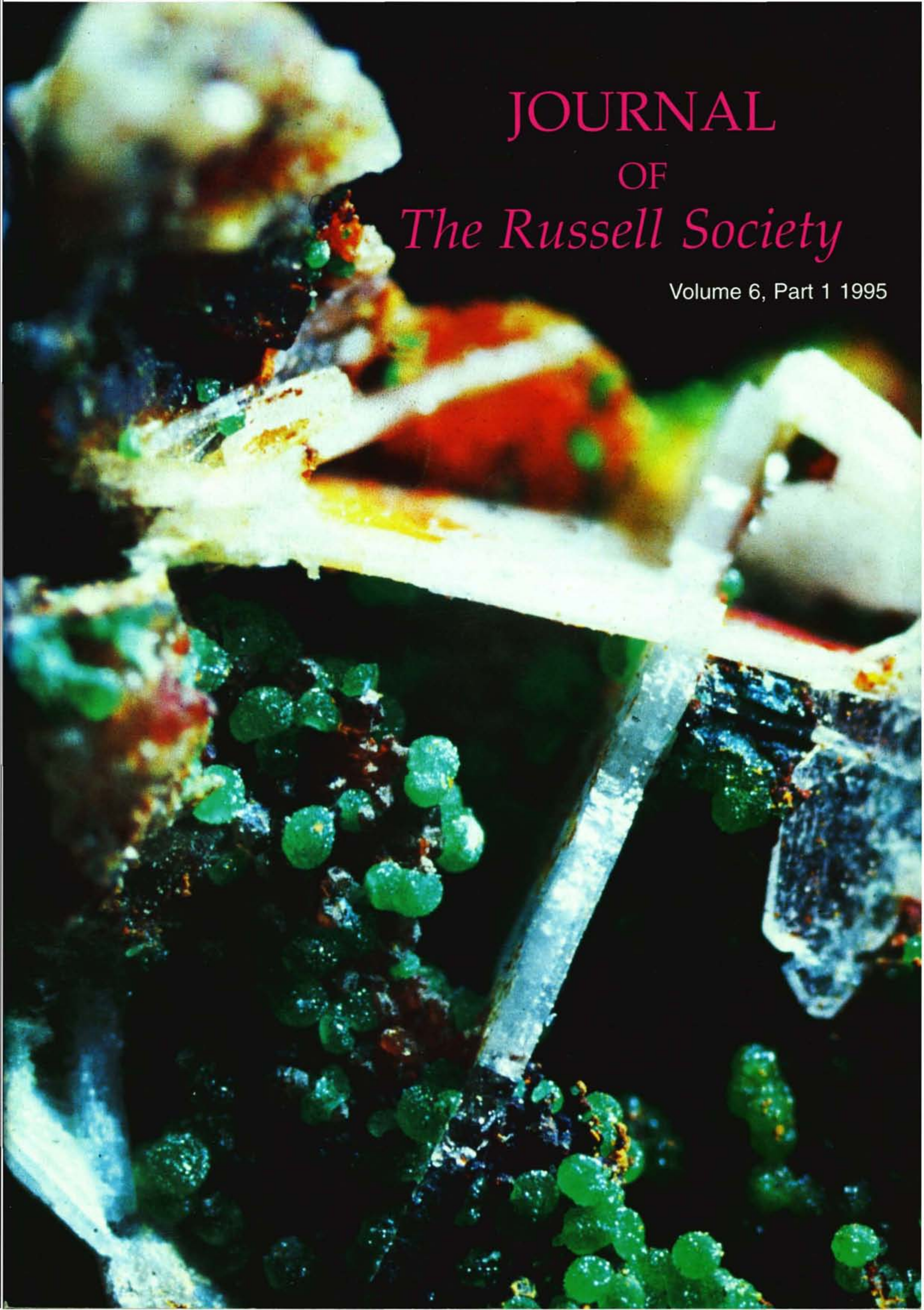
# JOURNAL
# OF
# *The Russell Society*

Volume 6, Part 1 1995



# JOURNAL OF THE RUSSELL SOCIETY

The journal of British Isles topographical mineralogy

**Aims and Scope:** The Journal publishes articles and reviews by both amateur and professional mineralogists dealing with all aspects of mineralogy. Contributions concerning the topographical mineralogy of the British Isles are particularly welcome. Notes for contributors can be found at the back of the Journal.

**Subscription rates:** The Journal is free to members of the Russell Society. Subscription rate for two issues £15. Enquiries should be made to the Journal Manager at the above address. Back copies of the Journal may also be ordered through the Journal Manager.

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**FRONT COVER:** Cuprian adamite, green globules up to 0.5 mm across on baryte. Nether Row Brow, Caldbeck Fells, Cumbria, England. M. Rothwell collection. Photograph by Mick Cooper.

# JOURNAL OF THE RUSSELL SOCIETY

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NOTES

# THE RUSSELL MEDAL

The Russell Society has this year awarded its Russell Medal to Dr R.F. Symes. This medal, named, like the Society, after the eminent British mineralogist Sir Arthur Russell (1878—1964), is awarded from time to time in recognition of distinguished contributions to topographical or systematic mineralogy or for work in the field of conservation of mineralogical sites or materials.

Bob Symes (right) receiving the medal from Brian Young, President of the Russell Society, at the Society's Annual Dinner held this year at Keble College, Oxford. (Photo: Nigel Moreton)

Dr Symes (Bob) needs little introduction to mineralogists. In his long career with the Natural History Museum, where he is now Keeper of Mineralogy, Bob has established himself as an expert in many areas of British mineralogy. He has worked in the Pennines, South Wales, Scotland and the Channel Islands, but is perhaps best known for his work in the Mendips and in Cornwall and Devon. Bob has been a keen supporter of the Russell Society from its earliest days and has been a friend and continuing source of encouragement and inspiration to very many of its members. He is one of an all too small number of amiable and extremely approachable 'experts'. His infectuous enthusiasm and strong belief in the important role of amateur collectors and societies in modern mineralogy have earned him an enviable reputation amongst amateurs and professionals alike.

During his presidency of this Society Bob's drive and enthusiasm for all things mineralogical were directed with great effect towards promoting the Society wherever and whenever possible. Under his leadership the Russell Society established a network of regional branches and grew rapidly to become a truly national society with a membership exceeding 500, a target he set for himself when he accepted the post as President.

In every sense Bob Symes is a truly worthy recipient of the Russell Medal.

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# GUEST EDITORIAL

What is a mineral? You and I know what we mean by the term, but I often get very bemused by the alternative meanings rather carelessly bandied about. Recently at a show cave in Derbyshire (which did indeed sell our sort of minerals) I saw a notice "Minerals on Sale Here" which went on to list various types of carbonated drinks as minerals. Also, in many lowland counties of England the County Plans give details of proposed mineral extraction, when what they in fact mean is sand and gravel — though admittedly quartz is a mineral. The other increasingly common usage is an expression of the trace element content of a product. When I was in hospital recently for a routine investigation, a charming lady came along one morning and asked to take a sample of my blood; I asked what it was for and was astonished to be told that it was to check "the minerals in your blood". I assured her that I was a Professor of Mineralogy and that one thing not in my blood were any minerals (I was deemed fit to be discharged soon afterwards)! But perhaps in one sense she was right; I'm sure that all readers of this journal have minerals or mineralogy 'in their blood'. But watch what you have in your stomach! There was a war-time story of a soldier suffering from indigestion who, vaguely recalling that one took bicarbonate to alleviate such a condition, swallowed some powdered natural chalk (carbonate being the next best thing presumably to bicarbonate) and died later from a perforated bowel due to silica sponge spicules in the chalk!

In a similar vein, a recent issue of a highly respected international journal concerned with analytical techniques published a paper entitled "Determination of mineral and trace elements in the diet ..." It seems that in the public understanding the word 'chemical' has become equated with toxicity; the chemists, seeking to avoid such implications, have thus begun to use 'mineral' instead. This is a trend which the mineralogical community must resist, before our own speciality becomes similarly besmirched in public understanding. I note, however, that the International Mineralogical Association has now promulgated a statement from the IMA Commission on New Minerals and Mineral Names stating that "in general terms, a mineral is an element or chemical compound that is normally crystalline and which has been formed as a result of geological processes". (See *Definition of a mineral* in this issue, p. 56).

A national advertising campaign is running currently in which someone is asked if he knows how to solve a particular problem. He doesn't, but "he knows a man that does". This is rather the approach I would recommend to mineral collectors who need to know just a little more about the specimens they find. They need to be aware of the numerous reference books giving various details as to the crystal system, chemical composition, appearance, type of occurrence and common associated minerals which are representative of their specimen. Most of us, alas, do not have X-ray identification facilities easily available. But even if we had, or alternatively an experienced professional mineralogist to offer an instant identification, there is still a lot more one needs to know about a mineral. It is little use knowing that a specimen is, say, polydymite, unless one appreciates that it is a rare ore of nickel. Similarly, if one found a specimen of strunzite one needs to know that it is a phosphate of manganese and iron and therefore one might hope to find other rare phosphates associated with it.

Mineral reference books vary in size, cost and accuracy, but two which are fairly cheap, readily available, and should be near at hand for every mineral collector are *Glossary of Mineral Species* by M. Fleischer and J.A. Mandarino, now in its 1995 edition, and *Mineral Reference Manual* (1991) by E.H. Nickel and M.C. Nichols. Both of these texts list minerals alphabetically, and give their chemical composition, crystal system and other essential details, including, in Nickel and Nichols, colour, hardness and density; both give key references. Even more authoritative, weighty (in all senses), and a bit more expensive are *Hey's Mineral Index*, now in an updated third edition (1993) by A.M. Clark of the Natural History Museum, which lists alphabetically all known minerals with details of their type locality and first description; and the *Handbook of Mineralogy* by J.W. Anthony, R.A. Bideaux, K.W. Bladh and M.C. Nichols, which aims to cover every mineral species recognised by Fleischer and Mandarino in a series of five volumes of which Vol. I on sulphides and Vol. II on silicates have so far appeared. This work has the interesting approach in that each species is described in just one page, no more and no less, so that for example orthoclase gets one page and so does yugawaralite. I would certainly expect any library with any pretensions to a decent coverage of the Earth Sciences to have these two larger works.

*Hey's Mineral Index* is of great use as it includes all known published mineral names, including varieties, synonyms and obsolete names (and also a number of common erroneous spellings); thus such old mining terms as 'iron-glance' and 'green lead ore' are listed. The *Handbook of Mineralogy* series gives many more details, such as the habit, twinning, cleavage, fracture, tenacity, hardness, density, transparency, colour, pleochroism and reflectivity; the type of geological occurrence, the associated minerals and a few prominent localities (mostly North American) are also listed. Students attending courses on the Earth Sciences will already be aware of *An Introduction to the Rock-Forming Minerals* (2nd edition) by W.A. Deer, R.A. Howie and J. Zussman, though, as its name implies, this text restricts itself to those minerals found in rocks and gives scant attention to ore and vein minerals.

For a more rounded approach one could of course consult *Mineralogical Abstracts*, a journal which appears quarterly and which prides itself in having in-depth informative abstracts and a very comprehensive annual author and subject index. In this ongoing publication the reader or enquirer will find full details of colour, properties, location and associated minerals in the Mineral Data and New Minerals sections (just two of 18 sections ranging from Age Determination to Topographical Mineralogy. If you are computer-minded, a CD-ROM package now available from Chapman & Hall is *MinSource*, which offers the user the last 14 years of *Mineralogical Abstracts* together with *Hey's Mineral Index* in its entirety, thus providing the enquirer or browser with some 70,000 abstracts plus 16,000 chemical definitions on a single CD-ROM. It is updated quarterly with the latest issue of *Mineralogical Abstracts* as soon as it is published.

Most of these sources are confined to word images, which inevitably leave the reader wanting to see what the mineral typically looks like. The world of minerals can be dramatically visual, and there is a host of illustrated books to choose from, far too numerous to list here (book reviews in this and other journals may help to make choices). Many are of the 'coffee table' variety, but the increasing availability of colour photographs has led to some provision for more serious collectors, one deserving mention being the *Encyclopedia of*

*Minerals*, by W.L. Roberts, G.R. Rapp and J. Weber, which, in addition to listing all the relevant properties of some 2200 minerals, presented (in the first, 1974, edition) nearly a thousand spectacular full-colour photographs of carefully chosen, mostly 'micro', specimens, including many rare species. To quote from their Preface: "When such minerals are photographed by careful, knowledgeable and dedicated technicians, the result is a good alternative to a personal view of the original". This whole work is dedicated to the Friends of Mineralogy, with which our society could perhaps be compared. The second (1990) edition of this *Encyclopedia*, by W.L. Roberts, T.J. Campbell and G.R. Rapp, is more up to date but contains only 330 photographs, largely of 'macro' specimens from public and private collections.

The late Neal Yedlin used to end his regular column on micromounting in the *Mineralogical Record* with the words "buy and use a good mineral book". It is hard to improve on such sound advice.

R.A. Howie

**ERRATA, VOLUMES 4—5**

**Volume 4, Part 1**:

p.21, RH col., line 2: *for* $Cu_6SnS_8$ *read* $Cu_8SnS_6$.

p.30, Fig.6 & p.32, Figs 8 & 9, captions: *for* flourite *read* fluorite.

**Volume 4, Part 2**:

p.46, Table I, column headings: *for* SX 3625 etc *read* SW 3625 etc.

p.90, LH col., line 11 from bottom: Whyte's Cleuch *should be under* Dumfries & Galloway Region.

p.91, RH col., line 2 from bottom, & p.92, LH col., line 8 from bottom: *for* Strathclyde *read* Dumfries & Galloway.

**Volume 5, Part 1**:

p.18, RH col., line 8 from bottom: *for* 557 881 *read* 557 781.

p.19, LH col., line 18 from bottom: *for* SK *read* SP.

p.64, RH col., line 25: *for* $Ag_2F$ *read* $Ag_2S$.

**Volume 5, Part 2**:

p.1 (Contents), Note on "Leadhillite from ...": *add* England to title.

p.104, Fig.2, near the top: *for* Cinoid ossicles *read* Crinoid ossicles.

**Shropshire *vs* Salop**:

In Volume 5, Part 2, the county of Shropshire was incorrectly referred to throughout as Salop. In the 1974 county reorganisations, Shropshire was indeed renamed Salop (the old Latin name for the county), but the name was changed back to Shropshire in 1980 (after it was pointed out that *salope* has a rude meaning in French!). *Therefore for* Salop *read* Shropshire on p.69 (Contents), line 19; p.91, RH col., lines 12 & 17; p.92, RH col., line 16 from bottom; p.94, Table II, footnotes 5 & 6; p.115, title of paper, and RH col., line 3 from bottom: p.116, LH col., line 2.

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# ELECTRON MICROPROBE TECHNIQUES IN MINERAL ANALYSIS

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**Electron probe microanalysis is the principal technique employed in the chemical analysis of minerals. In this review, the theoretical aspects of the technique are described, some applications to the study of minerals are presented, and the limitations are outlined.**

## INTRODUCTION

A fundamental aspect of the study of geology in general, and of mineralogy in particular, is the requirement of an accurate, detailed knowledge of the chemical composition of minerals. Early descriptions of minerals dating back to the 19th century have always included chemical information, and some of the most famous early mineralogists were either themselves highly skilled chemists, such as J.J. Berzelius, or had access to chemical laboratories. Classical chemical methods of analysis, although time-consuming and requiring separation before analysis, still have an important part to play in mineralogy, but are now largely superseded by physical microanalytical techniques, the foremost being electron probe microanalysis (EPMA). The role that EPMA plays in modern mineralogical research can be gauged from the fact that, of 259 papers published during 1994 in the journals *American Mineralogist, Canadian Mineralogist, European Journal of Mineralogy* and the *Mineralogical Magazine*, 64% incorporate data obtained by an electron microprobe.

New minerals, which are being discovered at the rate of 30—40 per year, cannot be accepted by the CNMMN (Commission on New Minerals and Mineral Names) without having had a chemical analysis performed on them. Other mineralogical studies relating, for example, to mineral characterisation (what they are), paragenesis (where they have formed, and under what conditions), and the evolution of mineralising fluids, all require analyses of the minerals themselves. Electron microprobes provide this information, and instruments now benefit from recent developments in electronics and the fast processing power of modern computers to make EPMA more than just a chemical analysis technique and, indeed, indispensable in all aspects of mineralogy. In this review we outline the general theories and principles behind EPMA, and illustrate some of its applications to mineralogical studies.

For more detailed information on the theories involved and on the various instrumental components, the reader is referred to one of the standard texts, such as Potts (1987), Reed (1993, 1995), or Scott and Love (1994). For a recent review of other microanalytical techniques in the earth sciences, Potts *et al.* (1995) is a recommended book.

## HISTORICAL BACKGROUND

Although there have been many major developments and refinements in EPMA over the past two or three decades, the technique really has its roots in some pioneering research between 1909 and 1914, when it was discovered that X-rays are emitted from a sample bombarded by electrons, and that these X-rays have wavelengths which are characteristic of the elements within the sample (Moseley, 1913, 1914). During the 1920s and 1930s, much of the research centred on establishing the interactions between X-rays and the atomic structures of crystals; this knowledge forms the basis of many of the theoretical aspects of EPMA. In the 1930s, the electron microscope was being developed, which provided a means of focusing an electron beam onto the specimen, but it was not until 1951 that Castaing, who was a post-doctoral student at the University of Paris, was able to combine these various lines of research to build a prototype electron probe capable of micro-area analysis. This proved to be a revolutionary innovation which has transformed the field of chemical analysis, particularly in metallurgical, material sciences and mineralogical studies, since it enabled the composition of a sample to be obtained on an area as small as 2 to 3 μm across, without destroying the sample. Conventional 'wet chemical' techniques would have required a significantly larger amount of sample for analysis, and would have consumed the sample.

The first commercial instrument was manufactured by Cameca in France in 1958. During the 1960s several companies produced electron microprobes and, with the development prior to this of electron beams that scanned across the specimen surface, scanning electron microscopes. Thus the related techniques of microanalysis and electron imaging became established in many of the scientific disciplines.

With developments in solid state electronics, a new type of X-ray detector was introduced in the late 1960s. This, a lithium-drifted silicon detector, was able to analyse a large region of the X-ray energy spectrum, and thus was capable of measuring the X-ray emissions from many elements simultaneously. Analysis with this type of detector has become routine since the 1970s and is known as Energy Dispersive X-ray Spectrometry (EDS). It complements the original method of using a diffracting crystal to select the characteristic wavelength of the X-rays, known as Wavelength Dispersive X-ray Spectrometry (WDS).

During the 1980s and 1990s, there have been major improvements, particularly in the electron beam stability and the reliability of electronic components, so that unattended overnight operation has now become routine. With developments in the speed, processing power and data-storage capacity of modern computers, the analysis and processing of digitised X-ray images and the data handling procedures have improved so radically that electron microprobes today no longer simply produce chemical analyses of minerals, but also provide new approaches to studying mineral systematics and processes.

## THEORETICAL CONSIDERATIONS

When a beam of electrons hits a specimen, many interactions take place within the sample, some of which can be used to provide information about the sample itself. The most important, in terms of EPMA, are schematically shown in Fig. 1.

*Secondary electrons* are emitted from effectively the surface of the sample (1 to 10 nm depth), and their detection

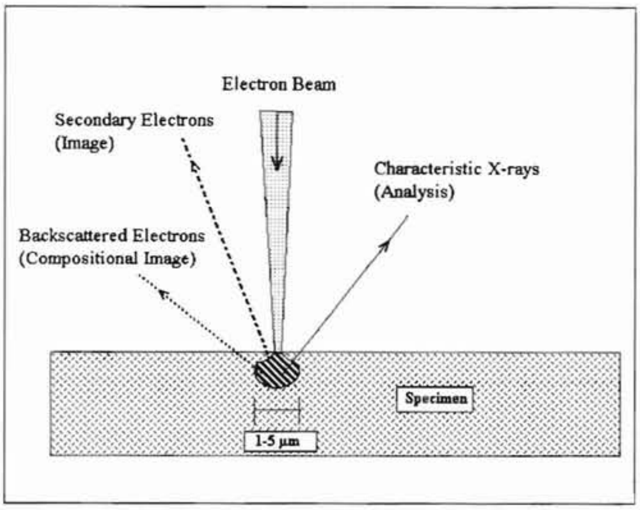

**FIGURE 1.** Effects of electron beam interactions with a mineral specimen.

provides the basis for high magnification imaging in the scanning electron microscope. In mineralogical studies, secondary electron images provide topographical information and are mainly used in the characterisation of crystal morphologies.

*Backscattered electrons* are also produced, but at a slightly greater depth (~10 nm); the intensity of these electrons depends on the mean atomic number of the elements in the sample. Thus, by detecting and measuring these electrons across samples of different composition, e.g. minerals intergrown in a rock, an image relating to the chemical compositions of the minerals can be obtained. Backscattered electron images are becoming increasingly used in mineralogical and petrological studies (e.g. Paterson *et al*., 1989) as they can provide information which cannot easily be obtained from standard optical microscopy: for example, compositional zoning and textural information within minerals (Fig. 2a); compositional differences between minerals (Fig. 2b); and the location of very small accessory minerals within rock samples.

Other specimen—electron interactions occur which are not discussed in detail here, but which also provide useful information in mineralogical studies. These interactions include the production of *auger electrons*, which can supply compositional information, particularly for the light (i.e. low atomic number) elements; *absorbed electrons*, which provide a combination of topographical and compositional information somewhat intermediate between secondary and backscattered electron images; *photons*, where some minerals (such as calcite or apatite) emit light in the visible or ultraviolet region (called *cathodoluminescence*) which can be characteristic of a particular chemical composition (see e.g. Marshall, 1988, for applications in mineralogy); and *phonons* produced by vibrations within the mineral lattice during electron bombardment, which are of importance only in that they can cause considerable local heating in the specimen and hence, particularly in hydrated minerals such as zeolites or clays, problems in chemical analysis by EPMA.

Of fundamental importance in EPMA is the production, identification and measurement of characteristic *X-rays* produced at a depth of 1—3 µm. When a high energy electron, generated by an electron microprobe, hits the sample, an electron from one of the inner orbital shells of an atom within the sample is ejected. The atom is now in an unstable ('excited') state, and an electron from an outer orbital shell will fall into the vacancy created to restore the atom to its stable ('ground') state. During this process, an amount of energy is released which is equal to the difference in energy between the two orbital shells involved. This process is shown schematically in Fig. 3. The characteristic X-ray energies emitted are designated by the Roman letter of the electron orbital shell containing the vacancy (i.e. K, L or M), and are suffixed by the Greek letter to denote the group to which the electron belongs (i.e. α, β, γ), and by a number to denote the relative intensities of the emission line (i.e. 1, 2, 3 ...).

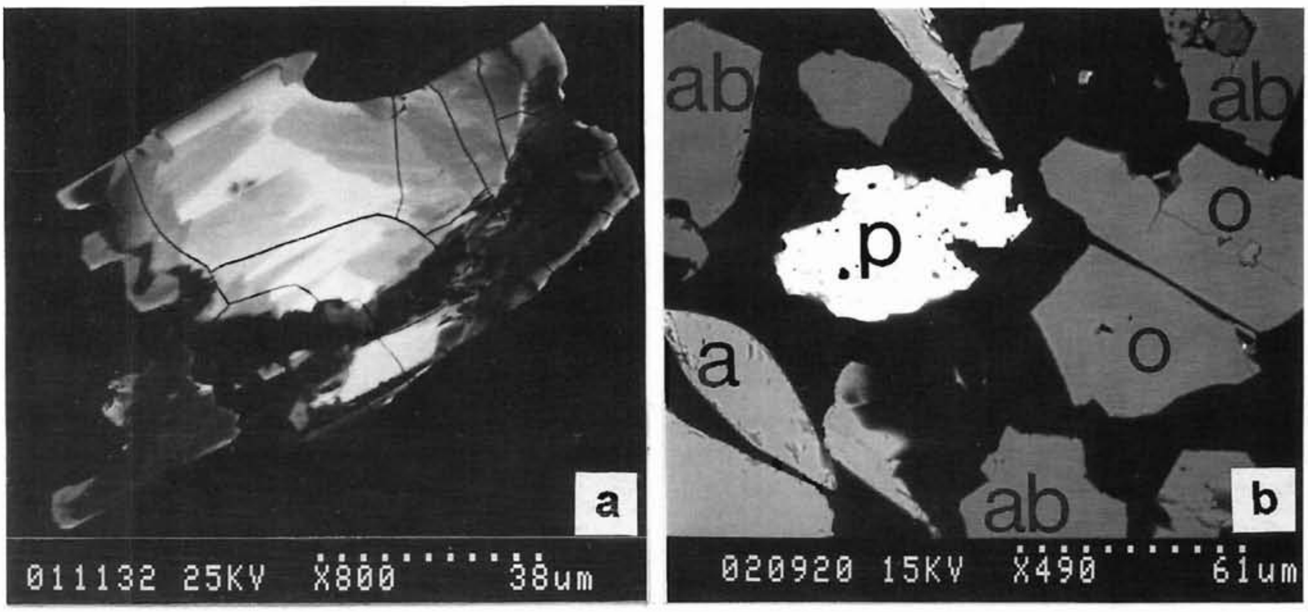

**FIGURE 2.** Examples of backscattered electron images to illustrate the advantages of compositional imaging. **(a)** Polished section of a crystal of zirconolite (essentially $CaZrTi_2O_7$) from Adamello, Italy, revealing a complex history of chemical zonation and corrosion features (Gieré and Williams, 1992). Scale bar 0.038 mm. **(b)** Grains of a pyrochlore-rich ore sample mounted in Araldite and polished. Each mineral species present was initially identified by its energy-dispersive spectrum; the minerals could then be readily correlated with the backscattered image, allowing rapid identification of all the grains and subsequent modal analysis using image analysis software. a = apatite, o = orthoclase, p = pyrochlore, ab = albite. Scale bar 0.061 mm.

Thus, in Fig. 3, the X-ray energies emitted are denoted Cu $K\alpha_1$ (energy = 8.047 KeV), representing the transition from the L to the K shell; Cu $K\beta_1$ (energy = 8.907 KeV) from the M to the K shell; and Cu $L\alpha_1$ (energy = 0.928 KeV) from the M to the L shell. In practice, X-rays of many specific energies are emitted, depending upon which orbital shells are involved; for example, there are at least 12 energy lines which correspond to the L spectrum, although some will be of very low intensity, and similar in energy.

For an electron to be ejected from the atom, the energy of the bombarding electron beam from the microprobe should be at least twice the energy of the emitted X-ray. Thus, for analysing Cu using the Kα line, the microprobe would typically be operated at 20 kV. In practice, elements from Be to Zn are analysed using the K lines, from As to Hf the L lines, and from Ta to U the M lines.

## INSTRUMENTATION

A schematic diagram of the important components comprising an electron microprobe is shown in Fig. 4, and the principles are outlined below.

### ELECTRON GUN AND COLUMN

The electrons are produced from an electron 'gun' by heating a tungsten filament to about 2400°C, and applying a negative potential (typically 10—30 kV) to accelerate the electrons away from the filament and down the electron 'column'. Magnetic lenses situated in the column focus the electrons into a beam of typically 0.2—1 μm diameter at the sample position. The gun, column and specimen stage are all under a high vacuum, this being necessary to maintain a stable electron beam.

### SPECIMEN STAGE

The rock or mineral samples and the standards are generally mounted as circular or rectangular polished sections (see below for details), placed onto a specimen holder, and inserted into position under the electron beam. Specimen stages usually accommodate several (generally up to six) specimens. Analysis positions can be selected using an optical microscope attached to the specimen chamber, or by secondary and/or backscattered electron imaging. Modern electron microprobes have automated x, y and z (focusing) movements with a position reproducibility of better than 1 μm, which allows unattended analysis of a large number of points under computer control.

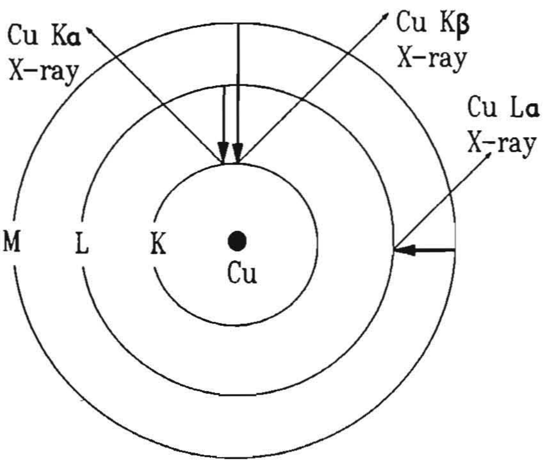

**FIGURE 3.** Simplified schematic diagram illustrating the emission of a Cu Kα X-ray from an L→K electron transition, Cu Kβ from an M→K transition, and Cu Lα from an M→L transition.

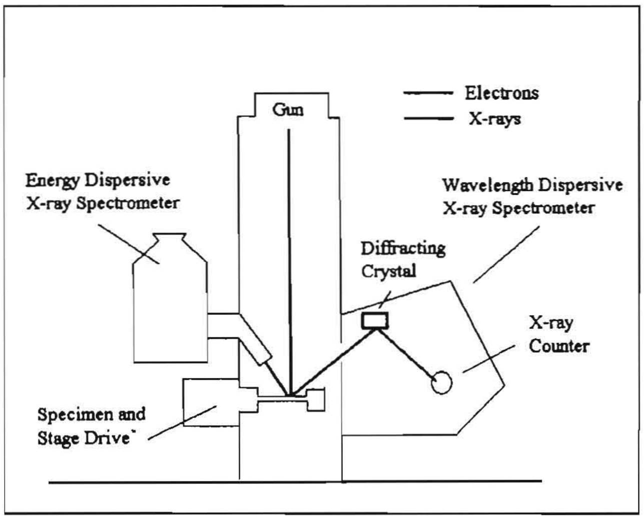

**FIGURE 4.** Schematic diagram of an electron microprobe.

### SPECTROMETERS AND DETECTORS

Spectrometers are used to isolate X-rays of a specific energy or wavelength, prior to their detection and measurement, as outlined in the following sections.

## X-RAY SPECTROMETRY

For accurate chemical analysis of minerals by EPMA, the detection and measurement of the characteristic X-rays generated by the mineral sample on bombardment with the electron beam are essential. Two related but distinct methods are employed: analysis on the basis of the energies of the X-rays, i.e. energy-dispersive spectrometry (EDS); and analysis on the basis of the wavelengths, i.e. wavelength-dispersive spectrometry (WDS). The wavelength λ (in Ångstroms) is related to energy E (in electron volts) by the expression $\lambda = 12396/E$.

In EDS, the X-rays of all energies emitted by the sample are simultaneously detected by a solid-state detector in which lithium atoms are implanted ('drifted') into a silicon wafer; this is called an Si(Li) detector. X-rays hitting the detector produce charged pulses that are proportional to the energy of the X-rays. The pulses are sorted according to size to produce an X-ray energy spectrum from which individual peak areas and hence the concentration of each element can be calculated.

In WDS, the emitted X-rays are first dispersed (like light by a grating) using a crystal of known structure to isolate the required wavelength (Fig. 5). The intensity of the line is then measured using a device called a gas-filled proportional counter. The analysing crystal reflects X-rays according to the Bragg equation, $n\lambda = 2d\sin\theta$, where λ is the wavelength in Ångstroms; *d* the interplanar spacing of the analysing crystal, in Ångstroms; θ the incident angle with the crystal plane (the Bragg angle); and n the order of reflection (an integer, usually 1). Thus, by changing the angle at which the incoming X-ray hits the crystal, the wavelength detected will change. Although most spectrometers can scan a wide range of θ values, four or five crystals with different *d*-spacings are needed to cover the complete range of wavelengths required for the analysis of elements from Be to U.

The main advantages and disadvantages associated with each system are summarised in Table I. Modern microprobes

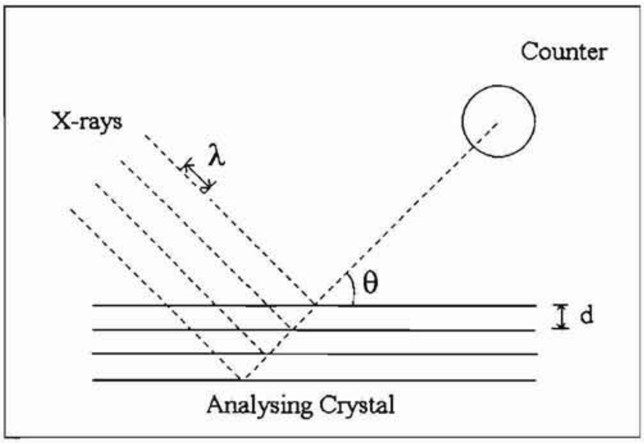

**FIGURE 5.** Schematic diagram illustrating the path of an X-ray of wavelength λ hitting an analysing crystal with interplanar spacing *d*, at an incident angle θ, in wavelength-dispersive spectrometry.

have both energy-dispersive and wavelength-dispersive systems available and, with appropriate software, it is possible to combine the two in the quantitative analysis of minerals (e.g. Ware, 1991), thus utilising the strengths of each system.

## QUANTITATIVE ANALYSIS

In many detailed mineralogical studies, the concentrations of each element within the mineral need to be established to a high degree of accuracy. To achieve this, the first requirement is that the mineral or rock specimen must have a flat, highly polished surface. This can be obtained by embedding the sample in a resin block, and polishing it on a series of laps using diamond or aluminium oxide 'grits', to a final grade of 0.25 μm. Alternatively, polished thin sections can be prepared by mounting the sample onto a glass slide and polishing it down to a thickness of 30 μm (e.g. Allan, 1984). The latter procedure has the advantage that the minerals can be viewed in both transmitted and reflected light optics, and that when observed under a petrological microscope, the optical characteristics of the minerals are identical with those in standard petrological thin sections. Finally, a thin conducting coating of carbon (typically 20—40 nm thick) is applied to the polished surface to dissipate any excess charge that may build up under the electron beam.

After selection of appropriate instrument parameters, i.e. the gun accelerating potential, electron beam current, spectrometer settings, etc., the intensities of the characteristic X-ray lines are measured. The *apparent* concentration $C_{\text{app}}$ of each element is then calculated using the equation:

$$C_{\text{app}} = \left(\frac{I_{\text{unk}}}{I_{\text{std}}}\right) C_{\text{std}}$$

where $I_{\text{unk}}$ and $I_{\text{std}}$ are the measured intensities for the unknown sample and the standard, respectively, and $C_{\text{std}}$ is the concentration of the element in the standard. The intensities are measured either as peak areas (in EDS), or as peak heights (in WDS). To obtain the true concentration, the apparent concentration so obtained needs to be corrected for 'matrix effects', i.e. the combined effects of the other elements present in the sample on the measured intensity of the element of interest. There are several mathematical ways of performing these corrections using iterative routines. Two procedures in common use are the *ZAF* method, where *Z* stands for an atomic number correction, *A* an absorption correction, and *F* a fluorescence factor; and the $\Phi(\rho z)$ (pronounced phi-rho-zee) method, which takes into account the depth distribution ($z$) of X-rays in the matrix, together with a calculation of the density ($\rho$). The calculations are now performed on-line and the results are obtained within a few seconds, although 20 years ago a dedicated main-frame computer was needed and it could take several hours before the results were known.

**TABLE I.** Comparison of the advantages and disadvantages of energy-dispersive and wavelength-dispersive analysis.

| | Advantages | Disadvantages |
|---|---|---|
| EDS | Many elements analysed simultaneously.<br>Rapid qualitative analysis.<br>No moving parts.<br>Lower specimen current.<br>Lower overall cost. | Peak overlap problems.<br>Poor detection limits — routinely 0.2—0.5 wt%. |
| WDS | Better spectral resolution — fewer peak overlaps.<br>Better detection limits — routinely 0.02—0.05 wt %.<br>More reliable, quantitative analysis. | Elements analysed sequentially.<br>Analysing crystal and detector need to be moved.<br>Higher specimen current — possible specimen damage. |

Implicit in these calculations is the measurement of an appropriate standard with a known concentration of the element being analysed. Ideally, the standard should have a concentration similar to that of the sample, to reduce the sample matrix effects. For most minerals this is not practical because of the large number of species present in the Mineral Kingdom, and generally the standards used are well-characterised, chemically homogeneous minerals, synthetic compounds, or glasses, and also pure metals. Most microprobe laboratories build up a 'library' of reliable standards through a combination of begging and borrowing from colleagues, separating suitable minerals, manufacturing chemically doped glasses, synthesising stable compounds, or purchasing standards from commercial sources.

With modern electron microprobes, quantitative analysis of 20 to 30 elements at concentrations above 0.05 wt % can be obtained in 10—15 minutes. Routine analyses of the major rock-forming minerals such as olivine, pyroxene, feldspar, etc., can be achieved in under two minutes, and several hundred analyses can be acquired during unattended overnight operation of the microprobe. Thus, detailed information on, e.g., chemical zonation within individual mineral grains, or element substitutions within mineral species, can be rapidly accumulated.

Thirty years ago, the mineral would first have had to be separated from its matrix, and even in a well-equipped laboratory the analysis of one mineral could have taken several days to perform. In addition, one could not have obtained the detailed spatial information on compositional zoning, for example. There are, however, some limitations to the quantitative analysis of minerals by EPMA which are outlined in a later section.

## QUALITATIVE ANALYSIS

When all that is required is to know which elements are present in a mineral specimen, it is often not necessary to have a flat polished surface, or to coat the sample with a conducting medium. Using backscattered or secondary electron imaging, excellent morphological detail, together with

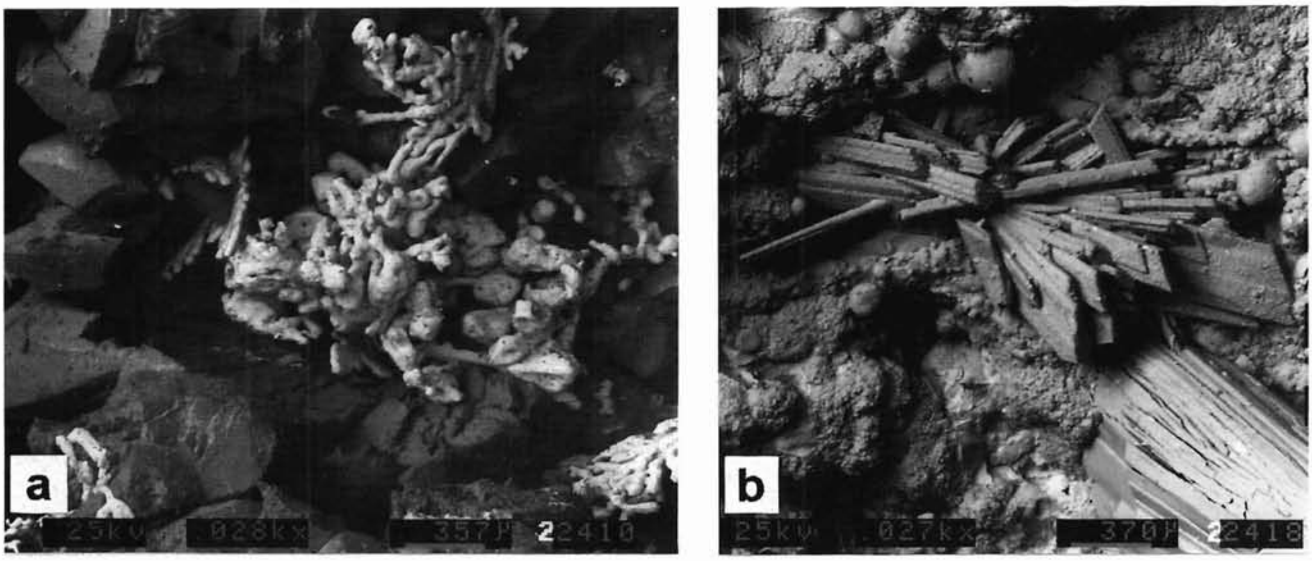

FIGURE 6. Examples of backscattered electron images of unpolished minerals on matrix, obtained using an ISI-ABT55 scanning electron microscope. See also Fig. 7. (a) Gold on quartz, Aquacate Mountains, Costa Rica. Scale bar 0.36 mm. (b) Symplesite on matrix of iron oxides and quartz, Mapimi, Mexico. Scale bar 0.37 mm.

rapid compositional information, can be obtained even on large 'hand-sized' mineral samples. This has an obvious advantage to the mineral curator, since rare or unique mineral grains need not be detached from their matrix, and the sample is unaffected by the analysis procedure.

Two examples of this application to specimens in the NHM collections are illustrated in Figs 6 and 7. In Fig. 6a the wiry morphology of gold grains in association with quartz can be clearly seen from the backscattered electron image of a mineral sample from the Aquacate Mountains, Costa Rica.

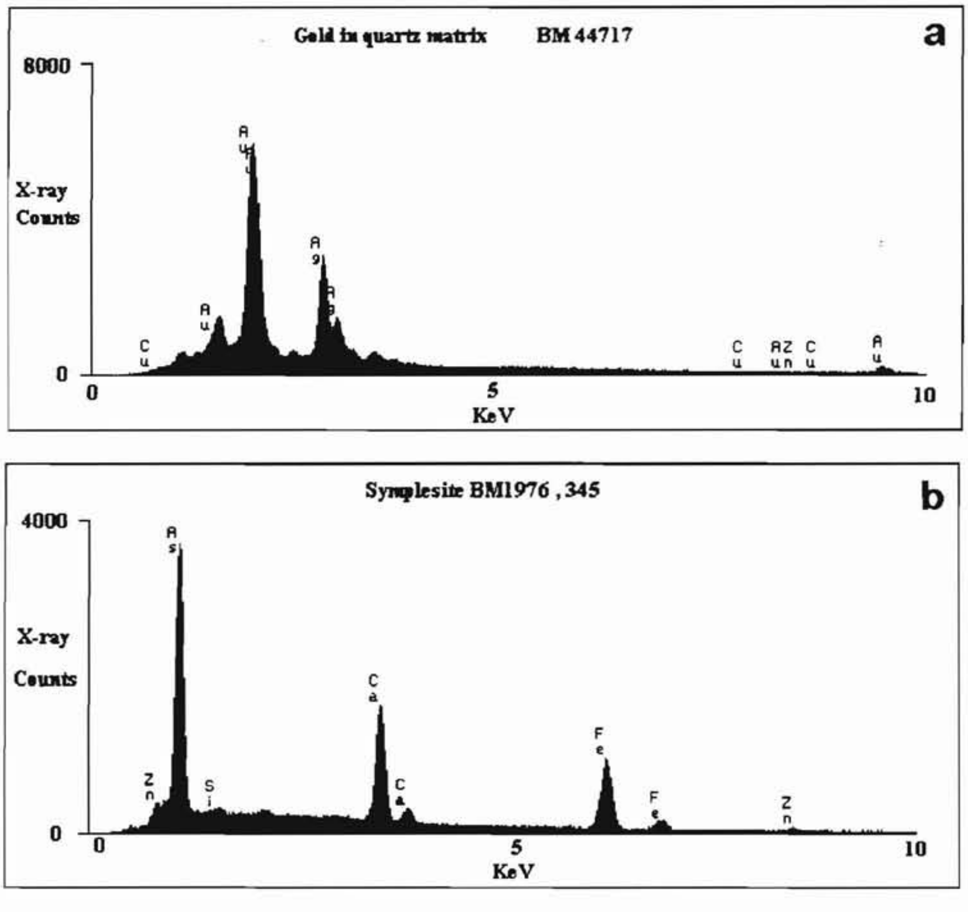

FIGURE 7a, b. Energy-dispersive X-ray spectra of samples shown in Fig. 6. The energy of the emitted X-rays is plotted on the horizontal axis, and the intensity on the vertical axis. The peaks are identified and labelled by the computer software.

The energy-dispersive spectrum of the gold grains (Fig. 7a) indicates that gold and silver are the major components but that copper is not present. In Fig. 6b, several crystals of a mineral suspected to be symplesite, $Fe_3(AsO_4)_2.8H_2O$, in a sample from Mapimi, Mexico, were shown from their energy-dispersive spectrum (Fig. 7b) to contain major concentrations of Fe and As, minor concentrations of Ca, and traces of Zn, in agreement with the composition of (calcian) symplesite. Spectra of the other minerals within the matrix established them to be a mixture of iron oxides and quartz. The specimen measured approximately 10 × 7 × 4 cm and this illustrates the capability of the scanning electron microscope to accommodate large specimens. It is also noteworthy that the spectrum accumulated very rapidly, the X-ray peaks corresponding to the individual elements being identifiable within seconds.

## X-RAY MAPPING

By selecting an element of interest, either as an energy 'window' in EDS, or a characteristic wavelength in WDS, and scanning the electron beam across the sample, an element distribution map (or 'X-ray map') is obtained. Such maps provide detailed information on chemical zoning within minerals, textural relationships that are sometimes not apparent from backscattered electron images, and mineral (or zonal) modal analysis.

Early electron microprobes displayed X-ray maps on a cathode-ray tube; the transient image could then be photographed for a permanent record. X-ray maps produced in this way were termed 'analogue maps'. On more modern instruments 'digital maps' can be obtained, in which the intensity of X-rays is recorded at each pixel of a grid (up to 1024 × 1024 pixels) and stored in computer memory. Such X-ray maps can be displayed as digitised images and manipulated in a variety of ways using image-processing software. Examples of digitised X-ray maps of a gold-bearing sample from Kalgoorlie, Western Australia, are shown in Fig. 8.

There are several differences between energy-dispersive and wavelength-dispersive maps. Mapping with an energy-dispersive system is often not specific to one element, since the map will be of a region of the spectrum likely to contain the characteristic X-rays of several potentially interfering elements. However, some manufacturers now provide software which sorts out such interferences so that the resulting X-ray map is more element-specific. With wavelength-dispersive systems, a characteristic X-ray line can usually be found which is free of interference from other elements, and hence the resulting map will be a true representation of the distribution of the element selected.

Using an energy-dispersive system, many X-ray maps can be acquired simultaneously (up to 32 on some instruments), whereas in a wavelength-dispersive system the number of X-ray maps obtained simultaneously depends on the number

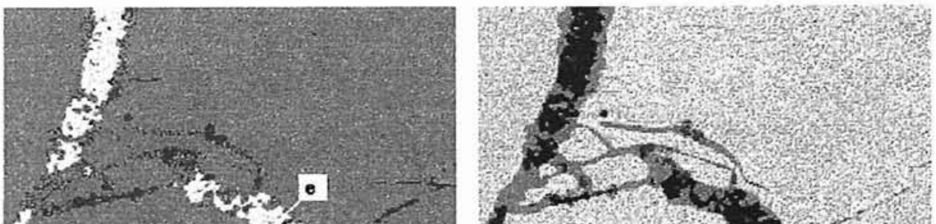

FIGURE 8. Digitised X-ray maps of the elements Au, Te, Ag and Cu in a polished section of an ore sample from Kalgoorlie, Western Australia (MI 1985,14674). Black represents low concentrations of an element and white, high concentrations, with intermediate concentrations in shades of grey. e = electrum, (Au,Ag); c = calaverite, $AuTe_2$; p = petzite, $Ag_3AuTe_2$; spots of high Cu concentration correspond to chalcopyrite. Scale bar 0.1 mm.

of spectrometers available (which can be up to five). Automation, however, allows several batches of elements to be mapped sequentially in unattended operation. With an energy-dispersive system, large areas of the specimen (typically 4 × 4 mm) can be mapped by moving the beam across the sample. However, in wavelength-dispersive mapping the X-ray map becomes defocused at low magnifications (<2000), and to produce X-ray maps of large areas the electron beam is held stationary while the specimen stage is moved. Software is now available for some energy-dispersive systems which provides a matrix-corrected analysis at each pixel position, so that the distribution maps can be quantified. For zoned minerals, a contoured compositional map can thus be displayed.

## RARE MINERAL PHASE LOCATION

By combining several features of EPMA, and using appropriate computer software to control the microprobe and monitor the results, rare mineral phases, for example discrete gold grains or rare-earth minerals, can be located automatically in rock sections and their positions recorded. This technique, developed by Jones (1990), utilises the fact that the signal measured by the backscattered electron detector depends on the composition of the mineral (the mean atomic number of its component elements). By selecting an energy 'window' within which the mineral will be detected, and searching the sample systematically by moving the stage in a grid pattern, the co-ordinates at which the detector signal matches the set window can be found. The mineral's identity can be confirmed by simultaneously measuring the intensity of the characteristic X-rays for one or more of its major elements. For example, in searching for gold grains in a rock section containing galena, three crystal spectrometers could be set at the wavelengths of Au (M$\alpha$), Pb (M$\alpha$) and S (K$\alpha$). At the end of the search, a printout of the matched co-ordinates from the backscattered electron detector and the corresponding intensity measurements from the spectrometers will indicate which of the located areas are likely to contain gold-bearing minerals, and which just sulphides. Using this technique and operating the microprobe unattended overnight, grains as small as 1 $\mu$m can be located in a sample area in excess of 10 cm$^2$.

## MINERAL IDENTIFICATION SOFTWARE

Backscattered electron images will often highlight minerals in rock sections which, even after analysis by the microprobe, are not immediately recognised by the mineralogist. Using computer software, of which there are several available (e.g. MinIdent, see Smith and Leibovitz, 1986), such minerals can be identified by comparing the composition determined by EPMA with those of known minerals stored in a large database. On some microprobes, this 'search and match' software can be directly interfaced with the microanalysis software.

## LIMITATIONS

In spite of many improvements in EPMA over the last two or three decades, traditional 'wet chemical' techniques are still necessary for the complete chemical analysis of some mineral species. Of the lighter (low atomic number) elements, only fluorine is now routinely analysed by EPMA (e.g. Potts and Tindle, 1989). Generally, neither carbon nor oxygen are analysed, their concentrations usually being calculated by stoichiometry (e.g. by adding oxygens in proportion to the amounts and valencies of the other, analysed elements), although quantitative analysis of oxygen by EPMA has been achieved with some success (e.g. Armstrong, 1988). $H_2O$ is not analysed directly, and hydrated minerals will therefore have analytical totals of less than 100%; in some cases $H_2O$ has been estimated from the analysis of oxygen (e.g. Nash, 1992). Lithium cannot be analysed by EPMA, and beryllium can be detected only with difficulty, so that other methods must be employed for these elements. Boron can be detected by EPMA with a suitable energy-dispersive detector or with an appropriate analysing crystal, and its quantitative analysis has met with some success (e.g. McGee *et al.*, 1991); the correction procedures for this element are, however, not well known. A major drawback is that EPMA does not normally distinguish between $Fe^{2+}$ and $Fe^{3+}$, although some studies have attempted to determine the oxidation state of iron in iron-bearing minerals with some success (e.g. Höfer *et al.*, 1994). Routinely, the $Fe^{2+}/Fe^{3+}$ ratio in minerals is calculated from the assumed stoichiometry.

Some minerals show varying degrees of instability under bombardment by the electron beam — e.g. clay minerals, zeolites, some carbonates, and hydrated minerals. This can result in poor analytical precision and accuracy. Although there are procedures which help to reduce specimen damage, such as operating the beam at a lower current, or 'defocusing' the beam in order to dissipate the energy over a larger area of the specimen, the best that can be achieved in these cases is often a semi-quantitative analysis. To assess the quality of an analysis in these situations, it may be compared with other published analyses for the mineral, if available.

## FINAL REMARKS

Although EPMA is now a mature analytical technique and an essential tool in many mineralogical studies, accurate quantitative analysis is often not easy or routine because of the complex chemistry of natural minerals. Accurate analysis requires many preparatory steps: the intrument operating parameters need to be optimised and, especially for trace element analysis, the background regions and potential spectral interferences must be accurately assesssed.

Future developmens in EPMA are likely to be (a) in the electronic components, to achieve even greater electron beam stability, particularly at high accelerating potentials, which would greatly improve the analysis of trace elements; (b) in the software for handling data and processing images; and (c) refinements of the matrix corrections and improvements in procedures for ultra-light element analysis.

Other microanalytical techniques, such as the ion microprobe, the nuclear microprobe, synchrotron X-ray microanalysis, and the laser microprobe, have been developed in the last decade (e.g. Potts *et al.*, 1995). These techniques will continue to find new mineralogical applications and will complement EPMA. However, the electron microprobe is likely to maintain its position as the principal method of analysing minerals well into the 21st century.

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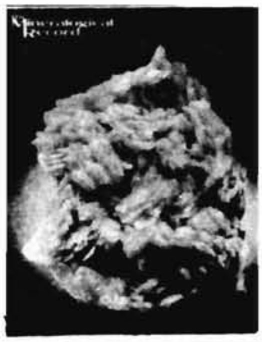

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# EARLY DEVELOPMENT OF MINERALOGY IN EDINBURGH, SCOTLAND*

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**The history of mineralogy in Edinburgh is briefly outlined by highlighting the main personalities involved. From the mid-eighteenth century until 1900 collections were amassed, studied and catalogued. Heritage collections can no longer be acquired, yet history reveals that many such collections declined or disappeared even though published works drew extensively upon their greatness.**

## INTRODUCTION

In the eighteenth century great artistic, intellectual and scientific advances occurred throughout many parts of Scotland; in particular, Edinburgh arose as a leading Scottish and, indeed, European, cultural city. The Scottish 'Enlightenment' took place from around the 1730s to the 1790s, and natural history, geology, and mineralogy became integral components. A coterie of Edinburgh professional men from academia, medicine, the law, banking and public life, through their intense interest in minerals, amassed considerable collections and elevated mineralogy from a curiosity to a highly respected science.

The advance in mineralogy is reflected by the growth in the size and functions of mineral collections. Many collections attain a zenith and then decline, yet they are the cornerstones from which our science has been and still is being projected. For example, a recent survey by the author of the *American Mineralogist* from 1916 to 1990, and the *Mineralogical Magazine* from 1877 to 1990, showed that 10% of new species came mainly from museum collections, with minor additions from university and private collections.

## SEVENTEENTH AND EIGHTEENTH CENTURIES

Sir Andrew Balfour (1630—1694) and Sir Robert Sibbald (1641—1722) were among the earliest mineral collectors and scientific naturalists in Scotland. They assembled collections of natural history objects which included approximately 250 mineral specimens. Sibbald (1697) catalogued their collections along Agricolan lines, for classification of natural history objects was then in its infancy. Sibbald's catalogue illuminates an interest in minerals in their own right, for morphology, colour, lustre and locality details are stated for many of the specimens. Not only was systematic mineralogy foremost, but so was regional surveying for economic minerals. Upon Balfour's death the collection was sold to Edinburgh University Museum. It is a tragedy that, less than a century after its acquisition, not a trace of it remained in the University.

The first professor of Natural History at Edinburgh University was the Reverend Dr John Walker (1731—1803; Fig. 1), who occupied the chair in 1779. Walker enrolled his first class during 1781, and in his initial lecture said "I am to teach a science I was never taught". John Walker actively pursued a teaching career until just before his death. For his profound influence in establishing geology as a science, and as a discipline within higher education, Walker is accredited with the title of 'Father of geological education'. Walker became a stimulating, eminent lecturer, and even professors enrolled for his classes. With his encyclopaedic scientific knowledge, art of demonstration, originality of thought, and passion to search for the truth, he inspired many future well-known scientists. An examination of Walker's class lists reveals Sir James Hall, the Father of experimental petrology, and Robert Jameson when the latter was only 18 years old. Walker worked from polished slabs (Fig. 2), utilized a microscope and chemical analysis, and evolved a hardness scale some 40 years before Mohs. Upon his death, his collection was removed from the University Museum by his Trustees and it has virtually all disappeared.

**FIGURE 1.** Dr John Walker of Edinburgh. From "Memoir of John Walker, D.D." in Jardine (1842).

## NINETEENTH CENTURY

Robert Jameson (1774—1854; Fig. 3) succeeded Walker and held the Chair of Natural History for fifty years. He amassed

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*Based on a paper presented at the Russell Society symposium on 'Mineralogy in the Field', Oxford, March 1995.

**FIGURE 2.** Polished slabs (*ca* 8 × 8 cm) used by John Walker for teaching. 'M.E.' on the labels denotes Museum Edinensis.

a huge collection of natural history objects, including 7000 mineral specimens. Jameson's mineralogy lectures revolved round morphological, physical and chemical characteristics, and the uses of minerals. He contributed to the mineralogical literature by publishing numerous papers and textbooks. Jameson's three-volume work, *System of Mineralogy*, appeared between 1804 and 1808. So great was the demand for this work, on a branch of science that was relatively new at the time, that a second edition appeared in 1816, and a third during 1820. Other major contributions followed, including another book, *Elements of Mineralogy* (1840a).


Robert Jameson

**FIGURE 3.** Signed portrait of Robert Jameson. Engraving by Schenk and Macfarlane, Edinburgh, of a pencil drawing by L. Chémar.

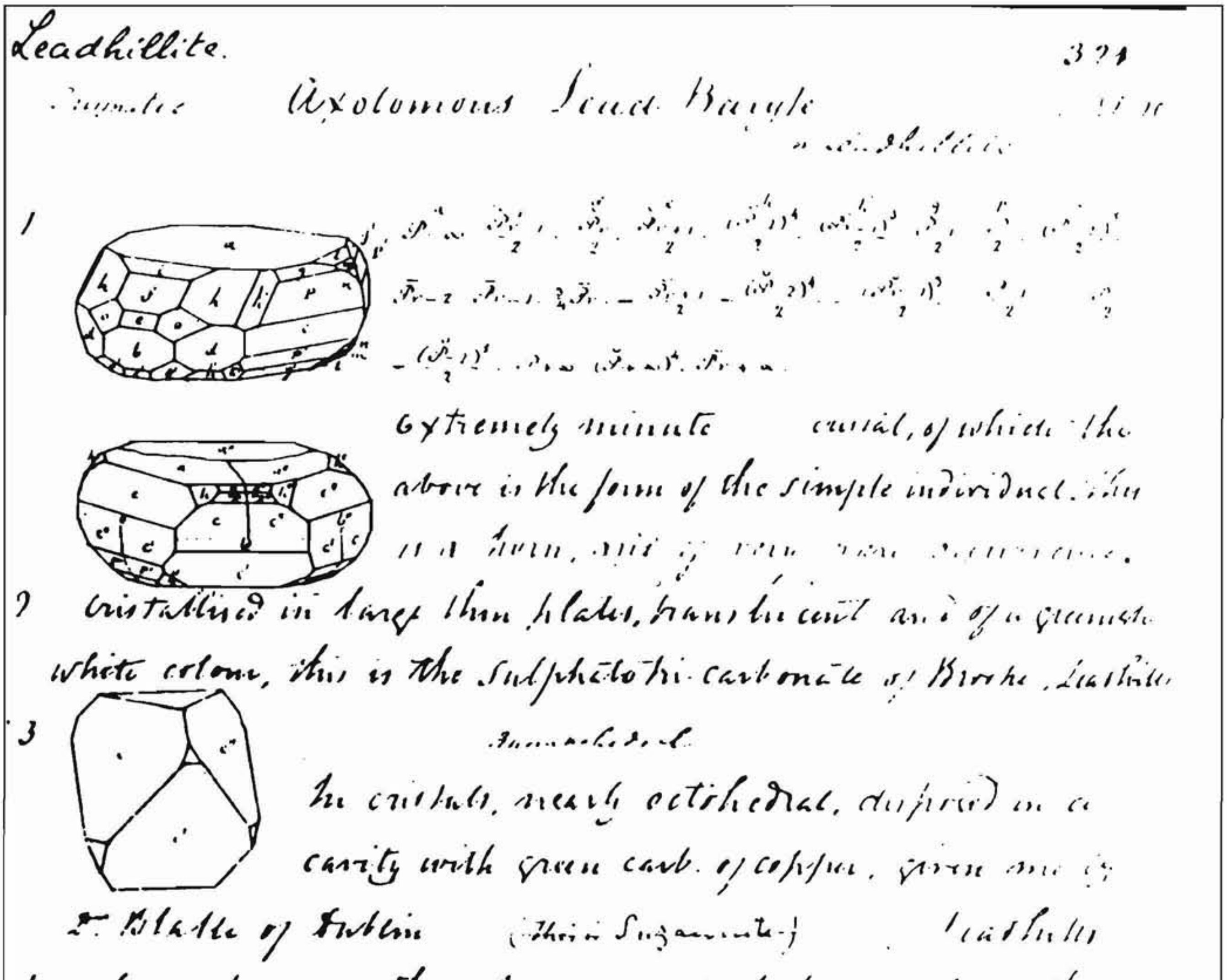
When describing a mineral Jameson commenced with the synonymy, followed by the external characters, i.e. the physical properties and morphology, whereafter he presented the chemical characteristics as ascertained under the blowpipe and by chemical analysis, then the paragenesis and finally the locality data. The foundations of descriptive mineralogy were clearly laid down slightly prior to and during Jameson's early career. Perhaps not surprisingly, modern reference works follow this successful pattern established some 190 years ago. In recognition of Jameson's contribution to mineralogy Haidinger (1825) immortalised his name by erecting the new species jamesonite. Greenockite, one of Scotland's rarest minerals, was analysed and named by Jameson (1840b). Jameson's influence in natural history and mineralogical circles was recognised worldwide, and he received honours from over fifty international scientific societies.

During 1817 Jameson issued instructions — one route was via the diplomatic service — on how to collect natural history specimens. Consequently specimens poured into the Edinburgh University Museum (Fig. 4) and pressure on space became extreme. He approached the government and Edinburgh Town Council for funds to construct a new museum. As a result, the present Royal Museum of Scotland (RMS) was founded in 1854 — the year of Jameson's death. The nucleus of the RMS General Mineral Collection is the *remnants* of Jameson's collection.

Surrounding and interacting with Jameson were the Edinburgh mineral dealer Alexander Rose (1781—1860) and the father and son Thomas Allan (1777—1833) and Robert Allan (1806—1863), both Edinburgh merchant bankers.

The sciences were a major interest in Alexander Rose's life. He fraternised with notable scientific men of the day,

**FIGURE 4.** Robert Jameson's Museum, Old College, Edinburgh. The etching *ca* 1822 was used by Jameson as a letter head and measured about 12.5 × 10 cm.



Leadhillite. 371

[illegible] Axotomous Lead Baryte [illegible]

[illegible] Leadhillite

1 [illegible]

Extremely minute crystal, of which the above is the form of the simple individual. This is a form, and of very rare occurrence.

2 Cristallised in large thin plates, translucent and of a greenish white colour, this is the Sulphato tri-carbonate of Brooke, Leadhills

3 [illegible]

In cristals, nearly octohedral, disposed in a cavity with green carb. of copper, given me by Dr Blake of Dublin (Their Suzannite) Leadhills

4 Same form as the above of a dark brown colour this is the truncated Rhombohedron of Brooke, [illegible] do.

5 Form similar to No 2 very beautifully cristallised and disposed on Baryte, do.

6 do in very minute cristals some of which are very perfect do.

7 do in cristals of considerable size and of a brownish colour do

8 very perfectly cristallised in translucent plates disposed in a cavity with acicular green Lead Baryte and accompanied with carbonate do.

FIGURE 5. Entry for leadhillite in the Allan-Greg catalogue; entries by Thomas Allan, crystal drawings and lists of forms by Robert Allan. Reproduced courtesy of the Natural History Museum, London.

including Sir Michael Faraday (1791—1867) and Sir David Brewster (1781—1868), who had the zeolite brewsterite named after him by Brooke (1822). Rose gave mineralogy classes in a house adjacent to his residence, opposite the University, and became Professor at Queen's College, Edinburgh. His lectures attracted architects, surveyors, engineers and general students, who were drawn to them by his outstanding teaching skills and the superb mineral collection with which he illustrated his talks. From eleven class members who attended his house lectures, a Geological Society was formed in December 1834, out of which grew today's Edinburgh Geological Society.

From a very young age, Thomas Allan began to develop a mineral collection. When Allan was 28 he visited Paris, and became acquainted with Haüy and Brochant. In 1808 Thomas Allan examined a shipment of Greenland minerals collected by Charles Lewis Giesecke in 1806, which had arrived in Edinburgh (Livingstone, 1993). Allan purchased the entire lot in 1808 and, upon cleaning the specimens, noted a black mineral which he tentatively identified as gadolinite. He gave the mineral to Thomas Thomson (1773—1852) who analysed it and named it allanite (Thomson, 1810). Allan compiled a collection in excess of 7000 specimens and actively exchanged specimens with Jameson and Count de Bournon.

The Austrian mineralogist Wilhelm Haidinger (1795—1871) stayed with Thomas Allan in Edinburgh for two years while he translated Mohs's *Treatise on Mineralogy*, which appeared in 1825. From Haidinger, Thomas and Robert Allan learned their morphological crystallography. With Haidinger Robert Allan ventured upon an extended mineralogical tour of Norway, Sweden, Germany and France. The two Allans catalogued their extensive collection, which is now the Allan-Greg collection in the Natural History Museum, London (Fig. 5). Robert Allan's most celebrated scientific work, *A Manual of Mineralogy* (1834), drew extensively upon their own mineral collection and on data gleaned during the European tour. This publication became a reference text for the *Manual of the Mineralogy of Great Britain and Ireland* by Greg and Lettsom (1858), which is still the only comprehensive mineralogical textbook covering the entire British Isles. The esteem generated by Robert Allan's book failed to pass unnoticed, and the publishers of *An Elementary Introduction to the Knowledge of Mineralogy* by William Phillips (1823) invited Robert to prepare a fourth edition. He retained Phillips's chemical classification but added details of 150 new species and close on 60 new figures to the revised book, which appeared in 1837.

A major figure in public life was Edinburgh-born Patrick Dudgeon (1817—1895), who also had developed a wide scientific reputation. He was a life-long friend of Professor Heddle and they, with others, founded the Mineralogical Society of Great Britain and Ireland in 1876. Dudgeon became a Trustee. and Heddle the second President of the Society. Dudgeon donated his collection of 2000 specimens to the Royal Museum of Scotland in 1890. As a measure of his dedication and mineralogical expertise, it contained about half the then known total number of species, which in 1890 was about 800.

The last character in this scenario is Matthew Forster Heddle (1828—1897; see Livingstone, 1990), who from 1862 was Professor of Chemistry at St Andrews University. Chemical analysis was his main method of identification; within the pyroxene, amphibole, feldspar, garnet, mica, and zeolite groups Heddle performed 257 analyses, for 7—10 elements per mineral. The Royal Society of Edinburgh awarded him their Keith Gold Medal for his studies into rhombohedral carbonates, and he launched the new species tobermorite from Scotland (Heddle, 1880).

Heddle contributed *one-third* of all the mineral species from Scotland known in 1901, and was responsible for *one-quarter* of all the British species. His collection of 7000 specimens came to the Royal Museum of Scotland in 1890 and 1894, and was displayed in 1895. Rarely does a national newspaper devote nearly half a page to a mineral collection, but *The Scotsman* (6 September, 1895) described his collection as "the finest national collection of the minerals of any one country in the world". Heddle began writing *The Mineralogy of Scotland*, which was posthumously edited by J.G. Goodchild and published in two volumes in 1901. Close on a century later this book remains the only major publication on Scottish minerals.

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# SUPERGENE U—Pb—Cu MINERALISATION AT LOE WARREN, ST JUST, CORNWALL, ENGLAND

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**A rich assemblage of supergene U—Pb—Cu minerals occurs in a small coastal exposure near Loe Warren, St Just, Cornwall. The supergene suite has been formed by the action of surface waters and sea spray on uraninite, chalcocite and chalcopyrite and contains a number of rare uranium species, several of which are new to Britain. Within the main part of the exposure three zones of mineralisation may be recognised. Rutherfordine, boltwoodite and vandendriessheite occur closely associated with uraninite at the NW end of the exposure. Trögerite and an unidentified calcium rare-earth uranyl carbonate hydrate also occur in this part of the exposure. The central region of the exposure contains few uranium species, but is rich in chalcocite and associated supergene products, including cumengeite, atacamite, lavendulan, and amorphous copper silicate. The SE end of the mineralised area contains kasolite, wölsendorfite, widenmannite, dewindtite, and an unknown basic lead uranyl carbonate.**

## INTRODUCTION

The stretch of coastline from Cape Cornwall to Pendeen Watch lies in the metamorphic aureole of the Land's End granite. This area hosted significant economic deposits of copper and tin which were exploited by several famous Cornish mines, notably Botallack, Levant and Geevor (Noall, 1970, 1972, 1973). Wheal Owles, which lies about 0.7 km west of Botallack village (Fig. 1), is perhaps best known for the tragic flooding in 1893 which led to its closure (Noall, 1973), and for minor amounts of cross-course uraninite (Dines, 1956) which have produced a range of interesting supergene uranium minerals within the mine (e.g.·Wolloxall, 1988; Elton *et al.*, 1994a. 1994b; Elton and Hooper, 1994).

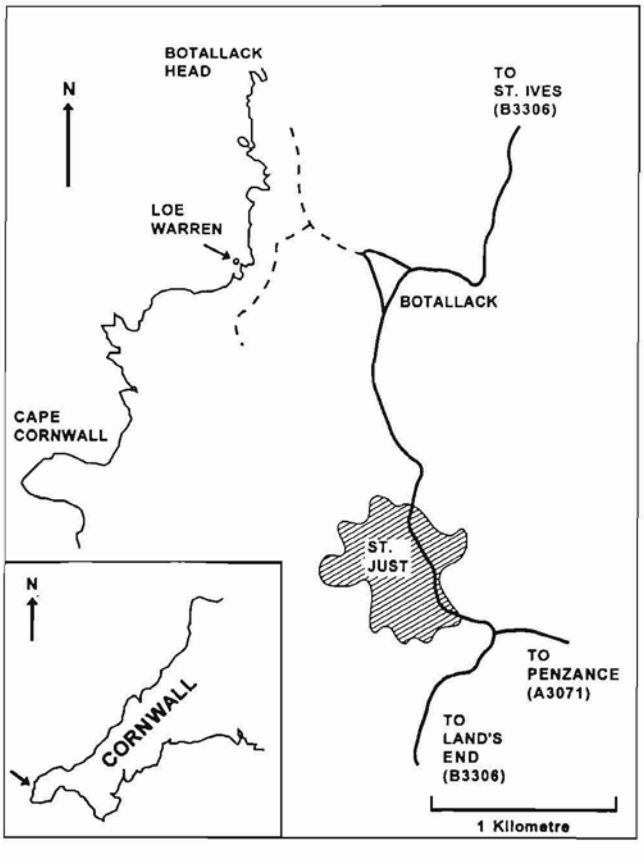

**FIGURE 1.** Location map.

Wheal Owles exploited a number of SE—NW trending lodes, several of which cross the coast between Wheal Edward zawn and a headland and large rock known as Loe Warren (National Grid Reference SW 3609 3297). Hanger lode, bearing copper, was formerly exposed in the cliffs in a zawn immediately east of Loe Warren, and was worked inland from this point along the Wheal Owles adit, which eventually connected with Cargodna incline shaft (SW 3628 3290). No evidence of these workings can be seen today, but a small mineralised area containing uraninite and chalcocite is exposed towards the back of the zawn (SW 3618 3297), and forms the subject of this paper. The zawn is nameless on mine plans and Ordnance Survey maps. Local collectors commonly refer to the exposure as 'Loe Warren' but, because this name applies strictly to the adjacent headland, the name 'Loe Warren zawn' will be used in this paper. ('Zawn' is a local term applied to small steep-sided sea-inlets resulting from the preferential erosion of mineralised veins or fissures).

## GEOLOGICAL SETTING

The shape of the Land's End peninsula corresponds roughly to that of the exposed granite. The granite was emplaced into country rocks consisting of middle to late Devonian argillaceous rocks and various basic intrusions. Metamorphism and metasomatism of the latter produced the great variety of hornfelses found today in the aureole (Mitropoulos, 1984). Aureole rocks are well exposed in a narrow coastal strip from Cape Cornwall to Pendeen Watch and consist mainly of laminated pelites interlayered with basaltic greenstones, basic intrusives and banded amphibolites. Fine-grained granite, leucogranite, and aplite pegmatite sheets are quite common at the contact zone (Mitropoulos, 1984; Jackson *et al.*, 1982). Khan (1972) recognised four major zones of metasomatic alteration within the aureole rocks, the arrangement of which depends on both distance from the contact and on the complexity of joint systems within the rock. The coastal rocks around Wheal Owles are substantially mafic hornfelses within the cummingtonite—cordierite—biotite and cummingtonite—anthophyllite—cordierite zones of Khan (1972).

Emplacement of the granite led to fracturing of the aureole rocks which was subsequently exploited by mineralising fluids. Jackson *et al.* (1982) provide a detailed description of mineralisation in the St Just district and recognise five types of mineralisation phenomena: metasomatism; barren pre- and post-joint pegmatites; mineralised sheet systems; mineralised fissure systems; and replacement bodies. Economic mineralisation within the Wheal Owles sett occurs within fissure veins. The vein systems, generally trending NW, typically carried cassiterite in the inland sections and copper sulphides in the coastal sections (Dines, 1956).

The more interesting mineralogical feature at Wheal Owles is the occurrence of late N—S trending veins carrying small amounts of lead, bismuth and uranium (Dines, 1956; Jackson *et al.*, 1982). Uraninite from Wheal Edward Cliff lode, ~200 m SW of Loe Warren, was dated at 58±3 Myr by Pockley (1964). Main stage mineralisation took place considerably earlier, at about 270 Myr, immediately, or soon, after emplacement of the granite (Jackson *et al.*, 1982). Local zones of feldspathised pelite are often associated with areas of potassium metasomatism. Fissure veins are also associated with local intense feldspathic and chloritic alteration (Jackson *et al.*, 1982).

## SAMPLE COLLECTION AND IDENTIFICATION

Specimens were collected from the exposure in Loe Warren zawn in 1992, 1993 and 1994. They were examined under a stereomicroscope and representative material was removed for qualitative energy-dispersive X-ray (EDX) analysis. All supergene uranium species were also examined by XRD. Other minerals not satisfactorily identified by EDX and physical properties were also examined by XRD. Where sufficient sample was available, diffractometry in Bragg-Brentano geometry was used, samples being ground by hand with acetone in an agate pestle and mortar and deposited on oriented silicon wafers or Mo foils. Powder photography using a 176 mm diameter Debye-Scherrer camera was carried out for some of the uranium species at the Natural History Museum, London (NHM); the relevant film numbers are given in the text. Quantitative EDX analysis and Fourier Transform IR spectroscopy were used to provide additional information for a number of species.

## MINERALISATION

The mineralised outcrop lies at the back of Loe Warren zawn, well above high tide mark, at the base of a slope of soil and rubble leading up the cliff (Figs 2 and 3). This debris, which has slumped from the cliff, is thought to obliterate the Wheal Owles adit and any former cliff workings on Hanger lode. Sporadic uraninite mineralisation can be traced along a NE—SW line for approximately 7 m across the back of the zawn. This line of weak mineralisation intersects or develops into a small, apparently NW trending, region rich in chalcocite with minor chalcopyrite, which also contained a rich pod of uraninite at its NW extremity. The line of uranium mineralisation was traced using a sensitive survey gamma monitor. At the NW end of the exposure, the region of enhanced radioactivity disappears beneath a large boulder and cannot be traced beyond. There is some evidence that it continues at depth. This comparatively rich region of mineralisation lies directly in the path of water draining from the slope behind. The water trickles over the exposure continuously, persisting even in dry weather, and probably originates from the buried adit.

The action of this water has produced an area of rich supergene alteration. The area is very small, about 2.5—3 m long and 0.5—1 m wide, but three zones of mineralisation can be recognised in the section presently exposed (Fig. 3). Lead and lead-uranium species occur predominantly at the SE end, nearest the base of the cliff; the middle of the exposure contains an area rich in chalcocite and associated supergene copper products but comparatively few uranium species; the NW end of the exposure (the seaward end) contained a nodule especially rich in uraninite which was surrounded by an alteration halo, the area below the uraninite being particularly rich in supergene mineralisation. This distribution of species may well change with depth.

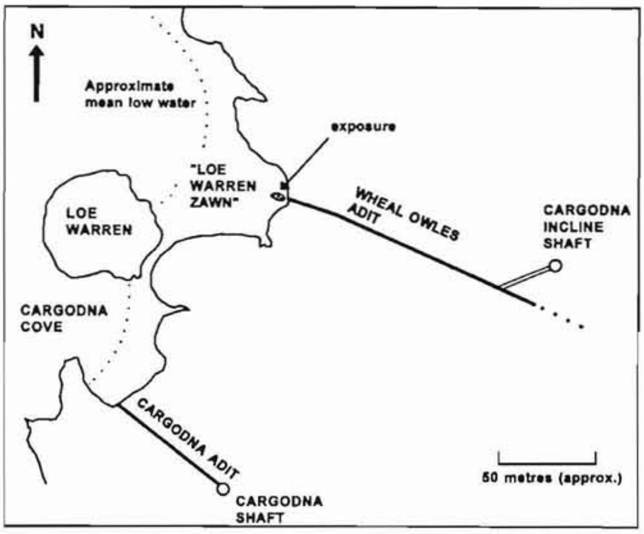

**FIGURE 2.** Sketch map of the area around Loe Warren zawn (based on mine plan number 211 part 1, dated 1879).

The following list of species concentrates on supergene minerals, but the main hypogene species are also included.

## MINERALS

### AMORPHOUS COPPER SILICATE

Joint planes and cracks in the rocks around the centre of the exposure are frequently coated with thin green and blue-green coatings. EDX analysis shows these coatings to be composed mainly of Cu and Si, often with traces of Cl, Pb and other elements. The crusts sometimes contain atacamite, malachite or cerussite, but XRD indicates that the bulk of the copper silicate is amorphous.

### ATACAMITE, $Cu_2Cl(OH)_3$

Atacamite occurs as tiny pale green to dark green anhedral crystalline masses and also as aggregates of generally subhedral crystals. The crystal habit appears to be identical with that of atacamite from Geevor mine, being composed of the rhombic prisms {110} and {011} and the pinacoid {010} (Fig. 4a). Atacamite occurs with malachite, amorphous copper silicate and, rarely, botallackite and cerussite. Only the metastable polymorphs atacamite and botallackite have been identified at Loe Warren zawn, and both occur near the surface of the Cu-rich part of the exposure. They are evidently of recent formation.

### BARYTE, $BaSO_4$

Baryte occurs rarely on specimens from the NW end of the exposure as tiny whitish square plates, associated with boltwoodite and zeunerite.

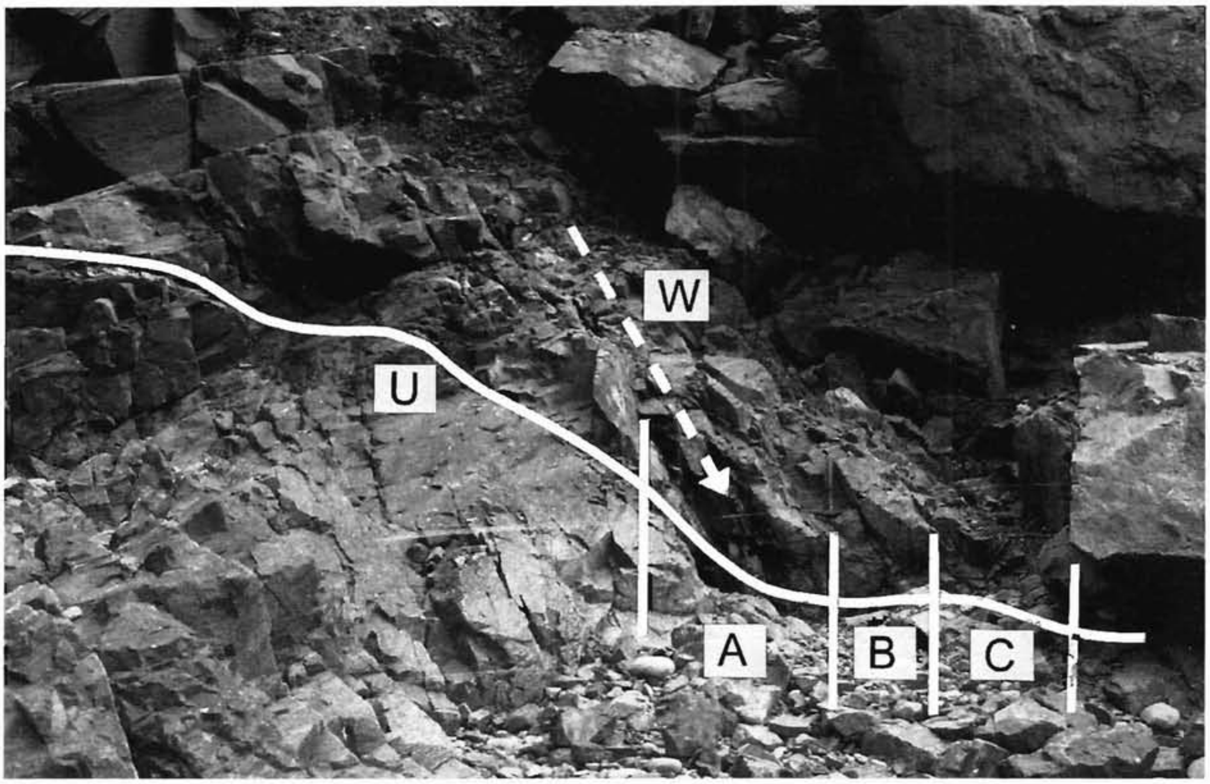

**FIGURE 3.** Exposure at Loe Warren zawn (photographed June 1994, facing south). The hammer is 33 cm long. The dashed line W indicates the flow of water over the exposure and the general strike of fractures in the rock. Line U marks approximately the line of enhanced radioactivity. A, B, C are the three zones of mineralisation discussed in the text; A is the SE zone, B the central zone, and C the NW (uraninite) zone.

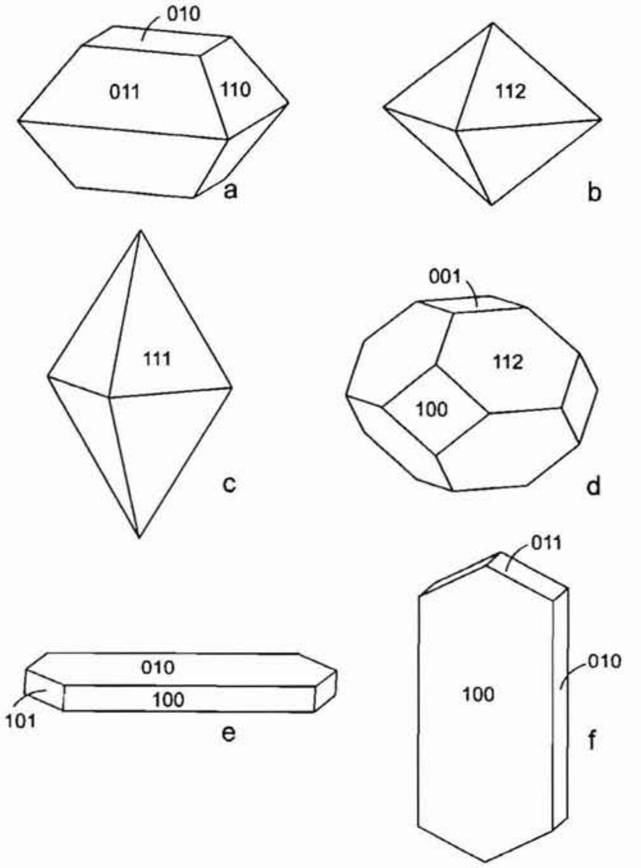

**FIGURE 4.** Crystal habits of: **(a)** atacamite; **(b, c, d)** cumengeite; **(e)** widenmannite; **(f)** wölsendorfite; from Loe Warren zawn.

## BOLTWOODITE, $(H_3O)K(UO_2)SiO_4$

Boltwoodite occurs at the NW end of the Loe Warren exposure lining joint planes in the rock with radiating and spherulitic crusts of bright greenish-yellow, sharply terminated, acicular crystals (Fig. 5a). Crystals may reach 0.05 mm in length, but are rarely more than 0.001 mm wide.

Since its original description from the Delta mine, Utah, USA (Frondel and Ito, 1956), boltwoodite has been found at many localities worldwide in a variety of geological environments. Boltwoodite is often found filling joint planes in host rock some distance from primary uraninite, or in the silicate zone of alteration surrounding the zone of hydrated uranyl oxides. Honea (1961) describes a number of locations. This is the second occurrence of boltwoodite in the British Isles, the first being at Needle's Eye, near Dalbeattie, south Scotland (Miller and Taylor, 1966), where it occurred with zeunerite through *in situ* alteration of pitchblende.

At Loe Warren zawn boltwoodite is associated with chalcocite and uraninite; the richer patches were found immediately below and around a nodule of uraninite. Boltwoodite is commonly found with rutherfordine, while vandendriesscheite and zeunerite also occur on several specimens. Boltwoodite appears to be the last formed of these minerals. Native copper and cuprite were noted rarely, as were baryte, connellite, kasolite, trögerite, and an unidentified calcium rare-earth uranyl carbonate hydrate. An isolated patch of greenish-yellow microcrystalline boltwoodite was found ~6 m NE of the main exposure, associated with a thin crust of uraninite lining joints in hornfels. Roberts *et al.* (1990) reported that most specimens of boltwoodite fluoresce a dull green under both short- and long-wave UV light, but none of the Loe Warren specimens exhibits any fluorescence.

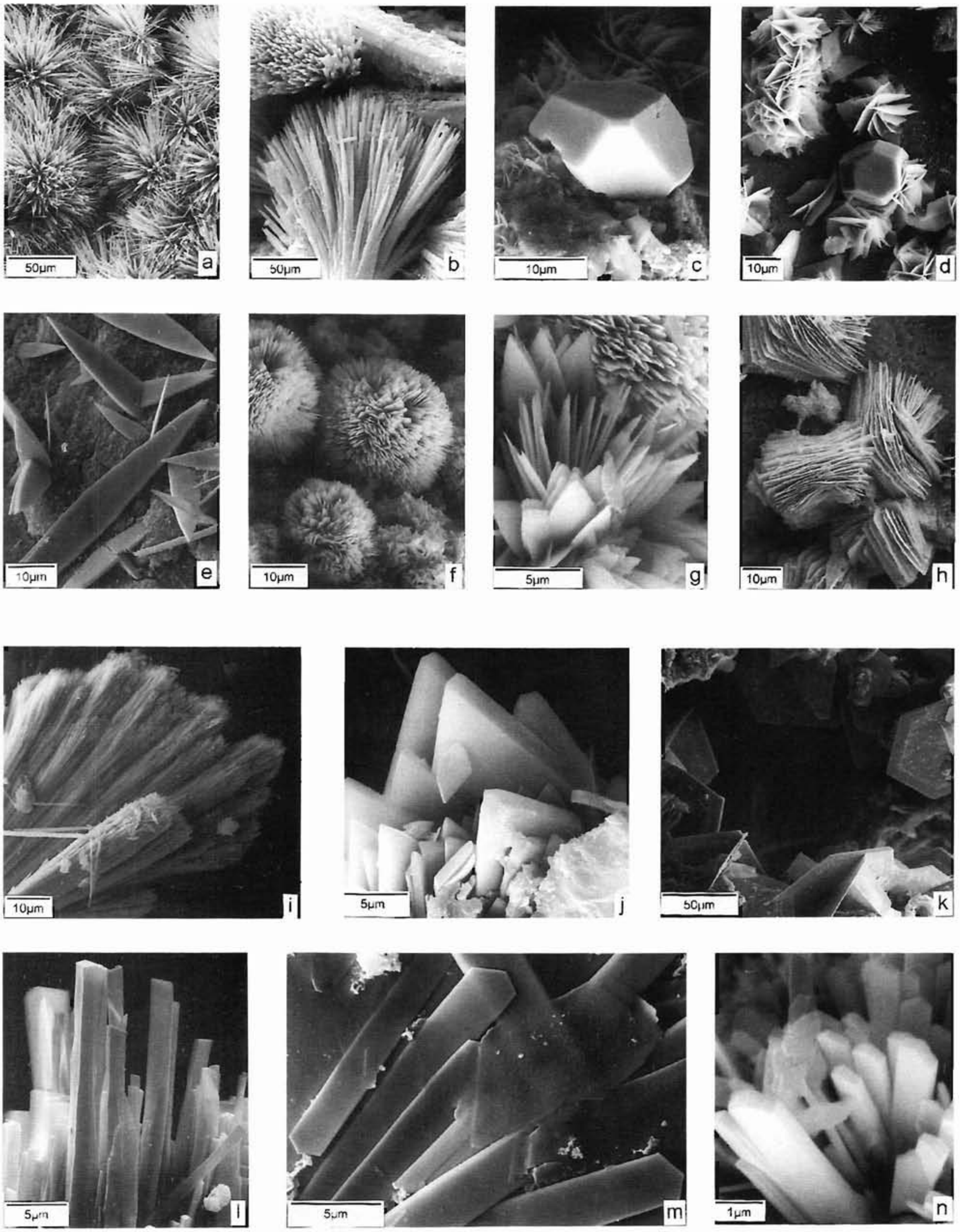

**FIGURE 5.** SEM photographs of minerals from Loe Warren zawn. **(a)** Boltwoodite, botryoidal crust of acicular crystals. **(b)** Connellite, divergent sprays on tabular arsenatian torbernite. **(c, d)** Cumengeite, with 'desert-rose' aggregates of flaky hexagonal crystals of an unknown basic lead uranyl carbonate; also a 'bow-tie' of dewindtite crystals (d, top centre). **(e)** Dewindtite of typical 'canoe-shaped' habit. **(f, g)** Kasolite, spheroidal aggregates of petaline crystals. **(h)** Lavendulan, typical 'books' of thin squarish plates. **(i)** Rutherfordine, spray of crystals. **(j)** Unidentified calcium rare-earth uranyl carbonate hydrate, tabular rhombic crystals. **(k)** Unknown basic lead uranyl carbonate, hexagonal crystals on cellular matrix; some carry thin laths of widenmannite. **(l)** Trögerite, flattened spray of acicular crystals (from NW end of exposure). **(m)** Widenmannite, crystals lying flat on the matrix. **(n)** Wölsendorfite crystals.

### BOTALLACKITE, $Cu_2Cl(OH)_3$

This species is scarce and occurs in the Cu-rich central region of the exposure, forming characteristic light bluish-green thin rectangular plates and flaky booklets. It is found with connellite and, on one specimen at least, is the earlier of the two minerals. It seems quite likely that the formation of the chloride minerals may be episodic, taking place when conditions are favourable, i.e. when the exposure receives considerable amounts of sea-spray. Botallackite is also found with, and on, kasolite.

### CALCITE, $CaCO_3$

Small anhedral patches of calcite occur within the hornfels matrix at the NW end of the exposure. EDX analysis shows a small amount of substitution by Mn. Chalcocite, boltwoodite, uraninite, malachite, and an unidentified calcium rare-earth uranyl carbonate hydrate are associated with the calcite. A few small euhedral crystals of chalcocite are enclosed by calcite.

### CERUSSITE, $PbCO_3$

Cerussite is intimately associated with an unknown basic lead uranyl carbonate, malachite, and widenmannite as a minor component of crusts coating joint faces in the rock at the SE end of the exposure. It occurs as white to colourless very slender acicular crystals; as stouter prismatic crystals, sometimes forming cyclic twins on {110}; as tabular crystals; and as small cream-coloured anhedral lumps. It is frequently associated with kasolite.

### CHALCOCITE, $Cu_2S$

Chalcocite is the major copper-bearing mineral at Loe Warren zawn and occurs disseminated through the mineralised area and as swarms of tiny veinlets. Occasionally, the veinlets open into narrow vugs allowing the development of small subhedral to euhedral hexagonal tabular, rarely prismatic, crystals. A little chalcopyrite occurs with, and is often enclosed by, the chalcocite.

Owing to its ubiquity, chalcocite is associated with virtually all the minerals found at Loe Warren zawn. Of particular interest is the very close association between dewindtite and chalcocite. Torbernite or arsenatian torbernite is also frequently associated closely with chalcocite. The reason for the close association between dewindtite and chalcocite is not clear; there may be some degree of coincidence in that the vugs containing chalcocite crystals are the only sufficiently open spaces within the matrix to allow development of dewindtite and torbernite crystals. Alternatively, reduction of mineralising fluids by chalcocite (a Cu(I) compound) may trigger precipitation of these uranyl phosphates from solution.

In the NW end of the exposure, chalcocite veinlets cut through massive and colloform uraninite.

### CHALCOPYRITE, $CuFeS_2$

Chalcopyrite occurs as anhedral patches, usually intergrown with chalcocite.

### CONNELLITE, $Cu_{19}Cl_4SO_4(OH)_{32}.3H_2O$

Connellite occurs mainly around the central region of the exposure, in the area rich in copper mineralisation, where it forms beautiful dark blue compact spherules, open spherules and, rarely, sprays of acicular crystals (Fig. 5b). It also forms botryoidal crusts which merge with amorphous copper silicate coatings. Associated minerals include chalcocite, zeunerite and zeunerite-torbernite intermediates, cerussite, lavendulan, and botallackite. Connellite is found with kasolite on two specimens and with dewindtite on just one.

Formation of connellite requires the relative absence of anions other than chloride with just traces of sulphate (Williams, 1990). The virtual absence of other secondary sulphates implies that sulphate ions are indeed scarce in the exposure. Connellite is found near the surface of the exposure and is one of the last minerals to have formed.

### COPPER, Cu

Anhedral flakes of native copper were noted on a few specimens from the NW end of the exposure, associated with zeunerite, boltwoodite, and cuprite; rutherfordine occurs on the same specimens, but not closely associated with the copper.

### CUMENGEITE, $Cu_{20}Pb_{21}Cl_{42}(OH)_{40}$

First reported in Britain at Newporth Beach, near Falmouth, Cornwall (Dean, 1982; Dean *et al.*, 1983), cumengeite has since been found at a number of Cornish localities, including Daymer Bay, near Polzeath; Trerubies Cove, near Delabole (see Ryback and Tandy, 1992); and notably at Gunver Head, near Padstow. The occurrence at Loe Warren appears to be the first in the West Penwith area of Cornwall.

Cumengeite is restricted to the SE end of the Loe Warren exposure and, although reasonably common, may easily be overlooked on account of the minute size of the crystals (typically 0.01—0.02 mm). The habit is dipyramidal {111} or {112}, or dipyramidal plus prism {010} and basal pinacoid {001} (Figs 4b,c,d and 5c,d). Crystals are transparent, of vitreous lustre and a deep, very slightly greenish, blue colour. The habit and appearance is very similar to that at Gunver Head, although at the latter locality cumengeite also occurs as opaque pale blue crystals and crusts.

At Loe Warren, cumengeite is of recent formation; this seems also to be the case at Newporth Beach (Dean, 1982) and at Gunver Head. Associated minerals include an unknown basic lead uranyl carbonate, cerussite, malachite, widenmannite, dewindtite, torbernite, and kasolite. At high tide, the locations for cumengeite at Newporth Beach and Daymer Bay are covered by sea-water, the action of which on galena or other lead minerals is presumed to give rise to the cumengeite. Both the Loe Warren exposure and that at Gunver Head lie well above the high water mark, but within reach of splash and spray in rough weather.

### CUPRITE, $Cu_2O$

A few red anhedral grains of cuprite were observed with boltwoodite and rutherfordine in very tight cracks in the host rock.

### DEWINDTITE, $Pb(UO_2)_3(PO_4)_2(OH)_2.3H_2O$

Dewindtite and renardite are hydrated lead uranyl phosphates with virtually identical X-ray powder patterns, but different formulae. Some confusion appears to surround the status of these minerals. In a study of synthetic lead uranyl phosphates, Ross (1956) showed that dewindtite was actually a mixture of lead autunite and renardite, and recommended its discretitadion. However, the name dewindtite has precedence and according to Clark (1993) the renardite component has now reverted to this name. However, dewindtite and renardite are treated as separate species in many recent references. In her studies, Ross (1956) showed the existence of a series extending from $Pb(UO_2)_4(PO_4)_2(OH)_4.nH_2O$ to $Pb_3(UO_2)_2(PO_4)_2(OH)_4.nH_2O$. Formation of specific members of the series depended on lead concentration in the mineralising solutions. The existence of such a series may explain variable analyses for dewindtite-like minerals reported in the literature (see Frondel and Cuttitta, 1954; Hogarth and Nuffield, 1954; Frondel, 1958).

At Loe Warren, dewindtite is always closely associated with chalcocite, the latter often forming small crystals. Dewindtite occurs as lemon-yellow, canoe-shaped, doubly-terminated, tapering laths, often forming tufts and divergent groups (Fig. 5e); also as spherulitic aggregates of similarly shaped, but more ragged, crystals showing evidence of subparallel growth, and as pale yellow powdery deposits on chalcocite. Besides chalcocite, dewindtite is frequently associated with kasolite and torbernite or intermediate members of the torbernite-zeunerite series, and sometimes with widenmannite, cumengeite, cerussite, botallackite, connellite and an unknown basic lead uranyl carbonate. Dewindtite appears to be later than torbernite-zeunerite and kasolite, but earlier than cumengeite, cerussite and botallackite. This is the first record of dewindtite from the British Isles.

### KASOLITE, $Pb(UO_2)SiO_4.H_2O$

Kasolite has been known from Loe Warren zawn for some time; specimens were originally found by A.C. Sparrow and C.H. Scheding in 1988 and identified at Oxford University Museum. Kasolite has also been identified at South Terras mine, St Stephen, Cornwall (R.S.W. Braithwaite specimen, NHM X-ray film 12846), associated with torbernite/metatorbernite and a phosphuranylite group mineral (Braithwaite, *personal communication*). The first British Isles occurrence of kasolite was at Tyndrum, Perthshire, Scotland, where it occurred with pitchblende (Harrison, 1957), and it has subsequently been found at "Chiapaval" [Chaipaval], South Harris (von Knorring and Dearnley, 1960) and at Helmsdale, Sutherland (Bowie *et al.*, 1970).

Kasolite occurs mainly towards the SE end of the Loe Warren exposure, lining joint planes in the rock with compact botryoidal crusts, fibrous crusts, and areas of discrete and intergrown compact or open spherules of radiating lath-like or petaline crystals (Fig. 5f,g). The colour is rather variable, from pale whitish-yellow through canary-yellow to dark yellow and orangy-yellow. Kasolite is frequently intergrown with aggregates and crusts of zeunerite-torbernite crystals. Tiny euhedral cumengeite is often seen with and on kasolite. The matrix usually contains disseminated chalcocite. Other associated minerals include (in order of frequency) dewindtite, cerussite, amorphous copper silicate, malachite, botallackite, connellite, wölsendorfite, and uraninite. Kasolite was originally found in oxidised parts of uraninite veins at Kasolo in the Shaba region of Zaire. Associated minerals there included torbernite and dewindtite (Frondel, 1958). It was formed by the action of meteoric fluids on earlier-formed secondary uranium minerals.

### LAVENDULAN, $NaCaCu_5(AsO_4)_4Cl.5H_2O$

Lavendulan is another rare chloride mineral which, like cumengeite, has been found at several localities in recent years. Lavendulan was first found in Britain in 1968 in uraniferous fissure veins near Needle's Eye, Dalbeattie, south Scotland, where it occurred as pale blue spherical aggregates up to 0.1 mm in size (Braithwaite and Knight, 1990). Lavendulan ("freirinite") was also reported by Harrison (1975) as sky-blue powdery deposits in concretions from Budleigh Salterton, Devon. Lavendulan has subsequently been found at a number of localities in Cornwall in different geological environments.

Lavendulan is very rare at Loe Warren zawn, having been observed on only one specimen from the middle part of the exposure. It forms sky-blue sheafy aggregates of extremely thin squarish plates (Fig. 5h). Lavendulan is a late mineral and is associated with zeunerite, amorphous copper silicate, and connellite.

### MALACHITE, $Cu_2CO_3(OH)_2$

Malachite occurs with other carbonate minerals at the SE end of the exposure and is also found sparingly with boltwoodite at the NW end. Malachite forms small patches and clumps of acicular crystals, and also occurs as tiny green blobs amongst the crusts of unknown basic lead uranyl carbonate and associated species.

### PYRITE, $FeS_2$

Pyrite occurs sparingly in veinlets, very rarely as tiny octahedra.

### RUTHERFORDINE, $(UO_2)CO_3$

Rutherfordine forms crusts, spherulitic aggregates and fan-shaped groups of lath-like crystals up to 0.1—0.2 mm long (Fig. 5i). The aggregates are dull green, rarely brown, and have a waxy lustre. Rutherfordine is most frequently associated with chalcocite and uraninite at the NW end of the exposure and appears to have formed in very tight cracks within the host rock. Boltwoodite is also a common associate, forming beautiful velvety crusts and spherules in more open vugs and cracks. Patches of dark yellow vandendriesscheite and occasional cuprite are present on a few specimens. Two specimens also contained trögerite adjacent to flattened sprays of rutherfordine in a very tight crack.

James (1945) records rutherfordine from South Terras mine, St Stephen, Cornwall, describing it as a yellow powder, but giving no other details. The occurrence has never been confirmed and, because detailed descriptions of rutherfordine did not appear until some years later (Frondel and Meyrowicz, 1956; Christ *et al.*, 1955; Clark and Christ, 1956), must be regarded as questionable. More recently, rutherfordine has been identified in schists at Boherkyle, near Graiguenamanagh, Co. Kilkenny, Republic of Ireland (Deevy, 1982). The occurrence of rutherfordine at Loe Warren zawn is the first authenticated in Britain.

### TORBERNITE, $Cu(UO_2)_2(PO_4)_2.10H_2O$

Extensive solid solution exists between torbernite and zeunerite, with substitution of $(AsO_4)^{3-}$ for $(PO_4)^{3-}$ depending largely on their relative abundance in the mineralising fluids. EDX analysis shows a range of compositions at Loe Warren, from essentially end-member torbernite through a range of intermediates to essentially end-member zeunerite. Torbernite and arsenatian torbernite appear more common towards the SE end of the exposure, while zeunerite or phosphatian zeunerite dominate at the uraninite-rich NW end.

Torbernite-zeunerite forms thin crusts of green rectangular tablets and also discrete spheroidal aggregates of tabular crystals. Pyramidal forms are rarely prominently developed. Members of the torbernite-zeunerite series are widely distributed through the main exposure, but are most commonly found with kasolite, dewindtite and associated species. Arsenatian torbernite is also found as a crust of thin transparent plates with kasolite and widenmannite in an isolated pocket of supergene uranium mineralisation about 3 m NE of the main exposure.

### TRÖGERITE, $(H_3O)_2(UO_2)_2(AsO_4)_2.6H_2O$

Trögerite occurs as flattened radiating groups of bright yellowish-green, transparent, acicular crystals on two specimens from the NW end of the exposure. Semi-quantitative EDX analysis and IR spectroscopy showed the mineral to be a hydrated uranyl arsenate. Small amounts of Fe, Mn, Cu and Si were observed in some analyses. Definitive data for trögerite appear to be lacking, but the X-ray powder pattern of the Loe Warren sample (NHM film 9628F) is similar to those of other specimens of trögerite from the NHM collections, although the patterns are somewhat variable. As with other autunite group minerals, variations in the state of hydration and chemical substitutions affect the powder pattern. Moreover, trögerite is known to undergo a phase transformation at room temperature (de Benyacar and de Abeledo, 1974).

The trögerite was found in very tight cracks in uraninite-veined, chlorite-rich matrix, associated with rutherfordine and cuprite; a little boltwoodite also occurred round the edge of one specimen. The crystals are prismatic, considerably elongated along one axis, and have square or rectangular cross-section. Some crystals are terminated by a plane orthogonal to the axis of elongation, others by a prism form with a large apical angle (Fig. 5l).

Trögerite from South Terras mine, St Stephen, was listed by Robson (1954) in his amendements to the 'Cornish Mineral Index'. However, no reference or other information was given, and the occurrence has not been confirmed, nor repeated in later publications. More recently, trögerite has been reported coating microscopic inclusions of pitchblende and filling fractures in bitumen from the Dalbeattie uranium locality, south Scotland (Eakin and Gize, 1992).

### UNIDENTIFIED CALCIUM RARE-EARTH URANYL CARBONATE HYDRATE

One specimen from the NW end of the exposure showed a number of tiny stellate groups of bright yellow tabular crystals. EDX and IR analysis showed the mineral to be a heavily hydrated calcium rare-earth uranyl carbonate. The rare earths were mainly Ce and Nd, with minor amounts of La. The mineral also occurred as a greenish-yellow crust showing little crystal form. The X-ray powder pattern (NHM film 9921F) was rather weak, but did not match known species of similar chemical composition. It is possible that the mineral is a partial metamict.

The crystals are tabular, generally with a rhombic outline (Fig. 5j), and form flattened, radiating aggregates. The matrix is hornfels containing patches of uraninite and calcite. The unidentified mineral occurred adjacent to a calcite veinlet; small euhedral crystals of chalcocite were embedded in the calcite. Thin crusts of microcrystalline boltwoodite covered parts of the specimen, and acicular malachite was also present. Some of the boltwoodite occurred on the malachite, indicating that malachite was the earlier formed mineral.

### UNKNOWN BASIC LEAD URANYL CARBONATE

An unknown basic lead uranyl carbonate is quite common at the SE end of the exposure, coating joint planes in the host rock with thin crusts composed of rosettes or spherulitic 'desert rose' aggregates of thin white translucent hexagonal plates up to 0.1 mm across (Fig. 5c,d,k). The mineral resembles hydrocerussite in habit but its X-ray powder pattern (NHM films 9638F and 9640F) does not match that of any known species. The infrared spectrum resembles that of widenmannite. EDX analysis of a number of samples consistently shows the presence of uranium at a Pb:U ratio of ~4:1.

The overall colour of the crusts is variable, including white, yellowish or greenish because of intimate association with other species, but individual crystals of the unknown mineral are colourless or white, or sometimes pale greenish-yellow when aggregated. Associated minerals include kasolite, cerussite, malachite, zeunerite-torbernite, cumengeite, widenmannite, dewindtite, botallackite and connellite. The unknown mineral also forms larger hexagonal plates up to ~0.2 mm across, encrusting cellular matrix together with many of the associated species listed above. The crystals show pyramidal modifications and exhibit subparallel growth and growth zoning (Fig. 5k).

### URANINITE, $UO_2$

Uraninite occurs as the colloform 'pitchblende' variety, mainly at the NW end of the exposure, although minor amounts may be found throughout the main exposure and along the line of enhanced radioactivity towards the NE. A particularly rich spheroidal mass of pitchblende occurred at the NW end of the exposure, surrounded by rather more disseminated patches and veinlets. The uraninite patch itself was largely devoid of secondary mineralisation, but joint planes in the rock around and particularly below its periphery were encrusted with boltwoodite and, less commonly, rutherfordine. Other associated minerals include vandendriesscheite, zeunerite, and rare wölsendorfite, copper and cuprite. The uraninite is frequently veined by stringers of chalcocite. Such intergrowths of uraninite with copper sulphides are typical of uranium occurrences around the Land's End granite (Ball *et al.*, 1982).

### VANDENDRIESSCHEITE, $PbU_7O_{22}.12H_2O$

Vandendriesscheite is rare at Loe Warren, occurring with boltwoodite and rutherfordine at the uraninite-rich NW end of the exposure where it forms thin dark yellow crusty patches on matrix rich in uraninite and chalcocite. It shows little obvious crystal form. The X-ray powder pattern showed relatively broad lines indicative of structural disorder or small particle size, or both. The pattern also showed a high background suggesting the presence of amorphous material. A number of other yellow hydrous uranium oxide or lead uranium oxide crusts, particularly those occurring as alteration rinds round uraninite, were examined by XRD and proved to be virtually amorphous. The poor crystallinity of minerals occurring in uraninite alteration rinds is well known and has hindered the study of such minerals in the past.

This is the second reported occurrence of vandendriesscheite in the British Isles, the first being at Dalbeattie, south Scotland, where it occurred as shiny orange spherical aggregates <0.1 mm across, with uraninite, uranophane and schoepite (Braithwaite and Knight, 1990).

### WIDENMANNITE, $Pb_2UO_2(CO_3)_3$

Widenmannite is an extremely rare mineral, previously known only from its type locality at the Michael mine, near Lahr, Black Forest, Germany (Walenta, 1976; Walenta and Wimmenauer, 1961). Widenmannite occurs at the SE end of the Loe Warren exposure as minute transparent to translucent lath-like crystals (Elton and Hooper, *in press*). It also occurs within shining pale yellow, white or greenish crusts which are composed of a rather variable and intimate mixture of species and coat joint planes in the rock. A large part of these crusts is an unknown basic lead uranyl carbonate occurring as hexagonal tabular crystals; other species present include cerussite, malachite, torbernite and minor cumengeite, kasolite and dewindtite.

Widenmannite forms lath-like crystals which are tabular {010}, considerably elongated along [001], and show the forms {100} and {101} (Fig. 4e). This habit is identical with that described by Walenta (1976). Widenmannite laths usually form randomly oriented mats or occur singly. On a few specimens the laths form larger stellate or divergent groups. The laths are generally less than 0.01 mm wide but may be up to 0.1 mm long (Fig. 5m). Individual laths are typically colourless; only when they are grouped together is the pale, slightly greenish, yellow colour perceivable.

One small patch of widenmannite occurred with arsenatian torbernite and kasolite on a matrix of dark biotite (containing a little Ti substituting for Fe) about 3 m NE of the main exposure, in a relatively dry area along the line of enhanced radioactivity (Fig. 3). The matrix contained tiny grains of fluorapatite.

At Michael mine, widenmannite occurred with cerussite, altered galena and kasolite. The oxidised zone there is rich in arsenates and the lead uranyl arsenates hügelite and hallimondite were also found with the widenmannite.

### WÖLSENDORFITE, $(Pb,Ca)U_2O_7.2H_2O$

Wölsendorfite is a relatively rare mineral at Loe Warren. It forms thin orange fibrous crusts composed of radiating prismatic or lath-like crystals (Fig. 5n). The crystals are generally tiny, up to ~0.01 mm long and just 0.001 mm wide. Using the unit cell of Protas (1957), rudimentary interfacial angle measurements on electron micrographs indicate that the crystals are elongated on [001] and flattened on [100], with forms {100}, {010}, and {011} (Fig. 4f).

One specimen was found at the NW end of the exposure, associated with boltwoodite. The others were found towards the SE end where the wölsendorfite was associated with kasolite, dewindtite, zeunerite and pyrite. On one specimen, crystals of zeunerite are clustered round the edges of the wölsendorfite crust. The paragenesis of the wölsendorfite is rather difficult to assess for it tends to occur beside, rather than on or under, its associated species. The appearance of some specimens strongly suggests sequential deposition by a retreating front of mineralising fluid.

This is the first reported occurrence of wölsendorfite in the British Isles. Its identity was confirmed by XRD (NHM film 9354F).

### ZEUNERITE, $Cu(UO_2)_2(AsO_4)_2.16H_2O$

Zeunerite occurs as crusts and spheroidal aggregates of small tabular crystals mainly towards the NW end of the exposure. Intermediate members of the zeunerite-torbernite series are far more frequent than end-members (see under torbernite for further comments). The source of arsenate ions at Loe Warren is not clear. No primary arsenic-bearing minerals have been identified, but it is possible that very small amounts of arsenopyrite may be disseminated with the other sulphides in the mineralised area.

## DISCUSSION

The paragenetic sequence for uranium species is not particularly well defined — much of the supergene mineralisation appears to be essentially contemporaneous, or in some cases episodic. As mentioned in the case of wölsendorfite, the appearance of some specimens strongly suggests sequential deposition by a retreating front of mineralising fluid. Fig. 6 shows a suggested paragenetic sequence for the formation of supergene species at Loe Warren zawn. Fig. 7 summarises the relationships between uranium minerals, giving an indication of both frequency of association and relative abundance within the exposure.

The paragenesis suggests the existence of four mineral assemblages. The associations with rutherfordine and uraninite at the NW end of the exposure form a distinct group mineralogically and spatially. Within the central and SE zones, three assemblages may be distinguished: silicates—phosphates—arsenates (kasolite, torbernite/zeunerite, dewindtite); carbonates (widenmannite, unknown basic lead uranyl carbonate, cerussite, malachite); and chlorides (cumengeite, etc.).

The formation of the chlorides cumengeite, atacamite, botallackite, connellite, and lavendulan is the easiest both to explain and to place in sequence. These minerals occur on the surface of the exposure in relatively low abundance and are clearly of recent formation. The role of seawater in the formation of some of these species is well known (e.g. Dean, 1982; Dean *et al.*, 1983; Williams, 1990). The mineralised area at Loe Warren zawn is never covered by the tide, but is within reach of sea spray and splash. It seems likely that the chloride mineralisation is episodic, occurring when conditions are favourable.

Deliens (1977b; see also Smith, 1984) describes the paragenesis of oxidised uranium minerals at Shinkolobwe, Zaire, showing a close relation of vandendriesscheite and rutherfordine to uraninite and to each other; and also of wölsendorfite to uraninite. These species were formed by direct alteration of uraninite. However, curite was the major precursor of many phosphates and silicates at Shinkolobwe, including kasolite which, in turn, is closely associated with torbernite and dewindtite. The latter phosphate-silicate group of associated species does not overlap significantly with the rutherfordine—vandendriesscheite—uraninite group of associations. This grouping is reminiscent of those at Loe Warren, although there is no obvious precursor for the SE zone miner-

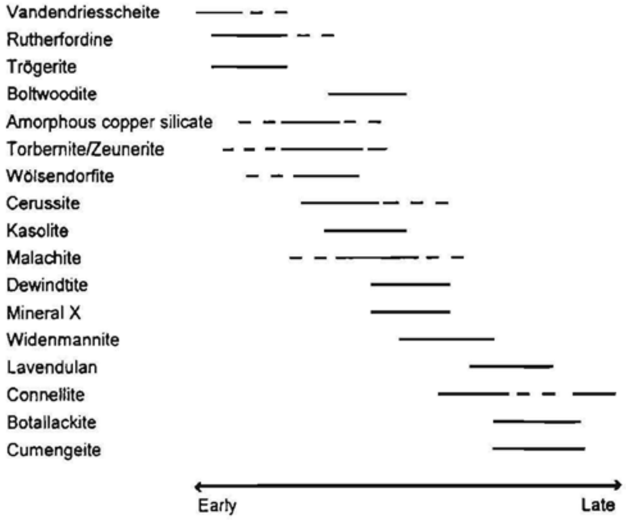

**FIGURE 6.** Paragenetic sequence for supergene species at Loe Warren zawn. The sequence is approximate owing to ambiguities in some associations. 'Mineral X' is the unknown basic lead uranyl carbonate.

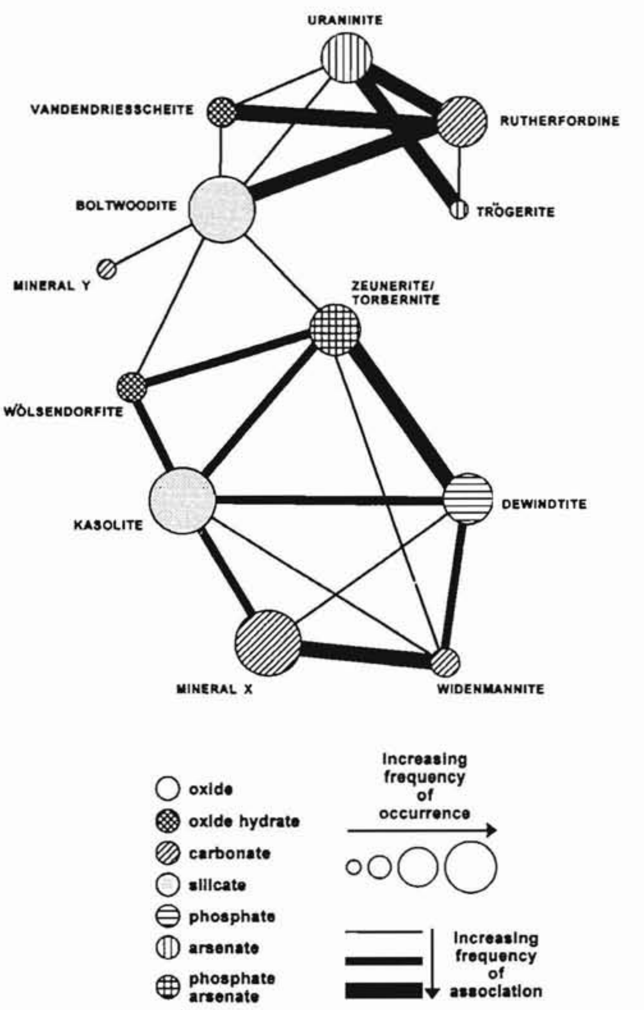

FIGURE 7. Associations between uranium species at Loe Warren zawn. The diagram attempts to illustrate frequency of association and relative abundance of individual minerals based on collected samples. 'Mineral X' is the unknown basic lead uranyl carbonate, 'Mineral Y' the unidentified calcium rare-earth uranyl carbonate hydrate.

als at Loe Warren. Widenmannite and the unknown basic lead uranyl carbonate appear to be the last-formed uranium species, and the uranium contained in them may have been derived from earlier secondary uranium species such as kasolite or torbernite.

Although both uranium and copper hypogene minerals occur in the Loe Warren exposure, no hypogene lead mineral has been identified. The age of uraninite in the exposure has not been dated, but that from the nearby Wheal Edward Cliff lode was given as 58±3 Myr by Pockley (1964). The young age of this uraninite has been taken as evidence of late-stage remobilisation of uraninite deposited earlier, and reprecipitation in fractures associated with Tertiary tectonics (Ball *et al.*, 1982). During remobilisation, some or all of the radiogenic lead would have been separated from the uraninite and redeposited elsewhere. This process has been recognised in some European deposits (Pockley, 1964). Although no significant amounts of galena were reported from Wheal Owles, late cross-veins in the region sometimes carried small amounts of argentiferous galena (Dines, 1956), presumably formed, at least in part, from radiogenic lead liberated during remobilisation. At Shinkolobwe, all of the lead is radiogenic; analysis of uraninite showed 7.02 wt % PbO (Gauthier *et al.*, 1989). Removal of this lead during supergene alteration of the uraninite produced the abundance and wide variety of Pb—U and Pb species in that deposit.

Assuming that uraninite at Loe Warren is of similar age to that at Wheal Edward, a little under 1% of the U would be expected to have been converted into Pb since remobilisation. If the uraninite is older (i.e. formed during the main stage of mineralisation) it could contain up to 3% of radiogenic Pb. Removal of part of this lead by supergene alteration of the uraninite seems a likely explanation for the presence of Pb—U and Pb species at Loe Warren, although it does not explain their distribution. It is also possible that a small amount of galena disseminated through the rocks of the exposure has been completely altered to supergene products.

Uranium has a relatively high geochemical mobility and readily forms carbonate and phosphate complexes in groundwater systems (Dongarra, 1984). It is quite possible that the species observed within the SE zone have been formed from components leached from higher up the cliff. Water samples collected from the location are neutral to slightly alkaline, consistent with the known conditions of formation of dewindtite (Ross, 1956).

Representative specimens of dewindtite, kasolite, widenmannite, wölsendorfite, vandendriesscheite, rutherfordine, the unknown basic lead uranyl carbonate, and associated species have been deposited at the Natural History Museum, London (NHM), and the University Museum, Oxford. Specimens of trögerite and unidentified calcium rare-earth uranyl carbonate hydrate are deposited at the NHM.

## ACKNOWLEDGEMENTS

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# SILICA-RICH EDINGTONITE AND ASSOCIATED MINERALS FROM LOANHEAD QUARRY, BEITH, STRATHCLYDE — A NEW SCOTTISH LOCALITY*

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**After a lapse of over 100 years, edingtonite has been rediscovered in Scotland at a new locality, Loanhead quarry, Beith, Strathclyde. It has an unusually high Si/Al ratio (3.7) and is associated with harmotome, natrolite, thomsonite, analcime, prehnite, baryte, calcite, hematite and, rarely, diaspore, native silver and ilmenite. The inter-relationship of these species is described and a paragenetic sequence is proposed.**

## INTRODUCTION

Edingtonite, $BaAl_2Si_3O_{10}.4H_2O$, is a rare barium zeolite first found in 1823 as a single specimen at Duntiglenan (National Grid Reference NS 489 735), 2.5 km ENE of Old Kilpatrick, Dunbartonshire, Strathclyde Region. It was described by Haidinger (1825) as closely associated with thomsonite, and named for the finder, Thomas Edington of the Phoenix Ironworks, Glasgow. Subsequently it was recorded from other nearby localities: two small quarries (NS 470 735 and 472 734) about 1 km NE of Old Kilpatrick; at Bell's quarry and the adjacent Bowling quarry (NS 447 738) about 2 km WNW of Old Kilpatrick; and in the Kilpatrick Hills about 8 km to the north (e.g. Greg and Lettsom, 1858; Heddle, 1901). According to Heddle (1855) it was always associated with baryte, harmotome and prehnite, but not with thomsonite.

There has been no record of edingtonite in the British Isles for well over 100 years until two recent finds, one at Squilver quarry, Shropshire, England (Hubbard and Enamy, 1993); the other at Loanhead quarry, Beith, Strathclyde Region, Scotland (this study). The mineralogy of Loanhead quarry has been described by Meikle (1989) who noted the occurrence of harmotome accompanying thomsonite and analcime. The edingtonite is closely associated with harmotome, thomsonite, natrolite, and very rare diaspore.

Loanhead quarry (NS 363 557, 2 km NE of Beith) works highly altered porphyritic basaltic lavas of the Clyde Plateau which are of Lower Carboniferous (Dinantian) age and thus contemporaries of the andesitic lavas at the type locality for edingtonite 20 km away. Significantly, a tholeiitic Tertiary dyke 30 m wide trends NW—SE across the quarry, relatively close to the site of the occurrences now recorded.

## EDINGTONITE

Loose material collected in 1993 close to the quarry face after blasting contained edingtonite associated with harmotome. The matrix consisted primarily of well-developed thomsonite crystals, pink and white analcime crystals, with specular and micaceous hematite and botryoidal prehnite. Partial dissolution of the matrix has left colourless to white irregular platy aggregates, later confirmed as prehnite by XRD by Dr Alan Dyer (*personal communication*).

A year later one of us (J.G.T.) noted, on the quarry face ~30 m west of the Tertiary dyke, a near-vertical prehnite vein intersected at about 30° by a baryte vein. Harmotome and edingtonite occurred in a contact alteration zone 12—20 cm wide and ~50 cm long. The matrix of this zone was mainly massive prehnite intergrown with well-developed thomsonite and natrolite accompanied by baryte and calcite. Dissolution channels of prehnite and thomsonite/natrolite (Fig. 1) were similar to those found earlier in the loose material. Recrystallised natrolite, prehnite, baryte, and calcite occurred within or close to these channels, as did rare but well-formed small crystals of ilmenite and several other species described below.

Edingtonite is similar in both occurrences. It forms colourless, highly transparent, equant or rectangular, complex wedge-shaped crystals up to 3 × 3 × 1.5 mm in size, occurring singly, in groups, and frequently as intergrown aggregates up to about 10 × 8 mm (Fig. 2). Sometimes edingtonite crystals are perched on, or are penetrated by, small well-formed thomsonite needles, and occasionally they partially enclose harmotome. It also occurs as random single crystals (<1 mm), often on edge and partly in, or on, botryoidal prehnite. Tiny single crystals (<0.3 mm) and intergrown groups (<0.6 mm) of edingtonite with inclusions of hematite occur in close association with small rosettes of blood-red platy hematite, also on botryoidal prehnite. These edingtonite crystals appear to have nucleated directly on small masses of hematite.

**FIGURE 1.** Natrolite, harmotome and edingtonite in dissolution channels, Loanhead quarry. Field width 40 mm.

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*A preliminary note was presented at the Russell Society symposium on 'Mineralogy in the Field', Oxford, March 1995.

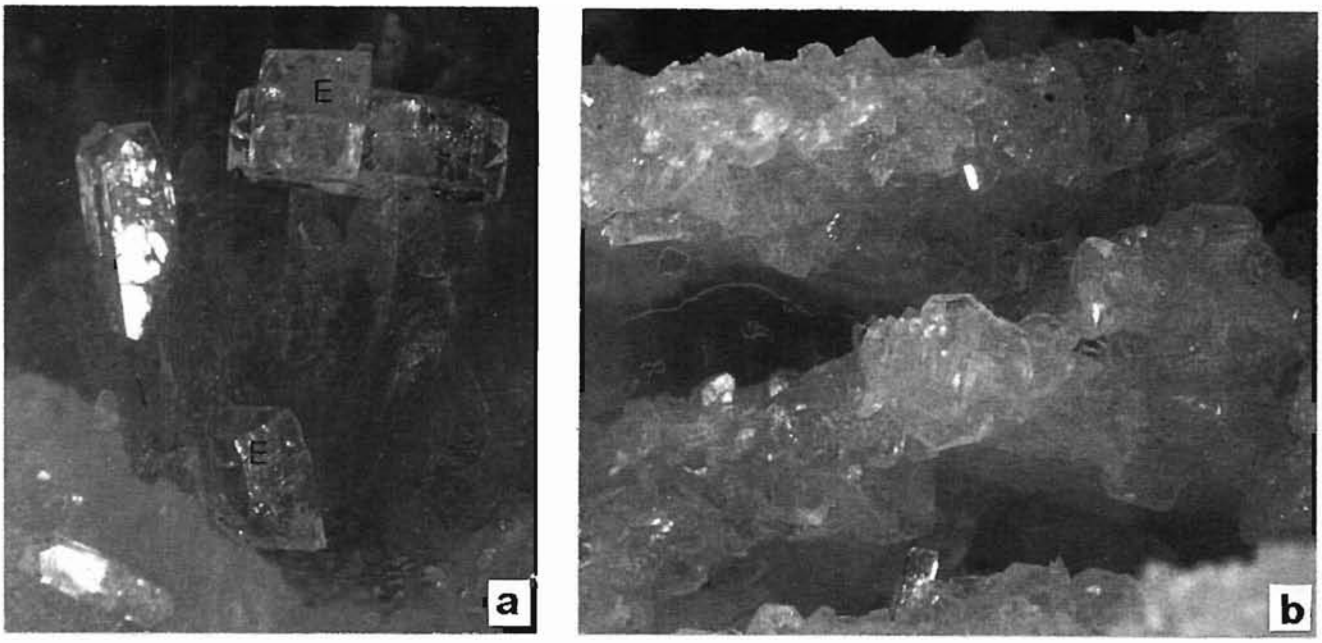

**FIGURE 2.** Edingtonite, Loanhead quarry. **(a)** Crystals (E) on harmotome twins. Field width 4.3 mm. **(b)** Aggregates of crystals. Field width 8 mm.

The habit of Loanhead edingtonite crystals resembles that figured by Greg and Lettsom (1858) and Heddle (1901), though rarely it occurs as phacoids with doubly-convex surfaces (Fig. 3), resembling those described by Goodchild (1903) on specimens in the Scottish Mineral Collection.

Despite the characteristic habit, some doubt as to identity was caused by examination of several of the complex wedge-shaped crystals which gave a biaxial positive rather than the usual biaxial negative sign of edingtonite (Gottardi and Galli, 1985). The species was, however, confirmed by XRD and EPMA. A probe analysis at the University of Wolverhampton, together with a thermogravimetric determination of water at the University of Salford, yielded the formula

$$(Ba_{1.01}Ca_{0.13})_{\Sigma 1.14}Al_{2.12}Si_{7.84}O_{20}\cdot 7.04H_2O$$

(Alan Dyer, *personal communication*). The Loanhead edingtonite is the most silica-rich yet discovered, with an Si/Al ratio of 3.7, which may account for its positive optical sign (Alan Dyer, *personal communication*). The unit cell composition of the Loanhead material is compared with published data for some other edingtonites in Table I. The Si/Al ratios in all other analysed edingtonites (Table I and analyses in Gottardi and Galli, 1985, and Tschernich, 1992) fall in the range 1.29—1.60.

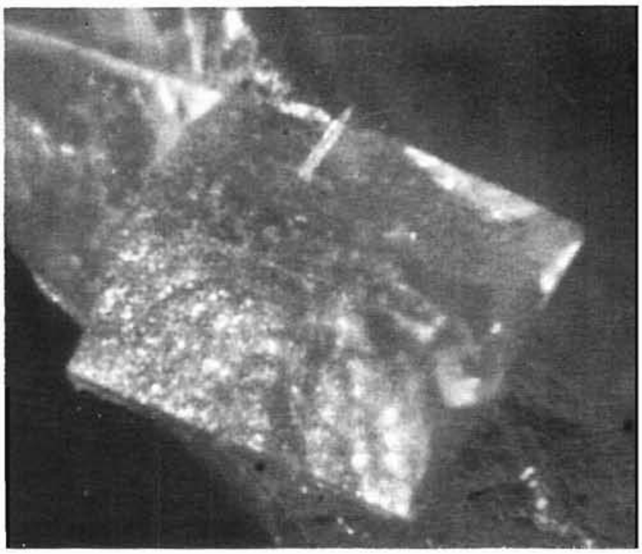

**FIGURE 3.** Edingtonite of phacoid habit, Loanhead quarry. Crystal size 0.47 × 0.43 mm.

## ASSOCIATED MINERALS

Harmotome, which is common and frequently closely associated with edingtonite, occurs as colourless, transparent, sharply-formed elongated crystals (<6 × 2 × 2 mm) displaying well-developed re-entrant angles similar to those of complex Marburg twins (Fig. 4a). Crystals without re-entrants, which seem comparable to Morvenite twins, are less frequent. Both types of crystal are often doubly-terminated and have been confirmed by XRD and XRF examination as harmotome. Additionally, it occurs very rarely as small (<0.6

**TABLE I.** Unit cell composition of edingtonite (atomic ratios on basis of 20 oxygens).

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Si | 7.84 | 5.99 | 5.94 | 5.94 | 5.96 |
| Al | 2.12 | 4.50 | 4.60 | 4.29 | 3.97 |
| Ba | 1.01 | 1.27 | 1.23 | 1.67 | 2.03 |
| Ca | 0.13 | — | — | trace | 0.02 |
| Na | — | — | — | trace | 0.01 |
| K | — | — | — | trace | 0.14 |
| $H_2O$ | 7.04 | 7.53 | 7.43 | 6.68 | 7.37 |
| Si/Al | 3.70 | 1.33 | 1.29 | 1.38 | 1.50 |

1—3 are electron microprobe analyses; $H_2O$ from thermogravimetry.

1. Loanhead quarry (this paper).
2. Squilver quarry, Shropshire (Hubbard and Enamy, 1993).
3. Ice River, British Columbia (Hubbard and Enamy, 1993).
4. Old Kilpatrick, Scotland (Heddle, 1855).
5. Böhlet, Sweden (Hey, 1934).

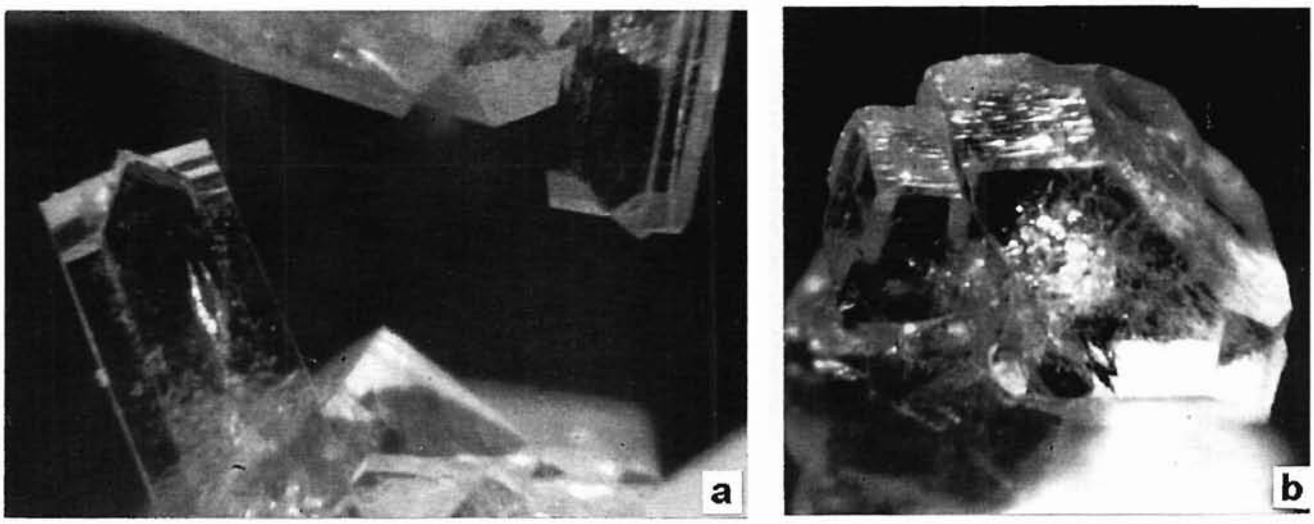

**FIGURE 4.** Harmotome, Loanhead quarry. **(a)** Marburg twins. The larger crystal is 0.9 mm long. **(b)** Perier twin. Crystal size 0.9 × 0.3 mm.

× 0.5 mm), equant, transparent, tetragonal-shaped crystals, also without re-entrants (Fig. 4b). However, striations which are present only on the termination faces are indicative of Perier twinning (Tschernich, 1992).

Diaspore occurred as two small aggregates in dissolution channels or cavities and in a similar manner to that previously described from nearby Hartfield Moss (Meikle, 1990). Native silver (confirmed by XRF) was found as flakes (<0.01 mm) and numerous wires (<0.8 × 0.005 mm) on and within botryoidal prehnite, adjacent to the diaspore. Ilmenite occurs rarely, as isolated small groups of three to four platy hexagonal crystals (<0.6 mm) in small cavities in botryoidal prehnite.

## DISCUSSION

Examination of the specimens shows that substantial dissolution of the principal matrix species has occurred, and there appear to be at least two suites of secondary minerals, particularly of the zeolites. Although there is no visible alteration of the intervening lavas, the close proximity of the Tertiary dyke probably gave rise to a localised hydrothermal system. The apparent recrystallisation of thomsonite, prehnite, calcite and hematite appears to confirm such an action.

Hydrothermal attack by a presumably silica-rich fluid undoubtedly occurred after the deposition of baryte and the formation of the analcime, prehnite, and thomsonite assemblages. Such a fluid would partially dissolve the prehnite and thomsonite/natrolite and also remove some baryte, resulting in the crystallisation of harmotome and later of edingtonite. The barium zeolites tend to be concentrated in or near the platy dissolution channels in the prehnite. The later natrolite, the diaspore, the late hematite, and perhaps the ilmenite, along with a second generation of prehnite, baryte and calcite, presumably followed from the same reaction.

The proposed paragenetic sequence is shown in Fig. 5. Exact temperature and pressure conditions for the crystallisation of harmotome are not known, although Tschernich (1992) considers a temperature range from 60 to 85°C to be representative for harmotome, while edingtonite is known to form in the late hydrothermal stages of volcanics. Analcime, thomsonite and natrolite tend to form at higher temperatures (Table II). The paragenetic sequence at Loanhead quarry accords with these trends. The rarity of edingtonite suggests that its formation requires an unusual combination of conditions.

Representative specimens from both occurrences have been presented to the Royal Museum of Scotland, Edinburgh (NMS G 1994), and to the Hunterian Museum, University of Glasgow.

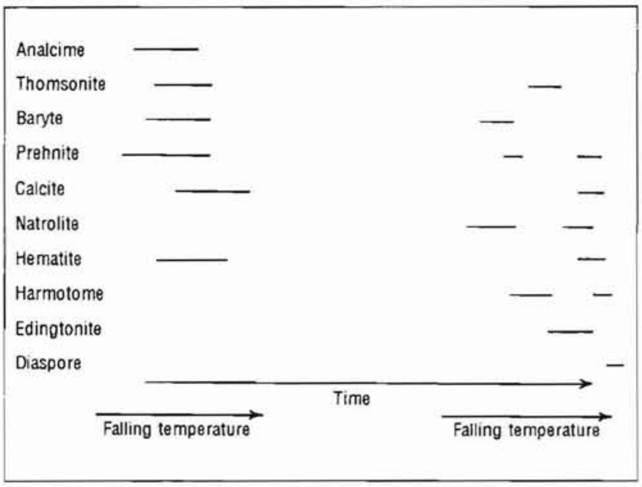

**FIGURE 5.** Probable paragenetic sequence of species in the prehnite vein alteration zone, Loanhead quarry.

**TABLE II.** Crystallisation temperatures of zeolites (from Tschernich, 1992).

| Species | Temperature/°C |
|---|---|
| Analcime | 60—300* |
| Thomsonite | 65—110 |
| Natrolite | 70—100 |
| Harmotome | 60—85 |
| Edingtonite | Late hydrothermal stages |

*Dominant above 175°C.

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# MINERALS OF MACHEN QUARRY, MID GLAMORGAN, WALES

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**The mineralisation at Machen quarry is associated with faults and joints within dolomitised limestone of Lower Carboniferous age. Galena and sphalerite, with minor pyrite and chalcopyrite, accompanied by baryte and calcite, are the main primary minerals. Extensive secondary mineralisation has taken place which has resulted in a wide range of attractive secondary minerals.**

## INTRODUCTION

Machen quarry (National Grid Reference ST 223 888) lies east of Machen village, Mid Glamorgan, south Wales, 7 km ENE of Caerphilly (Fig. 1). The quarry itself now straddles the boundary between Mid Glamorgan and Gwent, but both the village (named Machen Upper on older maps) and the quarry were in the former county of Monmouthshire. The quarry is actively working dolomitised limestone in a series of nine levels extending downwards from 250 to 70 m altitude.

Lead ore was mined in the Machen area in Roman times (Lewis, 1967), and possibly earlier. The close proximity of Roman settlements at Caerleon and Caerwent resulted in a demand for lead for roofing and piping. Smelted lead, lead ore, and pottery dating from the 1st and 2nd centuries AD were discovered in 1937 at Lower Machen (Tuck and Tuck, 1971), suggesting that the site may have been a small mining settlement. In 1965 the Bristol Exploration Club discovered a Roman lead mine at Cefn-Pwll-du and found coins of the 3rd century AD and pottery fragments within the mine workings (Tuck and Tuck, 1971).

Very little written historical evidence of mining in the Machen area has come to light. Medieval records refer to mining and smelting of lead in Glamorganshire and Monmouthshire in the 13th century. In 1665 a lease on the Machen silver-lead mines was granted by the owner, William Morris of Tredegar (Lewis, 1967). Archdeacon Coxe speaks in 1797 of "... Machen hill whose steep side is almost covered with Lime Kilns appearing like small caves in the rock" and also mentions "... mines of lead, calamine and coal" (Coxe, 1801). Lead deposits in the Draethen area were again exploited in the 19th century but these ventures were short-lived.

Recent blasting on level 9 of Machen quarry exposed small tunnel-like excavations in the quarry face. Many fragments of charcoal were found in the waste rock, which may indicate that fire-setting had been used.

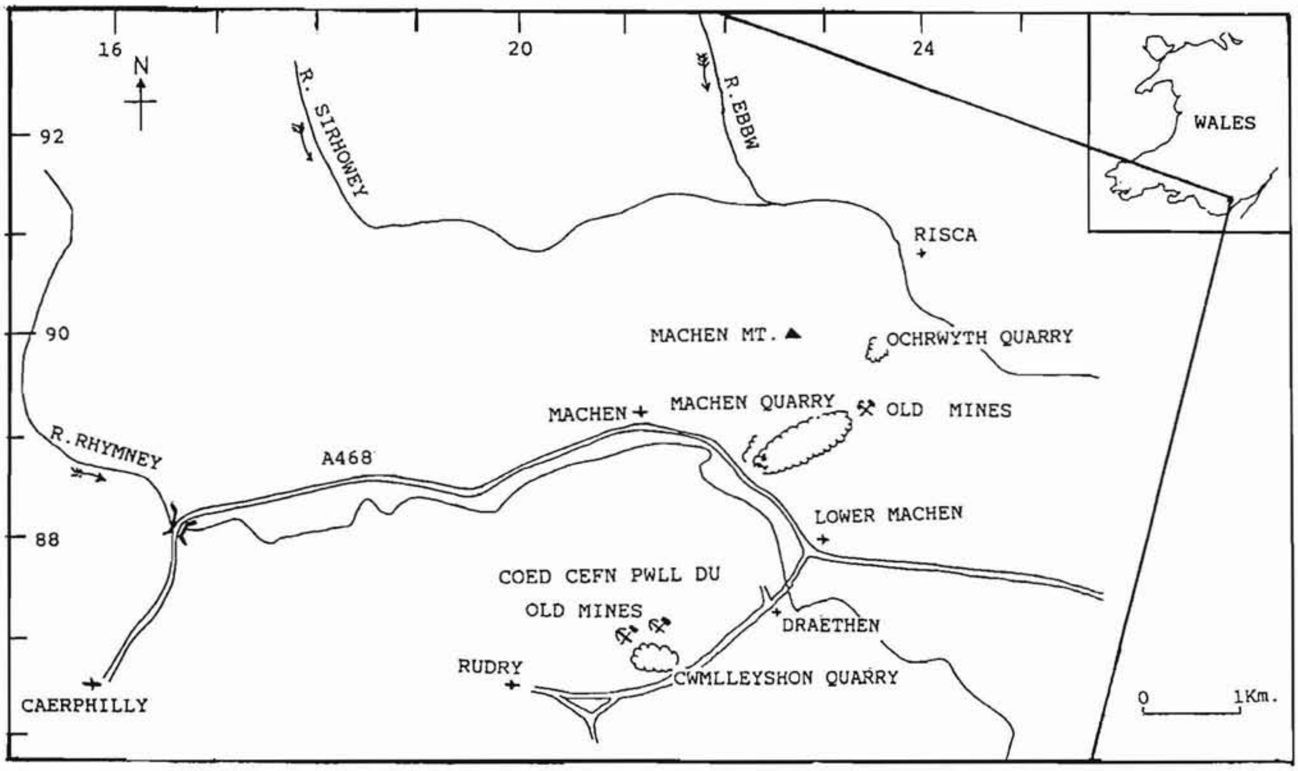

**FIGURE 1.** Location of Machen quarry.

## GEOLOGY

Machen quarry lies on the south-east rim of the South Wales coalfield basin, within an outcrop of Lower Carboniferous (Dinantian) age, sandwiched between Devonian Old Red Sandstone to the south-east, and Millstone Grit, Lower Coal Measures and Upper Coal Measures to the west and north-west (Fig. 2). The strata generally dip north-west and are associated with the Caerphilly syncline. North-east and east of the limestone outcrop are exposed Lower Limestone Shales and an oval-shaped inlier of Upper Old Red Sandstone, structurally complicated by the effect of the Machen anticline and syncline (Squirrell and Downing, 1969). Folding and faulting in the quarry is associated with the Hercynian orogeny of late Carboniferous times. The alignment of the Usk axis further east and north-east in relation to the normal E—W Hercynian structure was noted by Walmsley (1959). Numerous fractures and fissures occur in the working faces of the quarry and many of the vein structures are coincident with the direction of strike (Criddle, 1967). This is particularly prominent in the lead veins of the adjacent Draethen area. Structural control exercised by the Usk and possibly the Cardiff—Cowbridge anticlinal axes may be important.

## MINERALISATION

Mineralised vein structures at Machen quarry are of the fracture and infill type with local brecciation. Ore-bearing veins show large fluctuations in width, both down-dip and along the strike, and are usually developed along faults and joints. Locally, rich pockets of ore may fill most of the vein, only to pinch out further along the strike of the vein. The width of the veins varies typically from a few mm to 30 cm, and exceptionally to 1 m, with an average of 5 cm. Some veins consist almost entirely of dense white or pink baryte, and well-crystallised cockscomb baryte is fairly common in some of the calcite vugs. Recent quarrying on level 9 has exposed a 10-cm vein of baryte. Disseminated sulphides were originally present in the baryte but these have been oxidised and leached out, leaving cavities in which minerals such as aurichalcite, hemimorphite, and hydrozincite have crystallised. Further NE along the strike the vein contracted to a width of 5 cm and was composed almost exclusively of solid galena with a final-stage infill of white baryte (Fig. 3). More recently, quarrying lower down (level 7) has revealed several mineralised solution cavities. Deposited on the walls of some of the cavities were found large, rough octahedral crystals of galena on which were perched later-stage cockscomb aggregates of baryte crystals (Fig. 4). Cerussite and hemimorphite were abundant; smithsonite, previously rare at Machen, was locally common.

Although the lead veins at Machen are widespread throughout the quarry, copper mineralisation in the lead veins is very localised and is strongest in the veins running through the upper north-east side of the quarry. Zinc mineralisation, although more widespread, is also strongest in this part of the quarry.

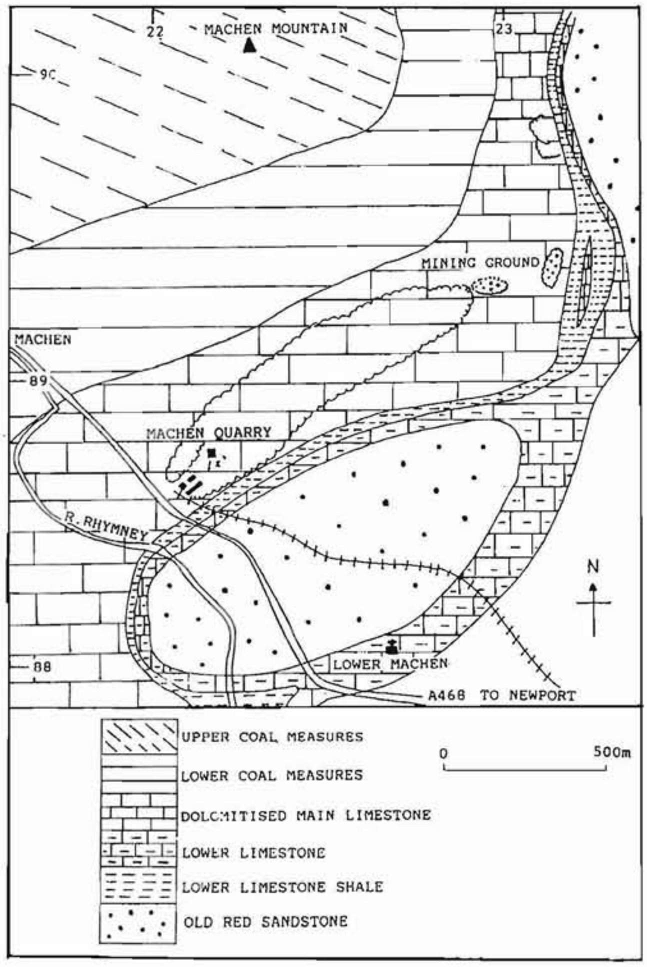

**FIGURE 2.** Sketch map of the geology of the Machen area. (Based on British Geological Survey sheet 149, one-inch series).

**FIGURE 3.** Galena vein with a final stage infill of baryte, from level 9, Machen quarry. The hammer is 25 cm long.

FIGURE 4. Baryte, cockscomb aggregates on rough octahedral galena crystals, from level 7, Machen quarry. Diameter of coin 18 mm.

## MINERALS

Machen quarry was originally known as a source of baryte and calcite specimens of reasonable quality, and occasional small crystals of cerussite and hemimorphite. From the mid-1980s, however, rich lead veins were periodically seen in the quarry faces as they advanced towards the ancient lead and zinc mines at Ochrwyth. The veins have yielded an interesting range of secondary lead, copper and zinc minerals, described below; some of these have already been mentioned by Bevins (1994). With the exception of mattheddleite, scotlandite and sulphur, examples of all the minerals listed here are held in the National Museum of Wales (NMW), Cardiff. Numbers prefixed NMW are specimen accession numbers; those prefixed X refer to identifications by X-ray powder diffraction at the NMW.

### ANGLESITE, $PbSO_4$

Anglesite is occasionally common in small cavities in galena and occurs as intergrown clusters or sprays of small translucent grey or whitish bladed crystals, or as transparent colourless bladed crystals, with a resinous to adamantine lustre. Small tabular crystals are less common. It is generally associated with cerussite crystals and with powdery bindheimite, the latter often as coatings. Anglesite crystals are typically <5 mm long, but very rarely reach 30 mm. Exceptional specimens collected in 1985 have transparent adamantine prisms up to 11 mm long (Bevins, 1994; NMW 85.62G.M1 and M2).

### AURICHALCITE, $(Zn,Cu)_5(CO_3)_2(OH)_6$

Aurichalcite (e.g. X776) occurs as attractive sprays of sky-blue to sea-green lath-like crystals (1—2 mm) often associated with hemimorphite, and very occasionally with malachite and rosasite. It lines small cavities (usually <5 mm but exceptionally 25 mm across) in the baryte—calcite gangue of Cu—Pb veins on the upper levels of the quarry, and is occasionally locally abundant. The specimens are among the finest from Wales; a colour photograph is reproduced by Bevins (1994).

### BARYTE, $BaSO_4$

Baryte is widespread as a gangue mineral associated with the lead and lead-copper veins. It is particularly common in the higher levels of the quarry where it forms attractive groups of cockscomb crystals, either white or in delicate shades of cream, orange, yellow or pink due to iron-staining (Fig. 4). The edges of the crystals are often lined with small colourless transparent or white calcite rhombs. Baryte also occurs as much rarer, 1 or 2-mm, clear tabular crystals, sometimes associated with goethite pseudomorphs after pyrite.

### BINDHEIMITE, $Pb_2Sb_2O_6(O,OH)$

Powdery, canary-yellow bindheimite (e.g. X853 on NMW 86.98G.M2) is commonly found in cavities in galena, often encrusting cerussite and anglesite crystals. No primary source of antimony has been identified at Machen.

### CALCITE, $CaCO_3$

Calcite is common and occurs as small, sharp rhombohedral crystals, often with cockscomb baryte, and as larger crystals, sometimes with dendritic inclusions of manganese oxides. The crystals are usually transparent, honey-coloured or white. Rarely, calcite occurs as etched translucent scalenohedra up to 5 cm long, and very rarely as blocky prisms with rhombohedral terminations, up to 10 cm in size. The latter are sometimes iron-stained orange and have attractive overgrowths of snow-white calcite crystals.

### CERUSSITE, $PbCO_3$

Cerussite is occasionally common as lustrous, colourless, transparent to milky-white, blocky crystals (1—2 mm) in cavities in galena, where it is associated with anglesite and bindheimite. It occurs less commonly as similar crystals associated with hemimorphite in the baryte gangue of the Pb—Cu veins, and rarely as reticulated masses up to 1 cm across. Exceptional complex platy crystals, or elongated tabular crystals, up to 35 mm long and sometimes with a red coating (probably hematite), were found in a lead vein exposed on level 7 in 1994. Associated minerals were galena octahedra coated with small cerussite crystals, white cockscomb baryte, and honey-coloured crystals of both hemimorphite and smithsonite. Cerussite also occurs rarely as crystals (1—2 mm) in small cavities in dolomitised limestone around the margins of the quarry.

### CHALCOPYRITE, $CuFeS_2$

Small masses of chalcopyrite, partially altered to goethite, were found in 1992 in the baryte—calcite gangue of a Pb—Cu vein exposed on level 9. Associated minerals were massive galena, hydrozincite, and small crystals of hemimorphite, aurichalcite, rosasite and, occasionally, malachite.

### CINNABAR, HgS

Cinnabar was found in 1985 as minute orange-red crystals, associated with galena and hemimorphite, in a 2-mm cavity in baryte (Bridges, 1990; NMW 89.43G.M7). Brick-red earthy coatings occurring in minor amounts in small cavities in galena found along the margins of lead veins on the upper levels of the quarry, or in small cavities in the baryte matrix, are also thought to be cinnabar.

DOLOMITE, $CaMg(CO_3)_2$

Dolomite occurs as typical saddle-shaped grey-brown rhombs up to 3 mm across, or as smaller brick-red crystals, both commonly associated with baryte and small goethite pseudomorphs after pyrite. It also occurs more rarely as cream-coloured crystals up to 3 mm across in small cavities in the unaltered limestone, occasionally with minute hemispheres of goethite(?) on the crystal faces.

FRAIPONTITE, $(Zn,Al)_3(Si,Al)_2O_5(OH)_4$

Fraipontite was identified from Machen in 1993 (Bevins, 1994; Goulding and Price, 1995), and was the first Welsh and third British Isles occurrence of this uncommon zinc-bearing clay mineral. It was associated with hemimorphite in an area rich in Cu—Pb—Zn mineralisation exposed on level 9, then the highest working level of the quarry, and formed individual pearly, greenish-yellow, six-sided laminar crystals (<0.5 mm), or as 'books' of such crystals. Although only two specimens with crystals were found, fraipontite occurring as small waxy creamy-white fractured botryoids has also been identified by the NMW (X851). As this latter material resembles hydrozincite, fraipontite may be overlooked and may be more common at Machen than hitherto thought.

GALENA, PbS

A number of lead veins run though the quarry. In places the principal vein is 1 m wide. Crystals of galena are extremely rare, typically forming small groups of dull, rough cubes up to 5 mm across, or similar but individual cubes and octahedra up to 10 mm across. Galena also occurs very rarely as crusts of 10 to 15-mm crystals coated with a later generation of baryte, hemimorphite and cerussite.

GOETHITE, FeO(OH)

Well-formed pseudomorphs of goethite after cubic or octahedral pyrite (rarely >8 mm) are occasionally found as small groups on unaltered limestone on the upper levels of the quarry. Very sharp pseudomorphs after pyrite cubes, and much rarer pseudomorphs after marcasite, both up to ~1 mm across, occur with small crystals of dolomite in association with baryte and calcite. Goethite also occurs in the overburden above the quarry as occasional small rust-coloured plates composed of botryoidal crystal aggregates after pyrite, with epimorphs after scalenohedral calcite on the reverse side. The largest such specimen is a shiny, black, water-worn crystal group 10 cm across and 5 cm thick. Goethite is also formed by partial alteration of chalcopyrite, q.v.

HEMATITE, $Fe_2O_3$ (?)

An ochreous material recently seen coating anglesite and cerussite crystals a dull brick-red is probably hematite.

HEMIMORPHITE, $Zn_4Si_2O_7(OH)_2.H_2O$

Hemimorphite is relatively common as aggregates of colourless to honey-coloured, radiating, tabular crystals, usually 1 mm but occasionally up to 4 mm across. It often forms a drusy lining in cavities up to 5 cm across in the baryte gangue of the lead veins, and is often intimately associated with aurichalcite.

HYDROZINCITE, $Zn_5(CO_3)_2(OH)_6$

Hydrozincite is found as occasional, but locally common, small grey to white bands; as botryoidal or powdery patches associated with aurichalcite, hemimorphite, chalcopyrite and galena (X840, X910); or as fibrous aggregates lining cavities in the baryte gangue (Fig. 5), on the upper levels of the quarry.

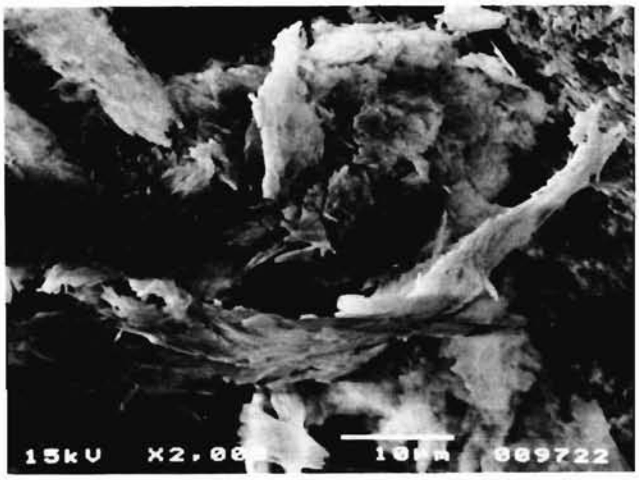

FIGURE 5. Fibrous hydrozincite, Machen quarry. SEM photograph. Scale bar 0.01 mm.

LINARITE, $PbCu(SO_4)(OH)_2$

Minute specks of bright blue crystalline material found in the typical baryte matrix of the lead—copper veins on the upper levels of the quarry, and having the appearance of linarite, were identified by the NMW as the selenite-selenate analogue schmiederite (X805), as were small, transparent, blue, bladed crystals (X909), rarely >1 mm long, found in a galena—baryte matrix associated with hemimorphite and sulphur(?).

We doubted this identification since the Machen crystals differed from light blue acicular schmiederite from Greystone quarry, Cornwall, identified by the Natural History Museum, London. Effenberger (1987) noted that natural schmiederite did not yield reliable X-ray data. Infrared examination by one of us (S.P.P.) of the Machen material gave a spectrum identical with that of linarite (except for an extra peak at 1114 cm$^{-1}$, probably due to an impurity), and showed no prominent absorption peaks expected for $(SeO_3)^{2-}$ and $(SeO_4)^{2-}$ (e.g. in the 720 cm$^{-1}$ and 860 cm$^{-1}$ regions, respectively). Absence of selenium was later confirmed by EPMA at University College, Cardiff (G. Kingston, *personal communication*). Thus the mineral is linarite, not schmiederite. Surprisingly, the EPMA revealed the presence of cadmium, but it is not known whether this is on the surface or within the structure.

Linarite is very rare at Machen, and this represents the first record for south Wales.

MALACHITE, $Cu_2(CO_3)(OH)_2$

Although malachite is relatively uncommon in south Wales, it is fairly widespread on the upper levels at Machen; well-crystallised specimens remain very rare. The best developed malachite occurred as globular aggregates of 1 to 2-mm crystals with calcite on limestone, and was found in 1992 in a small, earthy, iron-rich area of a calcite vein exposed on the top levels of the quarry. Microcrystals of malachite also occurred with aurichalcite, hemimorphite and rare massive chalcopyrite in the baryte gangue of a Pb—Cu vein exposed at the same time, and as minute spheroids on aurichalcite crystals.

MANGANESE OXIDES

Small manganese oxide dendrites, typically 5—10 mm across, are common. Well-formed dendrites up to 15 cm across, associated with a band of light-green clay or mudstone which was closely associated with the Cu—Pb—Zn mineralisation on level 9, were collected in 1993. Rare, small, dendritic inclusions within calcite crystals are thought to be a manganese oxide, perhaps pyrolusite.

### MATTHEDDLEITE, $Pb_{20}(SiO_4)_7(SO_4)_4Cl_4$ (?)

Mattheddleite is said to have been found in a lead vein exposed in the late 1980s, as very rare, free-standing, transparent, hexagonal crystals (≤0.5 mm) with pointed terminations. It was associated with supposed scotlandite (q.v.) and anglesite, on oxidised galena. We have not been authorised to publish other details or the name of the collector, but the mineral appears to have been identified only from its characteristic crystal morphology and appearance, and therefore requires confirmation.

### PYRITE, $FeS_2$

Although goethite pseudomorphous after pyrite occurs on the upper levels of the quarry, unaltered pyrite is extremely rare. An unaltered pyrite core within goethite, closely associated with galena, was found on the bottom level of the quarry in 1993.

### QUARTZ, $SiO_2$

Quartz is very rare but is occasionally found as opaque to transparent bipyramidal crystals (<10 mm) and is associated with dolomite and calcite crystals.

### ROSASITE, $(Cu,Zn)_2(CO_3)(OH)_2$

Rosasite was identified in 1992 by one of us (S.P.P.) using infrared spectroscopy among minerals encrusting massive chalcopyrite (q.v.) from level 9. Although generally rare, rosasite (e.g. X911, X913) was locally common in a minor mineralised vein exposed at the top of the quarry in Autumn 1993, occurring as blue-green spheroids (<1 mm) or botryoidal aggregates (<5 mm) in small cavities in the baryte gangue, and sometimes overgrown by later aurichalcite crystals. Rosasite also occurred as minute spheroids and aggregates on the aurichalcite.

### SCHMIEDERITE, $Pb_2Cu_2(SeO_3)(SeO_4)(OH)_4$ (?)

The mineral recorded as schmiederite (Bevins, 1994) appears to be linarite, q.v.

### SCOTLANDITE, $PbSO_3$ (?)

Scotlandite is said to have been found, associated with supposed mattheddleite (q.v.) and anglesite, on oxidised galena in a lead vein exposed in the late 1980s, as very rare, free-standing, transparent, adamantine, tabular crystals (≤2 mm) with curved faces. We have not been authorised to publish other details or the name of the collector, but the mineral appears to have been identified only from its characteristic crystal morphology and appearance, and therefore requires confirmation. The specimens would be exceptionally fine examples of this rare species.

At the time, Machen quarry was a prolific source of anglesite; such specimens should be carefully examined to see whether they contain material fitting the description of the supposed mattheddleite and scotlandite, so that it can be further studied.

### SMITHSONITE, $ZnCO_3$

Smithsonite is generally very rare at Machen. A creamy-beige botryoidal coating on galena (NMW 86.98G.M1a–c) is smithsonite, but other specimens suspected of being smithsonite have been identified as hemimorphite, which has a similar habit, but is generally white or pale cream in colour. Rare but much richer small translucent brown botryoidal groups and individual crystals (~2—3 mm) of smithsonite (X960; Fig. 6), occurring on baryte and associated with abundant hemimorphite and cerussite and rarer anglesite, were found in a rich pod of galena exposed on level 7 in July 1994. They are probably the best examples of smithsonite from south Wales.

**FIGURE 6.** Smithsonite, globular crystalline aggregates with hemimorphite prisms and blocky composite crystals of an unidentified mineral, Machen quarry. SEM photograph. Scale bar 0.5 mm.

### SPHALERITE, ZnS

Massive resinous brown sphalerite occurs rarely in small patches with other sulphides, but euhedral crystals have not been found.

### SULPHUR, S (?)

A minute yellow crystalline patch associated with linarite and collected from the Cu—Pn veins in 1994 is tentatively identified as sulphur from its appearance and characteristic decrepitation.

## DISCUSSION

Several generalisations can be made about the ore deposits in Machen quarry:

1. The deposits occur in dolomitised carbonate rock, formed at the margin of a sedimentary basin.
2. Mineralisation took place by cavity infilling and wall-rock replacement in an up-dip migration pattern.
3. The mineralogy is relatively simple, with galena and sphalerite as the main ore minerals, accompanied by pyrite, chalcopyrite, baryte and calcite.
4. The deposits are epigenetic, with sulphides emplaced in pre-existing pore spaces, fractures and fissure infill.
5. Igneous rocks are absent in the area.

Such criteria are characteristic of Mississippi Valley type deposits (Sverjensky, 1986).

Fluid inclusion and sulphur isotope data, which could shed more light on the origin of the deposit, are lacking. Isotopic evidence from galena occurrences at other localities within the Carboniferous limestone of south Wales suggests a mid-Triassic to early Jurassic age, i.e. 200—240 million years

(Fletcher *et al.*, 1992). The source of the base metals is unclear, but may have been the original limestone sediments. Bhatt (1975) has presented evidence for hypersaline conditions within the Main Limestone, and the formation of dolomite is known to be favoured by high salinity and high temperatures. Up-dip migration of saline basinal fluids, possibly via aquifers, would be capable of leaching trace metals from the sediments aided by seismic pumping (Sibson *et al.*, 1975) and geothermal gradients.

The close proximity of the Lower Coal Measures as a further or alternative source of metals may also have contributed to the base metal content of the deposit, by downward migration of fluids through faults and fractures followed by up-dip migration in the Main Limestone. The Old Red Sandstone which underlies the Main Limestone is an unlikely source of mineralisation because of its low porosity and permeability, and its poor properties as an aquifer. The almost complete absence of any base metal deposits in the Old Red Sandstone in the vicinity, and in the more extensive outcrops further north, argues against a deep-seated source of mineralising fluids (Foster-Smith, 1981).

Al-Kufaishi (1975) suggested that base metals were transported by downward leaching brines originating in Permian evaporites, now removed by erosion. Such an explanation seems plausible as most of the mineralisation in Machen quarry appears to be concentrated in the upper levels.

## ACKNOWLEDGEMENTS

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# STALACTITIC GALENA FROM LAMB BOTTOM, MENDIP HILLS, SOMERSET, ENGLAND

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**Galena, once mined in large quantities in the Mendip Hills, Somerset, commonly occurred as matrix-free nodules. Specimens of the rarer stalactitic formations of galena, some with tubular central cavities in the manner of carbonate speleothems, have been found recently at Lamb Bottom, West Harptree. They are described and compared with stalactites and helictites of sulphides from elsewhere.**

## INTRODUCTION

Mining for lead on Mendip dates from the period of the Roman occupation of Britain, and probably earlier, when the irregularly shaped, nodular, matrix-free masses of ore were won easily from shallow excavations. The geology, mining history and ore genesis of the area are well documented (e.g. Gough, 1930; Green, 1958; Alabaster, 1982; Ixer and Vaughan, 1993). Mineralisation occurred in episodic phases, probably from the late Triassic to early Jurassic periods, filling open joints and fissures caused by folding and faulting during earlier tectonic activity. Subsequent uplift and erosion produced a concentration of galena on the Mendip plateau. Extensive mining left a scenery of shallow worked-out opencasts or 'grooves' — the miners' 'gruffy ground'. Some of this ground was afforested at the end of World War II, principally Small Pitts and Row Pitts in Chewton Warren. The rest was left as grassy hummocks until recent years, when considerable land reclamation ironed out the evidence of centuries of mining activity. Some rough mined areas remain, most notably the Charterhouse orefield in central Mendip, and the orefield around Lamb Leer Cavern, at Lamb Bottom in West Harptree (Fig. 1).

There are only a few historical descriptions of the Mendip galena nodules and their appearance *in situ*, and very little of this material is preserved in museums. The earliest description seems to be from the Rev. Glanvil of Frome, who wrote in 1668 (Gough, 1930): "About two years since, one King of Wells in his Groove found a piece of Ore, in which they fancied the shape of a man, Eyes, Armes, Leggs, full Breast: The whole was about 4 inches in length". John Woodward (1665-1728), whose mineral and fossil collection is kept in the Sedgwick Museum, Cambridge, listed Mendip galena in his catalogue: "Thick set with tubercles and several pores or intervals, called honeycombe ore ... This sort of ore is found in the perpendicular fissures of stone in vast quantity ..." (Woodward, 1729). There are several of these large rough tuberose nodules, all apparently from Chewton Warren, in the Woodward collection. Another, smoother specimen is listed in the catalogue as typical of "lead ore found loose and independent". Other contemporary references to mining for lead ore were made by Dr A. Catcott (1728 etc.) in his *Diaries of Tours in England and Wales*, particularly the 1756 diaries for the Charterhouse area. More recently Green (1958) recorded nodules and large slabs of galena in old mining trenches.

A rare, and possibly unique, example of nodular galena occurring *in situ* underground was discovered recently in the 18th century Grebe Swallet lead mine at Charterhouse (National Grid Reference ST 504 555), which has been reopened and explored after floods revealed the site (Stanton, 1991). Nodules of ore of all sizes up to 28 kg in weight were found in clay- and rubble-filled fissures. Some of the nodules retain mamillated faces, with concave reverse faces, representing the growing side of the original vein, and the wall attachment side, respectively. Many of the nodules were much abraded during their passage down through the fissures, having been detached from their vein site.

Such nodules, coated with cerussite to various degrees and generally unabraded, along with the rarer stalactitic shaped specimens, may also be collected with diligent searching in the Lamb Bottom gruffy ground. They are described below, and compared with stalactitic sulphides from other parts of the world.

## STALACTITIC GALENA FROM LAMB BOTTOM

The main area of workings (ST 544 550) extends approximately east—west for 370 m and north—south for 320 m, and is bounded on the north by the pre-Triassic Lamb Leer fault, and on the west by a road (Fig.2). Galena was dug from 'grooves' (narrow opencast workings on veins), which roughly follow an east—west pattern, with some veins at

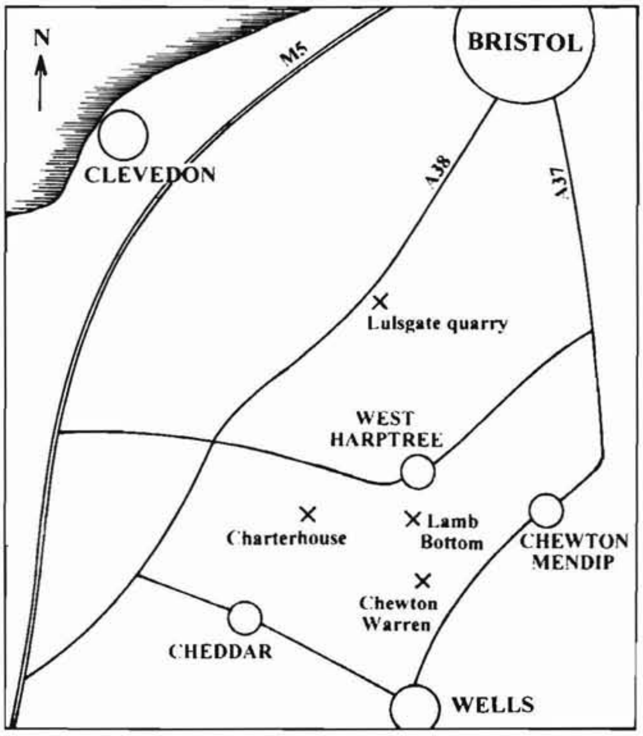

**FIGURE 1.** Location map.

right angles to these, and a network of intercommunicating joints. Lead was also mined in the 201-m deep Lamb Leer Cavern from at least as early as the mid-17th century. The cavern has been closed to explorers for a number of years. Most of the workings are in a calcite-mudstone facies of the Clifton Down Limestone; but in the eastern part they continue into the Hotwells Limestone division of the Lower Carboniferous. Iron was also mined from this eastern end in the 19th century; goethite, accompanied by small clear and often doubly-terminated quartz crystals, is more prominent on the tips here, and clusters of colourless tabular baryte crystals also occur. Lower Lias (Sutton Stone type) material occurs locally on the tips, sometimes spotted with patches of galena. In some deep grooves the bared limestone rock of the old veins, with traces of hydrous iron oxides, can be seen behind vegetation.

At the side of a shallow groove, *ca* 7.3 m long and 2 m wide and now only 1 m deep, at the western end of the workings, several specimens of galena were found grouped together just under the turf. Most of these were cauliflower-like or coralloidal nodules ranging in weight from 60 g to just under 1 kg, and most were well coated in cerussite, but some, and others found later elsewhere in Lamb Bottom, were shaped like long stalactites.

The stalactitic forms, up to 9 cm long, do not have a colloform or banded structure, but are composed of aggregates of crystals building outwards from a central core, seen in cross-section on broken specimens. Some show ferruginous ribs down their lengths (Fig. 3b), where they were attached to the iron oxide-coated wall rock, apparently in the vertical hanging manner of common carbonate speleothems. Other specimens are quite devoid of the iron attachments, and may have been freely projecting arrangements (Fig. 3a). Generally, the specimens found have broken terminations, but some are complete, with rounded ends, and one has a pointed end. More rarely, the stalactitic formations have hollow central tubes, up to 10 mm in diameter, through their length (Fig. 3d, 3e), and in several specimens brown ferruginous matter occupies a central tube. One broken stalactite shows, in cross-section, a hard inner core of limonite, surrounded by very soft powdery ferruginous dust, followed by a ring of calcite, and lastly a thick crust of crystalline galena. Among the more curious specimens, one galena stalactite, 42 mm long and sparsely encrusted with cerussite, has a central core of limonite which protrudes at both ends and which is rather angular in shape (Fig. 3c). Another galena stalactite, 35 mm long with a bluntly pointed end, is enclosed by coarse knobbly limonite.

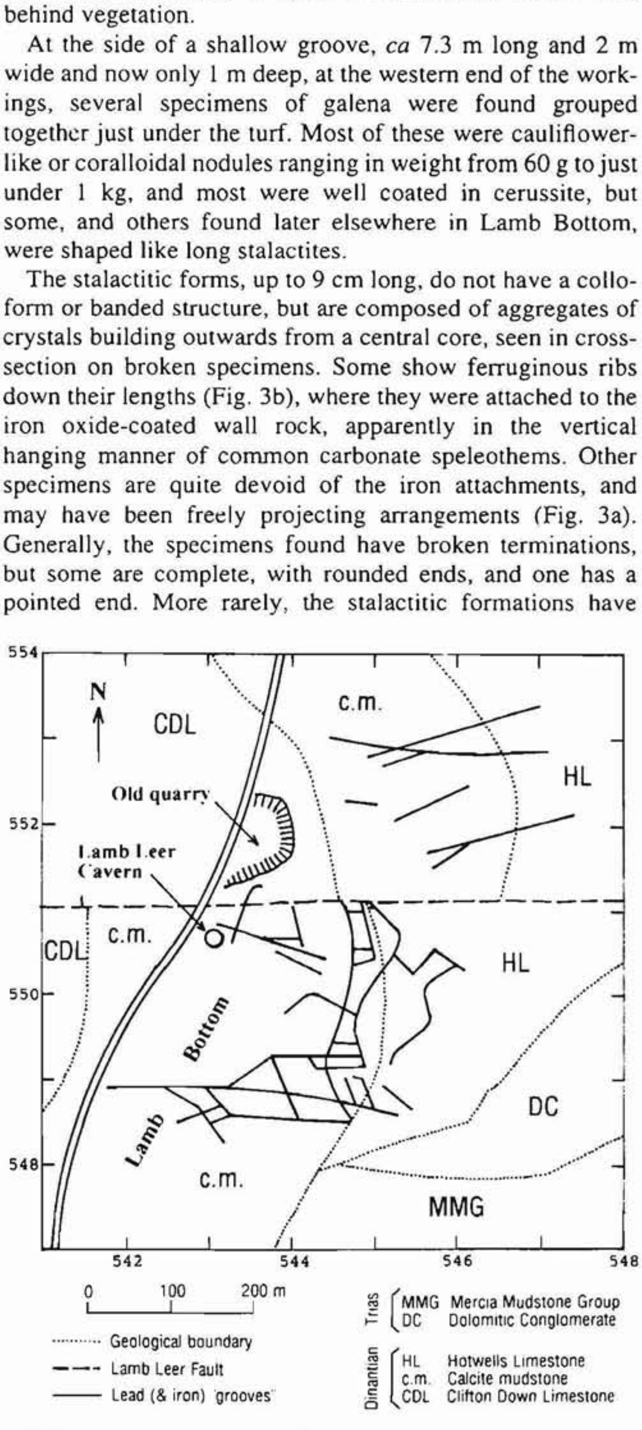

**FIGURE 2.** Geology of the Lamb Bottom area.

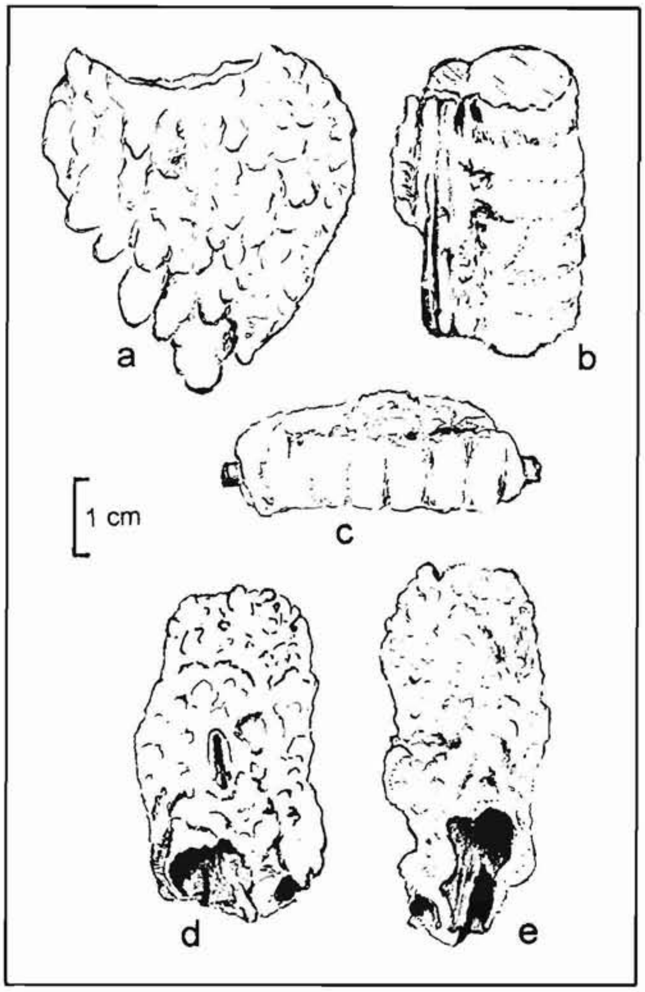

**FIGURE 3.** Stalactitic galena from Lamb Bottom, West Harptree, Somerset. **(a)** Stalactitic nodular aggregate composed of small galena crystals. **(b)** Two conjoined stalactites, lightly coated in cerussite, with broken surface showing crystalline galena, and projecting ferruginous ridges. **(c)** Angular core of limonite enclosed in galena, with a small area of cerussite on the upper surface. **(d, e)** Front and back views of a stalactite with tubular cavities through its length and a rounded termination. (Drawings by S. Cowdry. Specimens **a** and **c** from R. Hotston collection, **b**, **d**, **e** from S. Cowdry collection).

A search for stalactitic galena was made in other lead mining areas of Mendip. Only one site, at Greendown, Litton (ST 574 538), yielded very small (≤24 mm) stalactites of galena, one with a central canal 1 mm in diameter (Fig. 4), and in 1995 a group of three stalactites, 45 mm long, was found. Until recently, galena in a coralloidal or cauliflower-like form was to be found in a vein in Lulsgate quarry (ST 517 659) south of Bristol (C. Alabaster, *personal communication*).

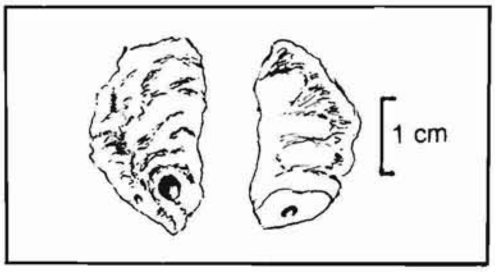

**FIGURE 4.** Views of the two ends of a galena stalactite with a small tubular cavity through its length, from Greendown, Litton, Somerset. (S. Cowdry specimen and drawing).

## STALACTITIC SULPHIDES FROM FOREIGN LOCALITIES

Stalactitic sulphides are known from elsewhere in the world and are especially associated with carbonate-hosted Mississippi Valley-type deposits or Irish-type deposits. Stalactitic galena, marcasite, and sphalerite/wurtzite were first described from the Upper Mississippi Valley—Tri-State area by Chamberlin (1882), from caves in Ordovician dolomites and limestones which were often full of water when first broken into.

According to Chamberlin (1882), "Both stalactites and stalagmites of the ores are found in them, not only those of a single mineral, as pyrite or calcite, but composite accretions. One form consists of an irregular reticulated core of galena, surrounded by from one to three inches of blende sphalerite, in radiant crystallization, coated on the exterior with pyrite, sparsely studded with small modified crystals of galena. These stalactites sometimes attain a diameter of six inches, and a length of a great as the height of the cavern will permit; in fact they sometimes form columns stretching entirely across the opening. Stalagmites, bearing galena on their summits, are said to be found here."

Other examples from Wisconsin, Illinois and Missouri have been described by Bain (1905, 1906), George (1925), Behre *et al.* (1937), and McKnight and Fisher (1970), and reviewed by Peck (1978).

In Europe sulphide speleothems have developed in the Middle Triassic dolomites of the Silesian—Cracow lead—zinc mining area of southern Poland (Bogacz *et al.*, 1970; Forti *et al.*, 1986; Motyka and Szuwarzynski, 1989), and in Carinthia and Slovenia of the northern Adriatic, where Triassic carbonates are host to galena and sphalerite stalactites and much banded sulphide (Winslow, 1894; Jicha, 1951; Di Colbertaldo and Feruglio, 1963). At Navan in Ireland, stalactitic aggregates of pyrite/marcasite, sphalerite and galena that are oriented at 90° to bedding planes have been the subject of much discussion but little agreement (Fontboté and Amstutz, 1986; Ashton *et al.*, 1986).

Old lead mines west of Tunis in north Africa have exploited ores found within Triassic to Miocene carbonates. Stalactites of galena interbanded with jordanite and calcite with minor sphalerite are present, as are 'potato' nodules and massive galena nodules (Superchi, 1970). The galena—jordanite stalactites illustrated by Superchi (1970, p. 82) show the closest external resemblance to the Lamb Bottom specimens.

## DISCUSSION

The stalactitic forms of galena are only rarely found on the spoil heaps on Mendip, and may not have been common even in former times. Elsewhere sulphide stalactites are recorded historically as relatively rare discoveries, and seldom illustrated. All of the occurrences of sulphide stalactites noted above are found in similar stratabound deposits, namely Mississippi Valley or Irish type. These epigenetic/syngenetic lead—zinc deposits occur within limestones and dolomites. Also, all of the stalactite formations mentioned were associated with crustifications, or layered deposits. Some very rare, beautiful, and unusual formations of galena, sphalerite and pyrite occurred in these host cavities, and are still the subject of heated discussion regarding their genesis.

The morphological similarities between sulphide and carbonate stalactites and their presence in open void spaces led Siebenthal (1915) to suggest a similar origin, by descending solutions depositing minerals into cavity spaces. Recently a similar genesis has been suggested for the stalactitic sulphides from Navan, Ireland, namely that they are the result of "solution overgrowths of gravity controlled crystalline growth structures in hydraulically dilated cavities" (I.K. Anderson in Ashton *et al.*, 1986).

However, the presence of stalactitic sulphide structures and an open central tube (if it is a primary feature) has suggested that fluids under hydraulic pressure being forced through fine pore spaces may be the responsible mechanism (Heyl *et al.*, 1959; Peck, 1978). This suggestion has been further strengthened by the discovery of sulphide chimneys with a central open tube surrounded by concentric sulphide layers, initially from the deep ocean floor, but now known to be associated with exhalative deposits in sedimentary basins (Sedex deposits) (Russell, 1992).

Yet other evidence suggests that some sulphide stalactites require unusual conditions for growth. The discovery in 1967 of gas-filled chambers decorated with sulphide speleothems growing in all directions, in Olkusz mine, Poland, and of similar chambers in Trzebionka mine in 1983, led to new theories on the formation of these deposits. Glazek (1992) proposed that sulphide speleothems can be formed wherever pore solutions with a high pressure of $H_2S$ are expelled from minute pores into a gas bubble with a lower $H_2S$ pressure.

Finally, as a counter to these suggestions, all of which require growth of the sulphide into open or fluid-filled void spaces, Fontboté and Amstutz (1986) have suggested that at Navan, Ireland, the stalactitic structures are due to the diagenetic replacement of earlier-formed calcite or baryte crystals by sulphide within the sediments, and not associated with void-filling in any way.

Nevertheless, the principle of sulphides forming unusual elongated stalactite-like shapes, sometimes apparently without gravity control, is well documented. It seems reasonable to suppose that the Mendip galena nodules and stalactites could have evolved in the same manner as those of similar deposits elsewhere.

### ACKNOWLEDGEMENTS

I wish to thank Richard Hotston, who found most of the best specimens of galena from Lamb Bottom, and who steadfastly maintained from the beginning that they were stalactitic. Thanks are also expressed to Dr Trevor Shaw, Dr Stewart Peck, and the staff of the Wills Library, Bristol University. The help of an anonymous referee in writing the foreign localities and discussion sections is gratefully acknowledged.

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# SULPHIDE, SULPHATE, PHOSPHATE AND CARBONATE MINERAL ASSEMBLAGES IN THE OXFORD CLAY, CASSINGTON-YARNTON AREA, OXFORDSHIRE, ENGLAND

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**Calcareous concretions and associated sediments, temporarily exposed in the Oxford Clay (Middle Jurassic), have yielded two suites of minerals, including pyrite, sphalerite, aragonite, calcite, gypsum, celestine, barian celestine, baryte, natrojarosite and vivianite, some of which are hitherto unrecorded from Oxfordshire. Differences between the two suites are ascribed to differences between the stratigraphic strata exposed. Comparisons are made with the mineralogy associated with similar concretions in the Oxford Clay at other British localities.**

## INTRODUCTION

Temporary shallow exposures of the Oxford Clay have provided a range of minerals both within and closely associated with calcareous concretions. Of the two suites described in this paper, one was exposed at National Grid Reference SP 461 121, 8 km NW of central Oxford, near the village of Cassington, during the construction of a new sewage treatment plant in the late 1970s. The other, more extensive, site was exposed at the NE corner of grid square SP 47 10 and the NW corner of square 48 10, between the A40 road and the Oxford to Hanborough railway, during sand and gravel extractions by the Amey Roadstone Corporation (ARC) in the early 1990s. This area is near the village of Yarnton. For convenience the two localities are called the Cassington (C) and Yarnton (Y) sites, respectively (Fig. 1).

## STRATIGRAPHY

Both exposures penetrated the Lower Oxford Clay (Middle Jurassic, Callovian), subzones *Kosmoceras phaeinum*, *K. grossouvrei*, and *K. obductum* at Cassington (in order of increasing age), and subzones *K. obductum* and *K. jason* at Yarnton. Since these beds dip very gently to the south-east, i.e. from C to Y, younger subzones might be expected at Yarnton. However, it is clear that at Yarnton, which is topographically lower, the proto-Thames has eroded the *K. phaeinum*, *K. grossouvrei* and most of the *K. obductum* subzones, and replaced them with Quaternary sands and gravels. Moreover, whereas at Yarnton aggregate extraction exposed only the surface layers of the surviving Callovian, at Cassington excavations for the sewage treatment works penetrated a greater depth of clay. Logging of the stratigraphy at Cassington was not possible, specimen collection being restricted to the contractor's spoil heaps for a brief period. The stratigraphy at a representative site at Yarnton is summarised in Fig. 2.

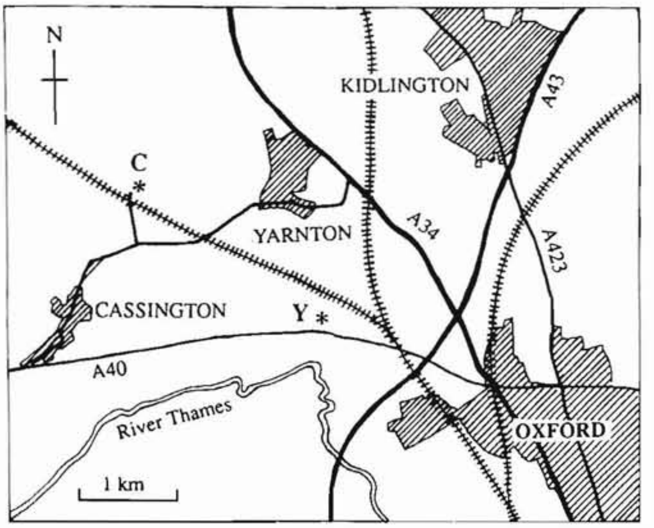

**FIGURE 1.** Locality map. The temporary exposures at Cassington (C) and Yarnton (Y) are described in this paper.

## CALCAREOUS CONCRETIONS

Grey calcareous concretions were abundant at both localities. All were rounded, ellipsoidal and flattened, and the larger ones were discoidal (Figs 3 and 4). They ranged in size up to 1.6 m along the major axes, and the few seen *in situ* were flattened in the vertical dimension, indicating compaction induced by the accumulating overburden of sediment. The smaller concretions (e.g. those at Yarnton at horizons 1.3 m and 2.1 m below the top of the *Jason* subzone) often contained complete ammonites. The larger concretions at deeper levels had fractured and had developed mineralised septa. These will be referred to as septarian concretions. They are highly calcareous, typically leaving only 12 wt % of insoluble residue after treatment with dilute HCl, in contrast with the associated clays which yield 96 wt % of insoluble residue.

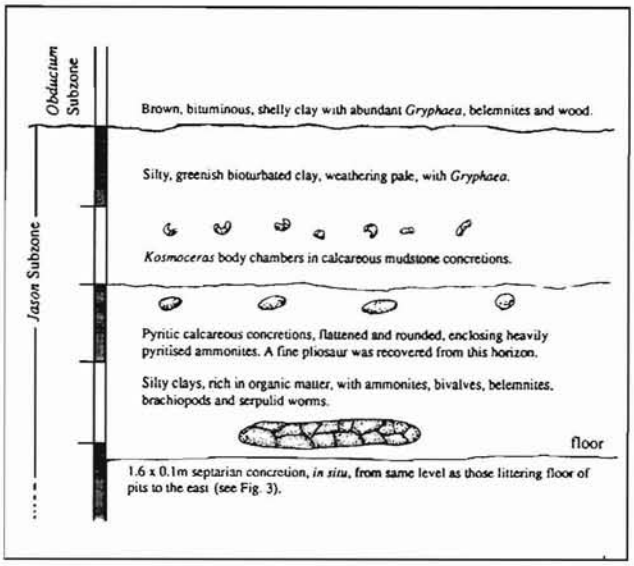

**FIGURE 2.** Simplified stratigraphic section at SP 479 108 in the Yarnton gravel pits, based on a composite by H.P. Powell and J.H. Callomon. This was the site from which H.P. Powell and others recovered a fine specimen of a 5-m long pliosaur, *Peloneustes philarchus*, now on display in the University Museum, Oxford. Vertical scale: 1 division = 1 metre.

FIGURE 3. Discoidal septarian concretions littering the floor of the Yarnton gravel pits at SP 482 108 in February 1992. Most, if not all, have become disoriented during digging operations. Photograph by H.P. Powell.

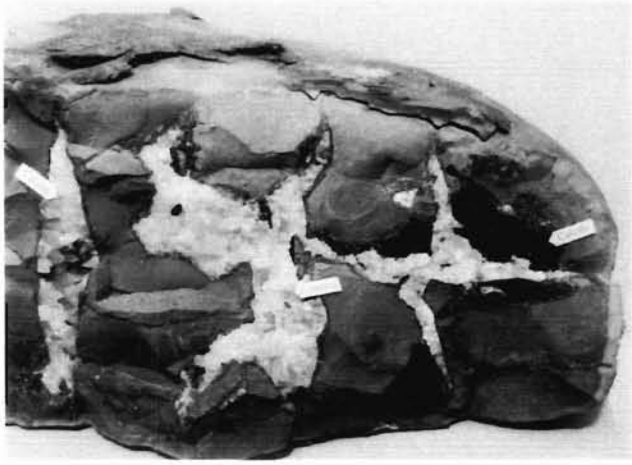

FIGURE 4. Interior of a typical septarian concretion from the Yarnton site. All the fracture walls are lined with brown scalenohedral calcite. The vertical fracture to the left is nearly filled with scalenohedral white calcite, and the central fractures are completely filled with celestine. Field width 36 cm.

## MINERALS

### PYRITE, $FeS_2$

Found at Cassington as microcrystalline coatings on some fracture walls of the septarian concretions. Where it occurs, it is always the first mineral to have grown in the septa. At Yarnton pyrite occurs in association with ammonite shells, especially *Kosmoceras jason* and *Indosphinctes*, in which it often forms extensive replacements.

### SPHALERITE, ZnS

Rarely found at Yarnton as platy crystals up to 2 mm long, within the clay- and calcite-filled body chambers of *Kosmoceras (Gulielmites) effulgens* in concretions 1.3 m below the top of the *Jason* subzone. The colour ranges from honey-brown to black with increasing size, so the sphalerite is probably iron-rich. It has not been noted at Cassington.

### ARAGONITE, $CaCO_3$

Aragonite is a major constituent of many of the ammonite shells and shell fragments at both localities.

### CALCITE, $CaCO_3$

Calcite is ubiquitous at both localities as clay-sized particles, especially in the concretions where it forms up to at least 96 wt % of the fine-grained rock. On the macroscopic scale calcite occurs abundantly at Cassington as scalenohedral (dog-tooth) crystals up to 8 mm long in the septarian concretions, growing directly on, and perpendicular to, the fracture surfaces; or separated from them only by a thin coat of pyrite. It is usually white, but occasionally brown. At Yarnton it is found with the same habit in the septarian concretions, typically directly on the fracture surfaces (pyrite apparently being absent here), where it is initially a dark brown colour. Where later overgrowths of calcite have crystallised, these are scalenohedral but white and coarser-grained (Fig. 4). Typically the narrowest septa are occupied by brown calcite only; those of intermediate thickness by brown and white calcite; and only the widest by brown and white calcite succeeded by celestine (Fig. 4).

### GYPSUM, $CaSO_4.2H_2O$

At Cassington, some concretions carry crusts up to 3 cm thick of platy, dirty-grey gypsum. In the associated clay it occurs (a) as large, discrete radiating clusters with individual crystals up to 35 mm long (Fig. 5); (b) as platy crystals, up to 1.5 mm long, sometimes in small clusters which may have acted as failed precursors of large clusters; and (c) as white powdery films. Gypsum has not been found within a concretion at Cassington, and has not been noted at Yarnton.

### CELESTINE, $SrSO_4$

Celestine, containing up to 0.79 wt % BaO (Table I), is the major fracture-filling sulphate in septarian concretions at both localities. It has crystallised after pyrite (where present) and calcite. When first observed on breaking open a concretion it is colourless, but develops a pale blue colour (or, very rarely, a faint pink tinge) after a few days. Przibram (1956) claimed that the blue colour of celestine is destroyed by heat, and restored by radiation, although he did not give temperatures, times, or radiation wavelengths. The Oxfordshire material does indeed

FIGURE 5. The largest gypsum cluster (11 × 11 cm) recovered from the Cassington site. Specimen OUM 25719.

**TABLE I.** Electron microprobe analyses (wt %) of celestine and barian celestine.

| | SrO | BaO | $SO_3$ | CaO | Total |
|---|---|---|---|---|---|
| 1 | 55.5 | 0.30 | 43.1 | 0.04 | 98.9 |
| 2 | 56.4 | 0.31 | 44.3 | n.d. | 101.0 |
| 3 | 55.6 | 0.31 | 43.5 | 0.06 | 99.5 |
| 4 | 55.2 | 0.44 | 44.2 | 0.04 | 99.9 |
| 5 | 55.4 | 0.55 | 44.1 | n.d. | 100.1 |
| 6 | 55.7 | 0.67 | 44.4 | 0.10 | 100.9 |
| 7 | 55.5 | 0.64 | 43.9 | 0.06 | 100.1 |
| 8 | 55.3 | 0.71 | 44.3 | 0.07 | 100.4 |
| 9 | 55.0 | 0.72 | 44.3 | 0.06 | 100.1 |
| 10 | 55.4 | 0.79 | 43.5 | n.d. | 99.7 |
| 11 | 51.3 | 3.43 | 42.9 | n.a. | 97.6 |
| 12 | 46.7 | 10.3 | 41.8 | n.a. | 98.9 |
| 13 | 46.7 | 12.8 | 41.4 | n.a. | 100.9 |

1—10 Celestine with minor Ba from the Yarnton site.
11—13 Barian celestine from the Cassington site.
n.d. = not detected above the detection limit of 0.02 for CaO.
n.a. = not analysed.
Fe was sought in samples 1—10, but not found above the detection limit of 0.08 for FeO.
Analyst: Dr Norman Charnley.

lose its colour on heating at 210°C for a few hours, but attempts to restore it by exposure to strong sunlight failed.

Barian celestine with up to 12.8 wt % BaO, i.e. $Sr_{0.85}Ba_{0.15}SO_4$ (Table I), has been found in narrow, discontinuous zones near the fracture walls, i.e. corresponding to an early stage of sulphate precipitation within the concretions. This variety (*barytocelestine*) remains white on exposure. In an apparently anomalous instance at Yarnton, minute ($\leq 6$ µm) euhedral crystals of very barium-rich celestine were found on the terminations of celestine 'scalenohedra' (Fig. 6). However the morphology of the celestine strongly suggests that it is pseudomorphous after calcite. If this is so, then the suggested order of crystallisation was calcite, barytocelestine and celestine (albeit pseudomorphous), in conformity with the observed sequence elsewhere.

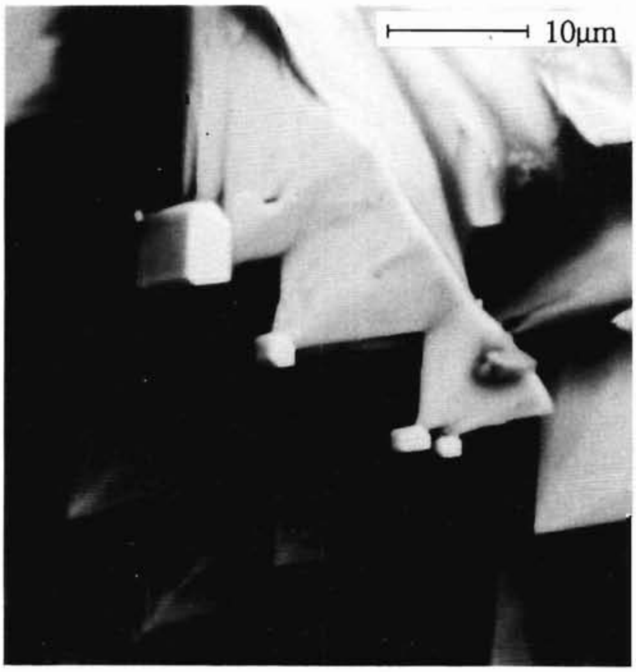

**FIGURE 6.** SEM photograph of minute euhedral barytocelestine crystals on the terminations of celestine crystals (probably pseudomorphous after calcite), from Yarnton. Scale bar 0.01 mm.

### BARYTE, $BaSO_4$

Baryte was not noted at Cassington, nor in the septarian concretions at Yarnton. It occurs at Yarnton rarely as snow-white powdery masses; as minute snow-white, elongated, radiating clusters associated with pyrite and calcite; and as brown, iron-stained, microcrystalline sheets in some of the smaller, pyritic, non-septarian concretions.

### NATROJAROSITE, $(Na,K)Fe_3(SO_4)_2(OH)_6$

This occurred at Cassington as microcrystalline, lemon-yellow films and nodular aggregates in the associated clays, and on some of the larger gypsum clusters. Its presence has been confirmed by XRD. Three EMP analyses gave Na/(Na+K) ratios of 0.81, 0.81 and 0.84. The minute crystals (Fig. 7) show both the habits listed by Palache *et al.* (1951): hexagonal plates flattened on {0001} and pseudo-cubic $\{01\bar{1}2\}$ crystals. Natrojarosite has not been found at Yarnton.

### VIVIANITE, $Fe_3(PO_4)_2.8H_2O$

This was found at Cassington, locally abundant in the clays associated with the concretions, as powdery bright blue films, sometimes along bedding planes, otherwise randomly distributed, and most notably as discrete bright blue spherical aggregates up to 4 mm in diameter. Its colour and stability have remained unchanged since its discovery in 1979, but since it was accessible only on spoil heaps there remains the possibility that its colour was different *in situ*. Its identity as vivianite, rather than as metavivianite or a mixture, has been confirmed by XRD on different samples in the 1980s and in 1995. However, its infrared spectrum differs from that of more coarsely crystalline vivianite (Fig. 8). This discrepancy awaits resolution, but it is worth noting here that Coxon and Flegg (1985), Birley and Young (1993), and Monica Price (*personal communication*) have separately reported a blue earthy mineral from Ireland, Northumberland, and King's Sutton (Oxfordshire), respectively, all yielding a vivianite XRD pattern; and that an 'anomalous' infrared spectrum similar to that of Fig. 8A was obtained

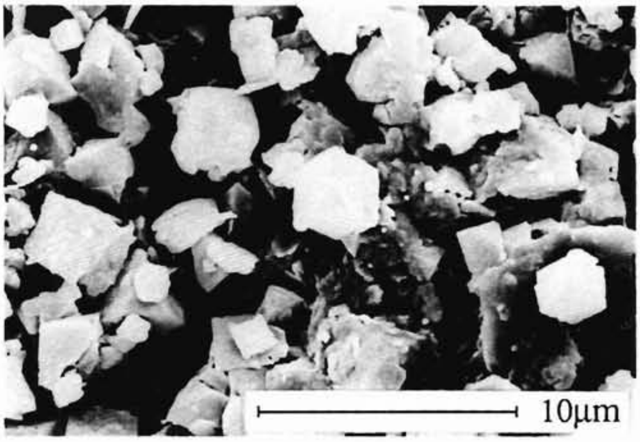

**FIGURE 7.** SEM photograph of natrojarosite from the Cassington site, showing two habits, pseudocubic and hexagonal plates flattened on {0001}. Scale bar 0.01 mm.

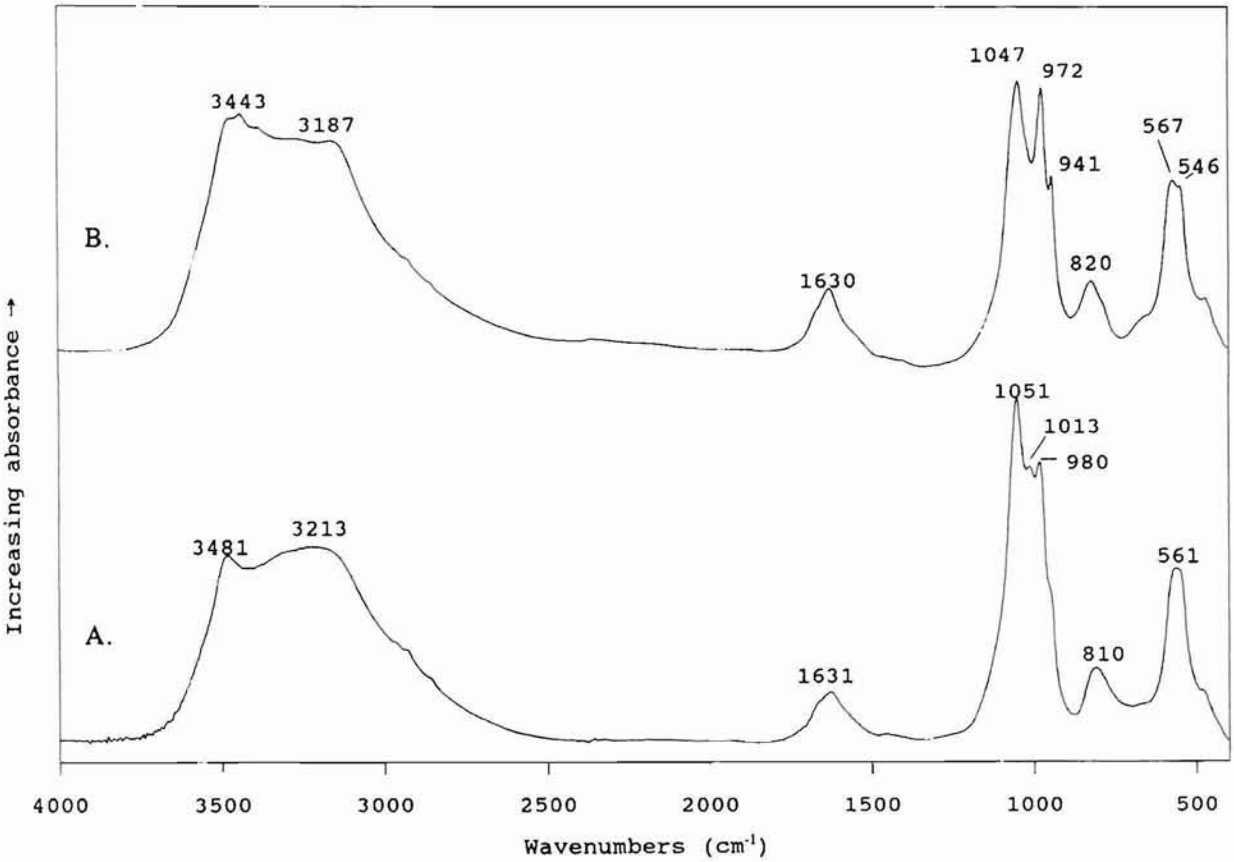

**FIGURE 8.** Infrared spectra of (**A**) blue earthy vivianite, Cassington, Oxfordshire (OUM 23969); (**B**) coarsely crystallised vivianite, Cornwall (OUM 16702). FTIR absorption spectra of powdered samples in KBr discs. Instrument: Mattson Galaxy Series 5000. Analyst: M.T. Price.

from blue powdery 'vivianite' from Sale Ees, Cheshire (G. Ryback, *personal communication*).

No vivianite was noted at Yarnton.

## DISCUSSION

Although only 3 km apart, the two sites described in this paper show some consistent differences in their mineralogy. These are tentatively ascribed to differences in the stratigraphic levels made accessible. Whereas it was possible to log the base of the *Obductum* and the upper 4 m of the *Jason* subzones at Yarnton (Fig. 2), at Cassington only material from the building contractor's spoil heaps was available for study, but fossil evidence showed that younger strata had been penetrated here. The minerals at Yarnton may have been formed in one or more of the *Kosmoceras phaeinum, K. grossouvrei* and *K. obductum* subzones.

To date the most comprehensive study of concretions and the associated diagenetic mineralisation in the Oxford Clay is that of Hudson (1978), who based his work mainly on material from Calvert and Bletchley (Buckinghamshire), Stewartby (Bedfordshire), and Norman Cross, near Peterborough (Cambridgeshire). The present paper draws attention to material from more recent exposures, which may enable such integrated paragenetic studies to be extended. Representative specimens from the localities described here are preserved in the Mineral Collections, Oxford University Museum, and samples can be made available to research workers.

Collectors should note that neither locality is now worth a visit. The Cassington sewage treatment plant (Thames Water) is fully operational, and there are no remaining geological exposures. The mineralogically productive area of the ARC gravel pits at Yarnton is now below the water table.

None of the research carried out thus far challenges Hudson's (1978) paragenetic interpretations. Many of the observations at the Oxfordshire sites are consistent with those made at Hudson's localities. Some interesting differences, listed below, suggest that further research on the geochemistry, diagenesis and mineralisation of these sediments is now overdue.

a) The dominant sulphate within septarian concretions in the Yarnton—Cassington area is celestine, with minor barian celestine (barytocelestine). Baryte, the only, and abundant, sulphate reported by Hudson (1978) has been found, but only in minute amounts in the non-septarian concretions.

b) Other sulphates, not noted by Hudson, are gypsum at Cassington, in a variety of modes; and natrojarosite at Cassington, in clays associated with the concretions.

c) The phosphate, vivianite, which occurs in clays associated with the concretions at Cassington, was not noted by Hudson.

d) The sulphide, sphalerite, although very rare at Yarnton, was not noted by Hudson at his localities.

### ACKNOWLEDGEMENTS

The author thanks Oxfordshire County Water Board (now subsumed by Thames Water) for access to the Cassington site in 1979, and Amey Roadstone Corporation for permission to collect on the Yarnton site in the 1990s. Especial thanks are due to my colleagues at Oxford University Museum, Monica Price and Philip Powell, for specimens, analytical data, faunal details and photographs, and for their comments on a draft paper. George Ryback made important contributions to the section on vivianite, for which I am grateful. EPMA, XRD and SEM data were provided by Norman Charnley and Colin Fagg of the Department of Earth Sciences, Oxford. Margaret Green, Karen Ritson, Guy Rogers and Morrison Thomas collected material at various times, and their help is gratefully acknowledged.

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# MINERALOGICAL SOCIETY

The Mineralogical Society was instituted in 1876. The general object is to advance the knowledge not only of Mineralogy but also of Crystallography, Geochemistry and Petrology, together with kindred subjects. This is done by publishing scientific journals, books and monographs, and by arranging or supporting scientific meetings. The Society speaks for Mineralogy in Great Britain linking with British science in general through the Royal Society and cooperating closely with the Geological Society. It maintains liaison with European mineralogists as a member Society of the European Mineralogical Union, and it is the body which nominates British representatives to the International Mineralogical Association.

The four interest groups within the Society are very active in arranging more specialised meetings and technical discussions in the following fields: Clay Minerals, Applied Mineralogy (study of industrial and ore minerals, including coal) Geochemistry (including cosmochemistry), and Metamorphic Studies.

The **Clay Minerals Group** promotes the advancement of clay science and clay technology as applied to all aspects of pure and applied research and industrial uses. Interests of its members cover a wide spectrum, including mining and mineral processing, soils and plant nutrition, crystallography, sedimentary geology, ceramics, petroleum engineering and medicine. Regular meetings are held two or three times a year. The group publishes reference monographs on specific aspects of clay science, and is responsible for the journal Clay Minerals.

The **Applied Mineralogy Group** aims to encourage study and research in applied aspects of mineralogy, such as ore mineralogy and ore microscopy, industrial mineralogy and petrology (including mineralogical aspects of refractories, slags, ceramics, concretes and other building materials), mineral fuels (including nuclear minerals and coals), environmental mineralogy (e.g. toxic and nuclear waste, minerals and health problems such as asbestosis), and fluid inclusion studies (in relation to ores and hydrothermal systems in particular). The group organises meetings and short courses and facilitates publication of conference proceedings and monographs.

The **Geochemistry Group** is the largest and most important specialist group to represent all aspects of this subject in Britain. In addition to the conventional areas of igneous, metamorphic and sedimentary geochemistry, and cosmochemistry, the group's activities encompass such interdisciplinary research areas as environmental, bio- and hydro-geochemistry. The group also promotes exchange of knowledge on the applications and development of relevant new techniques as they arise. Thematic meetings are held each year, which are sometimes international or in collaboration with other specialist groups; an annual research meeting is also held for informal presentations, particularly from research students. The group is developing its educational role through geochemical workshops and short field study meetings.

The **Metamorphic Studies Group** is a joint specialist group of the Mineralogical Society and the Geological Society, and was inaugurated in 1981 to promote all aspects of field and laboratory studies relating to metamorphic rocks. Meetings on particular themes are held each year, and field excursions are organised periodically. In March, an annual meeting is held (usually at Burlington House, London W1) on 'research in progress' when short papers on all aspects of metamorphism are invited, and research students are particularly encouraged to participate.

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Applicants may be elected as Ordinary Members who may receive any two or all three of the Society Journals, or as Associate Members, who may take any one Journal, or none at all. Associate members may not take a full part in the management of the Society, but otherwise have the same privileges as Ordinary Members. Full time students may join as Ordinary Members at a reduced rate. A limited number of distinguished mineralogists may be elected as Honorary Members.

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The Society presents two medals annually: the Mineralogical Society-Schlumberger Award to a scientist to recognise scientific excellence in mineralogy and its applications; and the Mineralogical Society-Max Hey Medal which is awarded to a scientist under the age of 35 in recognition of research of excellence.

The Society also has a postgraduate student bursary, a senior bursary and a student award scheme. The bursaries are awarded for attendance at meetings appropriate to the interests of the Society, for fields or site visits or to further the research aims of the individuals involved. The student award scheme grants two years' of membership to the best undergraduate students in the second year of a three-year degree or third year of a fourth year degree course in each of the geology departments in the British Isles.

Further details about the Society are available from the General Secretary, Mineralogical Society, 41 Queen's Gate, London SW7 5HR, UK. Tel. +44 (01)71 584 7516, Fax +44 (0)171 823 8021, e-mail k_murphy@minersoc.demon.co.uk.

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# NOTES

## WULFENITE FROM CORNWALL, ENGLAND

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Wulfenite is considered to be a rare mineral in the British Isles, but is being reported from an increasing number of localities (Rothwell and Mason, 1992). Despite Cornwall having the largest variety of mineral species of any British county, only one confirmed occurrence of wulfenite has been published. This is a wulfenite-stolzite intermediate on a single specimen from Holmbush mine, Callington, collected by A.W.G. Kingsbury in 1968 and identified by XRD at the Natural History Museum, London (J.G. Francis *in* Rothwell and Mason, 1992). A second suspected find at Greystone quarry, Lezant, reported in the British Micromount Society Newsletter No. 20 (1990), was subsequently found to be of crocoite (Rothwell and Mason, 1992). However, unpublished reports indicate further finds at this quarry, one of which has been confirmed as wulfenite at the Natural History Museum. We have now identified wulfenite at two additional localities in Cornwall.

### WHEAL GOLDEN, PERRANZABULOE

The main lode at Wheal Golden follows the coast for over a kilometre, and as it crosses a series of small headlands it is clearly visible in the cliff faces along with the associated old workings. At the southern end it is intersected by the Perran Iron lode, and at the northern end it meets a large cross-course at Holywell Bay. The average width of the lode is about 1 m, and it consists mainly of chalcedonic quartz and quartz showing a comb structure, with fluorite and galena (Dewey, 1921; Dines, 1956).

In June 1993 one of us (M.G.H.M.) collected specimens rich in pyromorphite from a small overgrown dump at National Grid Reference SW 757 591, adjacent to Allan's shaft in the Wheal Golden sett, and noticed small crystals of presumed wulfenite on some specimens. They form transparent orange crystals, up to 0.7 mm long but usually 0.2—0.3 mm, of sharp bipyramidal habit, very sparsely scattered among grass-green pyromorphite crystals (<0.5 mm) on the surface of a limonitic, schistose 'killas' veined with milky quartz. The crystal shown in Fig. 1 was analysed using SEM with an energy-dispersive analyser by Mr Tony Ball at the Camborne School of Mines, and shown to contain major lead and molybdenum, tungsten being absent. It is therefore confirmed as wulfenite.

Wheal Golden is a classic locality for pyromorphite (Greg and Lettsom, 1858). The IR spectrum of this pyromorphite, which tends to form long spiky crystals, shows no arsenate absorptions, so it is end-member pyromorphite with no or negligible mimetite content. White blades of anglesite (<0.5 mm; identified by IR) are scattered among the pyromorphite in cavities in quartz veins in pale brown 'killas'. Other species found on the dumps are galena, tetrahedrite, chalcopyrite, dolomite, siderite, cerussite and linarite. In addition, cumengeite and phosgenite have been collected (M.G.H.M.) from lode outcrops in the cliffs.

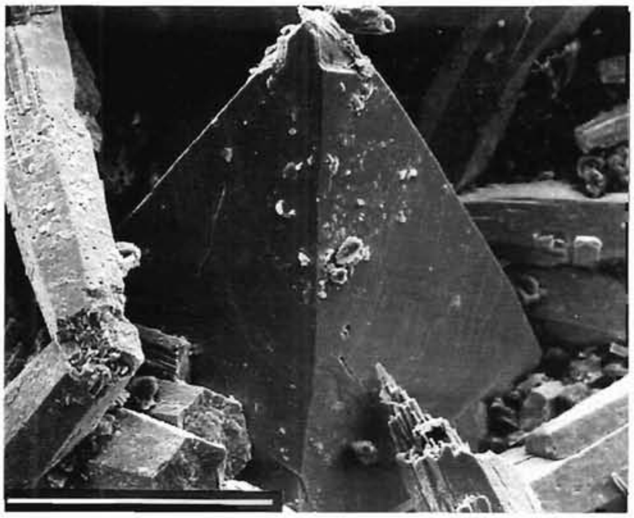

**FIGURE 1.** Wulfenite, bipyramidal crystal among pyromorphite crystals, from Wheal Golden. SEM photograph by A. Ball. Scale bar 0.1 mm.

### WHEAL MARY ANN, MENHENIOT

Wulfenite was found (M.G.H.M.) in 1994 at Wheal Mary Ann, on a dump at SX 287 635. This mine lies nearly 1 km north of Menheniot Church, in a country rock of soft grey slate and interbedded volcanic rock of Upper Devonian age (Dewey, 1921). It was the deepest major lead producer in Cornwall, being worked to a depth of over 550 m and a distance of nearly 2 km, to where it meets the Honey and Trelawney mines to the north (Dines, 1956). The dumps have produced some spectacular specimens of fluorite and baryte (Rudler, 1905), and were reworked for fluorite in the early 1970s.

The wulfenite forms bright orange, equant, bipyramidal crystals (<0.3 mm) and also tabular crystals (<1 mm) scattered on very pale green pyromorphite. The pyromorphite forms coatings of tiny crystals, typically ~0.05 mm long, lining solution cavities in a vein of colourless granular quartz carrying scattered galena. One specimen displays a 0.3 mm tabular wulfenite crystal on baryte. An electron microprobe analysis (Table I) by Mr D. Plant of the crystal shown in Fig. 2 indicates that, like the Wheal Golden material, it is tungstate-free wulfenite. For analysis, the photographed crystal was detached, mounted in epoxy resin, polished, and coated with carbon. It was analysed using a Cameca Camebax instrument fitted with a wavelength-dispersive spectrometer, and galena and molybdenum metal standards.

**TABLE I.** Electron microprobe analysis of wulfenite from Wheal Mary Ann, recalculated as wt % oxides.

| | 1 | 2 |
|---|---|---|
| PbO | 61.0 | 60.8 |
| $MoO_3$ | 38.3 | 39.2 |
| Total | 99.3 | 100.0 |

1. Average of four spot analyses of the crystal illustrated in Fig. 2. Tungsten looked for, not detected.
2. Theoretical for $PbMoO_4$.

Other minerals found on the dumps include pyrite, baryte, calcite, siderite, anglesite, cerussite, linarite, and the well-known pseudomorphs of chalcedony after baryte and octahedral fluorite.

A recently found specimen shows tiny white crystals of late-generation apatite clustered on quartz crystals in a cavity. They are associated with colourless pyromorphite in short prismatic crystals, needles, and spiky crystals resembling aragonite, and also with gypsum and snow-like flaky coatings of anglesite. All these species were identified by IR spectroscopy.

## ACKNOWLEDGEMENTS

The authors would like to thank Mr D. Plant, of the Geology Department, University of Manchester, for SEM photography and EPMA; and Mr Tony Ball and Mr Simon Camm of the Camborne School of Mines for SEM work on the Wheal Golden material.

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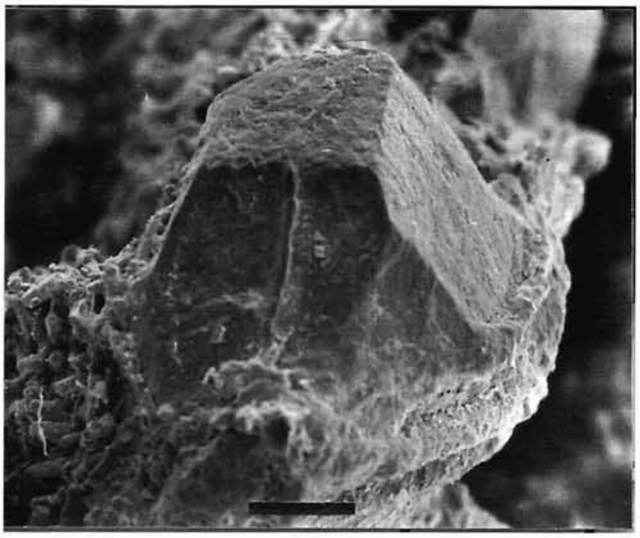

**FIGURE 2.** Wulfenite crystal (analysed) from Wheal Mary Ann. SEM photograph by D. Plant. Scale bar 0.1 mm.

Dines, H.G. (1956). *The Metalliferous Mining Region of South-West England.* Memoirs of the Geological Survey of Great Britain. 2 vols.

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# WULFENITE: A NEW FIND IN DERBYSHIRE, ENGLAND

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Crich quarry (centred on National Grid Reference SK 342 557) is now a very large quarry in the Carboniferous (Viséan) Limestone inlier at Crich, Derbyshire, and has swallowed up a number of old lead mines, including the Glory mine in the northern part, at around SK 342 560. During January 1994 two of us (J.I.W. and M.C.) were exploring a partly excavated vein in the northern part of the quarry, near SK 343 559, in the Glory mine area, and came across a thick pod of galena, about 2 × 0.3 × 0.25 m in size. Some of this galena displayed good cerussite crystals in spaces at the interface with fluorite and baryte gangue. On closer examination of this material, some crystals resembling wulfenite were found which prompted return visits to the site. Revisits were timely, as the find site has now been quarried away, and no more material has been found more recently.

A Fourier Transform IR spectrum of one of the crystals was measured in Nujol mull, between KBr plates, over the range 400—4000 cm$^{-1}$, and matched that of wulfenite,

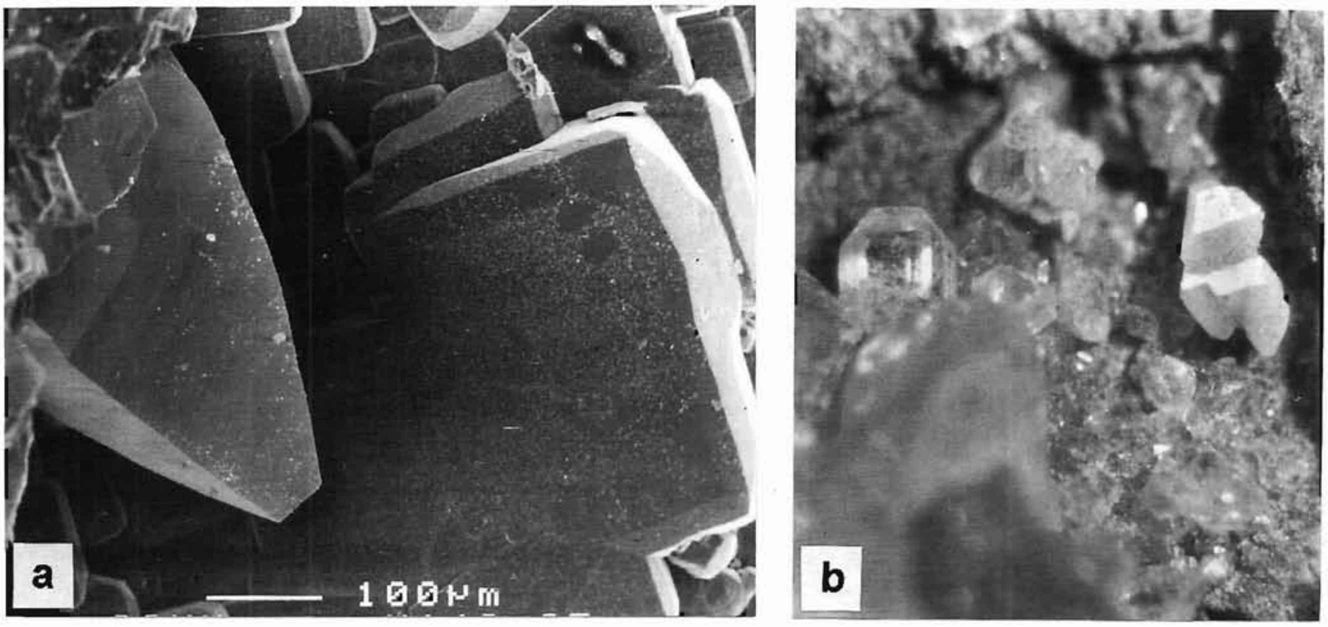

**FIGURE 1.** (a) Wulfenite, orange-yellow crystal 0.5 mm long (left centre; analysed), on pale lilac fluorite, from Crich quarry. SEM photograph by D. Plant. Scale bar 0.1 mm. (b) Sulphur, pale yellow aggregate 0.8 mm long (right centre), with cerussite crystals on galena, from Crich quarry. R.S.W. Braithwaite specimen (94—23) and photomicrograph.

although the spectrum of the analogous tungstate, stolzite, is almost indistinguishable. A microchemical test, however, gave 'molybdenum blue', confirming the presence of molybdate and suggesting that the crystals are wulfenite. This was corroborated by EMPA by Mr D. Plant of the crystal illustrated in Fig. 1a, which also indicated the absence of tungstate (Table I). For analysis, the crystal was detached, mounted in epoxy resin, polished and coated with carbon. It was analysed using a Cameca Camebax instrument fitted with a wavelength-dispersive spectrometer, and galena and molybdenum metal standards.

The wulfenite forms almost white to orange-yellow to reddish-orange crystals 0.05—2 mm in size, some of tabular habit but mostly steep bipyramidal (Fig. 1a). They are perched on galena and on the gangue minerals adjacent to it, in particular on colourless to pale lilac fluorite, and on off-white platy baryte. Associated minerals include cerussite crystals of various habits <7 mm long, and occasionally native sulphur crystals <1 mm long, some of classical bipyramidal habit and showing well-defined faces (Fig. 1b). Such sulphur crystals are unlike most British examples, which occur as ill-defined rounded crystals. Calcite and occasionally quartz are other associated minerals. The native sulphur (oxidation state 0) is an intermediate in the oxidation of sulphide (oxidation state −2) in galena to sulphate (oxidation state +6). In the carbonate-rich environment at this locality, and in the presence of molybdenum, cerussite and wulfenite have formed in preference to anglesite as the end-products of galena oxidation.

**TABLE I.** Electron microprobe analysis of wulfenite from Crich quarry, recalculated as wt % oxides.

| | 1 | 2 |
|---|---|---|
| PbO | 61.0 | 60.8 |
| $MoO_3$ | 38.4 | 39.2 |
| Total | 99.4 | 100.0 |

1. Average of five spot analyses of the crystal illustrated in Fig. 1a. Tungsten looked for, not detected.
2. Theoretical for $PbMoO_4$.

Wulfenite is rare in the Pennine orefields, but a single brown crystal has been reported before from Crich, at SK 345 554, several hundred metres south of the new find (Rothwell and Mason, 1992). Possibly the most remarkable feature of the current find is its highly localised richness; although some specimens show sparsely scattered wulfenite crystals, others show hundreds of crystals packed together.

## ACKNOWLEDGEMENTS

The authors would like to express their sincere thanks to the manager of Crich quarry for allowing us to investigate something that may otherwise never have come to light, and to Mr D. Plant of the Geology Department, University of Manchester, for SEM photographs and EPMA.

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# WELL-CRYSTALLISED FRAIPONTITE FROM MACHEN QUARRY, MID GLAMORGAN: A FIRST WELSH LOCALITY

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In the late summer of 1993, samples were collected by one of us (J.G.) from lead—zinc-bearing veins in the Carboniferous Limestone at level 9 of Machen quarry (National Grid Reference ST 223 888), near Caerphilly, Mid Glamorgan, Wales, the mineralogy of which is described by Plant and Jones (1995). Examination of the brecciated calcite—baryte—galena vein material under the microscope revealed cavities containing transparent, euhedral crystals of hemimorphite, sometimes with cerussite, baryte and anglesite. Two of the cavities also contained pearly, pale green, hexagonal or pseudohexagonal crystals up to 0.4 mm across, occurring singly and as foliated masses on hemimorphite (Fig. 1). There was some massive, buff material close to the crystals. The crystals and massive material were analysed at Oxford University Museum. Energy-dispersive X-ray analysis showed the presence of Si, Al and Zn with traces of Cu and Fe. Although the very small sample sizes resulted in low X-ray diffractometer line intensities, the four strongest lines matched those of fraipontite. This supports analyses carried out on samples in the National Museum of Wales (Bevins, 1994, p. 69). A marginally closer match was made to the $1H$ polytype (PDF 34-782) than to the $2M_1$ polytype (PDF 14-366).

Fraipontite, $(Zn,Al)_3(Si,Al)_2O_5(OH)_4$, is an uncommon zinc-bearing member of the kaolinite-serpentine group. Crystals are very rarely observed. It was first described in 1927, probably from the Vieille Montagne mines, Belgium, and has been subsequently found at Lavrion, Greece; Ojuela mine, Durango, Mexico; Tsumeb, Namibia; and a few localities in the USA (Anthony *et al.*, 1995, p. 265). It has also been recorded at two localities in North Yorkshire: associated with hemimorphite and smithsonite in the Copperthwaite vein in Swaledale (Ryback and Tandy, 1992); and with gibbsite in the Virgin Moss vein, Wensleydale (Young *et al.*, 1992). Machen quarry is the first recorded locality for fraipontite in Wales.

In the North Yorkshire occurrences, fraipontite was formed as a supergene mineral with sphalerite as the probable source of zinc. The occurrence at Machen shows marked similarities. Here fraipontite is also of supergene formation in the Carboniferous Main Limestone, and, as in Yorkshire, hemimorphite predominates over smithsonite in the mineralised veins, indicating a good supply of silicon. Both silicon and aluminium could have been derived from overlying mudstones and sandstones which have subsequently been eroded away, while sphalerite is present on level 9 and at lower levels of the quarry.

**FIGURE 1.** Scanning electron micrograph of pseudohexagonal crystals of fraipontite, with baryte (B) and prismatic crystals of hemimorphite. J. Goulding specimen. Scale bar 0.1 mm.

Fraipontite appears to be rare at Machen quarry. Massive material of similar appearance, collected from level 7, proved not to contain zinc. Despite extensive searches, only these two well-crystallised specimens (one is lodged in the Oxford University Museum as OUM28838), along with a small number of massive samples (cf. Bevins, 1994; Plant and Jones, 1995), have been recovered to date.

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# BAVENITE FROM SHAP GRANITE QUARRY, CUMBRIA, ENGLAND

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Bavenite, $Ca_4Be_2Al_2Si_9O_{26}(OH)_2$, is a rare secondary beryllium mineral occurring chiefly in granitic rocks. In the British Isles it has been recorded only from fissures crossing aplite and calc-silicate hornfels at Meldon, Devon (Dearman and Claringbull, 1960). This note reports a second occurrence, at the Shap granite quarry, Shap, Cumbria (National Grid Reference NY 558 084). A colour photograph of this bavenite from Shap was published recently, without a description (Cooper, 1991).

Bavenite was found in a loose block of rather drusy, feldspar-rich facies of the granite. In this rock, which has not been seen *in situ*, the abundant large phenocrysts of pink perthitic feldspar characteristic of Shap granite are surrounded by a groundmass of pink feldspar, abundant dark-green mica, and some scattered pyrite. Small (<1 mm) terminated feldspar crystals, together with dark-green mica which locally contains included minute colourless apatite crystals, project into numerous drusy cavities up to 8 mm across. Titanite, scheelite, epidote and calcite also occur as euhedral crystals in these cavities. Bavenite was found in a few of the cavities as clear, colourless, platy crystals up to 0.8 mm across, typically in diverging aggregates up to 5 mm across (Fig. 1 and Cooper, 1991); a few crystals showed bevelled edges. Bavenite was suspected from the habit and optical properties, and confirmed by powder XRD (NHM X-ray No. 8496F). On all specimens bavenite encrusts feldspar crystals, and appears to be a late-stage mineral in the cavities. No other beryllium minerals have so far been reported from the Shap granite or the surrounding metamorphic aureole.

**FIGURE 1.** Bavenite, colourless platy crystals on feldspar, in cavity in granite, Shap, Cumbria. Author's specimen MYM 1212. Field of view 1.6 mm.

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# BEYERITE, $(Ca,Pb)(BiO)_2(CO_3)_2$, A MINERAL NEW TO THE BRITISH ISLES, FROM CUMBRIA, ENGLAND

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Examination of a specimen (RSWB 87—15) from Buckbarrow Beck, Cumbria, containing material provisionally identified as russellite, failed to reveal any russellite. Crusts of small radiating clusters of pale yellow-green needles fitting the description of russellite from this locality (Young *et al.*, 1986; 1991) proved to contain carbonate, and the IR spectrum of this material, initially suspected to be that of bismutite, was shown to match closely the spectrum of beyerite, $(Ca,Pb)(BiO)_2(CO_3)_2$, reported by Jones and Jackson (1993), including the rather weak absorptions between 1032 and 909 $cm^{-1}$ attributed by them to impurities, and the weak triplet near 1750 $cm^{-1}$. An X-ray powder diffractometer trace of this material confirmed its identity with beyerite, showing a good match with the data for beyerite on JCPDS powder diffraction file card No. 22—1067.

The find is of particular interest since beyerite (which is not to be confused with the aluminium hydroxide bayerite) is not only of very rare occurrence, but has not been reported before from the British Isles.

The specimen was among material collected by Brian Young in 1986 from a vein on the west side of Buckbarrow Beck, Corney Fell, Waberthwaite, Cumbria, at a point (National Grid Reference SD 1367 9097) ~50 m SW of an old trial level, and described by Young *et al.* (1986). Other specimens from this locality should be checked for the presence of beyerite.

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# TROILITE FROM GLENELG, HIGHLAND REGION, SCOTLAND: THE FIRST BRITISH ISLES OCCURRENCE

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Tiny flecks and grains (up to 2 mm) of a bronze-coloured sulphide were discovered during examination of specimens of impure marble collected from Sgiath Bheinn (National Grid Reference NG 822 188), south of Còsag, Glenelg, Lochaber District, Highland Region. Upon analysis, these proved to be troilite with minor admixed pyrrhotite (R. Thompson, *personal communication*) and cubanite (P.G. Hill, *personal communication*). C.T. Clough (in Peach *et al.*, 1901) noted that marble occurred in the western Lewisian inlier of Glenelg, but did not mention sulphide mineralization. The troilite is associated with spinel, diopside, clinohumite, quartz and phlogopite.

Approximately 0.2 g of the bronzy sulphide mineral was hand-picked to provide a bulk sample from which X-ray powder diffraction photographs, electron microprobe analyses and magnetic measurements were made. Eakle (1922) noted that troilite and pyrrhotite were distinguishable by their reaction to immersion in dilute sulphuric acid. He observed that "The acid immediately attacks troilite and generates hydrogen sulphide ... Pyrrhotite remains inert in the acid". The same test was undertaken by the author on the Glenelg sulphide and a sample of pyrrhotite using a solution of 1 molar sulphuric acid. The Glenelg material reacted with the acid while the pyrrhotite remained inert.

X-ray powder diffraction photographs were taken using a 114.6 mm diameter Philips Debye-Scherrer camera and Mn-filtered Fe-K$\alpha$ radiation. The sharpest photograph was selected and measured. The results, together with the published patterns of troilite and pyrrhotite, are given in Table I. The lines from the Glenelg material were indexed on a hexagonal cell using the Appleman-Evans (1986 revision) indexing program and cell parameters were calculated as $a = 5.978$, $c = 11.707$ Å. These compare with 5.96 and 11.76 Å from Ramdohr (1980), and 5.958 and 11.74 Å from Anthony *et al.* (1990).

Magnetism is an important property of iron-bearing minerals and three types are: *ferromagnetism*, where all the electron spin moments are aligned parallel to each other and have equal strengh and direction, giving a strongly magnetic material; *antiferromagnetism*, where the spin moments are parallel and equal but act in opposite directions, thus cancelling out each other and producing a nonmagnetic material; and *ferrimagnetism*, where the spin moments are parallel and in opposite directions but of unequal strength, thus giving strong to moderately magnetic material. Pyrrhotite is ferrimagnetic, whereas troilite is antiferromagnetic (Deer, Howie and Zussman, 1992). Two grains of the Glenelg sulphide were submitted for magnetic analysis. In this test, an increasing magnetic field is applied to a material that increases its magnetism until a point is reached when the material is completely saturated and no increase in magnetism is recorded. The value of the magnetism at this point is called the *saturation magnetism* ($M_{sf}$). The more strongly ferrimagnetic the material, the larger the $M_{sf}$. Weakly ferrimagnetic or antiferromagnetic minerals exhibit very low or zero saturation values. The $M_{sf}$ values for the Glenelg grains were measured, giving values of 0.12 and 0.10 $Am^2kg^{-1}$, compared with a value of ~17 $Am^2kg^{-1}$ for pyrrhotite. Given that pure troilite is antiferromagnetic, the $M_{sf}$ values for the grains were attributed to admixed pyrrhotite. The pyrrhotite content was calculated as 0.7 and 0.6%, respectively (R. Thompson, *personal communication*).

Four grains were selected and EPMA was undertaken using a Cameca Camebax with energy-dispersive analyser and a pyrite

**TABLE I.** X-ray powder diffraction patterns for troilite and pyrrhotite.

| 1 | | | 2 | | | 3 | | |
|---|---|---|---|---|---|---|---|---|
| *d*/Å | I | *hkl* | *d*/Å | I | *hkl* | *d*/Å | I | *hkl* |
| 5.163 | 5 | | 5.40 | 20 | | | | |
| 4.749 | 15 | 100? | 4.74 | 10 | 101 | | | |
| 4.507 | 5 | | | | | | | |
| 3.572 | 20 | | | | | 3.45 | 3 | 110 |
| 2.988 | 50 | 110 | 2.98 | 40 | 110 | 2.981 | 30 | 200 |
| 2.927 | 15 | 004 | | | | 2.879 | 4 | 002 |
| 2.656 | 60 | 112 | 2.66 | 60 | 112 | 1.653 | 40 | 201 |
| 2.522 | 15 | 201 | 2.52 | 10 | 201 | | | |
| 2.310 | 5 | | | | | | | |
| 2.150 | 5 | 203 | 2.14 | 10 | 105 | | | |
| 2.093 | 100 | 114 | 2.09 | 100 | 114 | 2.072 | 100 | 202 |
| 1.925 | 20 | 211 | 1.923 | 30 | 211 | | | |
| 1.746 | 20 | 213 | 1.748 | 10 | 213 | | | |
| 1.720 | 40 | 300 | 1.719 | 50 | 300 | 1.724 | 25 | 220 |
| 1.637 | 15 | 116 | 1.634 | 30 | 116 | | | |
| | | | | | | 1.614 | 6 | 203 |
| 1.595 | 5 | 107 | 1.595 | 5 | 107 | | | |
| 1.501 | 5 | 215 | 1.501 | 5 | 215 | | | |
| 1.467 | 10 | 008 | 1.469 | 30 | 008 | | | |
| 1.443 | 5 | 222 | 1.445 | 20 | 222 | 1.445 | 4 | 401 |
| | | | | | | 1.440 | 10 | 004 |
| 1.422 | 5 | 311 | 1.422 | 5 | 311 | | | |
| 1.348 | 5 | 313 | | | | | | |
| 1.330 | 15 | 224 | 1.331 | 40 | 224 | | | |
| | | | | | | 1.326 | 9 | 402 |
| 1.316 | 10 | 118 | 1.319 | 10 | 118 | | | |
| | | | | | | 1.299 | 4 | 204 |
| | | | 1.284 | 5 | 401 | | | |
| | | | 1.271 | 5 | 217 | | | |
| 1.224 | 10 | 315 | 1.224 | 20 | 315 | | | |
| 1.188 | 5 | 320 | 1.188 | 10 | 226 | | | |
| 1.172 | 5 | 218 | 1.179 | 10 | 321 | | | |
| 1.139 | 15 | 323 | 1.135 | 20 | 323 | | | |
| 1.119 | 20 | 308 | 1.119 | 40 | 308 | | | |
| 1.108 | 15 | 412 | 1.108 | 30 | 412 | | | |
| | | | 1.091 | 10 | 1.1.10 | | | |
| 1.054 | 15 | 414 | 1.054 | 30 | 414 | | | |
| 1.024 | 10 | 407 | | | | | | |
| 0.994 | 20 | 330 | | | | | | |

1. Troilite, Glenelg.
2. Troilite, Del Norte Co., California. (JCPDS 11—151).
3. Pyrrhotite, synthetic. (JCPDS 25—411).

**TABLE II.** Analyses of troilite (wt %).

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Fe | 62.70 | 63.0 | 64.1 | 63.53 |
| Cu | — | — | 0.05 | — |
| S | 35.40 | 35.0 | 36.1 | 36.47 |
| Total | 98.10 | 98.0 | 100.25 | 100.00 |

1. Del Norte Co., California (Eakle, 1922).
2. Cranbourne meteorite (Berry and Thompson, 1962).
3. Glenelg. Average of 8 spot analyses on four grains.
4. Calculated for FeS.

standard. The results (Table II) clearly indicate that the Glenelg material matches other troilite analyses from the literature. From the analysis of the Glenelg material, the Fe:S ratio was calculated as 1.02:1.00, giving an iron content of 50.5 at. %. Yund and Hall (1968) reported a miscibility gap between troilite and pyrrhotite below 140°C, with iron in troilite ranging from 49.83 to 50.07 at. % and in pyrrhotite from 48.12 to 49.30 at. %. The Glenelg material falls well outside the pyrrhotite range but almost within the troilite range.

This is the first recorded occurrence of troilite in the British Isles. The material has been deposited in the Scottish Mineral Collection of the National Museums of Scotland (NMS G 1995.23.1).

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# RUTHENIRIDOSMINE FROM THE OCHIL HILLS, SCOTLAND: THE FIRST BRITISH ISLES OCCURRENCE

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During examination of alluvial gold from two localities in the Ochil Hills, Tayside Region, three grains of a light grey metallic mineral were separated and identified as the rare mineral rutheniridosmine, (Os,Ir,Ru).

A number of platinum group minerals (PGMs) have been recorded from Scotland. Prichard *et al.* (1981) noted minute grains of iridosmine [(Os,Ir)] and laurite ($RuS_2$) in chromite from Shetland. Tarkian and Prichard (1987) described grains of irarsite [(Ir,Ru,Rh,Pt)AsS] with rims of hollingworthite [(Rh,Pt,Pd)AsS] from the Shetland ophiolite complex. Prichard *et al.* (1987) noted minute crystals of genkinite [$(Pt,Pd)_4Sb_3$], a single grain of geversite ($PtSb_2$), grains of hongshiite (PtCu), a single grain of platinum, a single grain of potarite (PdHg) within chromite, and several unnamed PGMs, also in the Shetland ophiolite. A single euhedral grain of sperrylite ($PtAs_2$) was recovered from panning concentrates from the Huntly area, Aberdeenshire (Gunn *et al.*, 1990). Palladseite ($Pd_{17}Se_{15}$) and palladium have also been noted as inclusions in alluvial gold from Smid Hope Burn and Craigierig Burn in the Southern Uplands of Scotland (Leake *et al.*, 1993). Rutheniridosmine has not been reported from Scotland.

The Ochil Volcanic Formation, which together with the Dundee Formation constitutes the Arbuthnott Group, is of Lower Devonian age. The rocks of the Arbuthnott Group form a line of hills which stretch from Stirling to the north Fife coast near St Andrews. The Ochil Hills are the westernmost portion of this chain. The predominant rock types are pyroxene-andesite, trachyandesite and hornblende-andesite lavas which are intercalated with tuffs and agglomerates. Cutting through the lavas and clastic rocks are several intrusions of diorite and also dykes and sills (Francis *et al.*, 1970).

Two light-grey subhedral metallic grains (ca 1.9 × 0.9 × 0.9 and 2 × 1 × 1 mm) were separated from alluvial gold samples from Chapel Burn (National Grid Reference NO 013 095), 5 km NNE of the Glen Devon Youth Hostel, and Cloan Burn (NN 970 095), 5 km NNW of the hostel, respectively. These two localities lie about 4.5 km apart, in Perth and Kinross District, Tayside Region, some 19 km SW of Perth. A third, much smaller grain (ca 0.5 × 0.5 × 0.5 mm) was also found in the Cloan Burn gold sample and this was used for X-ray diffraction. In addition, grains of a much softer, silver grey, mercurian silver were found at both localities. All three grains were initially examined by X-ray fluorescence spectrometry, using a Philips/Edax PV9500 EDS with DX-4 upgrade. This established the presence of major ruthenium, osmium and iridium. Two grains were then selected, one for electron microprobe analysis (EPMA) and one for powder X-ray diffraction (XRD).

XRD was carried out on a Philips Debye-Scherrer 114.6 mm diameter camera using Cu-K$\alpha$ radiation at 30 kV and 20 mA. The resulting pattern was rather poor with broad indistinct lines and some preferred orientation due to the malleability of the grain, but matched the published pattern of rutheniridosmine (Harris and Cabri, 1973).

Energy-dispersive EPMA was carried out on a Cameca Camebax. In the absence of osmium and ruthenium standards, rhenium, iridium and platinum were used in place of osmium; and niobium, molybdenum, rhodium and silver for ruthenium. The instrument was calibrated for these metals and the counts were interpolated to obtain a count rate for Os and Ru. The analyses were undertaken in two batches, the first acting as a trial run allowing a second run after minor modifications to the calibration. The results are given in Table I along with other published rutheniridosmine analyses. In both batches rhodium, which could not be analyzed accurately at that time because of peak overlap with ruthenium, is estimated at 3.5 wt % (P.G. Hill, *personal communication*). The analyses also show the presence of approximately 5% platinum. From these analyses (assuming 3.5% Rh) we can

**TABLE I.** Analyses of rutheniridosmine (wt %).

| | Os | Ir | Ru | Pt | Pd | Rh | Fe | Cu | Ni | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 38.9 | 39.0 | 21.1 | — | — | 1.0 | — | — | — | 100.0 |
| 2 | 40.4 | 35.9 | 15.8 | 3.7 | 0.5 | 2.1 | 0.1 | — | — | 98.5 |
| 3 | 33.1 | 41.4 | 19.0 | 1.6 | 0.7 | 2.3 | 0.1 | — | — | 98.2 |
| 4 | 66.3 | 18.8 | 9.9 | 2.8 | 0.3 | 1.7 | — | 0.1 | — | 99.9 |
| 5 | 48.8 | 41.9 | 7.0 | 2.4 | 0.12 | 0.89 | 0.15 | — | 0.02 | 101.28 |
| 6 | 33.8 | 27.9 | 29.8 | 4.0 | 2.8 | 1.7 | 0.2 | — | — | 100.2 |
| 7 | 34.7 | 30.7 | 27.9 | 5.1 | — | 3.5* | — | — | — | 101.9 |
| 8 | 34.4 | 30.3 | 26.5 | 5.4 | — | 3.5* | — | — | — | 00.1 |

*Estimated figure.

1. $Os_{0.33}Ir_{0.32}Ru_{0.33}Rh_{0.02}$. Hokkaido, Japan (Aoyama, 1936).
2. $Os_{0.35}Ir_{0.31}Ru_{0.26}Pt_{0.03}Pd_{0.01}Rh_{0.03}Fe_{<0.01}$. Atlin, British Columbia, Canada (Harris and Cabri, 1973).
3. $Os_{0.28}Ir_{0.35}Ru_{0.31}Pt_{0.01}Pd_{0.01}Rh_{0.04}Fe_{<0.01}$. Ruby Creek, British Columbia, Canada (Harris and Cabri, 1973).
4. $Os_{0.60}Ir_{0.17}Ru_{0.17}Pt_{0.02}Pd_{<0.01}Rh_{0.03}Cu_{<0.01}$. Papua New Guinea. (Harris and Cabri, 1973).
5. $Os_{0.45}Ir_{0.38}Ru_{0.12}Pt_{0.02}Pd_{<0.01}Rh_{0.02}Ni_{<0.01}$. Heazlewood, Tasmania, Australia (Cabri and Harris, 1975).
6. $Os_{0.26}Ir_{0.21}Ru_{0.43}Pt_{0.03}Pd_{0.04}Rh_{0.02}Fe_{<0.01}$. Trinity River, California, USA (Snetsinger, 1971).
7. $Os_{0.27}Ir_{0.24}Ru_{0.41}Pt_{0.04}Rh_{0.05}$. Batch 1 (mean of 7 spot analyses), Ochil Hills, Scotland (this paper).
8. $Os_{0.27}Ir_{0.24}Ru_{0.40}Pt_{0.04}Rh_{0.05}$. Batch 2 (mean of 10 spot analyses), Ochil Hills, Scotland (this paper).

derive the formulae $Os_{0.27}Ir_{0.24}Ru_{0.41}Pt_{0.04}Rh_{0.05}$ for batch 1 and $Os_{0.27}Ir_{0.24}Ru_{0.40}Pt_{0.04}Rh_{0.05}$ for batch 2. Inclusions of platinum were also noticed and analyzed (Table II).

The name ruthenosmiridium (not rutheniridosmine) was first used by Aoyama (1936) to describe small hexagonal tin-white grains found in placer gold deposits. Analysis (see Table I) gave the formula $Os_{0.33}Ir_{0.32}Ru_{0.33}Rh_{0.02}$. Hey (1963) reviewed the nomenclature of the natural Os—Ir alloys and suggested that the terms osmiridium and iridosmine be defined thus: *osmiridium*, cubic alloys with Os<32 wt %; *iridosmine*, hexagonal alloys with Os 32-80 wt %. Using Hey's classification, Strunz (1966) redefined Aoyama's hexagonal phase as ruthen-iridosmium. Harris and Cabri (1973) examined the nomenclature of Ru—Os—Ir alloys and, using new analytical data, added the following modifications to Hey's definitions: *ruthenosmiridium*, cubic alloys with Ir<80 wt % of (Ru+Ir+Os) and Ru>10 wt % of (Ru+Ir+Os); *rutheniridosmine*, hexagonal alloys with Os<80 wt % of (Ru+Ir+Os) and Ru>10 wt % of (Ru+Ir+Os). Harris and Cabri (1973) also stated that, because optical and X-ray data for iridosmine and rutheniridosmine are virtually indistinguishable, it is the compositional information that allows them to be designated as iridosmine or rutheniridosmine, and this is supported by data compiled by Cabri (1981). Thus the analysed grain from the Ochil Hills is identified as rutheniridosmine.

The source of the rutheniridosmine is unclear. At Talnotry, near Newton Stewart, Kirkcudbrightshire, a mineralized diorite was found to contain very low concentrations (generally <1 ppm) of PGMs (Stanley *et al.*, 1987). However, neither Cloan Burn nor Chapel Burn pass through any of the small diorite intrusions of the Ochils. A study by Crocket (1981) showed that very low concentrations of platinum group elements can also occur in basalts and other mafic rocks, but these are generally of the order of 0.7—27 ppb. A tiny inclusion in alluvial gold from nearby Borland Glen contained 2.94 wt % Pd (Coats *et al.*, 1991) but otherwise, to the author's knowledge, no platinum group elements have been found previously in the Ochil Hills. Further geochemical surveying of the area may reveal more information.

This is the first recorded occurrence of rutheniridosmine in the British Isles. The material is deposited in the Scottish Mineral Collection of the National Museums of Scotland (NMS G 1955.20.1 and 1955.21.1).

**TABLE II.** Analysis of platinum inclusions in rutheniridosmine from the Ochil Hills (wt %).

| | Os | Ir | Pt | Ru | Rh | Fe | Ni | Total |
|---|---|---|---|---|---|---|---|---|
| Spot 1 | 1.27 | 3.12 | 82.59 | 0.17 | 1.71 | 9.67 | 1.49 | 100.02 |
| Spot 2 | 0.80 | 2.77 | 82.37 | 0.11 | 1.71 | 9.59 | 1.50 | 98.87 |
| Spot 3 | 0.97 | 2.93 | 82.02 | 0.18 | 1.77 | 9.58 | 1.53 | 98.98 |

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*Journal of the Russell Society*, 6(1), 56–57 (1995).

# DEFINITION OF A MINERAL

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## INTRODUCTION

In response to suggestions from the mineralogical community that a new definition of a mineral, compatible with recent technological advances, should be promulgated, the IMA Commission on New Minerals and Mineral Names (CNMMN) has taken the initiative in producing the definition embodied in this paper. The paper is the end-product of active discussion of the subject within the CNMMN over a period of several years, and represents a general consensus of the CNMMN membership.

Although the main purpose of this definition is to provide internal guidelines for the work of the CNMMN, it is hoped that it will be also be generally accepted by mineralogists and other earth scientists. However, if serious objections are raised with respect to any parts of the definition, the possibility of further revisions will be considered.

## GENERAL

In general terms, a mineral is an element or chemical compound that is normally crystalline and which has been formed as a result of geological processes. This statement suffices to include the vast majority of substances that are generally accepted as minerals, but there are some substances that do not conform entirely to these requirements and it is therefore necessary to consider where the dividing line between mineral and non-mineral should be drawn, and what exceptions to the general statement should be permitted. The remainder of this document is devoted to an examination of these aspects.

## CRYSTALLINITY

The term 'crystalline', as generally used in mineralogy, means atomic ordering on a scale that can produce an 'indexable' (i.e. with Miller indices) diffraction pattern when the substance is traversed by a wave with a suitable wavelength (X-ray, electrons, neutrons, etc.). However, some naturally-occurring substances are non-crystalline. Such substances can be divided into two categories: amorphous — substances that have never been crystalline and do not diffract X-rays or electrons; and metamict — those that were crystalline at one time, but whose crystallinity has been destroyed by ionizing radiation. Some mineralogists are reluctant to accept amorphous substances as minerals because of the difficulty in determining whether the substance is a true chemical compound or a mixture, and the impossibility of characterizing it completely; some prefer to call such substances 'mineraloids'. However, some amorphous substances (e.g. georgeite, calciouranoite) have been accepted as minerals by the CNMMN.

With modern techniques it is possible to study amorphous phases more effectively than was possible in the past. Spectroscopic methods associated with a complete chemical analysis can often identify an amorphous phase unequivocally. In fact, appropriate spectroscopies (e.g. IR, NMR, Raman, EXAFS, Mössbauer) can reveal the three-dimensional short-range structural environment of each element (chemical bonds). Of course, without the possibility of obtaining a complete crystal structure analysis, which can give coordinates and nature of the atoms, the necessity of a complete chemical analysis is more stringent with amorphous material than with a crystalline phase.

The basis for accepting a naturally-occurring amorphous phase as a mineral could be:

- a series of complete quantitative chemical analyses that are sufficient to reveal the chemical composition of all the grains in the specimen;
- physico-chemical (normally spectroscopic) data that prove the uniqueness of the phase;
- evidence that the material cannot produce an "indexable" diffraction pattern, both in the natural state, and after treatment with some physico-chemical solid-state process (e.g. heating).

Metamict substances, if formed by geological processes, are accepted as minerals if it can be established with reasonable certainty that the original substance (before metamictization) was a crystalline mineral of the same bulk composition. Evidence for this includes the restoration of crystallinity by appropriate heat treatment and the compatibility of the diffraction pattern of the heat-treated product with the external morphology (if any) of the original crystal (e.g. fergusonite-(Y)).

A special case of non-crystalline naturally-occurring substances are those that are liquid under ambient conditions. Water, in its liquid form, is not considered to be a mineral, but its solid form, ice, is. Mercury, however, is recognized as a mineral even though it does not occur in a crystalline state on Earth. Petroleum and its non-crystalline bituminous manifestations, are not regarded as minerals.

## STABILITY UNDER AMBIENT CONDITIONS

Many minerals were formed under conditions of high temperature and/or pressure and are metastable under ambient conditions; others may tend to hydrate or dehydrate when removed from their place of origin. Such minerals may require special procedures to prevent their decomposition before the investigation is complete. The use of special procedures in the investigation does not preclude the acceptance of a metastable or unstable substance as a mineral if it can be adequately characterized and if it meets the other criteria for a mineral.

## EXTRA-TERRESTRIAL SUBSTANCES

Extra-terrestrial substances (meteorites, moon rocks, etc.) were apparently produced by processes similar to those on Earth, and therefore such processes are now called geological, even though the term 'geology' originally meant the study of rocks on this planet. Consequently, naturally-occurring components of extra-terrestrial rocks and cosmic dusts are regarded as minerals (e.g. the lunar mineral tranquillityite).

## ANTHROPOGENIC SUBSTANCES

Anthropogenic substances are those produced by Man, and are not regarded as minerals. If such substances are identical to minerals, they can be referred to as 'synthetic equivalents' of the minerals in question.

## GEOLOGICALLY-MODIFIED ANTHROPOGENIC SUBSTANCES

Chemical compounds formed by the action of geological processes on anthropogenic substances have, on occasion, been accepted as minerals (e.g. the Laurium 'minerals' formed by the reaction of sea-water with ancient metallurgical slags). However, in the modern era, when many exotic materials are produced, the possibility arises that such substances can be placed in a geological environment to produce reaction products that might otherwise qualify as new minerals. The CNMMN has therefore ruled that, in future, chemical compounds formed by the action of geological processes on anthropogenic substances cannot be considered as minerals.

Some chemical compounds formed by the action of geological processes on rocks or minerals that have been exposed to such processes by activities of Man (e.g. mine openings, ore dumps, road cuts, etc.) have been accepted as minerals in the past and, if the exposure was inadvertent, i.e., not done with the express purpose of creating new minerals, then such products can be accepted as minerals. Chemical compounds caused by mine fires are considered to be a special case, as it is not always clear whether there has been human involvement in initiating the fire, and such substances are therefore not accepted as minerals.

## BIOGENIC SUBSTANCES

Biogenic substances are chemical compounds produced entirely by biological processes without a geological component (e.g. urinary calculi, oxalate crystals in plant tissues, shells of marine molluscs, etc.) and are not regarded as minerals. However, if geological processes were involved in the genesis of the compound, then the product can be accepted as a mineral. Examples of acceptable minerals of this kind are substances crystallized from organic matter in black shale or from bat guano in caves, and the constituents of limestones or phosphorites derived from marine organisms.

(Publication approved by the Commission on New Minerals and Minerals Names of the International Mineralogical Association)

*Journal of the Russell Society*, **6**(*1*), *58–60* (*1995*).

# BOOK REVIEWS

Wilson, W.E., The History of Mineral Collecting 1530-1799. With notes on twelve hundred early mineral collectors. *Mineralogical Record*, vol. **25**, No. 6. The Mineralogical Record, Tucson, 1994. 243 pp. Price $24.00.

This Special Issue commemorates the 500th anniversary of the birth of Georgius Agricola (Georg Bauer, 1494—1555), the Father of Mineralogy and the Father of Mineral Collecting. The book is divided into two major sections: the narrative text, arranged by century and (for the 18th century) by country, and the reference section consisting of an annotated census of all known collectors active before 1799, a bibliography of their published collection catalogues, and a general bibliography.

The earliest known surviving mineral specimens are two native silvers from Schneeberg, Saxony; in 1477 miners encountered the convergence of 12 silver-bearing veins in the St Georg mine, and at this junction a mass of solid silver 4 × 1 × 2 m in size and weighing ~20 metric tons was uncovered. Turning to the 18th century, after a description of the French scene (including colour photographs of some of the specimens from the collection of René Just Haüy), there is a 27-page documentation of collecting in Great Britain (including Scotland and Ireland). Here details are given of the collections of Sir Hans Sloane, John Woodward, William Borlase, Philip Rashleigh, A.J. Forster, Charles Greville, James Sowerby, Alexander Crichton, James Smithson and William Phillips, among others. Similarly, accounts are given of collectors in Germany (Goethe, Werner) and Austria (von Born, Zois), Hungary, Bohemia, the Low Countries, Switzerland, Italy, Russia, the Scandinavian countries, Spain (and Mexico), Portugal (and Brazil), and America. A fascinating reproduction of the 25 guidelines for visitors to mineralogical museums to follow (C.F. Nickelio, 1727) includes a plea for "cleanly scrubbed hands" (rule 1) followed later by (rule 18) "everyone should be wary of having sticky hands and light fingers"!

As is usual with *Mineralogical Record* publications, the work is well illustrated, with drawings, coloured sketches of minerals (e.g. from the works of Rashleigh and Sowerby), and colour photographs. In his concluding chapter, the author points out that the beginning of mineral collecting in the 16th century was a necessary prerequisite to the development of the first systematic classification schemes for minerals, and also led to the developing interest in the chemical analysis of minerals and to the study of their structure and physical properties.

This book gives a truly fascinating description of the birth of our science and at $24 should be snapped up by all mineralogists while it is available. Regular subscribers to *Mineralogical Record* will have already received their copies.

R.A. Howie

Anthony, J.W., Bideaux R.A., Bladh K.W. and Nichols, M.C., *Handbook of Mineralogy, volume II, Silica, Silicates.* (In two parts.) Mineral Data Publishing, Tucson, 1995. xvi + 904 pp. Price $135.00. ISBN 0-9622097-1-6.

I was delighted to receive for review volume II, parts 1 and 2 of the *Handbook of Mineralogy*, covering silica and the silicates. In part this is because these are an extremely valuable pair of books to have on one's shelf, but also because volume II of this work has appeared only five years after publication of volume I, which covered elements, sulfides and sulfosalts. In many cases subsequent parts only follow many years later, while sometimes they don't even follow at all.

The format of volume II is the same as for volume I (see the review in volume 4, part 1 of this *Journal*). The data for each species detailed are presented on a single page, with information covering: mineral name, idealised chemical formula, crystal data, physical properties, optical properties, cell data, X-ray powder pattern (7 strongest lines), chemistry (up to 4 analyses), occurrence, association, distribution, name, location of type material, and references.

What makes this any more useful than obvious competitors in this area of the mineralogy book market? To me the useful features are: the presentation of a chemical analysis (or analyses) for every mineral entry, which is particularly useful when working back from obtained electron microprobe or scanning electron microprobe energy dispersive data; the 'distribution' of the species (up to a dozen localities worldwide); the whereabouts of type material; and the up-to-date nature of the references listed.

The concluding comment in my review of volume I was that I sincerely hoped that "all of these proposed volumes see the light of day". However, it is regrettable that John Anthony is not with us to see publication of volume II. We all very much enjoyed John's company during his all too brief stay in the National Museum of Wales, in Cardiff. I feel honoured to have shared some of his time.

R.E. Bevins

Stoiber, R.E. and Morse, S.A., *Crystal Identification with the Polarizing Microscope*. Chapman & Hall, New York & London, 1994. xiv + 358 pp. Price £24.95. ISBN 0-412-04821-3.

The petrographic microscope is still the basic tool for many mineralogists and petrographers and in the correct hands can reveal a wealth of information about an unknown mineral. However, both its application, and the theoretical basis behind its use, can be daunting to the novice. There has thus always been a need for a good introductory text to mineral identification using the microscope, and this book is the latest offering on this topic.

This text attempts to explain, from first principles, how the petrographic microscope can be used in mineral identification. Over the last couple of decades such 'classical' microscopic techniques for mineral identification have tended to assume less importance, even in such traditional bastions of academic learning as universities (rather like the old flame test for determining elemental compositions). These days, for a final definitive determination, the mineralogist is much more likely to resort to the electron microscope or X-ray methods. However, not everyone is able to call on such resources, and often there is a need for a method of mineral identification that is both quick and relatively cheap.

The authors have the benefit of many years of teaching mineralogy to students and this experience is revealed in the book. The text is clear and well laid out, and there are numerous diagrams. There are also several 'recipes' (i.e. procedures to adopt when attempting to identify an unknown) with examples. An understanding of the theory behind the practice is not essential to carry out these experiments, but it helps. Therefore the theoretical aspects are covered in some detail and such topics as the nature of light, dispersion, refractive index, interference figures, and anisotropy are all included. There are also two appendices: one contains tables listing the criteria which can be used to distinguish important rock-forming minerals, the other deals specifically with the identification of asbestos minerals.

Although the procedures described are in theory applicable to any mineral which is able to transmit light, the technique is essentially restricted to the more common rock-forming minerals. (It is not, of course, applicable to opaque sulphides and metal oxides). But it could be used to great effect on the wide array of secondary minerals which so interest many collectors, and it has the distinct advantage that it is cheap (at least after the initial acquisition of a microscope!) and therefore potentially within the reach of the serious amateur mineralogist. Unfortunately, relevant data for such minerals are not contained in this text, and are still mostly 'buried' in the scientific literature.

The book may be heavy going for many readers of this journal and it is only recommended for the committed enthusiast. But, if you have a petrographic microscope and need a good, economical introduction to its use in mineral identification, then this is clearly the book for you!

D.H.M. Alderton

Sinkankas, J., *Gemology: An Annotated Bibliography*. Scarecrow Press, Methuchen (New Jersey) & London, 1993. 2 volumes, xxxiii + 570 and 608 pp. Price $180. ISBN 0-8108-2652-6.

This is the first ever comprehensive bibliography of gems and precious and semi-precious stones, listing on 1166 large pages nearly 7500 items, mostly books but also some journal articles, published between 1500 and 1985. Many of these are from the library of John Sinkankas, the well-known writer on gems and minerals and a book connoisseur. He describes in great detail the title pages (some of which are reproduced) and the binding, paper quality, pagination and contents of the books, distinguishing between different editions if they exist. He also adds his personal assessment (occasionally frankly rude!) of their accuracy and importance.

The arrangement is by authors (from Uuno V. Aarne to Erika Zwierlein-Diehl), for many of whom brief biographical sketches are given. Most names were unfamiliar to me, but some mainstream mineralogists are listed. Thus L.J. Spencer (1870—1959) gets a paragraph of compressed biography and 7 items (5 of them various printings and editions of his *A Key to Precious Stones*, as well as cross-references to several further items which Spencer co-authored or edited. Among entries that may interest British mineralogists are a few old catalogues, such as: *Catalogue of Minerals in St. George's Museum, Sheffield* (1877—1886), "very rare"; *Catalogue of the Collection of Siliceous Minerals. Given to and Arranged for St. David's School, Reigate* (1883); *Catalogue of Familiar Minerals in the Museum of Kirkcudbright* (1884), also "very rare". All these were by John Ruskin, the art critic and amateur mineralogist.

Few of our readers will buy this book, on grounds of its specialisation and cost (a kind friend lent it to me for review). But do try to see a copy if you can. It is a monumental labour of love by an erudite author, fascinating to browse through, and hiding nuggets of useful information even for those not particularly interested in gemmology.

G. Ryback

Tyler, I., *Seathwaite Wad and the Mines of the Borrowdale Valley*. Blue Rock Publications, Carlisle, 1995. 220 pp., 87 photographs, 11 maps and sections, 7 pencil sketches. Price £13.99. ISBN 0-9523028-1-0.

In the foreword to his book the author comments that little has been written about Cumbria's famous graphite, or 'wad', mine. Certainly this may be so for its history, though a considerable literature exists on the mineralogy and the geology of this unique deposit. The book is, however, principally concerned with the history of the 'wad' mine and the neighbouring small metal mines and trials.

By way of introduction a single page is devoted to the geology of Borrowdale. There follows a short series of brief descriptions of so-called remote trials before several pages of text, photos and sketch maps are directed to the lead and copper mines of the Borrowdale valley. The bulk of the book is then devoted to a detailed historical account of the wad mine itself. The text is illustrated with photographs, both of sites as they exist today and some interesting reproductions of old photographs and documents. A number of specially drawn sketches, at least some executed in Borrowdale graphite, are included. Various tables of production figures follow, as well as lists of miners, etc., a glossary of mining terms, and a bibliography.

It is good to see an appreciation of the importance of the geology and mineralogy to an historical work of this sort. However, the reader unfamiliar with Lake District geology will learn little from the section entitled "Geology of Borrowdale". It is not as it claims a resumé of 'basic structure'; rather it is a series of sketchy notes on a few individual sites which belong in the appropriate sections on the following pages. Some reference should have been included in the bibliography to a few of the more easily accessible texts on basic Lake District geology.

The metalliferous mines and trials of the valley are discussed in a rather confused and rambling fashion which is difficult to follow without a detailed mine plan to hand. Some help could have been provided by way of relevant sketch maps or plans at sensible points in the text. A site map of the mines (minus scale) appears at the end of this section and the only plan included is of a particularly simple working of minor importance.

The numbered chapters on the 'wad' mine are logically ordered and are written in a more accessible style than those which precede them. Some indication of the earlier uses of graphite, and hence the reason for its great value, would have been useful and would help to account for the almost obsessive concern with security which seems to have characterised the working life of the mine. The text clearly reflects the author's detailed documentary researches. However, as in many books of this genre, the author seems to have included indiscriminately every piece of information discovered in his research. One is left with the clear impression that, had he discovered the name of the mine owner's son's pet rabbit, this too would have been included! Aficionados of detail of this sort will no doubt enjoy the lists of miners, production figures and pencil makers, etc., which appear as appendices. The glossary of mining terms offers a useful lifeline to those untutored in mining, though such definitions as "Copper — a mineral" or "Lead — a metal gained from the ore of galena [sic]" are rather bizarre.

The half-tone photographs, most of which reproduce very well, are somewhat inexplicably grouped into separate blocks, rather disrupting the text. Two of the maps lack a scale and two of the sections show no orientation.

Bearing in mind these criticisms, and providing one is prepared to skim over the first 60 pages, which seem like an over-long and unnecessary overture, Ian Tyler deserves acknowledgement for taking on the task of setting down the history of one of Britain's most interesting and unique mineral deposits.

B. Young

# NOTES FOR CONTRIBUTORS

## TYPESCRIPTS

Papers should be typed, preferably on A4 paper, on one side only, with double spacing and wide margins. All pages should be numbered. Three complete copies should be submitted to the Editor. Each paper will be reviewed by two referees. Submission of a paper to the Journal is taken to imply that it has not been considered for publication elsewhere. Material accepted for publication can not be published elsewhere in the same form without the consent of the Editor.

The submitted material should normally contain original observations or experimental results relating to mineral occurrences in the British Isles, although other suitable topics may be considered. Full articles should include an abstract of up to 250 words summarising the significant points of the paper; notes (up to 1500 words) do not require an abstract. Review articles, which are usually invited, are also published occasionally.

## FORMAT AND PRESENTATION

Papers should be submitted in the style and format of the Journal, and divided into appropriate sections and subsections. A recent issue of the Journal should be consulted for examples. Words to be printed in italics should be underlined in the typescript. Titles of papers should be adequately informative.

Authors should present their material with clarity and conciseness. Results and discussion should not normally be intermingled. Identification of the less common minerals should be supported by sufficient proof (X-ray diffraction, analyses, etc.). It may not be necessary to reproduce such data in full in the text, but they should be supplied to the Editor if required by the referees in the course of their assessment. For mineral occurrences of particular note (e.g. new occurrences in the British Isles or at a particular locality) authors are strongly encouraged to record the specimen number and the institution or collection where the specimen is lodged. National Grid References should be given for localities described in the text (the format is, e.g.: ST 4015 7185, ST 401 718, ST 40 71).

## FIGURES

All figures should be numbered with consecutive Arabic numbers, and referred to in the text as Fig. 1, etc. Figures must have descriptive captions, and a list of these is to be typed on a separate sheet of the typescript.

Line drawings, crystal diagrams, maps, etc., should be of a quality suitable for direct reproduction, with appropriate line thicknesses and letter sizes. The Editor will arrange artwork for authors who do not have access to such facilities. Photographs should be submitted as good, glossy, black-and-white original prints of maximum possible contrast. The scale must be indicated, either on the photograph or by specifying, e.g. frame width or crystal size in the caption.

Draft line diagrams and good photocopies of photographs will suffice for attachment to the submitted typescripts, but a set of original photographs must be supplied at the time of submission; fair-drawn line diagrams will be needed only after acceptance of the paper.

## TABLES

Tables should be numbered consecutively with Roman numbers, and referred to in the text as Table I, etc. Each table should have a descriptive title, separated from the table by a horizontal line. Another horizontal line should mark the end of tabulated data; any footnotes should be placed below this.

## TERMINOLOGY

Authors must adhere to the nomenclature and terminology of the International Mineralogical Association. The most recent *Glossary of Mineral Species* (at present the 6th edition, by M. Fleischer and J.A. Mandarino, 1991) can be used as a guide to mineral nomenclature, but where this conflicts with *Hey's Mineral Index* (1993) or *Mineralogical Magazine* and *Mineralogical Abstracts* usage, the Editor will advise on the preferred nomenclature. Chemical nomenclature should conform to the rules of the International Union of Pure and Applied Chemistry. Crystal structure studies should be reported in the manner outlined by the International Union of Crystallography (*Acta Crystallographica*, **22**, 45 (1967)).

## ABBREVIATIONS

Except for common non-scientific abbreviations and those for standard units of measurement, abbreviations should be spelt out in full at their first mention in the article, e.g. 'platinum group mineral (PGM)'. If used, 'n.d.' in tables must be defined ('not determined' or 'not detected'). The following abbreviations may be used without explanation:

XRD = X-ray diffraction
XRF = X-ray fluorescence analysis
EPMA = electron probe microanalysis (electron microprobe analysis)
EDX = energy dispersive analysis (same as EDA, EDAX, EDS)
SEM.= scanning electron microscope or microscopy
TEM = transmission electron microscope or microscopy
IR = infrared
UV = ultraviolet
NGR = National Grid Reference

## REFERENCES

References should be indicated in the text thus: (Brown, 1967) or 'as stated by Brown (1967)'; (Green and Brown, 1985) for two authors; (Green *et al.*, 1986) for three or more authors. If two or more references would give rise to identical citations in the text, they may be distinguished by appending 'a', 'b', etc. to the publication year.

A list of references in alphabetical order should form the last section of each paper. Some examples of the style used are given below; note that journal names are given in full. References to Newsletters and similar publications will not normally be allowed. Papers *in press* may be included provided they have been accepted for publication and the journal name is given. Personal communications and unpublished work (except M.Sc. and Ph.D. theses) should not be included here but can be cited in the text, thus: (A. Brown, *personal communication* or *personal communication*, 1992), (B.C. Green, *unpublished work*).

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**BACK COVER:** Opal (4 × 3 cm), Gunheath china clay pit, St Austell, Cornwall, England. G. Ryback photograph and specimen (83–4, collected by D. J. Creba in 1977).