed inside an adjacent tray (number 13343) in the store. The monitor transmitted temperature and relative humidity data at three minute intervals to a remote data logger.

The results are summarised in Figures 1 and 2, where they are compared to the data from the continuous monitoring of the store in two other locations. The void space outside the tray experienced variations in %RH which were somewhat less extreme than that measured elsewhere in the store (Figure 1), and the %RH values were also slightly lower. Figure 2 shows that the environment within tray 13343 remained at a roughly constant temperature, similar to that in the store outside the tray. Humidity inside the tray varied from about 35 to 43 %RH over the course of a week. This variation is significantly less than that outside the tray and elsewhere in the store, where values between about 26 to 74% RH were measured. This confirms that the trays in this area exert a strong buffering effect on RH.

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[*] Location: Level 3, Aisle AT, 6.4

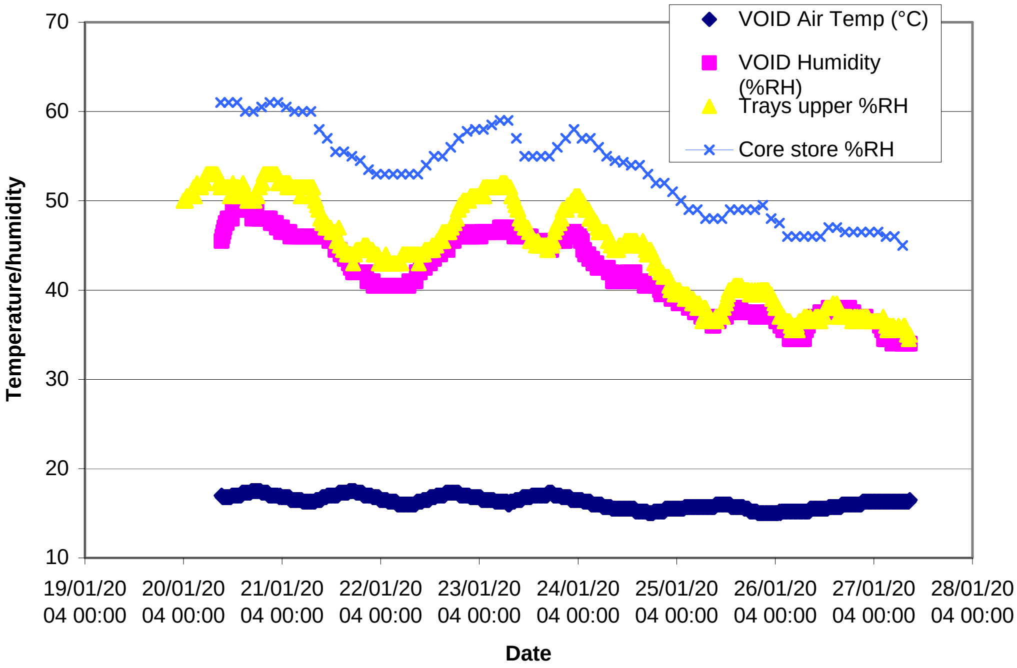

Figure 1 Environmental conditions in space where tray 13344 had been kept, 20-27th Jan 2004 (Pink/black). Compared to RH at top of tray store (yellow) and in main core store (blue).

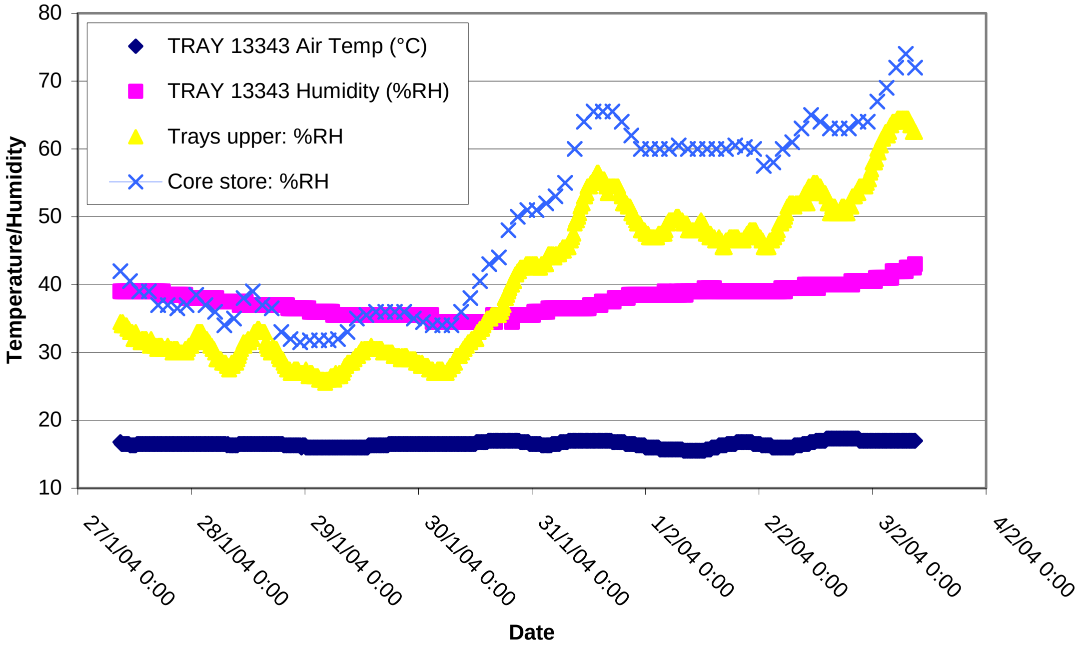

Figure 2 Environmental conditions inside tray 13343, 27th Jan - 3rd Feb 2004 (pink/black). Compared to %RH at top of tray store (yellow) and in main core store (blue).

7 Mineralogy and petrography of degradation process

The pyrite decay product ‘dust’ was analysed by Scanning Electron Microscopy (SEM) and X-Ray Diffractometry (XRD) to determine the minerals present and ascertain how they formed. Some goniatite specimens in glass vials which had undergone only partial decomposition (see Plates 1 and 2) were also examined by SEM.

7.1 SCANNING ELECTRON MICROSCOPY

Samples of the ‘dust’ were prepared for SEM by sprinkling onto a sticky carbon tab on an aluminium stub mount. The partially degraded specimens were mounted directly in the SEM chamber. A Leo 435VP SEM was used in Variable Pressure (i.e. low vacuum) mode; this meant that it was not necessary to coat any of the specimens with a conducting film, thus allowing non-destructive examination of intact fossil specimens. The microscope was operated at an accelerating voltage of 20 KV in both Secondary Electron and Back-Scattered Electron modes. Semi-quantitative chemical analysis of individual phases was performed using energy-dispersive X-ray microanalysis (EDXA).

7.1.1 DUST

The overwhelming majority of the dust consists of secondary hydrated Fe sulphates, surrounding lesser amounts of partially corroded pyrite (Plate 3). There is what appears to be an early, amorphous or poorly ordered phase (Plate 4) with a high Fe/S ratio of about 2.6 and minor Al and Si. The main reaction product phase (Plate 5), developing later, is tabular and has an Fe/S ratio of about 0.77, close to that of römerite ($Fe_3(SO_4)_4.14H_2O$). It also contains minor amounts of Al. Also present amongst the reaction products are rare crystals of sulphur, about 100 microns in diameter (Plate 6).

7.1.2 Goniatite specimen Sy1511

The surface of this specimen was seen to be heavily coated in oxidation products. These consist mainly of Fe sulphates and rare sulphur crystals (Plate 7). The chief sulphate phase forms relatively coarse, well-crystallised tabular to platy grains. Some sulphur crystals are corrosion-pitted. Other Fe sulphates include: an abundant, finer-grained phase forming hexagonal plates (Plate 8) which is relatively sulphate-rich; and a ‘string-like’ phase (Plate 7) which is probably highly hydrated as it appears dark in Back-Scattered SEM. The ‘strings’ are actually long thin, sheets curled and slightly twisted perpendicular to their long axes. Some original pyrite is present, partially decomposed although some cubic grain surfaces appear relatively uncorroded (Plate 9).

After initial inspection, secondary surface coatings were brushed off this specimen. It was then re-examined to reveal pyrite surfaces pitted by corrosion holes which are filled with secondary sulphates (Plate 10).

7.1.3 Goniatite specimen Sy 1541

This goniatite specimen, like Sy1511, still has much of its pyrite surface visible but is partially and variably coated with secondary Fe sulphates (Plate 11). The major secondary phase appears to form thick rhomb-shaped plates and a few long ‘string-like’ Fe sulphate grains are also present (Plate 12).

7.1.4 Goniatite specimen Sy1551

This specimen is a tiny goniatite, shown in Plate 13 where the partial and variable extent of the secondary Fe sulphate coating is visible. The original pyrite surface has undergone some cracking: (Plate 14) and sulphate phases are growing in the cracks, including fine grained hexagonal plates of an Fe-Al-K sulphate, possibly jarosite (Plate 15; Figure 1). Adjacent to these, a block, secondary sulphate phase has itself undergone some corrosion (Plate 16).

7.2 X-RAY DIFFRACTOMETRY

Two methods were employed to prepare the 'dust' reaction product material for analysis by XRD. Firstly, about 3g of the material were ground up under pure ethanol in an automatic agitator to produce micron-sized grains. The resulting slurry was then left for several days at ambient temperature in a fume cupboard until the ethanol had evaporated. The material was then ground again, dry, in an agate pestle and mortar and back-loaded in an aluminium sample-holder to produce a non-oriented mount. There was concern that during the drying process, some of the minerals may have altered due to different relative humidity conditions from those in which they formed. Therefore a second sample was prepared by grinding a smaller amount of material by hand, under acetone, in an agate pestle and mortar. The resulting slurry was transferred to a silicon wafer and left for a much shorter time (about 5 minutes) to evaporate at ambient temperature, leaving an oriented mount. The silicon wafer is cut in a particular crystallographic orientation which results in it making almost zero contributions to the XRD trace and so is ideal for analysing very small amounts of material. As the material is able to settle on the wafer surface, it can become oriented such that the basal (*00l*) reflections appear relatively stronger on the XRD trace.

The XRD traces for the two preparations are shown in Figures 4 and 5. Both samples consist of some iron sulphate phases along with some pyrite. (Note that non-crystalline phases, and those present at concentrations of less than about 5%, are undetectable by XRD.) The two traces differ in the relative proportions of different iron sulphate phases (e.g. Figure 6), implying that some phase transformation has taken place during the preparation of at least one sample. The quick-evaporated sample consists mainly of römerite ($Fe_3(SO_4)_4.14H_2O$) with minor coquimbite/paracoquimbite ($Fe^{3+}_2(SO_4)_3.9H_2O$). The slow-evaporated sample contains minor amounts of römerite and intermediate amounts of coquimbite/paracoquimbite but is comprised mostly of melanterite ($Fe^{2+}SO_4.7H_2O$).

7.3 DISCUSSION

The table below compares the three Fe sulphate phases identified by XRD.

Mineral	Formula	H_2O/Fe	H_2O/ SO_4	Fe/SO_4	Quick evaporated (acetone)	Slow evaporated (ethanol)
Melanterite	$Fe^{2+}SO_4.7H_2O$	7	7	1	-	Major
Römerite	$Fe^{2+}Fe^{3+}_2(SO_4)_4.14H_2O$	4.7	3.5	0.75	Major	Minor
Coquimbite	$Fe^{3+}_2(SO_4)_3.9H_2O$	4.5	3	0.67	Minor	Middle

At 20 ºC, coquimbite is unstable above 73% RH, while melanterite is stable between 57 and 95% RH (Alpers *et al.*, 2000; Dean, 1978; Howie, 1992). The author was unable to find any data on the stability of römerite with varying relative humidity.

The sample which had been prepared in acetone evaporated quickly and contained mainly römerite. The samples which had been prepared with ethanol evaporated much more slowly (in a fume cupboard); it contained very little römerite and mainly consisted of melanterite, which is more hydrated than römerite and is stable at higher RHs. This suggests that water may have been absorbed during the slower ethanol evaporation process, altering römerite to melanterite. The relative humidity in the fume cupboard was therefore monitored over a period of several weeks. This was carried out several months after the initial procedure and so ambient weather conditions were very different. However, relative humidity in the fume cupboard was found to vary greatly, between 10 and 65%, over this period and so it is entirely possible that the melanterite in the slow-evaporated sample formed at the expense of other Fe sulphate phases (probably römerite) which became unstable at higher humidities.

Römerite is triclinic and known to take a tabular form, while coquimbite is hexagonal and can be prismatic or platy. Thus the XRD findings are compatible with the SEM observations of a major tabular sulphate with an Fe/S ratio of about 0.77 (possibly römerite) and lesser amounts of a relatively sulphate-rich phase which forms hexagonal plates (possibly coquimbite).

The literature on pyrite oxidation in the natural or mining environment (e.g. acid mine drainage or naturally weathered pyritic shale) records many secondary sulphate phases including melanterite, jarosite, coquimbite and römerite (Alpers *et al.*, 2000; Jerz and Rimstidt, 2003). It has been found that the first phases to form are the divalents, including melanterite, while the trivalents, including römerite and coquimbite, form later, in a gradual process of increasing degree of oxidation. The literature on pyrite oxidation of museum samples suggests that a wide range of phases can form. Melanterite is noted as a common early phase which can oxidise further to other sulphates (Howie, 1992). These trends of gradual oxidation and sequential formation of divalent followed by trivalent products are the opposite of that observed in the BGS museum samples where melanterite was not an early product. This is presumably because the relative humidity was not high enough to support the formation of melanterite during specimen storage.

Crystalline sulphur and possible jarosite were both noted by SEM amongst the reaction products, but in very small quantities, which is presumably why they were not detected by XRD. Jarosite has been observed in degraded museum samples (Buurman, 1970) but no literature mentioning elemental sulphur in degraded pyrite museum collections has been found. A natural occurrence of both jarosite and elemental sulphur as weathering products of pyrite is noted by Nickel (1984). Elemental sulphur was shown to have a very limited stability field in the aqueous Fe-SO_4-H_2O-O_2 system, existing only at pH less than 1 and Eh close to +0.3. It was suggested that sulphur may have formed metastably. Note that these stability fields apply to a system in the presence of excess water, unlike the situation of the BGS collections.

In the BGS collections, the pyrite oxidation process may have continued until oxygen levels (and pH?) in the tray reached a critically low level and sulphur may have begun to form at the expense of Fe sulphate phases. Some sulphate phases did show signs of minor corrosion (e.g. Plate 16). Some sulphur crystals also showed signs of corrosion (Plate 7), implying that stable conditions for sulphur (such as low oxygen levels) did not persist. This would be expected, as oxygen should have been able to ingress slowly into the tray.

8 Comparative specimens

It was decided to carry out a brief inspection of a different storage tray that also contained damaged specimens from the Coal Measures, to see what similarities and difference might exist between the two subsets of specimens. Tray 13362 was selected. It contains material from nearly 200 feet of the Coal Measures in the Woolley Moor 1 borehole (SK36SE 5). The borehole was drilled 1958 and the specimens were stored at the Leeds Kippax store until 1985 when they were transferred to Keyworth.

Most of the material in the tray has not experienced any damage due to pyrite decay (Plate 17). However, the tray contains 8 specimens from the Alton Marine Band (Bu 1623 to 1630), 6 of which have extensive damage due probably to pyrite oxidation (see Table 1). The specimens are shown in Plate 18. The tray does not contain any specimens from the horizons immediately above the AMB and so the material is not directly comparable with tray 13344. The specimens from the AMB include fish scales, Lingula, Pow?ideniella, goniatites (Bu1629 and 1630) and a possible sponge. Pyrite decay has resulted in the precipitation of white reaction products which have forced apart the laminae of the rock matrix (see Plate 19). The pH of the reaction products from the worst affected specimen (Bu 1630) was tested (using the same method as described in Section 5) and found to be 3.5.

The environmental conditions in this tray were investigated by placing a temperature/relative humidity monitor inside the tray for a week. The results (Figure 3) show very little variation in relative humidity (39.5 to 41%)during the period of measurement.

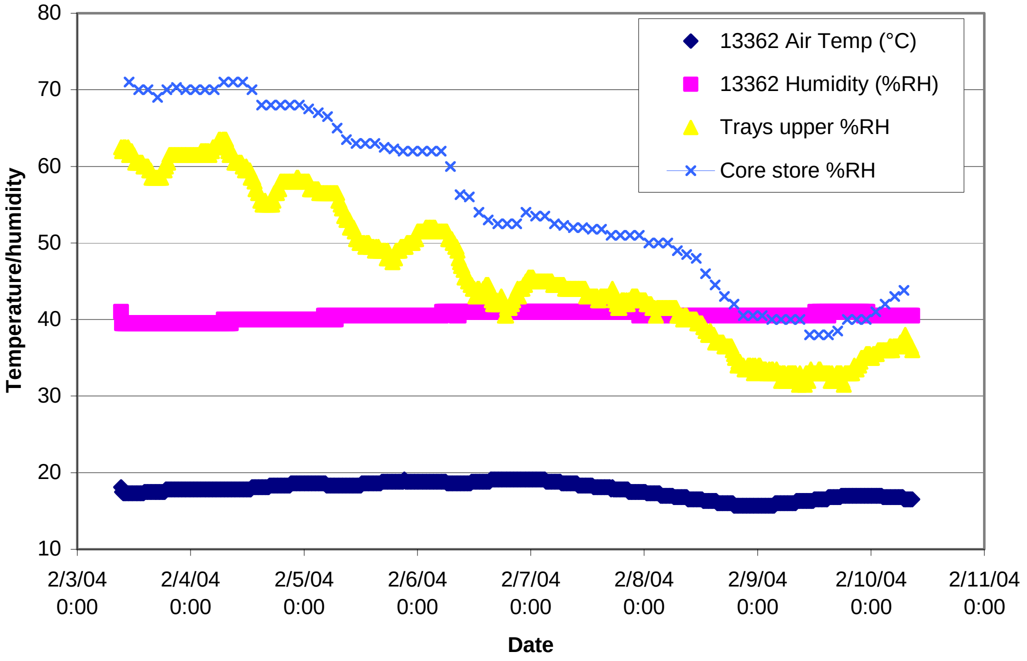

Figure 3 Environmental conditions inside tray 13362, 3-10th Feb 2004 (pink/black). Compared to %RH at top of tray store (yellow) and in main core store (blue).

Thus there are several factors which could contribute to the Woolley Moor material (tray 13362) being less damaged by pyrite decay than the Stubben Edge specimens of tray 13344:

- *Relative humidity*: measurements suggest that RH may vary less than in tray 13344, although the measurements in the two tray environments were not made simultaneously.
- *Geological horizon*: Woolley Moor specimens are from the Alton Marine Band while Stubben Edge Hall specimens are from 10 feet above it; the latter unit could contain more pyrite or more organic matter.
- *Matrix of specimens*: Woolley Moor specimens are borehole pieces, not individual fossils.
- *Fossil Genus*: most of the destroyed Stubben Edge Hall specimens are/were goniatites, whereas there are few goniatites in the Woolley Moor collection; this fossil Genus may develop particular pyrite microtextures which are more susceptible to decay. Fossil Genus may also exert a control on the amount of organic material in the rock or the amount of sulphide available for pyrite formation.

- *History between collection and final storage*: Stubben Edge Hall specimens may have encountered wetter conditions.
- *Weathering on site*: the rocks at the Stubben Edge Hall site may have been partially weathered prior to collection, whereas the Woolley Moor specimens were from an unweathered borehole core.

9 Discussion

9.1 ENVIRONMENTAL CONDITIONS

The environmental conditions under which the specimens have been stored are not known because for most of their history there was no continuous environmental monitoring. The petrographic and mineralogical study of the reaction products was carried out with the aim of establishing the conditions under which these phases formed. The main reaction products were found to be the hydrated Fe sulphates coquimbite and römerite. Hydrated Fe sulphates are very sensitive to relative humidity (and to a lesser extent temperature). Coquimbite may be unstable above 73% RH. No stability data was found for römerite but it readily altered to melanterite during one of the sample preparation processes. Since melanterite is stable above 60% RH, this suggests that the römerite may have formed and persisted in the collections at <60% RH. If true, this implies that extremes of RH may not be needed for catastrophic pyrite decay.

Previous authors have suggested that RH should be kept below about 60% to guard against pyrite decay and that if specimens are rich in organic carbon it may be necessary to keep them at less than 30% RH. The current study suggests that some specimen collections may need to be stored well below 60% RH.

The monitoring of relative humidity in a tray near to the storage location of this material shows that the trays strongly buffer RH to close to 40%, even when the rest of the store experiences large variations in RH. This implies that catastrophic pyrite decay may occurred in a tray even though the %RH was kept close to 40%.

9.2 OTHER FACTORS INFLUENCING DECAY

A number of factors are identified in the literature as affecting the degree of pyrite decay, for example the amount of pyrite and organic carbon in the specimens. The comparison of specimens from different trays, units and sites was made to assess which factors may be important in this case.

Relative humidity, geological horizon, fossil Genus, storage conditions immediately after sampling and prior to final storage and on-site weathering all emerged as potential factors influencing or initiating pyrite decay. Of these, the fossil type was not investigated in much detail, i.e. no attempt was made to compare fossil Genus with degree of decay. Relative humidity is the only factor that can be controlled but previous work suggests that it may not be possible to prevent pyrite decay once it has begun.

10 Conservation

The nine surviving specimens of the Stubben Edge Hall collection will be treated with the Ammonia Vapour Method for pyrite decay to prevent further deterioration, and the specimens will be routinely monitored at 6 monthly intervals.

11 Conclusions.

A collection of mainly goniatite specimens collected from the Westphalian Coal Measures at Stubben Edge Hall were found to have undergone catastrophic damage, resulting in the complete destruction of 56 specimens, and extensive damage to the remaining nine, all from a single storage tray in the BGS collections at Keyworth.

The damage was shown to be due to the oxidation of pyrite and the subsequent formation of larger volume hydrated Fe sulphates; mainly römerite ($Fe^{2+}Fe^{3+}_2(SO_4)_4.14H_2O$) with lesser amounts of coquimbite ($Fe^{3+}_2(SO_4)_3.9H_2O$). Occasional crystals of elemental sulphur and possible jarosite (ideal formula $KFe^{3+}_3(SO_4)_2(OH)_6$) are also amongst the reaction products. Elemental sulphur has not previously been recorded as a pyrite decay product in museum specimens. It is indicative of extremely acidic, oxygen-poor conditions.

Most of the damage appears to have occurred since the specimens were transferred from Leeds to Keyworth in 1985. However, pyrite oxidation may have been initiated much earlier than this and once begun can be self sustaining.

Previous work suggests that pyrite oxidation can generally be prevented or inhibited by storing samples at relative humidities of less than 60%. If specimens contain large amounts of organic carbon it may be necessary to store them at less than 30% to inhibit pyrite decay.

Environmental monitoring carried out in the area where the tray was stored, and in an adjacent tray, suggests that the relative humidity is kept generally between 35 and 45%, even when extremes of 25 to 75% are recorded elsewhere in the store. This implies that catastrophic damage can happen to pyite specimens even when the %RH can be kept close to 40%. However, the monitoring was only carried out for one week in each location; a full annual record needs to be made to assess the long term conditions of storage.

The main reaction products are probably stable at relative humidities of less than 60%, and so could have formed in the environmental conditions that seem to be present in the Keyworth store.

A comparison with similar material from similar geological units was made. No other material was as badly damaged as the Stubben Edge Hall specimens and the possible factors contributing to their more extreme damage could include: exact geological horizon (potentially affecting amount of pyrite and organic carbon present); weathering conditions at the collection site; storage conditions immediately after sampling and prior to final storage in the BGS collection; and fossil specimen Genus (potentially affecting pyrite microstructure).

Any correlation between fossil Genus and degree of damage was not investigated and it is recommended that this be carried out for both the Stubben Edge Hall specimens and all the comparator specimens.

The nine surviving specimens will be treated with ammonia vapour to prevent further deterioration, and monitored at 6 monthly intervals.

Appendix 1 Plates

Plate 1 Tray 13344 shortly after opening, with packaging paper removed, showing grey ash-like products of pyrite oxidation (mainly on the left) and a few surviving fossil specimens (mainly on the right).

Plate 2 Tray 13344 after removal of reaction products. The central two columns of specimens are those from 10 feet above the Alton Marine Band (AMB) which survived pyrite decay due to being stored in glass phials. Specimens on the left are from 15 feet above AMB and are unaffected by pyrite decay, as are those on the right, collected from a different location.

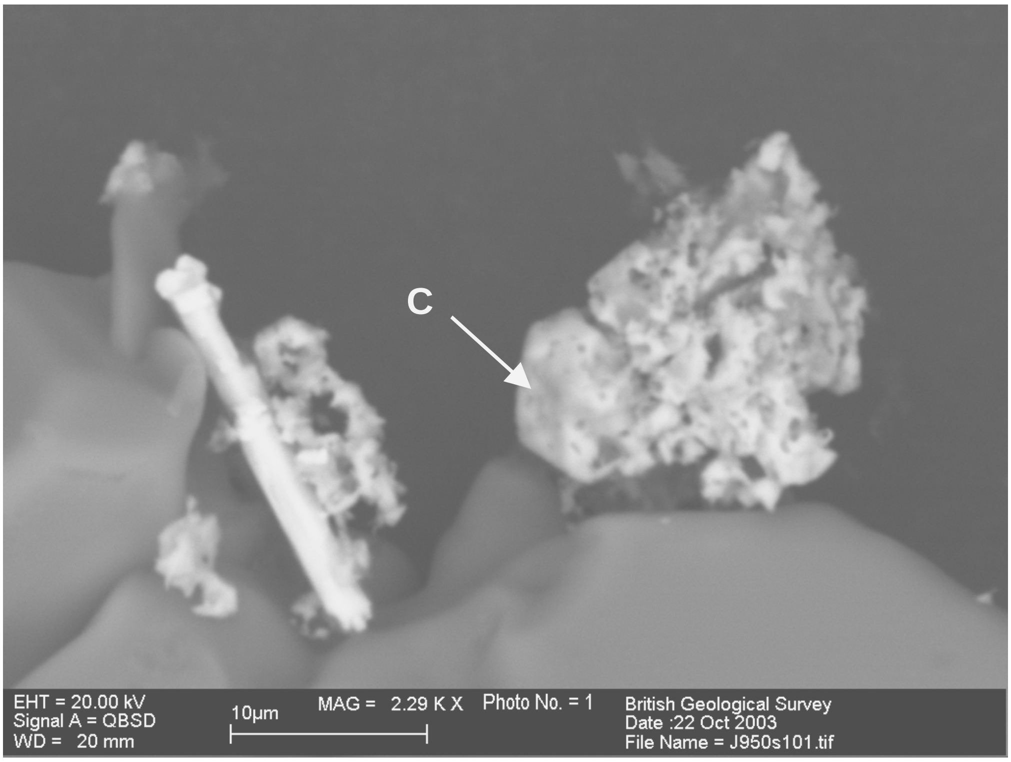

Plate 3 SEM image showing remnants of pyrite in the 'dust'. The original cubic morphology of one grain can still be seen (C), now pitted by corrosion.

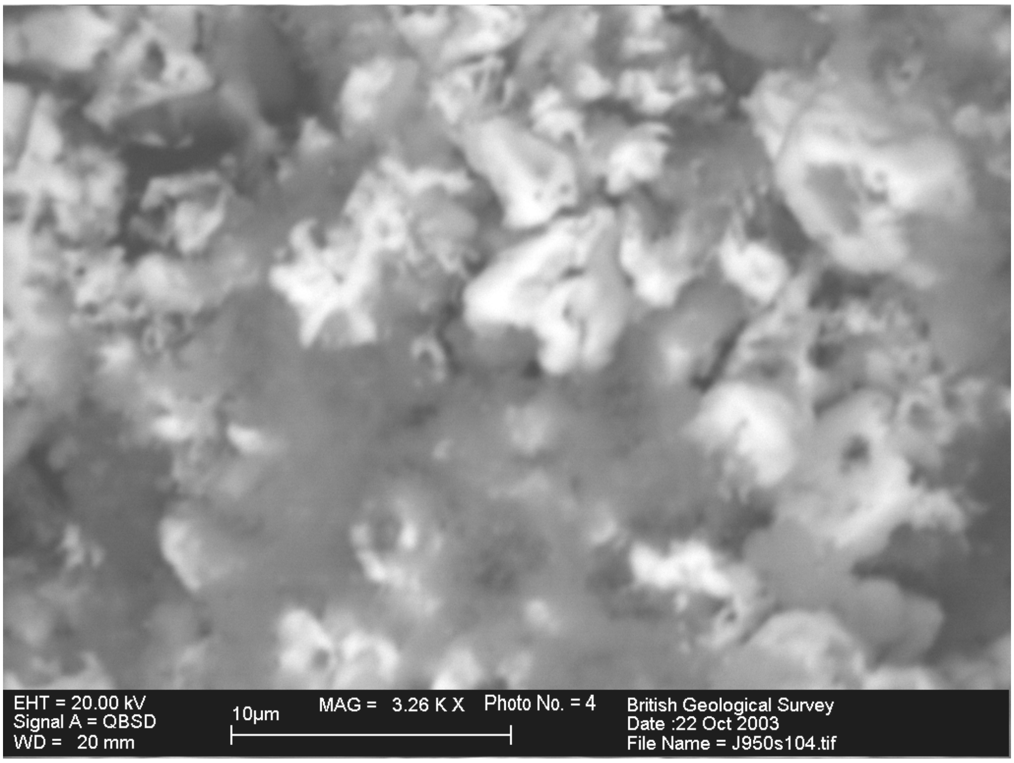

Plate 4 Early ?amorphous high-Fe sulphate (grey) surrounding degraded pyrite (bright).

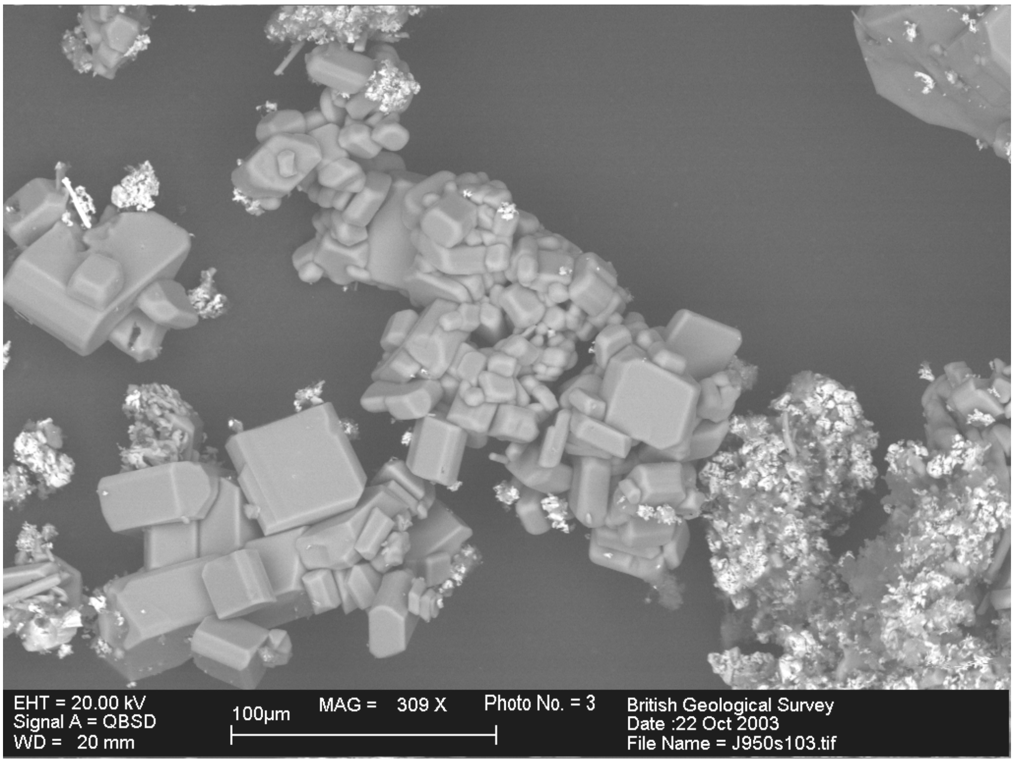

Plate 5 Secondary sulphate and primary pyrite.

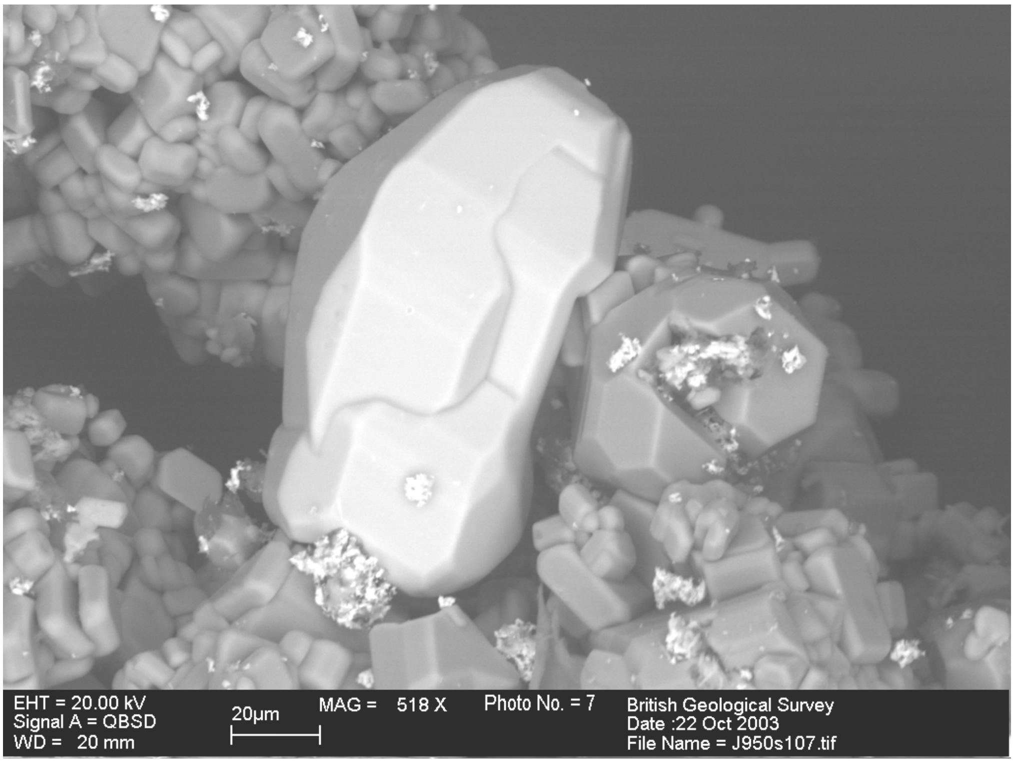

Plate 6 Sulphur crystal in the ‘dust’.

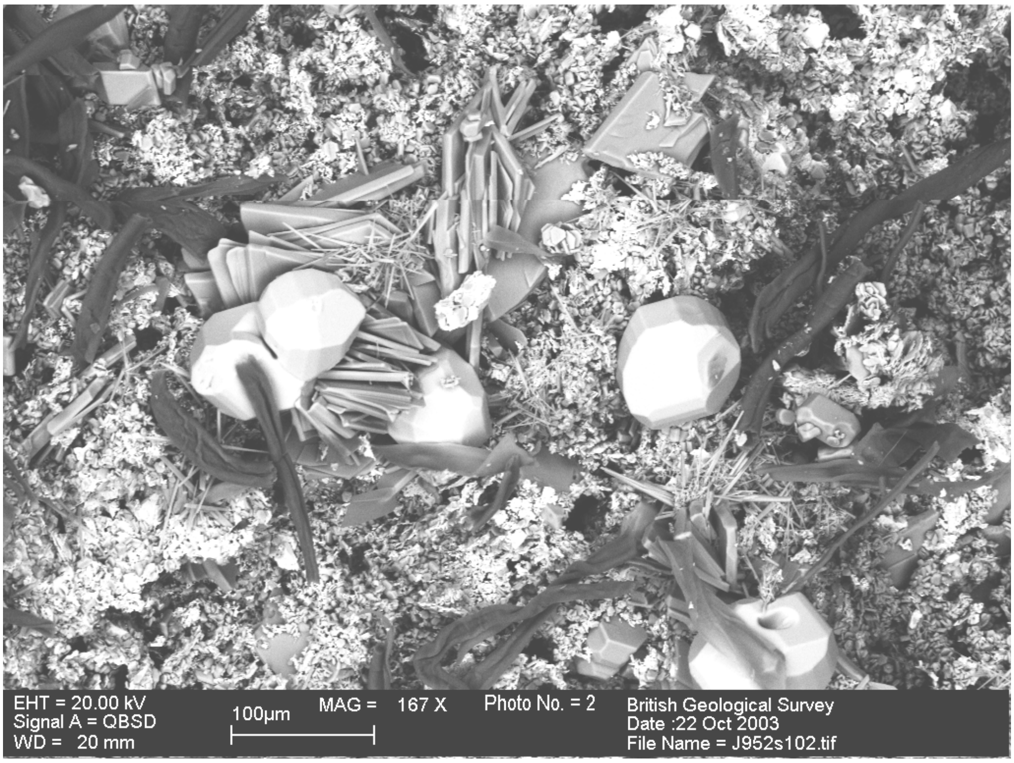

Plate 7 SEM image of surface of specimen Sy1511, showing sulphur crystals (bright, equant) and various Fe sulphate phases: pale grey, tabular crystals; poorly ordered, dark grey 'string-like' grains; and finer-grained hexagonal plates (see Plate below). Note that the sulphur crystal to the lower right is corrosion-pitted, implying that later reactions or changes in ambient conditions have made it unstable. The needle-like crystals are a Ca-bearing secondary phase, possibly formed from the reaction of acids with Ca carbonate in the original specimens. It was not possible to identify them, partly because uncontaminated chemical analyses could not be obtained.

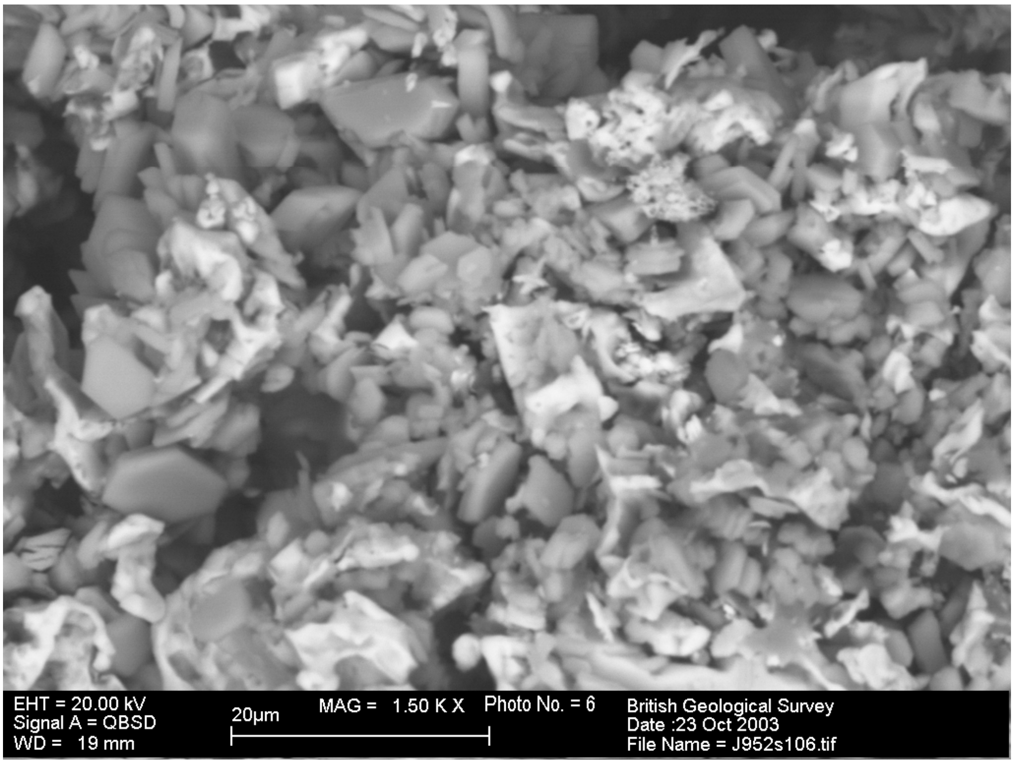

Plate 8 SEM image at higher magnification showing the relatively fine grained hexagonal plate-shaped Fe sulphate phase (grey) growing amongst remnant pyrite (bright).

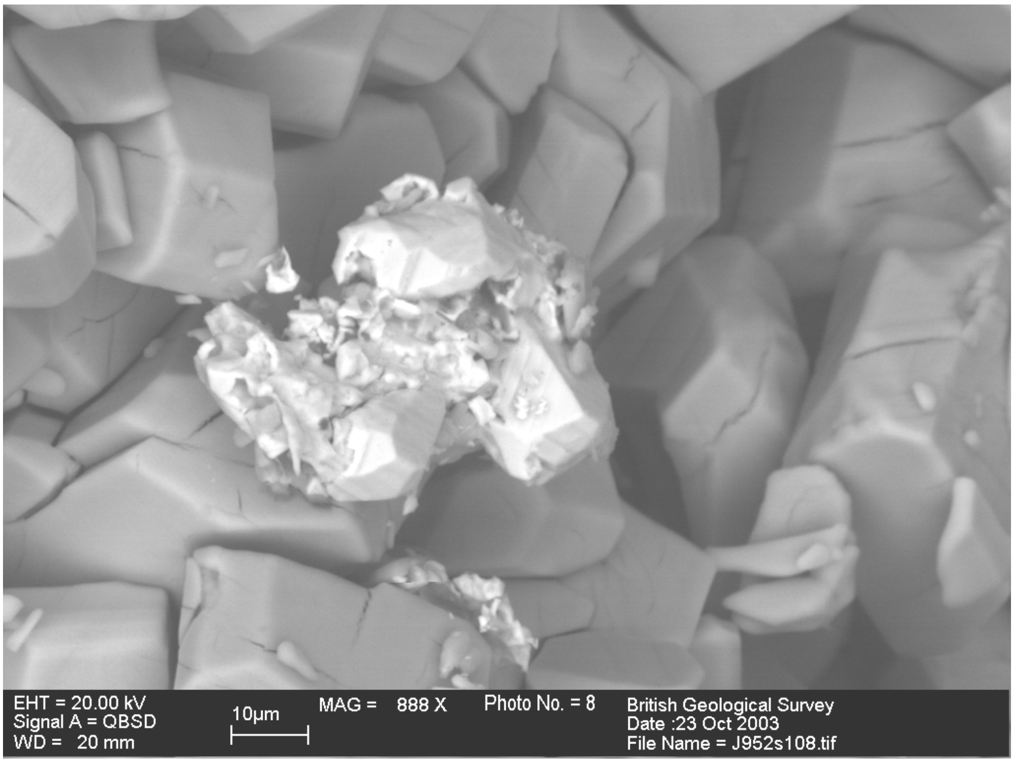

Plate 9 Remnant grains of pyrite (bright), partially corroded, surrounded by secondary sulphate (grey). Note uncorroded surfaces of the cubic pyrite grains.

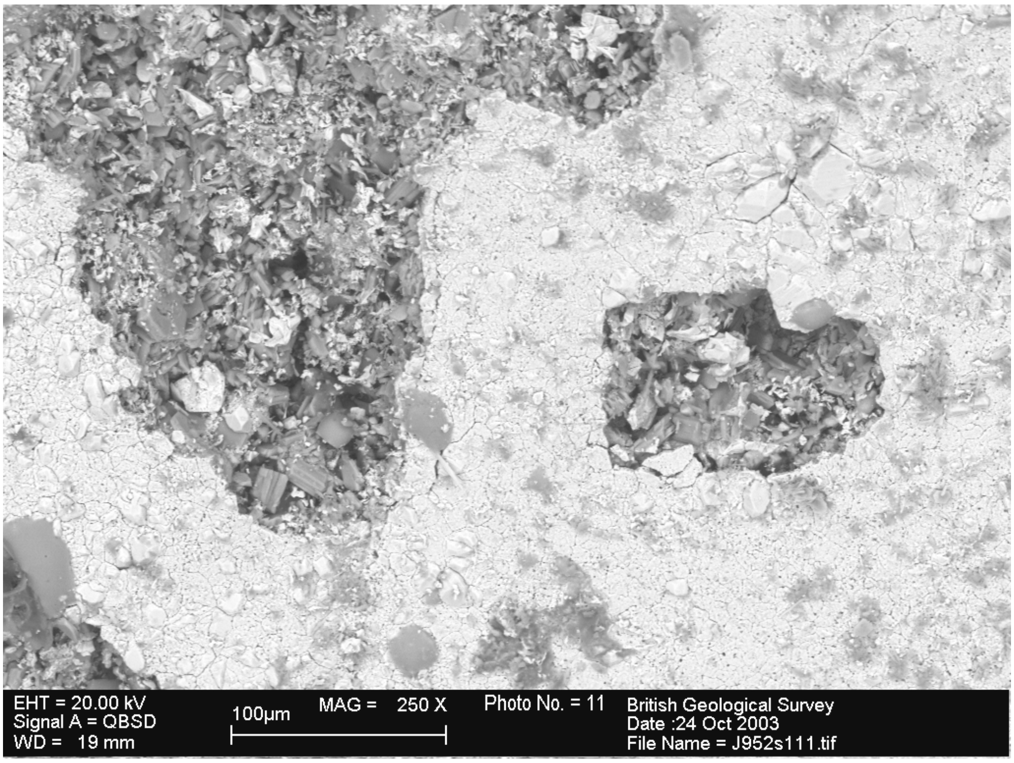

Plate 10 The bright area is the pyrite surface of the fossil specimen; dark areas are corrosion holes filled with secondary sulphate phases.

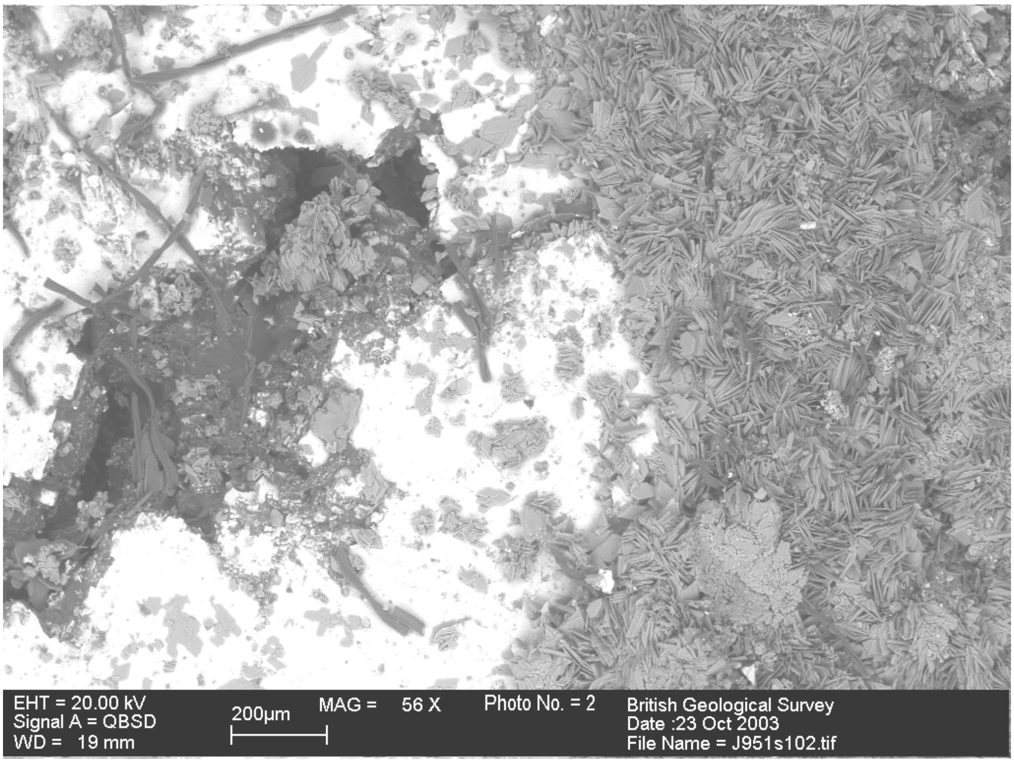

Plate 11 This shows specimen Sy1541 with some of the original pyrite surface preserved (bright) but other areas heavily coated in secondary Fe sulphates (grey material).

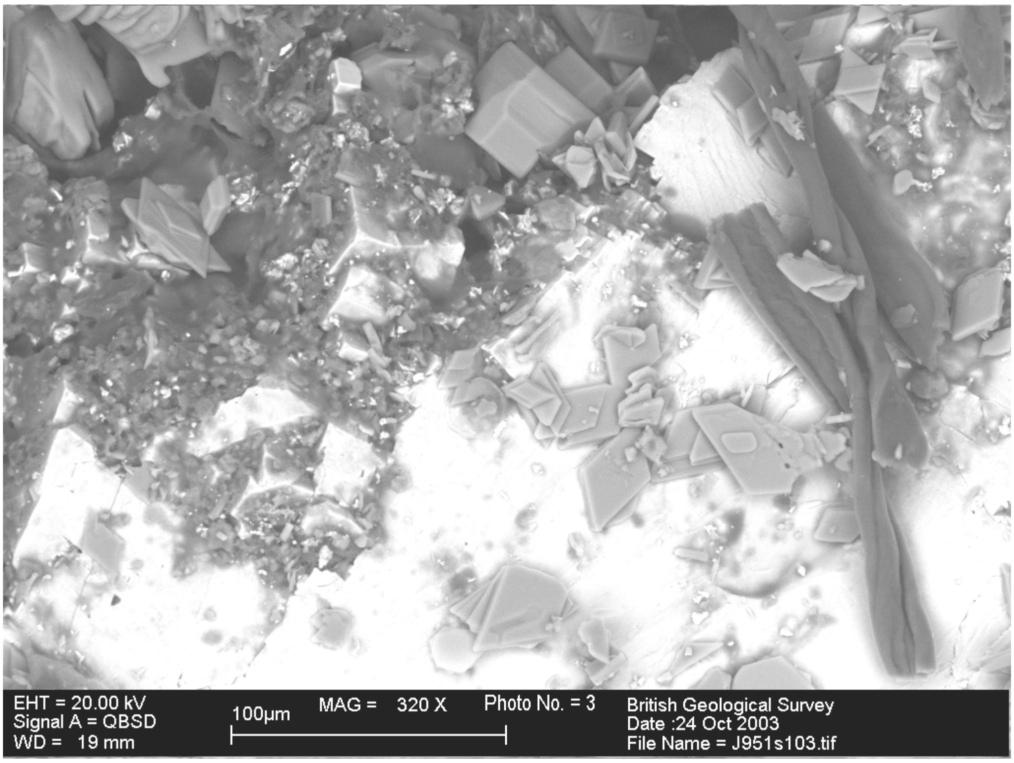

Plate 12 This more magnified image shows the morphologies of two of the secondary Fe sulphates: the rhombic plates (mid-grey) and the 'string-like' grains (dark grey) which are actually long thin sheets, slightly curled and twisted perpendicular to their long axes.

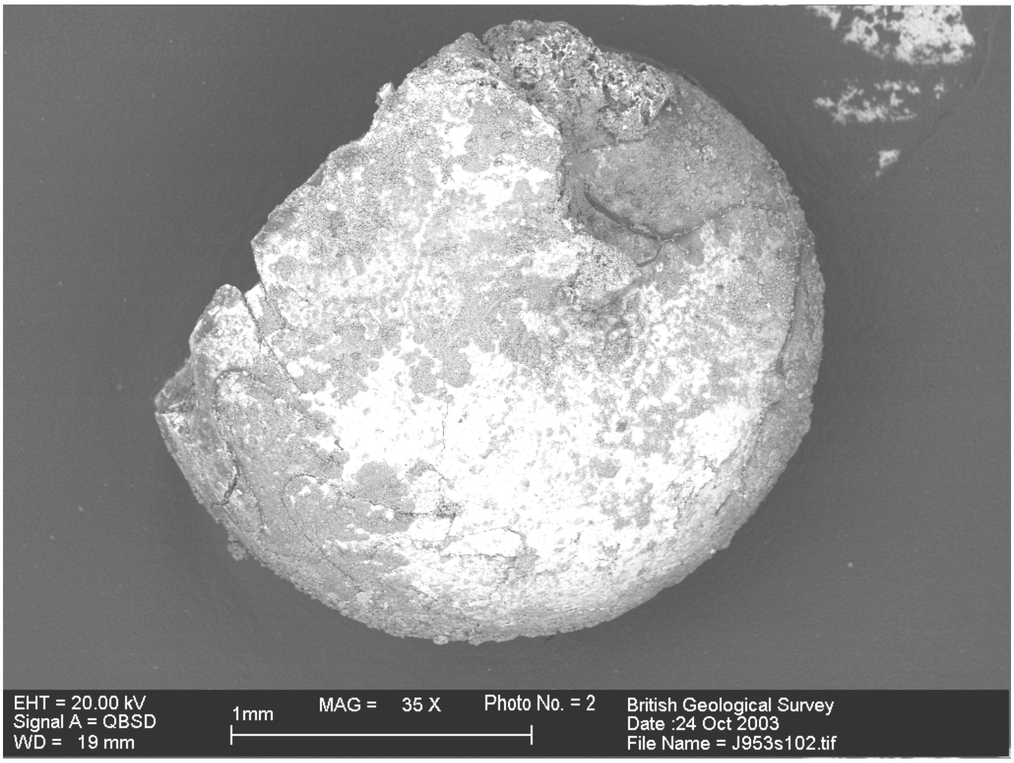

Plate 13 This ammonite specimen (Sy1551) still retains much of its original pyrite surface (bright) but more than half of this is now coated in secondary Fe sulphates (grey). Note the suture lines still visible to the lower left.

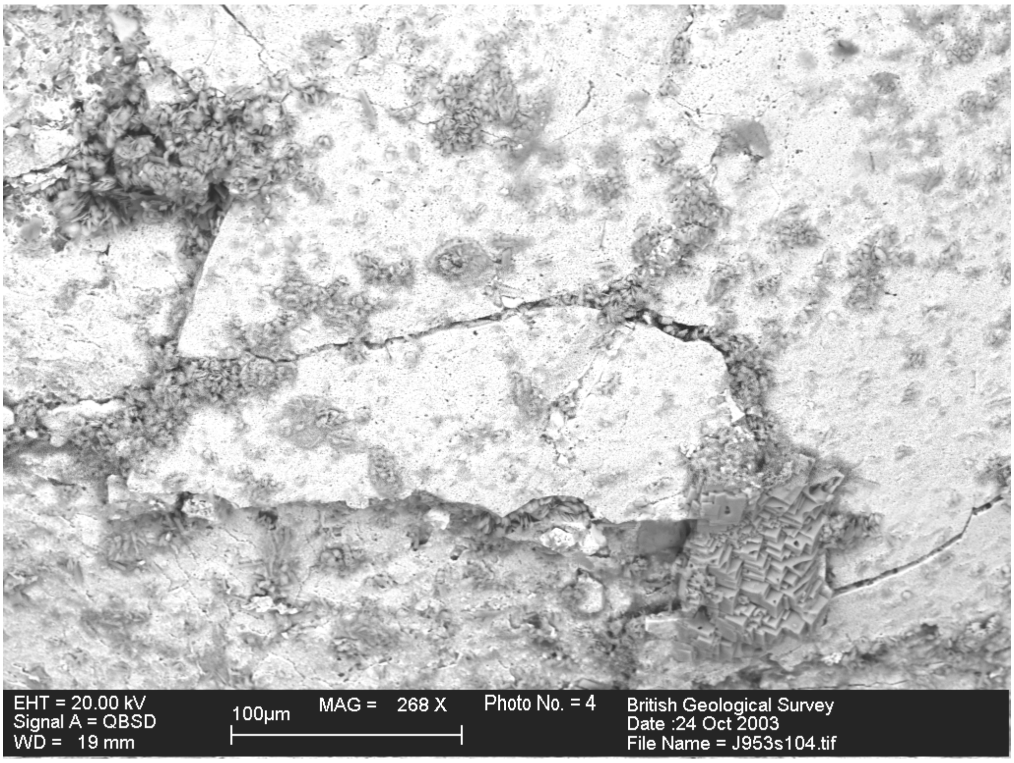

Plate 14 Enlargement of Plate 11 showing cracks in the original pyrite surface, in which secondary Fe sulphates are growing.

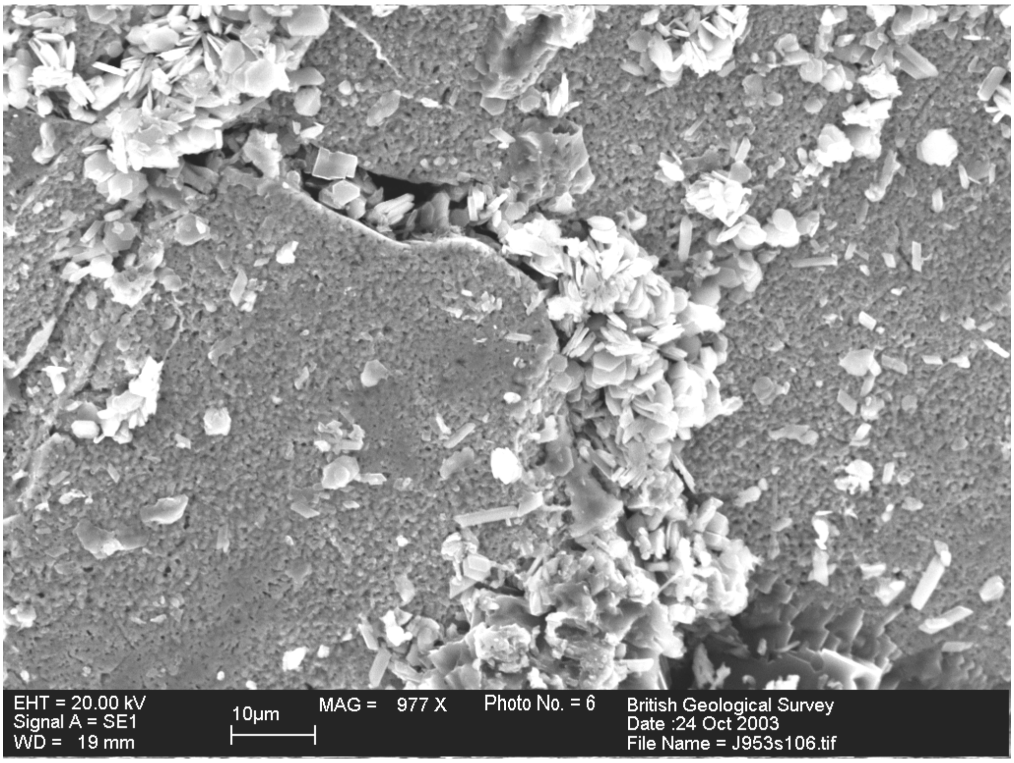

Plate 15 This Secondary Electron image is a more highly magnified view of Plate 12, showing secondary hexagonal plates growing in a crack in the pyrite surface.

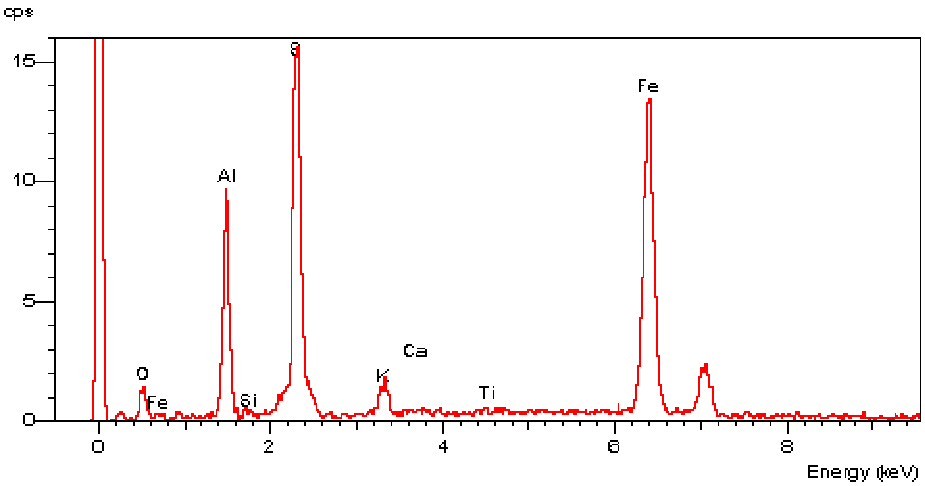

Figure 4 Energy-dispersive X-ray spectrum showing the chemistry of the hexagonal plates of Plate 15.

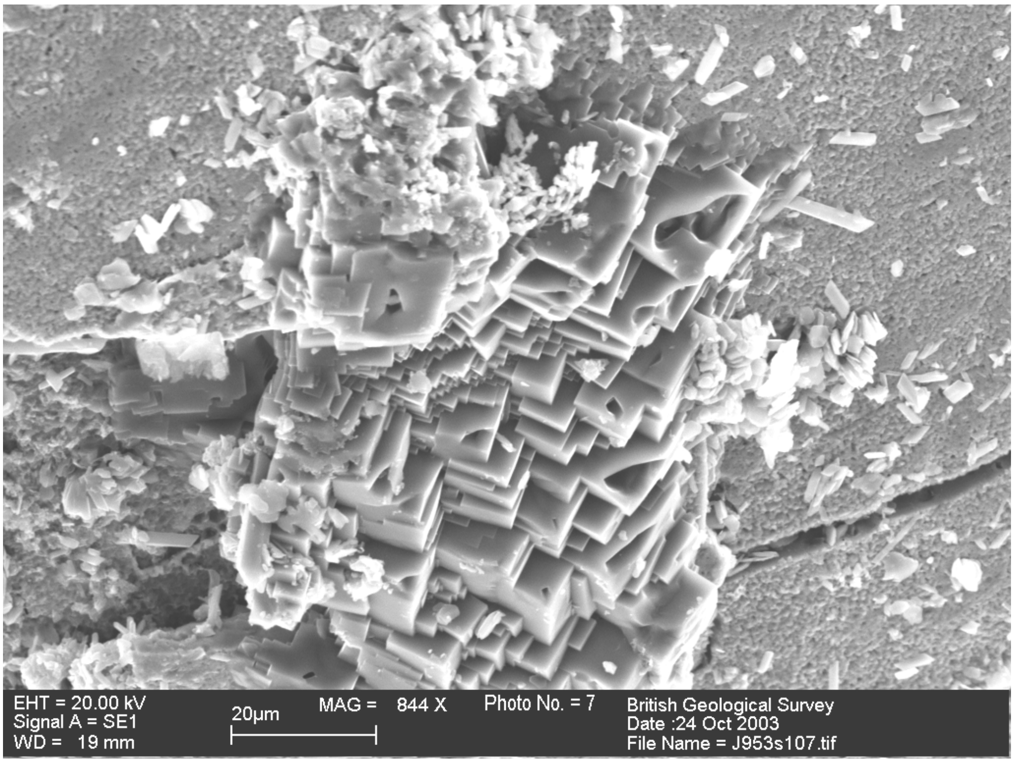

Plate 16 Back-Scattered Electron image taken just below Plate J953s106, showing another secondary sulphate phase which has undergone some corrosion.

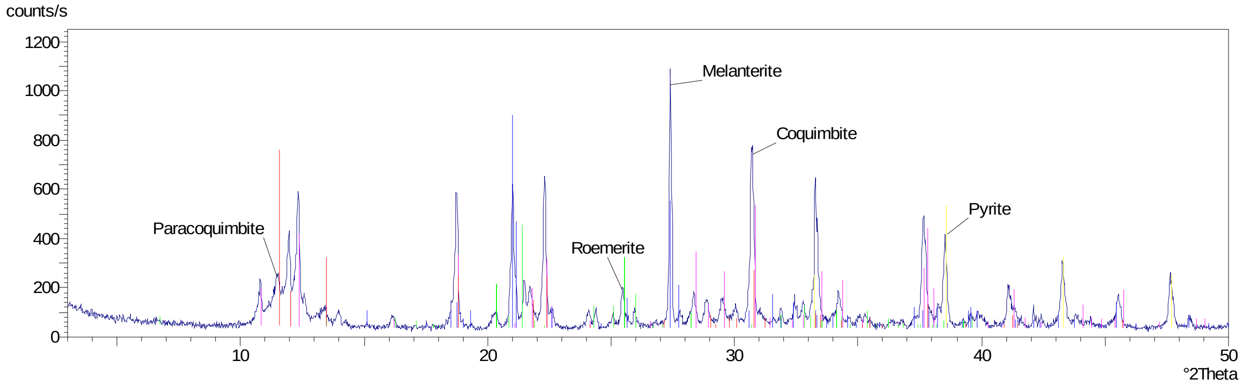

Figure 5 XRD trace of the grey 'dust'. Non-oriented bulk sample mount made from sample which was micronised in ethanol and evaporated slowly in fume cupboard. Blue lines = melanterite; green = römerite; pink = coquimbite; red = paracoquimbite; yellow = pyrite.

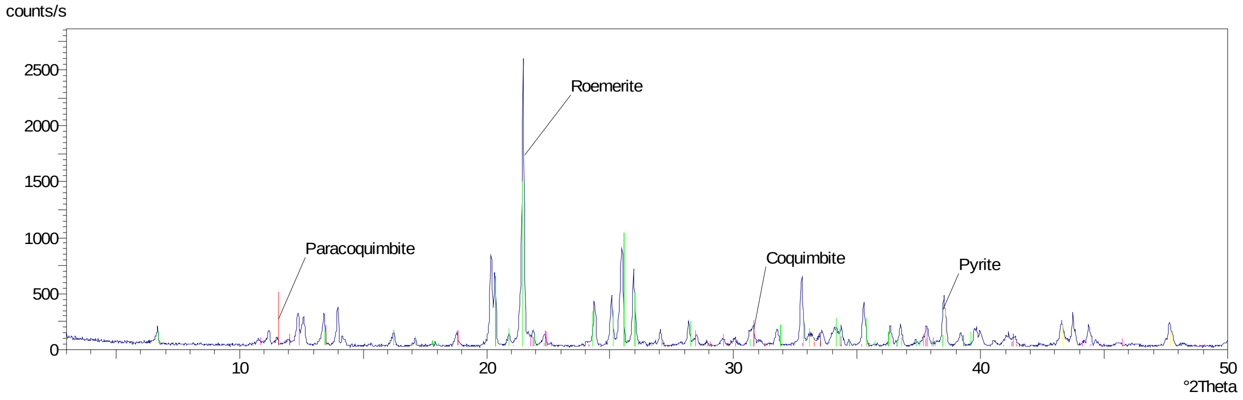

Figure 6 XRD trace of the grey 'dust'. Oriented, silicon wafer mount of sample which was ground in acetone and evaporated quickly. Green lines = römerite; pink = coquimbite; red = paracoquimbite; yellow = pyrite.

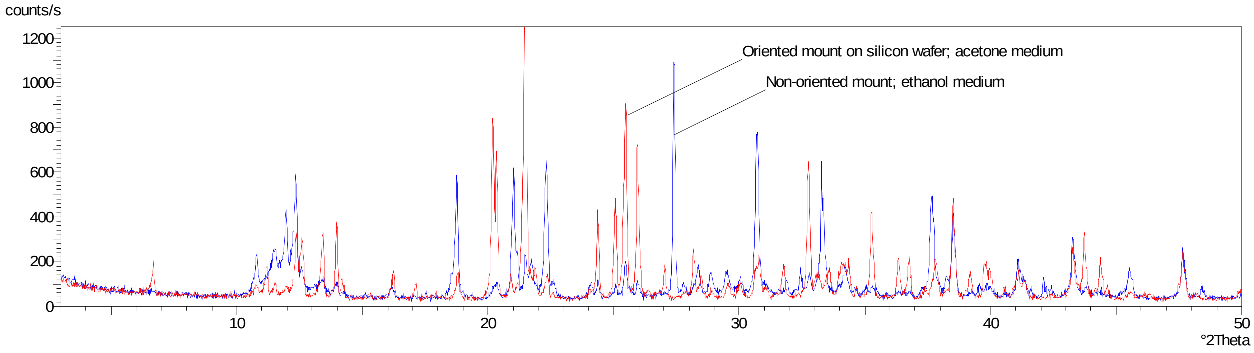

Figure 7 Comparison of the two XRD traces of Figures 4 and 5, showing different relative amounts of Fe sulphate phases in the two samples, presumably due to different preparation methods.

Plate 17 Tray 13362, containing material from 200 feet of Westphalian Coal Measures from the Woolley Moor 1 borehole.

Plate 18 Specimens Bu 1623 to Bu 1630 from tray 13362.

Plate 19 Specimen Bu 1630 from tray 13362, Woolley Moor 1 borehole. This shows how pyrite damage has resulted in the precipitation of white reaction products between laminae. The sample has subsequently become delaminated.

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