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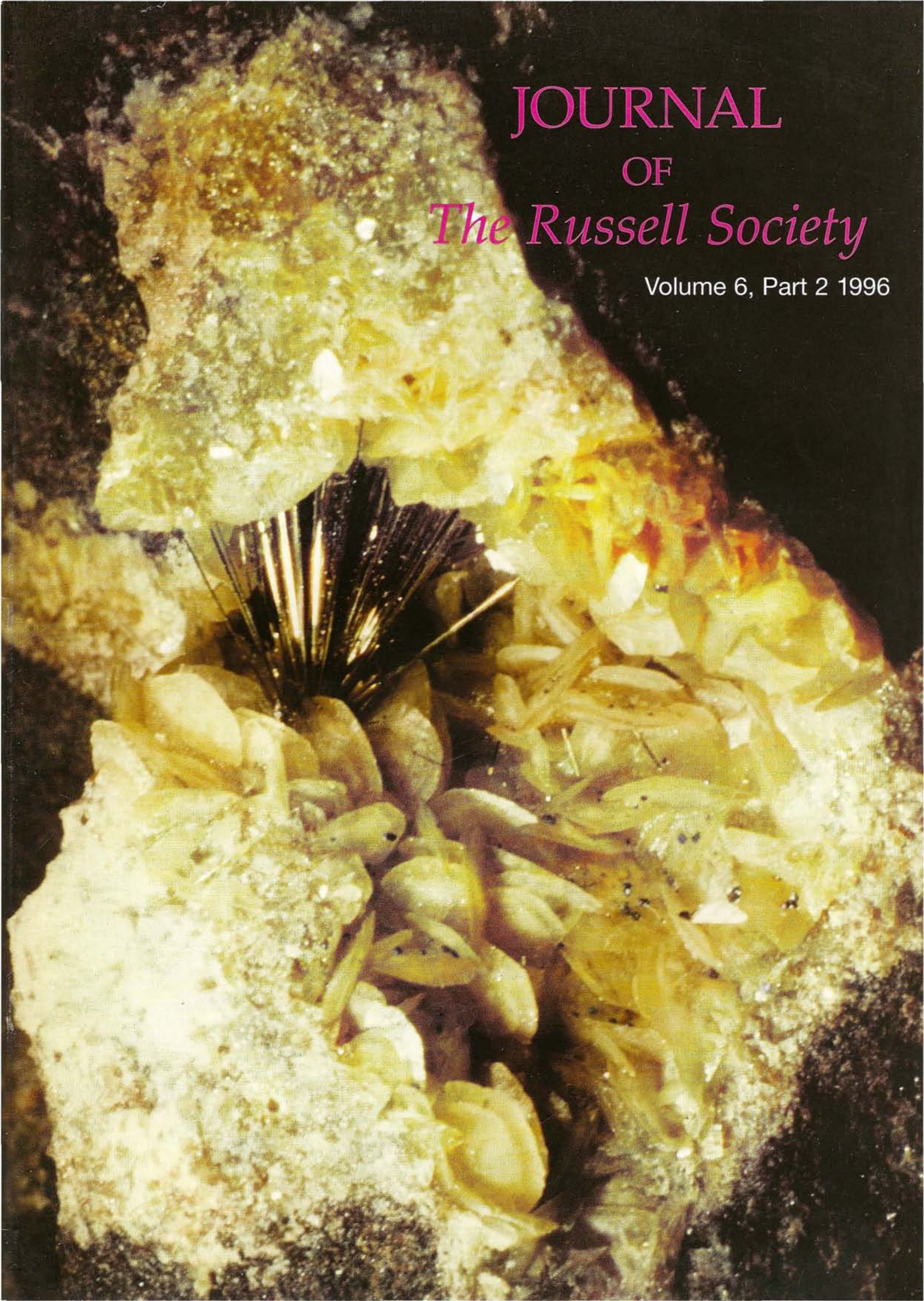

JOURNAL OF THE RUSSELL SOCIETY

The journal of British Isles topographical mineralogy

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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 in the last issue of the Journal, or obtained from the editor.

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FRONT COVER: Millerite, acicular crystals up to 7 mm long, on crystallised siderite. Ferndale, Rhondda Fach, Mid Glamorgan, south Wales. Peter Wallace specimen and photograph.

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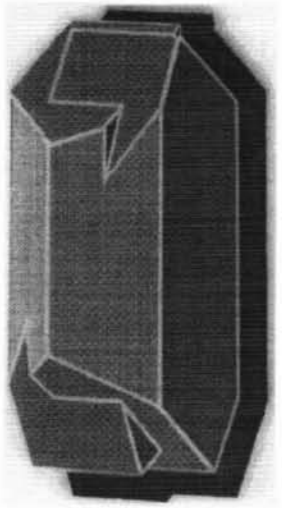

The **Mineralogical Society** was instituted in 1876. The general object is to advance the knowledge not only of mineralogy but also of crystallography, geochemistry and petrology, together with kindred subjects. This is done principally by publishing scientific journals, books and monographs, and by arranging or supporting scientific meetings. The Society speaks for Mineralogy in Great Britain, linking with British science in general through the Royal Society and co-operation 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.

There are five Special Interest Groups within the Society which are very active in arranging more specialized meetings and technical discussions in the following fields: Clay Minerals, Applied Mineralogy, Geochemistry, Metamorphic Studies, and Mineral Physics.

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.

The **Applied Mineralogy Group** aims to encourage study and research in applied aspects of mineralogy, such as ore mineralogy and ore miscroscopy, 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 disposal, minerals and health problems such as asbestosis), and fluid inclusion studies (in relation to ores and hydrothermal systems in particular).

The **Geochemistry Group** is a joint specialist group of the Mineralogical Society and the Geological Society, and is the largest and most important specialist group to represent all aspects of 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 **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 organized periodically.

The **Mineral Physics Group** was formed in 1995. It was set up to advance the understanding of the fundamental physical and chemical processes that determine the properties of minerals.

The Society has an extensive publications list and a large stock of back issues of its journals. Please contact the publications office for a copy of the list. The Mineralogical Society-Chapman & Hall Special Series is available from the offices of Chapman & Hall, 2–6 Boundary Row, London SE1 8HN, UK. Tel. (0171) 865 0066. Discounts are available to members of the Mineralogical Society. The CD-ROM, ***MinSource***, containing 15 years' of *Mineralogical Abstracts* is also available from Chapman & Hall and a very substantial discount is obtained by proof of membership of the Mineralogical Society.

Full details of membership, Society meetings and publications are available from the **General Secretary, Mineralogical Society, 41 Queen's Gate, London SW7 5HR. Tel. +44 (0)171 584 7516, fax +44 (0)171 823 8021, e-mail k_murphy@minersoc.demon.co.uk.**

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FLUID INCLUSIONS: ANALYSIS AND APPLICATIONS

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Fluid inclusion research is one the principal methodologies for examining fluid processes, ancient and modern, in the Earth's crust. In this review, the main procedures for analysing fluid inclusion are described, and some of the research applications are presented.

INTRODUCTION

What are fluid inclusions, where do they occur and how are they observed and analysed? Moreover, what type of information do they provide about geological processes? These are questions that even an experienced geologist or mineralogist may ask.

Natural crystal growth is rarely perfect. Flaws range from point defects on the atomic scale to larger defects on the macro scale. Fluid inclusions are small samples of liquid trapped in these imperfections whilst the crystal was growing. They vary considerably in form, size and composition. Fig. 1A shows a relatively simple two-phase gas–liquid inclusion (in this case, an aqueous brine + water vapour). Fig. 1B illustrates that an inclusion can contain more than one liquid; here it comprises liquid water, liquid carbon dioxide and carbon dioxide gas. A fluid inclusion can also contain precipitated salts. Fig. 1C illustrates a multi-solid–gas–liquid inclusion consisting of several salt crystals within an aqueous brine. Furthermore, they do not necessarily have to contain water. In Fig. 1D the liquid phase comprises heavy hydrocarbons and a light hydrocarbon-rich gas phase.

In theory, fluid inclusions should occur wherever a mineral has crystallised in the presence of a fluid. The term fluid is used in the broadest sense and represents all types of liquid (e.g. water, oil and silicate melts) and gas (e.g. carbon dioxide and methane). It follows that fluid inclusions should occur in a wide range of geological environments. Examples of minerals containing fluid inclusions are calcite, as precipitated from groundwaters (e.g. stalactites); hydrothermal quartz in ore deposits; pyroxenes in high-grade metamorphic rocks; and droplets of quenched silicate melt (now a glass) in phenocrysts in a range of igneous rocks. However, the study of fluid inclusions is usually restricted to a small number of transparent minerals such as quartz, carbonates and fluorite (Table I).

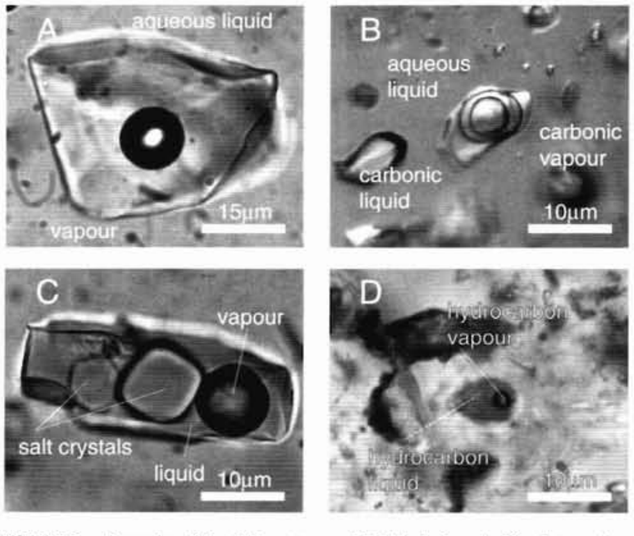

FIGURE 1. Examples of the different types of fluid inclusion. **A:** Simple two-phase aqueous brine + vapour (hosted in fluorite from the North Pennine orefield). **B:** Complex gas–liquid fluid inclusion comprising liquid water, liquid carbon dioxide and carbon dioxide gas (hosted in vein-quartz associated with mesothermal gold mineralisation). **C:** Multi-solid–gas–liquid inclusions consisting of several salt crystals, concentrated aqueous brine, and vapour (hosted in vein-quartz from the Birch Tor tin deposit, SW England). **D:** Two-phase gas–liquid inclusion, the liquid phase consisting of heavy hydrocarbons and the gas phase of lighter hydrocarbons (hosted in diagenetic vein-calcite).

TABLE I. Minerals in which fluid inclusions are most commonly studied.

Host mineral	Examples of applications
Quartz	Gold mineralisation, sedimentary diagenesis
Fluorite	Pb–Zn deposits
Halite	Evaporite formation, palaeoclimates
Calcite	Hydrothermal ore deposits, sedimentary diagenesis
Baryte	Hydrothermal ore deposits, sedimentary diagenesis
Garnet	Metamorphic petrology, skarn formation
Pyroxene	Metamorphic petrology, skarn formation

Fluid inclusions are generally small (<100 μm) and have to be observed using an optical microscope. The microscope is the fundamental 'analytical' tool of all fluid inclusionists, as careful and detailed petrography is a prerequisite for interpreting the data obtained from the wide variety of sophisticated analytical techniques available to the fluid inclusion researcher. The description of these techniques forms the main part of this article and a selection of them is discussed in more detail. However, the main objective is to show how the analysis of fluid inclusions can provide valuable information about processes in the earth sciences. This is exemplified by a short literature survey. In 1995, over three hundred articles containing an element of fluid inclusion research were published in the scientific literature. The subject matter mainly concentrates on classical studies of ore genesis. However, wide-ranging topics such as metamorphic processes, climatology, modelling of modern aquifers, waste disposal of carbon dioxide on the sea floor, sedimentary diagenesis, physical chemistry (thermodynamics), and measurement of palaeostress are covered in a significant number of papers.

HISTORICAL ASPECTS

The existence of fluid inclusions has been known for several centuries and a good historical account, from which this synopsis is taken, is given by Roedder (1984). Fluid inclusions were first described in the English scientific literature by Boyle (1672), who describes a large moving bubble in quartz. However, the first attempts at fluid inclusion analysis on large (~1 cm^3) fluid inclusions, using 'traditional' wet chemical techniques, were by Breislak (1818), Davy (1822), Brewster (1823), Nicol (1828) and Dwight (1820). Sorby (1858) was the first person to propose a theoretical framework for fluid inclusion analysis. He stated that the gas bubble visible in many fluid inclusions was the result of differential shrinkage between the trapped fluid and the enclosing mineral. Thus, he maintained, the temperature at which the fluid was trapped could be estimated by heating the sample and measuring the temperature at which the gas bubble disappeared. It is remarkable that this work, without the aid of modern analytical techniques and a knowledge of fluid thermodynamics, still forms with a few modifications and caveats the basis of modern microthermometry. This hypothesis has not been without its antagonists, who have been reluctant to accept fluid inclusion data for two main reasons. The first is that many inclusions are secondary in nature, i.e. they have been trapped in micro-fractures after the host mineral crystallised and, therefore, do not document the temperature of crystallisation but record a later fluid event. Secondly, it was argued that inclusions do not remain closed systems throughout geological time (e.g. Skinner, 1953; Osborne and Haszeldene, 1993; see also the discussion by Worden *et al.*, 1995). Although 'leakage' is an accepted phenomenon it is important to state that, irrespective of their history, fluid inclusions represent the only real samples of ancient crustal fluids. Moreover, fluid inclusionists have developed petrographic criteria to counter these criticisms.

ANALYTICAL TECHNIQUES

A wide variety of analytical techniques is used to study the chemistry and physical properties of fluid inclusions. They fall broadly into two types: microanalysis of individual fluid inclusions, and analytical methods that extract many thousands of fluid inclusions from their mineral hosts for bulk analysis.

MICROTHERMOMETRY

Fluid inclusion microthermometry concerns the analysis of individual fluid inclusions and underpins all other analytical techniques. It is the most widely used methodology, requires little capital outlay and could be practised by an enthusiastic amateur with access to a petrological microscope. Moreover, it is probably one of the few areas of the earth sciences where the dedicated amateur can make a real contribution to modern scientific thinking. The equipment comprises a small computer-controlled heating – freezing stage, which is fitted to a near-standard petrological microscope (Fig. 2). The only extra requirements for microthermometric analysis are an additional extra-long working distance high-powered objective and a long working distance sub-stage condenser. Samples for microthermometric analysis are usually prepared as free-standing doubly polished wafers between 100 and 200 μm thick. However, they can also be made as doubly polished thin-sections (30–50 μm thick) mounted on a glass slide or cover-slip (Fig. 3). The latter technique is more technically demanding and is usually reserved for studies of fluid inclusions hosted in diagenetic cements.

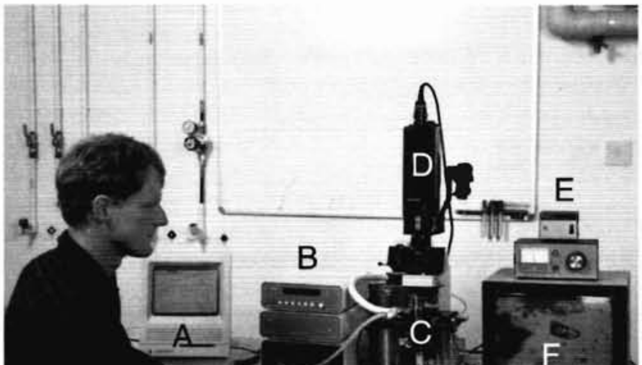

FIGURE 2. Microthermometric analysis equipment. **A:** Micro-computer for storing data and digital images. **B:** Linkam heating–freezing equipment. **C:** Leitz Ortholux II petrological microscope. **D:** Video camera for displaying and recording live images. **E:** Power supply for camera and microscope. **F:** TV monitor to display live images from the petrological microscope.

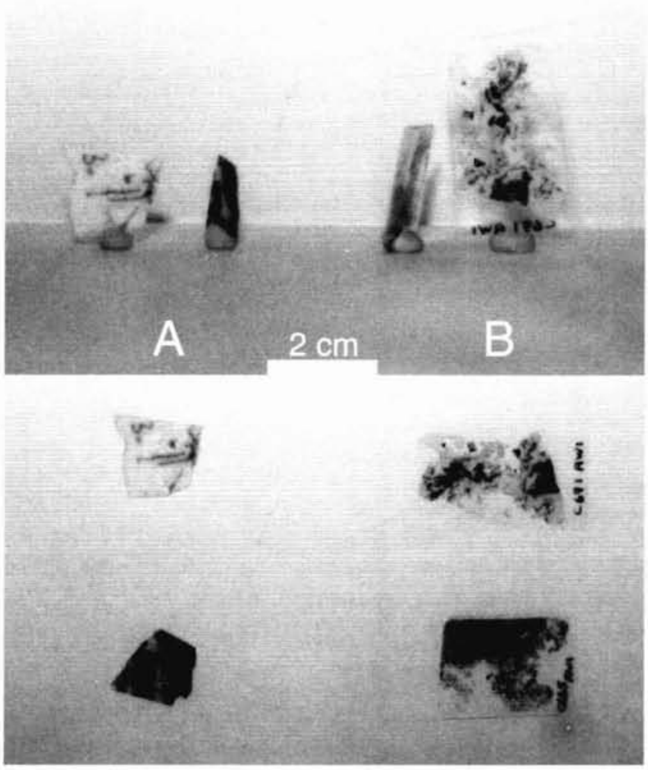

FIGURE 3. Types of samples used in fluid inclusion microthermometry. **A:** Free-standing doubly polished fluid inclusion wafer (100–200 μm thick). **B:** Doubly polished thin section (30–50 μm thick) mounted on a glass cover-slip.

Correct interpretation of data obtained from more sophisticated analytical techniques is dependent on a thorough knowledge of the compositional variations and distribution of fluid inclusions obtained through petrography and microthermometry.

Microthermometry provides qualitative to semi-quantitative information on the chemistry of the fluid inclusion and the physical conditions (pressure P and temperature T) at which the fluid was trapped in the mineral. The principles behind microthermometric analysis concern the careful observation and recognition of phase changes in the fluid inclusions. Accurate measurement of the temperature (to ± 0.1°C) at which phase changes take place makes it possible, by referring to experimentally determined fluid systems, to derive pressure, temperature, molar volume and chemical (PTVX) estimates of the state of the fluid. It is not within the scope of this article to describe in detail the wide variety of phase changes that occur in natural fluid inclusions, and the interested reader is referred to two texts (Shepherd *et al.*, 1984; Roedder, 1984) which deal comprehensively with this topic. However, to show how microthermometry is employed in fluid inclusion analysis the phase changes depicted in Fig. 4 can be used to illustrate the general technique.

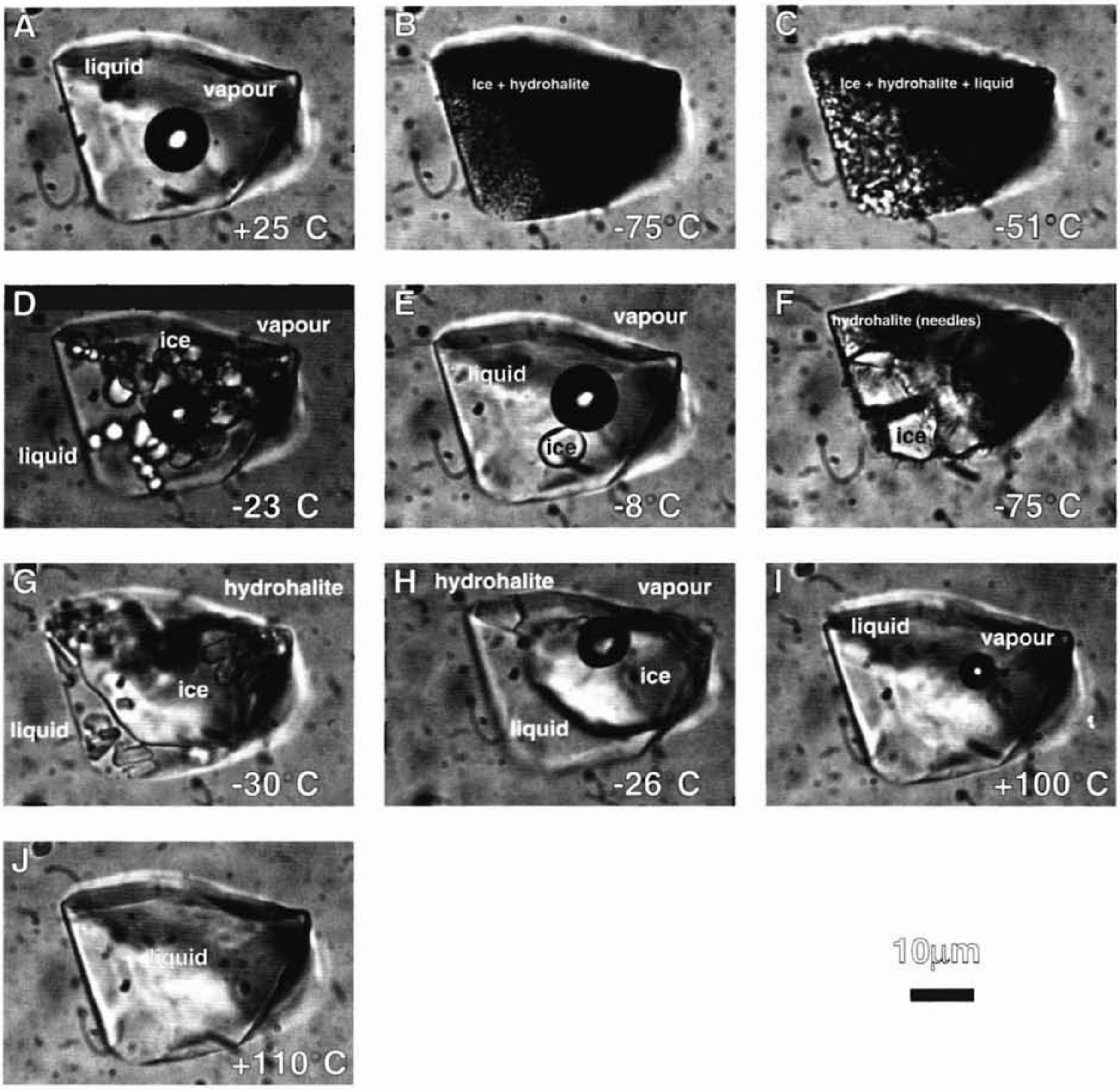

FIGURE 4. An example of the types of phase change observed during microthermometry (see text for a detailed description of events). **A:** T = 25°C; gas–liquid fluid inclusion. **B:** T = –75°C; fluid inclusion completely frozen. **C:** T = –51°C; granularity in the fluid inclusion marks the first appearance of liquid and is used as an estimate of eutectic temperature. **D:** T = –23°C; inclusion comprises liquid + vapour and a number of small ice crystals. **E:** T = –8°C; inclusion comprises liquid + vapour and a single ice crystal. **F:** T = –75°C; re-freezing the inclusion has caused hydrohalite to nucleate; because a single ice crystal was grown the location of hydrohalite can be clearly observed (*cf.* 4B). **G:** T = –30°C; inclusion consists of liquid + vapour, a single ice crystal and several hexagonal plates of hydrohalite. **H:** T = –26°C; now the inclusion only consists of single crystals of ice and hydrohalite, making the task of measuring the melting of these two phases far easier. **I:** T = 100°C; inclusion is close to homogenisation and the vapour bubble has decreased in size (*cf.* 4A). **J:** T = 110°C; inclusion has totally homogenised and now consists only of liquid.

TABLE II. First melting temperatures for a variety of salt–water systems (after Borisenko, 1977).

Chemical system	Eutectic temperature (°C)
H_2O–NaCl	–21.2
H_2O–$MgCl_2$	–33.6
H_2O–$CaCl_2$	–49.8
H_2O–NaCl–$CaCl_2$	–52.2
H_2O–NaCl–KCl	–23.5

Fig. 4A shows a liquid–vapour inclusion at room temperature. The first stage in microthermometric analysis is to completely freeze the contents of the fluid inclusion using the heating–freezing stage. Once the inclusion has frozen (Fig. 4B) it is slowly warmed and the temperatures at which subsequent phase changes occur are carefully measured. In the case of the illustrated inclusion, at –51.0°C it starts to appear granular (Fig. 4C). This temperature marks the first appearance of liquid and approximates to the eutectic of the system: –51.0°C is close to –52.2°C, the eutectic temperature in the system NaCl–$CaCl_2$–H_2O (Table II). The inclusion now contains liquid, vapour, ice, and a salt hydrate (hydrohalite, $NaCl.2H_2O$). The observation of first melting, which is independent of salinity, is used to infer the number and type of salts dissolved in the fluid. Heating to –23°C leaves several ice crystals but no hydrohalite (Fig. 4D). Further warming to –8.0°C leaves just a single ice crystal (Fig. 4E). Between –51.0 and –23.0°C hydrohalite has melted. Often this phase change is difficult to observe. To make the change easier to observe the inclusion is again cooled to –75°C and now the location of hydrohalite in the inclusion can be clearly observed (Fig. 4F). Warming the inclusion to –30.0°C results in several hexagonal hydrohalite crystals (Fig. 4G). Heating the inclusion a few degrees further to –26°C results in just a single hydrohalite crystal (Fig. 4H), which melts at –25.0°C. Warming to –7.0°C causes the last crystal of ice to melt (not shown). This completes all the observations for this inclusion below room temperature. However, the temperature at which the vapour phase disappears (the homogenisation temperature) is still to be determined. This phase change is used to estimate the temperature at which the inclusion was trapped in the mineral. On heating to 100°C the vapour bubble has decreased markedly in size (Fig. 4I) and at 110°C the inclusion comprises only liquid and is said to have homogenised (Fig. 4J). This process would be repeated for 20 to 40 inclusions with the aim of covering all types of compositional and petrographic variation. In a typical fluid inclusion study 10 to 30 samples would be similarly analysed.

Having made the measurements, how are they interpreted? First we can convert the observational data into compositional information using knowledge gained from experimental studies of phase equilibria. The first melting temperature indicates that the system $NaCl–CaCl_2–H_2O$ would be an appropriate model for this particular fluid inclusion. Fig. 5 illustrates the phase relationships in this system and the liquid line of descent shows the phase behaviour for the inclusion described above. At temperatures below –52°C the inclusion comprises ice + hydrohalite + vapour and when the inclusion is heated to –52.2°C the first liquid appears. As the inclusion is warmed, melting of the solids progresses and the composition of the resultant liquid is constrained by the ice – hydrohalite cotectic (line A–B) until at –25.0°C the last crystal of hydrohalite melts and the bulk composition of the liquid is free to move into the ice-field. The temperature at which hydrohalite melts can then be used to calculate the $NaCl/(NaCl+CaCl_2)$ weight ratio of the inclusion by finding the intersection of the tie-line (dotted line in Fig. 5) with the $NaCl–CaCl_2$ axis; in this case 0.79. On further warming, the last ice crystal melts at –7.0°C. This last temperature gives the bulk salinity of the inclusion: 11.3 weight percent NaCl + $CaCl_2$ equivalent. Fluid inclusionists routinely use a range of computer programs to estimate fluid inclusion compositions, rather than the time-consuming graphical interpolation method illustrated here. However, the graphical method illustrates how the observation of phase changes in a fluid inclusion can be used to estimate fluid compositions qualitatively and semi-quantitatively.

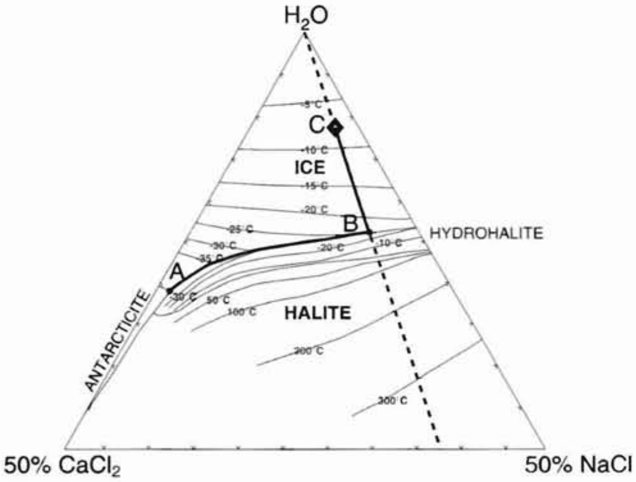

FIGURE 5. Triangular phase diagram for the system $NaCl–H_2O–CaCl_2$ (after Naden, 1996), showing the liquid line of descent for the inclusion illustrated in Fig. 4. Point A: T = –52°C; eutectic point in the system. As the inclusion is warmed it follows the cotectic (A–B) until at point B (–25°C) the last crystal of hydrohalite melts. A tie-line (dashed-line) between the H_2O apex of the diagram and this point can be used to calculate the Na:Ca ratio. On further warming, the composition of the liquid moves into the ice field, following the tie-line (B–C) until point C where the last crystal of ice melts at –7°C. Point C gives the bulk composition of the liquid.

Lastly, the homogenisation temperature of the inclusion gives an estimate of the minimum trapping temperature of the inclusion and, if the inclusion was trapped during mineral growth (i.e. it is a primary fluid inclusion), the minimum temperature of mineral formation. The reason why the homogenisation temperature is only a minimum estimate is that unless the fluid inclusion was trapped on the liquid–vapour curve the trapping temperature is dependent on pressure, a parameter which has to be determined independently. This is illustrated in Fig. 6 which is a pressure – temperature diagram for the system $NaCl–H_2O$ (a reasonable approximation for our inclusion). Point A shows the inclusion at room temperature. As it is warmed the inclusion follows the liquid—vapour curve until point B, where it homogenises. At this point, the inclusion is no longer constrained to the liquid–vapour curve and is free to move into the liquid field along a line of constant density (an isochore). The position of this isochore depends on the fluid inclusion composition and the homogenisation temperature. Points C and D represent different trapping conditions along an isochore, and inclusions trapped under any of these P–T conditions will homogenise at the same temperature (point B). Thus, unless an independent means of estimating pressure at the time of trapping (a geobarometer) is available, the trapping conditions cannot be uniquely determined.

Inclusions trapped on the liquid–vapour curve (point B in Fig. 6) are a special case. Here, the homogenisation temperature uniquely defines the P–T conditions of trapping. However, to prove that trapping on the liquid–vapour curve has occurred requires careful petrography to show that two fluids were trapped in equilibrium – a phenomenon called heterogeneous trapping. A detailed description of this phenomenon is given by Pichavant *et al.* (1982) and Ramboz *et al.* (1982). Furthermore, fluid inclusions that have been heterogeneously trapped commonly represent systems where a single fluid has split into two. This is analogous to opening a bottle of sparkling mineral water where the sudden lowering of pressure results in the release from solution of gaseous carbon dioxide.

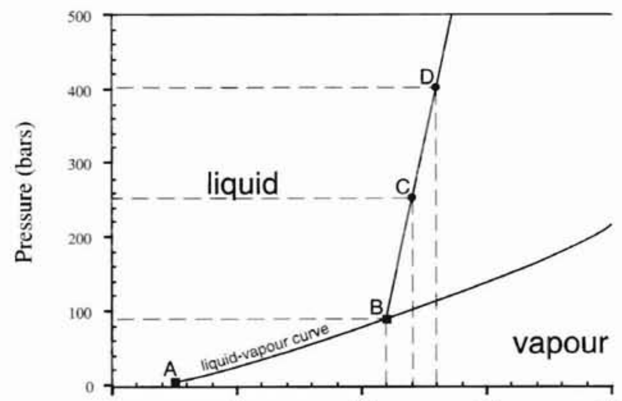

FIGURE 6. P–T diagram showing the location of the isochore for the inclusion illustrated in Fig. 4. Point A corresponds to the inclusion at room temperature. Point B is the homogenisation temperature of the inclusion. Points C and D show two possible P–T trapping conditions for this homogenisation temperature. To obtain the true trapping temperature an independent measure of pressure must be obtained.

This extremely important process is commonly termed boiling, phase separation, or fluid immiscibility. Moreover, its occurrence during mineral deposit formation can dramatically alter the chemistry of the ore fluid and it is recognised to be one of the most important processes in the genesis of an ore deposit.

BULK CHEMICAL ANALYSIS OF FLUID INCLUSIONS

A single gram of quartz may contain over twenty thousand fluid inclusions. This represents approximately 1000–2000 ppm or 0.1–0.2 % (by weight) of fluid trapped in quartz. It is possible to extract this fluid and determine its chemical composition using a variety of analytical techniques such as ion chromatography, mass spectrometry (MS), atomic emission spectrometry (AES), and optical emission spectrometry (OES). Although these analytical techniques are very powerful, with detection limits in the sub-ppm range, bulk extraction of fluid inclusions has several drawbacks. First, the large number of inclusions means that fluid may be extracted from several different types of fluid inclusion, giving very precise but geologically meaningless chemical data. It is therefore necessary to screen samples petrographically before analysis to show that they contain predominantly only one type of fluid inclusion. Furthermore, while extracting fluid from the sample, it is possible to contaminate it with impurities from the surface of the quartz or from small mineral inclusions. Thus a scrupulously clean analytical procedure is needed.

The precise sample preparation technique used depends on the type of analysis being undertaken. However, detailed petrography and microthermometric analysis of the samples is essential, so that only those containing predominantly one type of fluid inclusion are selected for bulk chemical analysis. Approximately 5–10 grams of the selected quartz is crushed and screened to give an average grain size between 1 and 0.5 mm. This grain size is a compromise between liberating mineral impurities in the quartz and preserving the fluid inclusions. The quartz is cleaned several times in hot strong acid, rinsed several times in hot ultra-pure water to remove most of the impurities adhering to the surface of the quartz, and then carefully hand-picked under a binocular microscope to produce a clean quartz sample. Two final clean-up procedures are used to remove any remaining impurities. One technique involves cleaning quartz in an electrolytic cell for several weeks. This removes any ionic species adsorbed on the surface or along micro-fractures in the quartz. The second involves ultrasonic cleaning in an organic solvent such as trichloromethane to remove organic contaminants.

Extraction of the inclusion fluid is achieved using one of two procedures. The first is to crush the quartz to a fine powder, which is then leached by the addition of a solvent (usually ultra-pure water). This takes up into solution any ionic species present in the fluid inclusions, and the resulting solution can then be analysed. Crushing also releases the volatile components from the fluid inclusions, which can then be isolated and analysed either for individual species or, if there is enough fluid, for stable isotope ratios. The second extraction method is to heat the quartz to between 400 and 600°C which causes the fluid inclusions to rupture (decrepitate). This is normally reserved for the determination of volatile constituents. Decrepitation also causes the non-volatile constituents of the fluid inclusions to precipitate along micro-fractures and these can then be leached by the addition of a suitable solvent and analysed separately.

CRUSH-LEACH ANALYSIS

Crush-leach analysis is used to determine the ionic species present in fluid inclusions (details of the analytical technique are described in Bottrell *et al.*, 1988). Because the total amount of inclusion fluid released by crushing can never be accurately determined it is not possible to give precise absolute abundances of the elements determined by this method and results are commonly normalised to one of the major components in the fluid (usually sodium). However, if accurate microthermometric data are available for the sample, it is possible to use the composition of the fluid determined from microthermometry to give a semi-quantitative estimate of absolute abundances.

An example of the application of crush-leach analysis is the investigation of the granite-related Th–U–REE mineralisation in the Capitan Mountains, New Mexico (Campbell *et al.*, 1995). Careful petrography and microthermometry identified four main types of fluid inclusion. Type I are multiphase inclusions comprising liquid + vapour + halite (NaCl) + sylvite (KCl), with three or more other daughter minerals (e.g. anhydrite and hematite). Type II inclusions are similar to Type I inclusions but do not contain as many 'exotic' daughter minerals (e.g. anhydrite and hematite). Type III inclusions comprise liquid + vapour with only one daughter mineral (halite). Type IV inclusions consist only of liquid + vapour. Detailed knowledge of fluid inclusion petrography and microthermometry allowed Campbell *et al.* to select appropriate samples for crush-leach analysis. Fluids extracted from quartz and fluorite samples were analysed for F, Br, Cl, I and SO_4 by ion chromatography. Inductively coupled plasma (ICP)–AES and ICP–MS were used to analyse for Na, K, Ca, Mg, Al, Ba, B, Li, Cs, Rb, Sr, Fe, Mn, Pb, Zn, Cu and total rare earths. Detection limits for each component in the leached fluid were in the order of 2 ppm. Normally, results of analyses are quoted relative to sodium, but in this case accurate microthermometry allowed the reconstruction of leachate data to absolute abundances showing trace element concentrations in the range 50–2000 ppm for elements such as Li, Ba, Sr, Rb, Pb, Zn and total rare earth elements. Fe and Mn, which cannot be detected microthermometrically, were shown to be major constituents of the fluid (1–2 wt %). Furthermore, the halogen ratios indicated by crush-leach analysis were one of the most distinctive features of the mineralisation and indicated assimilation of evaporites by ascending granitic magmas.

GAS ANALYSIS

Gas analysis is another bulk technique for analysing the volatile components (e.g. H_2O, CO_2, CH_4, N_2) within a fluid inclusion. As with crush-leach analysis, scrupulously clean samples are required for analysis. Fig. 7 shows the volatile analysis equipment used at the British Geological Survey and Fig. 8 shows typical gas mass spectra obtained with such equipment. Gas analysis is mainly used to study ore deposits where the hydrothermal fluid had a high content of dissolved volatiles, e.g. mesothermal gold (H_2O–NaCl–CO_2±CH_4±N_2) and granite-related tin–tungsten (H_2O–NaCl±CO_2±CH_4±N_2) mineralisation. Volatile data, in conjunction with stable isotope data (see below) can be used to model fluid–rock interactions and to identify possible fluid sources.

In a fluid inclusion study of black-shale hosted gold mineralisation in the Dolgellau Gold Belt of north Wales, Shepherd *et al.* (1991) showed, by microthermometric analysis, that gold mineralisation was related to unmixing of an H_2O–NaCl–N_2–CH_4–CO_2 hydrothermal fluid. Bulk analysis of the inclusion volatiles hosted in mineralised vein quartz, with

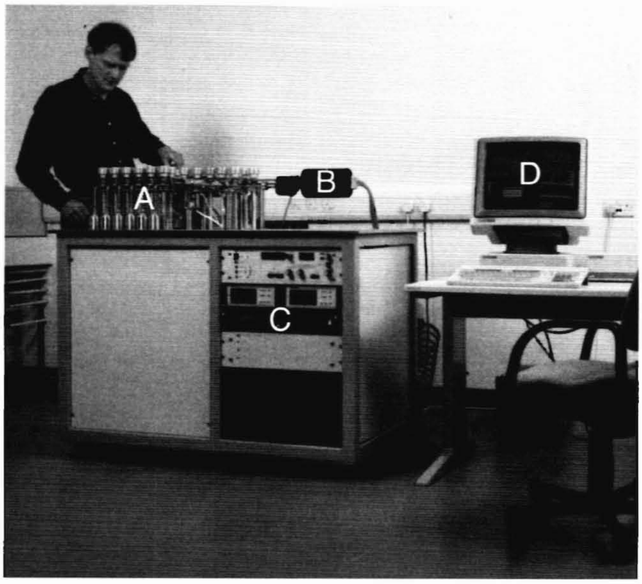

FIGURE 7. Gas analysis equipment used at the British Geological Survey. **A:** Computer-controlled high-vacuum line for extracting and separating fluid inclusion gases. **B:** Fast- scanning quadrupole mass spectrometer. **C:** High-sensitivity pressure gauges. **D:** Hewlett Packard computer for automated analysis.

accompanying gold assays, showed a strong positive correlation between inclusion volatiles (CH_4, N_2, CO_2/CH_4) and gold grade. This was related to intense interaction between the ore fluids and graphitic shales, which resulted in the breakdown of carbonaceous matter and ammonium-bearing micas and introduced CH_4 and N_2 into the ore fluids. On reaching gas saturation the ore fluid unmixed and gold precipitated. The correlation between inclusion volatiles and gold grade was so strong that it prompted Shepherd *et al.* to suggest that bulk volatile analysis could be used as an exploration tool.

ISOTOPE ANALYSIS

The most widely practised isotopic techniques are those of hydrogen, oxygen and carbon. Fig. 9 shows the extraction line at the British Geological Survey for stable isotope analysis (isotopic analysis is undertaken off-line in a gas source mass spectrometer). Stable isotopes in studies of hydrothermal processes are commonly used to document and identify fluid sources, mixing of different types of fluid, boiling during ore precipitation, and fluid–rock interaction. Sample preparation and extraction techniques may differ slightly between laboratories. However, the general technique described above is applicable to all.

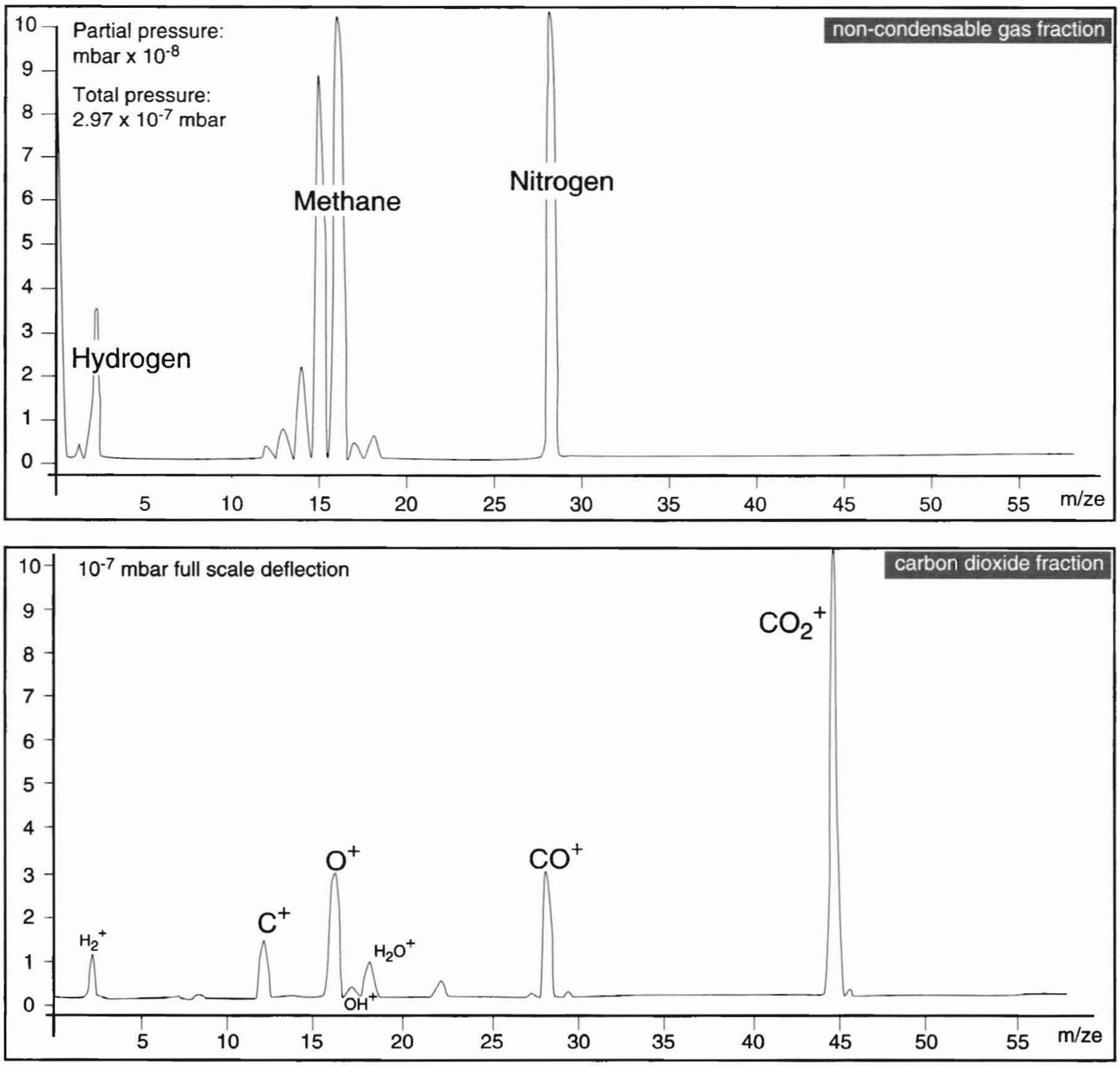

FIGURE 8. Fluid inclusion gas mass spectrum, showing peaks for methane, nitrogen and carbon dioxide. Horizontal scale gives ion mass divided by ion charge (usually 1); peak heights are proportional to the number of ions detected.

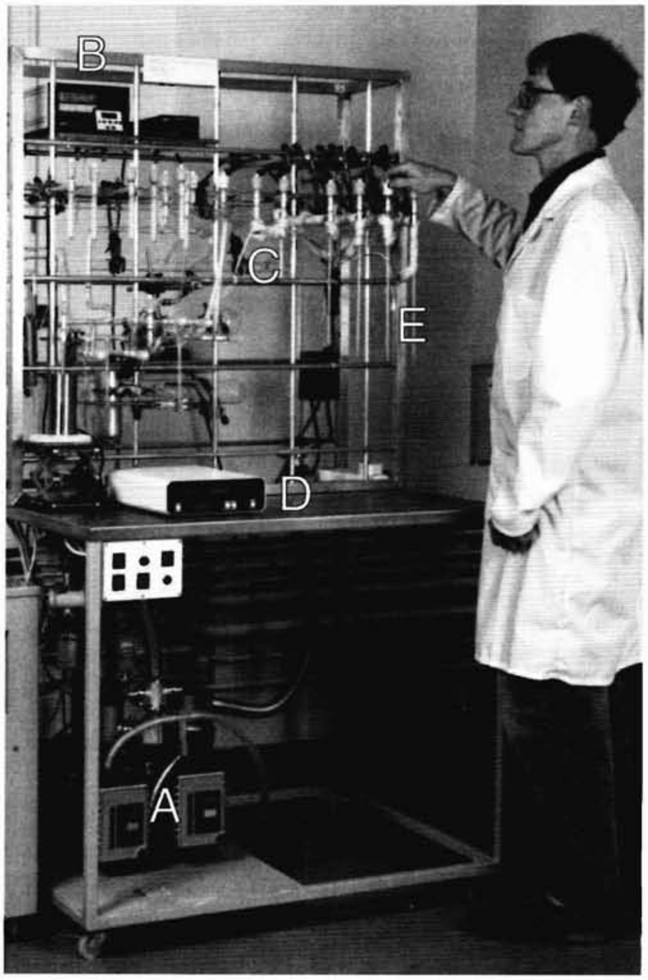

FIGURE 9. Fluid inclusion extraction line for stable isotope analysis. **A:** High-vacuum pumps. **B:** Pressure gauges. **C:** High-vacuum glass extraction line. **D:** Temperature controller for decrepitating the sample. **E:** Glass tubes for holding samples.

The ratios of stable isotopes in a mineral (e.g. $^{2}H/^{1}H$, $^{18}O/^{16}O$) vary depending on the processes involved in its formation. The results of stable isotope analysis are usually expressed as positive or negative deviations (δ, measured in parts per thousand or ‰) from standard internationally accepted values for each isotope pair.

Wilkinson *et al.* (1995) used $\delta^{18}O$, δD and $\delta^{13}C$ signatures of fluid inclusions in vein-quartz from southwest England to show how several generations of hydrothermal fluid migrated through a segment of Palaeozoic crust during the Variscan orogeny. They were able to identify fluids of metamorphic, mixed magmatic–metamorphic, meteoric and basinal brine origin. The mixed magmatic–metamorphic fluid was the main fluid responsible for the Sn–W mineralisation, and there must have been some input from the metamorphic rock that surrounds the Cornubian batholith. In addition, the stable isotope signatures showed that the Pb–Zn mineralisation in the region was unrelated to magmatism and that the fluids and metals were sourced from basinal brines, probably associated with the development of Permo-Triassic basins.

A less widely used methodology is the analysis of radiogenic isotopes of trace metals in the fluid inclusions (Rb, Sr, Sm, Nd, Pb). As with all bulk analytical techniques, sample purity and a prior knowledge of the distribution of fluid inclusions within a sample, gained through petrography and microthermometric analysis, are critical factors in obtaining high-quality data.

Precise radiometric ages for ore deposits are notoriously difficult to obtain, since ore minerals generally do not contain significant concentrations of radioactive elements such as potassium, rubidium or neodymium to allow their use as geochronometers (ore minerals in uranium deposits are an obvious exception). Ore deposits are commonly dated by analysis of the associated alteration assemblage minerals (e.g. micas and feldspars), which contain sufficient amounts of rubidium and potassium for radiometric age determination. However, this is not without its problems, as the fluxes of fluid associated with hydrothermal processes commonly mean that these ages are reset. The need to find a solution to these problems provided the driving force behind using inclusion fluids, which are commonly high in elements such as rubidium, strontium and potassium, as geochronometers.

For the radiogenic isotope analysis of inclusion fluids, two main methodologies have been developed: determination of $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios in fluid inclusions hosted in quartz; and determination of $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios in fluid inclusions hosted in sphalerite. Rubidium and strontium are present only at the ppm level in fluid inclusions. Moreover, quantitative extraction and precise analysis of such small amounts of material without contamination and loss presents a considerable problem. The description of the various techniques that have been developed for radiometric isotope analysis of inclusion fluids is beyond the scope of this article. However, the interested reader is referred to Pettke and Diamond (1995) for an excellent critique of the various procedures.

In spite of these difficulties, fluid inclusions have provided unequivocal ages for a number of mineral deposits (Scrivener *et al.*, 1994) and acted as isotopic tracers of fluid evolution (Halliday *et al.*, 1990), which would not have been possible using conventional isotopic dating and tracing techniques. For example, one of the major problems in ore deposit geochronology is the timing of Mississippi Valley-type (MVT) mineralisation with respect to geological evolution of the sedimentary basins that host, or are located close to, the mineralisation. Three main models have been proposed for the origin of the mineralising fluid: (i) over-pressuring of sediments during rapid burial or hydrocarbon generation; (ii) topographically driven flow; and (iii) basin compression and thrusting. Dating of MVT mineralisation would provide a method of discriminating between these hypotheses. Christensen *et al.* (1995), in a study of MVT mineralisation in the Canning basin, Australia, used fluid inclusions in sphalerite to obtain accurate ages of 375±3 Ma, 355±14 Ma and 363±12 Ma on different samples from the area. These were consistent with early de-watering (30 to 50 Ma after the initiation of basin extension) from over-pressured zones in the sedimentary pile, rather than later brine expulsion associated with hydrocarbon generation in the late Carboniferous.

CHEMICAL ANALYSIS OF INDIVIDUAL FLUID INCLUSIONS

As already stated, microthermometry provides only semi-quantitative chemical data on the major elements in the fluid phase and very little information on the trace constituents. Bulk analysis techniques can measure trace elements but interpretation of the results will always be equivocal, to a greater or lesser degree. What is required is the ability to undertake high-sensitivity, high-precision and high-accuracy analyses of single fluid inclusions, though the small size of fluid inclusions presents a challenge. They are generally less than 1,000 μm^3 in size, equivalent to <1 nanolitre (10^{-9} l) of fluid, and contain only 10–500 picograms (10^{-12}g) of major constituents (e.g. Na, Ca, Cl) with femtograms (10^{-15}g) of trace elements (e.g. Zn, and Pb). Most work has focused on non-destructive micro-beam techniques. Although such techniques do not require the extraction of fluid, the small size of the inclusions present problems of obtaining a large enough 'signal' for meaningful chemical analysis. The micro-beam would have to penetrate beneath the mineral surface to produce a signal from the fluid inclusion. Thus, techniques such as Fourier-transform infra-red (FTIR) and especially Laser Raman spectroscopy, which are not as susceptible to matrix effects as is EPMA, have become the most widespread tools for the analysis of individual fluid inclusions. Laser Raman has proved to be extremely useful in determining minor amounts of gases (CO_2, CH_4, N_2) present in a fluid inclusion and is commonly used to help reconstruct fluid compositions of geologically complex fluids that contain significant amounts of such gases. However, only polyatomic volatile species are 'seen' by FTIR or Laser Raman spectroscopy. To provide detailed information on the trace element chemistry of the inclusion, fluid inclusionists have taken two approaches. The first was to use high-energy micro-beams (e.g. synchrotron radiation) to overcome the problem of producing a large enough signal from a fluid inclusion located beneath the surface of the sample. The second development concentrates on extracting the fluid for analysis, using a laser. The extracted fluid is then analysed employing high-sensitivity analytical techniques such as ICP–MS or ICP–AES (e.g. Shepherd and Chenery, 1995; Moissette *et al.*, 1996).

NON-DESTRUCTIVE MICROBEAM TECHNIQUES

Synchrotron radiation is emitted when charged particles such as electrons or positrons are accelerated. In an electron storage ring, radiation is generated as the electrons are guided, by magnets, around a closed loop. The radiation can be 'tapped' and collimated into a small beam as little as 5 µm across that is suitable for X-ray fluorescence (XRF) microanalysis. The high energy of the beam results in significant surface penetration of the sample and permits the analysis of fluid inclusions. It has the sensitivity (ppm range) and multi-element capabilities (all elements with atomic number above 13) that make it suitable for the analysis of individual fluid inclusions located close to the surface of the mineral. However, to obtain a quantitative analysis from a synchrotron XRF (SXRF) spectrum is not simple. First, there is the problem of subtracting the X-ray spectrum produced by the host mineral; secondly, accurate prediction of X-ray absorption and generation efficiency from the fluid inclusion and host mineral (quartz) are required; and thirdly, the precise geometry of the inclusion must be known to calculate its volume. Rankin *et al.* (1992), Vanko *et al.* (1993) and Mavrogenes *et al.* (1995) describe techniques for overcoming some of these limitations. SXRF can undoubtedly provide qualitative to semi-quantitative data concerning the distribution of major and trace (>200 ppm) elements in fluid inclusions; quantitative estimation is certainly more difficult and further research is required. However, SXRF has advantages in that it is non-destructive, and is particularly useful for identifying daughter minerals in fluid inclusions. In studies of deposits where the hydrothermal fluid is particularly concentrated (e.g. rare earth pegmatites and porphyry copper deposits), the ability to identify daughter phases can provide important information on the nature of the mineralising fluids.

Two techniques similar to SXRF are proton-induced X-ray emission (PIXE) analysis and proton-induced gamma-ray emission (PIGE) analysis. They are analogous to EPMA but utilise a high-energy (*c.* 3–4 Mev) beam of protons rather than electrons. As with SXRF, obtaining quantitative data from a PIXE spectrum is not simple and raises the same problems (see Ryan *et al.*, 1990 and 1991).

Heinrich *et al.* (1992) used PIXE microanalysis to investigate the distribution of ore metals in fluid inclusions hosted in a quartz–cassiterite vein in the Mole Granite, New South Wales, Western Australia. Two types of coexisting fluid inclusions were identified microthermometrically: high salinity (~30–45 weight % total dissolved solids) multi-solid inclusions and low salinity vapour-rich fluid inclusions. They were interpreted as an equilibrium assemblage of exsolved magmatic brine and vapour. Semi-quantitative to quantitative PIXE microanalysis performed on both inclusion types revealed a marked fractionation between the brine- and vapour-rich inclusions, with most elements being strongly fractionated into the brine-rich inclusions. Copper was an exception and was preferentially partitioned into the vapour phase by an order of magnitude (~900 ppm in the brine-rich and 10,000 ppm in the vapour-rich inclusions). This was an important discovery as copper concentrations are two orders of magnitude greater in the vapour phase than would be predicted from published partitioning data for copper into chloride fluids. Hence copper must be complexed by another ligand such as reduced sulphur. This has important implications for genetic modelling as most models assume that copper in porphyry copper deposits is transported as a chloride complex. This research shows how important it is to obtain at least semi-quantitative trace element data on individual fluid inclusions.

LASER EXTRACTION TECHNIQUES

Although analytical techniques using synchrotron and proton radiation are non-destructive and provide analytical information in the ppm range they require access to large-scale reactor facilities and cannot be used as a routine analytical tool. Inductively coupled plasma (ICP) mass-, emission- and absorption spectrometers are more widely available. However, these are destructive techniques and require sample introduction. How do you extract 1–10 nano-litres of inclusion fluid from a mineral and transfer the sample to a ICP mass spectrometer without sample loss or fractionation? Recent developments in laser technology mean that it is now possible to focus accurately a high-powered laser to a spot size of 2–5 µm and to remove ('ablate') small amounts of material from the surface of a solid, with the laser acting as a very accurate micro-drill or probe. Thus, in theory it should be possible to interface a laser ablation microprobe (LAMP) with an ICP mass spectrometer, to 'drill' into a fluid inclusion and to release the contents for analysis. At the British Geological Survey, Shepherd and Chenery (1995) have developed such an apparatus (Fig. 10) and have shown that it is capable of analysing a wide range of elements in individual fluid inclusions 10–60 µm in diameter (1–25 nanolitres of fluid). As part of their study they analysed fluorites from the north Pennine orefield and the Kit Hill–Gunnislake area of southwest England, and were able to detect ore-forming elements such as Pb, Cu and Zn (Fig. 11). Further technique development has resulted in semi-quantitative to quantitative determination of chlorine to bromine ratios, which can be used to determine fluid origins and fluid–rock interactions (T.J. Shepherd, *unpublished data*). Although synchrotron and proton radiation techniques can provide extremely important information concerning element concentrations and speciation, LAMP ICP–MS is more widely accessible and is most likely to be the technique for routine analysis

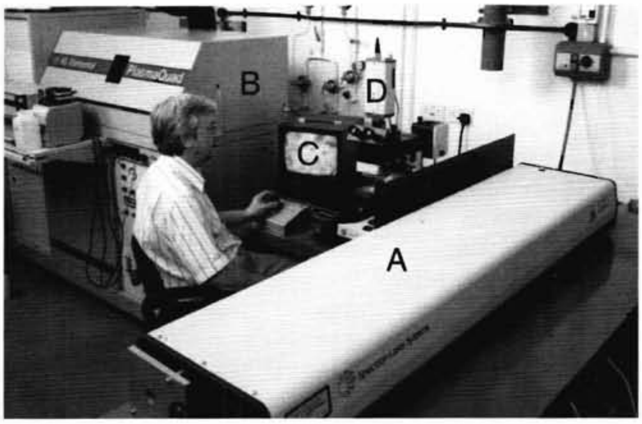

FIGURE 10. Laser Ablation ICP–MS equipment at the British Geological Survey for the chemical analysis of single fluid inclusions. **A:** Spectron Laser Systems Nd–YAG laser. **B:** VG Elemental Plasma Quad ICP mass spectrometer. **C:** TV monitor for observing sample and laser microprobe. **D:** Leitz microscope for focusing laser beam and observing sample.

of individual fluid inclusions in the future.

THEORETICAL STUDIES

Not all fluid inclusion studies are confined to the study of natural samples. In fact the interpretation of fluid inclusion data relies to a greater or lesser degree on an understanding of the physico-chemical characteristics of experimentally and theoretically determined systems, such as NaCl–H_2O and NaCl–CO_2–H_2O. Originally, much of this work was undertaken using specially designed high pressure–high temperature apparatus. Furthermore, the studies were undertaken from a chemical engineering rather than a geological standpoint. This, coupled with the highly corrosive nature of the fluids under examination, meant that data were not available in areas of most interest to fluid inclusionists, and prompted them to develop techniques for fabricating synthetic fluid inclusions. Sterner and Bodnar (1984) have developed a technique where cylinders of Brazilian quartz, free of fluid inclusions, are heated to 350°C and rapidly quenched in water to induce micro-fracturing in the quartz. The fractured quartz is then packed into platinum capsules, with appropriate amounts of water and salts to produce the desired fluid composition. The capsules are then heated in the pressure apparatus to the desired P–T conditions and the fluid causes the micro-cracks to heal and trap fluid inclusions at known PTVX conditions. Synthetic fluid inclusions have been used to investigate a number of chemical systems of geological interest (Table III), and these data, in conjunction with earlier investigations, provide the framework for interpreting a wide range of microthermometric data. Furthermore, as synthetic fluid inclusions have known PTVX properties, they are invaluable as calibration and evaluation standards for all the various analytical techniques described above.

APPLICATIONS

As stated earlier, wherever a mineral has precipitated from a fluid there is scope for a fluid inclusion study, and some brief examples have already been cited above. Here, I would like to concentrate on some applications to specific geological problems. They range from studies of ore genesis, the modelling of sedimentary basin evolution, pressure–temperature reconstructions in metamorphic petrology, and the petrogenesis of igneous rocks, to the formation of evaporites. Fluid inclusions not only provide geological information, but also provide data on phase equilibria in synthetic systems that are of considerable use to the physical chemist.

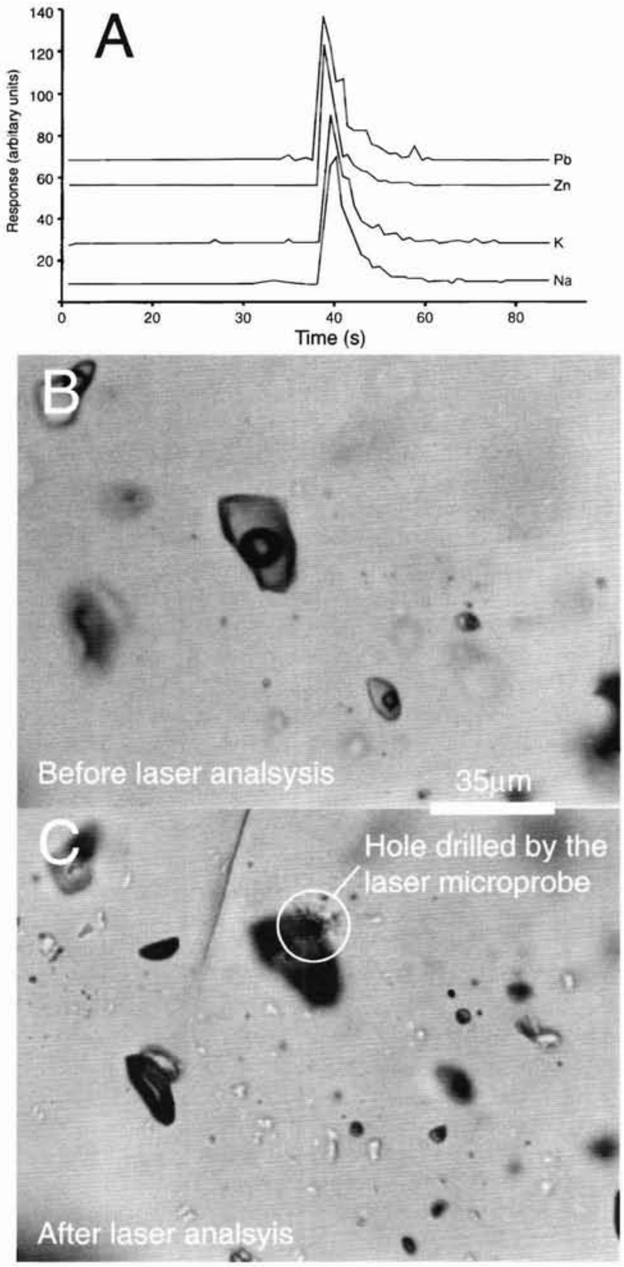

FIGURE 11. A: Mass spectrum of a single fluid inclusion hosted in fluorite from the North Pennine orefield. The y-axis shows the response of the ICP mass spectrometer in arbitrary units and the x-axis is time (seconds). While the laser probe is drilling into the inclusion there is no response from the instrument. After about 30 seconds the fluid inclusion ruptures and releases its contents (approximately 1 nanolitre of inclusion fluid) and the instrument records the presence of lead, zinc potassium and sodium in the fluid (T.J. Shepherd, *unpublished data*). **B:** Fluid inclusion before analysis, with the liquid and gas phases clearly visible. **C:** Fluid inclusion after analysis. It is now empty and all the fluid has been extracted. Note that none of the surrounding inclusions have been damaged by the laser; thus confirming that the analytical signal relates to a single fluid inclusion.

ORE DEPOSITS

The most common use of fluid inclusions is in the study of the genesis of ore deposits, and the literature on the subject is voluminous. Through such research, fluid inclusionists now understand the types of fluid involved in the majority of classes of hydrothermal ore deposit (Table IV).

An excellent example is the study of gold–quartz veins in the

TABLE III. Systems investigated using synthetic fluid inclusions.

System	Applications
$NaCl–H_2O$	Epithermal gold deposits, paleogroundwaters
$CaCl_2–H_2O$	MVT base metal deposits, sedimentary diagensis
$NaCl–H_2O±CO_2$	Metamorphism, Archaean gold
$NaCl–KCl–H_2O$	Porphyry copper deposits
$NaCl–CaCl_2–H_2O$	MVT deposits, sedimentary diagenesis, mid-ocean ridge hydrothermal activity

Italian Alps by Diamond (1990), who showed how a number of analytical techniques can be integrated to characterise the pressure, density, temperature and compositional evolution of vein-forming hydrothermal solutions, and to identify the relationship between fluid processes and gold deposition. Careful petrography revealed two distinct inclusion types: low-CO_2 (15–25 volume % carbonic liquid) and high-CO_2 (85–95 volume % carbonic phase). These inclusions occur in five separate generations and gold (10–100 μm grain size) was shown to be coeval with each of them. Thus fluid inclusion analyses could be directly related to the processes of gold mineralisation. Microthermometry showed that, semi-quantitatively, these inclusions comprise a low salinity aqueous brine with <3 wt % total dissolved solids and a carbonic liquid with traces of other volatiles (CH_4, N_2). Laser Raman spectroscopy was used to identify and characterise trace gas components, and crush-leach analysis quantified the ionic species in the hydrothermal fluid. The combination of microthermometry, Laser Raman spectroscopy and crush-leach analysis was then used to estimate a fluid composition (in mole percent) of 90.9 H_2O, 5.9 CO_2, 1.47 Cl, 1.49 Na, 0.15 N_2, 0.06 K, 0.02 S, 0.02 Ca, 0.003 Mg and 0.002 CH_4. These results, combined with high-temperature (200–300°C) microthermometric data and thermodynamic modelling, were then employed to estimate P–T conditions for the main mineralisation as being between 300°C, 1300 bars and 240°C, 650 bars. Fluid immiscibility was observed only in the latest generation of fluid inclusions, associated with calcite + tetrahedrite + galena + gold. This is an alternative hypothesis to current models for the formation of mesothermal gold deposits, which relate the deposition of economic gold to processes involving unmixing of carbonic and aqueous fluids.

SEDIMENTARY DIAGENESIS

Fluid inclusions trapped in diagenetic minerals (e.g. carbonate cements and authigenic quartz overgrowths) present a unique opportunity for examining the evolution of pore-fluid chemistry, oil migration and changing P–T conditions during the burial of a sedimentary sequence. For example, Narr and Burruss (1984) studied the origin of fracture porosity and permeability in a carbonate hydrocarbon reservoir and identified coexisting brine and hydrocarbon fluid inclusions. Microthermometric data on both types of fluid inclusion allowed them to reconstruct the pressure–temperature conditions of fluid inclusion trapping by reference to the experimentally and theoretically determined PTVX properties of hydrocarbon and salt–water systems. They estimated that the two coexisting fluids were trapped at approximately 130°C and 350 bars. Furthermore, the coexistence of hydrocarbon and brine inclusions documents the pressure and temperature at which the hydrocarbon migrated into the reservoir. However, the applicability of fluid inclusion studies to sedimentary diagenesis is not without difficulties. One of the major problems is the possibility of fluid inclusion 'resetting' by a higher temperature event during burial. Approaches to solving this problem are discussed by Burruss (1989), and involve careful petrography and microthermometry to check for internal consistency of observations. However, if 'resetting' has occurred this does not mean that the data are invalidated, as they now record the maximum temperatures to which the inclusions have been exposed and may help define a maximum palaeogeothermal gradient for the well site.

PALAEOGROUNDWATERS AND PALAEOCLIMATE

A rapidly evolving field of fluid inclusion research is the study of ancient (<1 Ma) and modern waters. To date most of the studies have focused on palaeoclimatic studies using fluid inclusions trapped in evaporites. Roberts and Spencer (1995), in a study of modern halite precipitating in an ephemeral lake in the Badwater Basin, Death Valley, California, developed a microthermometric technique for analysing primary fluid inclusions trapped in halite. They found that fluid inclusion homogenisation temperatures obtained from the halite closely mirrored the measured lake temperatures and duplicated seasonal variations. The microthermometric study was then extended to cover halite beds in lake sediment cores from the same locality to see if these patterns were repeated in evaporites up to 192,000 years old. The homogenisation results were unable to resolve fine-scale seasonal variation, but still recorded palaeotemperatures in the range 5–35°C. The presence of pseudomorphs of hydrohalite, a mineral that is only stable below ~0.1°C, indicated that between 186 and 120 thousand years ago temperatures were 10–15°C cooler than at present. This type of research is still in its infancy and there are

TABLE IV. Some types of hydrothermal ore deposits and their associated fluid chemistry.

Type of mineralisation	Fluid chemistry and general P–T conditions
Porphyry copper deposits	Very high salinity, high temperature magmatic $NaCl–KCl±CaCl_2–H_2O$ fluids
Mississippi Valley Type Pb–Zn deposits	High salinity, low temperature $NaCl–CaCl_2–H_2O$ fluids commonly associated with hydrocarbon-bearing fluid inclusions. Low temperatures (generally < 200°C)
Granite-associated Sn–W mineralisation	Low to moderate salinity, mainly magmatic $NaCl–H_2O$ fluids with minor amounts of dissolved gas (CO_2, CH_4). Moderate to high temperatures (300–500°C)
Epithermal gold	Low salinity, moderate temperature $NaCl–H_2O$ fluids with trace volatiles (e.g. CO_2, CH_4). Mineralisation commonly associated with boiling phenomena at ~200–250°C
Mesothermal (Archaean-type) gold	Moderate to high temperature $NaCl–H_2O–CO_2±CH_4±N_2$ fluids. Mineralisation commonly associated with immiscible fluids at moderate temperatures (250–400°C).

many problems still to be resolved. but the approach has great potential for climatological research.

THE FUTURE

Current trends in fluid inclusion research are towards developing routine quantitative analysis of individual fluid inclusions. In terms of the quality of data there is a broad analogy with that obtained by EPMA during late 1960s and early 1970s. The techniques are able to produce quantitative data, but the number of analyses that can be undertaken is relatively small. Considering the number of fluid inclusions in a sample (thousands or millions) this presents a major sampling problem. How representative is the small number of quantitative multi-element, multi-species analyses of the range of palaeofluids present in a sample? Currently, this problem is overcome by using careful petrography and microthermometry to identify 'typical' fluid inclusions for detailed analysis. This enables the high-quality information provided by the more sensitive techniques to be related to the fluid inclusion paragenesis obtained through petrography. However, a future goal is the automation of the various techniques to produce high-sensitivity 'fluid inclusion maps' showing the distribution of trace elements in different generations of fluid inclusions. This is analogous to the detailed X-ray element maps that can be produced by modern electron microprobes (see Williams and Spratt, 1995).

CLOSING REMARKS

In a review article of this type it is not possible to deal in any detail with specific aspects of fluid inclusion research. However, I have tried to show how fluid inclusion analysis is applicable to a range of topics in the earth sciences and that these techniques can be used to glean pertinent information about fluid processes, ancient and modern, within the Earth's crust. Where possible I have directed the interested reader to literature that deals comprehensively with individual topics such as microthermometry and the use of modern high-precision equipment in fluid inclusion analysis. I especially wanted to show that there is a greater breadth to fluid inclusion studies than just a convenient geothermometer used in the study of ore deposits – a common misconception held by many professional geologists.

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MINERALOGY OF SNELSTON MINE, NEAR ASHBOURNE, DERBYSHIRE, ENGLAND

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Snelston mine is situated on a Lower Carboniferous Limestone inlier close to the south edge of the Derbyshire limestone dome and protrudes through Triassic sediments. Dolomitisation of the surface of the limestone acted as a barrier to downward percolating mineralising fluids, resulting in a concentration of copper and lead minerals which were mined sporadically over a period of at least 100 years. The paper describes the minerals found at Snelston mine, and discusses the geology and mineralisation of the deposit.

INTRODUCTION

Snelston mine (National Grid Reference SK 154 414) is located near the village of Snelston, between Ashbourne and Uttoxeter, Derbyshire (Fig. 1). Copper and lead minerals were recovered principally between 1869 and 1873, and again from 1909 to about 1921. More recently, Snelston mine has been commonly known as Isolation Mine but, although this name was believed to be locally current in the 1940s (R.J. King, *personal communication*), it is not found in any official documents and it is uncertain when it was introduced.

A large depression just east and south of the mine was an old quarry, called for convenience in this paper the North quarry, which has been infilled largely with a slurry of coffee grounds from a nearby factory, making the surface unstable and unsafe to walk on. There is a second quarry (SK 153 412) across the road to the south, referred to here as the South quarry, currently used as a refuse tip and nearly totally filled; access is possible but very restricted. South quarry was known variously as Birchwoodpark Quarry, Birchwoodpark Stone Quarries, and Birchwoodpark Lime Works in the past, and is currently called Birchwood Quarry by Derbyshire County Council.

The geology of the immediate area and the layout of the mine itself are largely obscured by vegetation and by material dumped in the adjacent quarry. Having been used as a rubbish dump, the area has a large number of 'remains' which may or may not have been associated with the mine. In particular, there is a substantial amount of slag and clinker which appears to be recent infill material. Occasional pieces of slag found buried and associated with mineralised material, however, may be contemporary with mining or with the lime kilns which were also sited here.

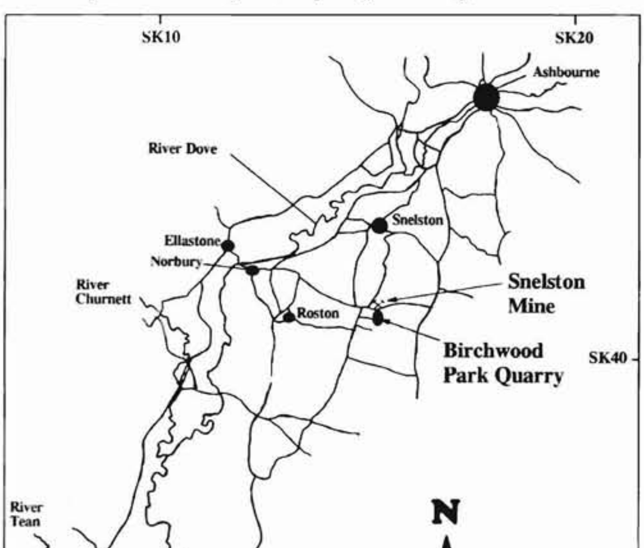

FIGURE 1. Location map.

HISTORY

Farey (1811) makes several references to mining in this area, the principal of which are: (a) "Birchwood-park ... in Limestone (in the Red), Lead, Fluor, green Spar"; (b) "In a Stone-pit on the south side of Birchwood-moor Houses ... I saw several strong veins of rose-coloured Barytes with thin strings of Lead Ore in them in ... a Gravel Rock? foreign to the Derbyshire strata, as Alderley Edge is." On a map dating from 1828, South quarry was already extensive and was referred to as a lime works. Quarries and kilns, as well as old shafts and a chimney, are marked on subsequent Ordnance Survey maps. A detailed account of the interesting history of Snelston mine has been published elsewhere (Jackman, 1996).

Lead and copper ore production is recorded by Dewey and Eastwood (1925) and by Burt *et al.* (1981) for two periods, 1869–73 and 1909–18. No further reference has been found for the first period, but information about the second period can be found in company records in the Public Record Office, Kew, Surrey. Snelston Copper Mine Limited was formed in 1910 to exploit the deposit, and over 600 tons of copper ore and 250 tons of lead ore were extracted before the company went into voluntary liquidation in 1922. Since then there has been no metal mining at Snelston but limestone quarrying continued in South quarry until 1957, when the boundaries of the limestone had been reached and water ingress prevented the quarry floor from being lowered any further. North quarry had already ceased operation by 1904 (Bemrose, 1904). The sites of both quarries have been used as rubbish tips for some time, and the old mine workings are undoubtedly flooded and inaccessible. Water ingress to the mine was always a major problem.

GEOLOGY AND MINERALISATION

Snelston mine is located in gently rolling countryside at the edge of a Lower Carboniferous (Dinantian) Limestone periclinal inlier 6 km south of, but at depth continuous with, the Derbyshire Carboniferous Limestone dome (Chisholm *et al.*, 1988). The Snelston pericline is roughly elliptical (*ca* 800 × 200 m), with the main axis lying NNE–SSW, and is completely surrounded by Triassic deposits which are them-

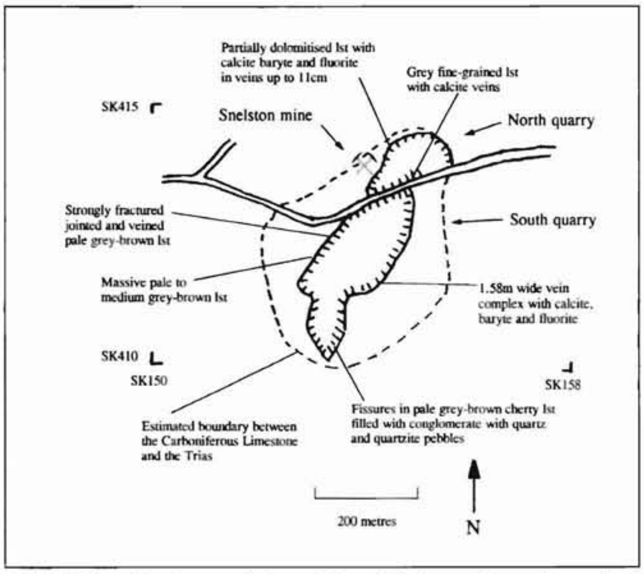

FIGURE 2. Sketch map of the position of Snelston mine and associated quarries relative to the boundary of the inlier. (After BGS Sheet SK14 SE, 1955).

selves largely covered by drift (Fig. 2). Farey (1811) mentioned "yellow" [Magnesian] limestone, and "gravel rock" which he appeared to recognise as being unusual for the area, and observed that the limestone protruded through "the Gravel" – presumably the Triassic deposits or perhaps glacial drift. Mello (1866) noted that "an isolated mass of mountain limestone very curiously protrudes through the Keuper Marl ... near to Snelstone".

The unconformable junction between the Triassic Mercia Mudstone Group ('Keuper') marls and sandstones, and the underlying Dinantian limestone, can be seen in South quarry. The surface of the limestone had been heavily eroded before being covered by Triassic rocks, and shows sand- and clay-filled fissures and caverns (Bemrose, 1904; King, 1968). Only about 6 m of the top of the limestone are now exposed in the east face of the quarry, which dips away in the southern corner. Similarly, the remaining face at the SW of the quarry dips away both to SE and to NW. According to Chisholm *et al.* (1988), the Sherwood Sandstone Group, normally underlying the Mercia Mudstones, abuts the limestone in the south of South quarry. The limestone exposed at Snelston is generally grey but both silicified limestone and (brown) dolomitised limestone also occur (Bemrose, 1904). The sandy fissure-fill is either loose or cemented with quartz and/or calcite, so that it may resemble quartzite or be described as a calcareous sandstone (Bemrose, 1904).

The economic mineralisation at Snelston occurred chiefly in the Trias, in calcareous sandstones of the Mercia Mudstone Group at or near the junction with the limestone, which is dolomitised at the unconformity (Dewey and Eastwood, 1925). The mine was worked for galena and cerussite as well as for chalcopyrite, chalcocite, malachite and azurite. Chalcopyrite and chalcocite are now scarce on the dumps, but malachite can be frequently found cementing Mercia Mudstone Group sandstones and lining joints and cavities. More sparing lead and copper mineralisation is present below the unconformity, in clay- and sand-filled pockets in the limestone, and as veinlets in the dolomitised limestone.

Both Bemrose (1904) and R.S.W. Braithwaite (*personal communication*) have referred to vertical veins in South quarry containing fluorite, baryte and calcite together with some copper mineralisation. Vertical veins of calcite with minor chalcopyrite and malachite are currently exposed in the north face of South quarry. In the east face there are vertical fissures and cavernous pipes, either lined with nodular and cockscomb baryte, or filled with red clay enclosing baryte. One of these also had colourless fluorite cubes lining patches on the face closely associated with baryte. This is presumably the 5.2 ft (1.6 m) wide vein complex referred to on the 1955 1:10560 geological map as containing calcite, baryte and fluorite.

MINERALS

The available study material dates largely from three collecting periods: (a) specimens collected by Arthur Russell in 1917, and those from the Garnett Collection, probably also obtained during the second mining period; (b) specimens collected in the early 1960s by R.J. King and R.S.W. Braithwaite; (c) specimens collected recently (from about 1980) by a small group of collectors.

The Natural History Museum, London (NHM) now houses the Russell specimens (see Appendix), together with two undated MS notes which are quoted below under azurite and malachite, respectively. They appear to be notes for a planned systematic mineralogy of the British Isles by Russell, arranged under mineral species. There was no file for chalcocite.

Specimens from the collection of C.S. Garnett of Matlock, Derbyshire (who published papers on Derbyshire minerals in 1920–1923) are now in the NHM and in the King Collection in the National Museum of Wales (NMW). Those in the NHM were purchased from Gregory, Bottley & Co. in 1951, and one of them is recorded as having originated from C. Pattinson – presumably Chas Pattinson, the mine manager at Snelston mine in 1912 (*Kelly's Directory of the Counties of Derby and Nottingham* for 1912). Possibly other specimens in the Garnett Collection were also supplied by Pattinson. Material collected by R.J. King is also housed in the NMW (see Appendix).

Minerals are now not easy to find and much patience is needed; visits to the limited exposures often yield nothing or only malachite stains. It is improbable that the old workings will ever be accessible, owing to flooding by water and the coffee slurry.

ANGLESITE, $PbSO_4$

Small colourless bladed crystals (<2 mm) are associated with galena and linarite in sandstone. Braithwaite (*personal communication*) found anglesite in 1960 with a brilliant blue fluorescence in long-wave UV light. A specimen in the King Collection (NMW) has anglesite with galena, collected in 1980.

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

Very rare but has been found as aggregates of silky crystals (<2 mm) in vugs in quartz (G.W. Fletcher, *personal communication*).

AZURITE, $Cu_3(CO_3)_2(OH)_2$

A. Russell noted (undated MS in NHM): "In 1917 I collected some beautiful specimens of azurite at this mine ... The azurite occurs as crusts of small deep blue prismatic crystals lining with malachite cavities in the sandstone which sometimes contain dull greyish-black superficially altered patches of chalcocite. Beautiful little crystals of cerussite are often implanted on the azurite." Russell specimens in the NHM display crusts of azurite crystals in vuggy sandstone and have associated malachite, cerussite, and massive chalcocite. Azurite was also recorded by Dewey and Eastwood (1925) and Braithwaite (1983). Azurite can still be found, rarely, as blocky microcrystals (<1–2 mm) associated with malachite on a limonitic matrix, and also as aggregates of platy crystals with malachite in the sandstone.

BARYTE, $BaSO_4$

The occurrence of baryte-bearing veins in South quarry has been mentioned above. Some of these exposures may now be obscured by infill, but pinkish nodular and cockscomb baryte was found in 1994 in the east face of South quarry; goethite pseudomorphs after pyrite(?) form inclusions in the baryte and are scattered over the surfaces. D.I. Green (*personal communication*) reports baryte from the mine dumps, as thin, colourless, often pseudohexagonal plates.

BROCHANTITE, $Cu_4SO_4(OH)_6$

Braithwaite (1983 and *personal communication*) noted emerald-green brochantite from the Snelston inlier and confirmed the identity by wet chemical methods.

CALCITE, $CaCO_3$

Calcite is rarely present at the mine site as small (~5 mm) translucent scalenohedral and rhombohedral crystals. It is found more often as infilling blocks with large cleavage faces, or as larger aggregates of intergrown scalenohedra, in material apparently from near the sandstone–dolomitised limestone junction. Vugs in this calcite sometimes enclose malachite or, rarely, wulfenite. Occasionally the calcite is transparent and contains inclusions of native copper or malachite. Bemrose (1904) reported calcite in veins as well as cementing sandstone. Braithwaite (*personal communication*) collected scalenohedral crystals, nail-head crystals with specks of chalcopyrite, and pink calcite with malachite crystals on corroded chalcopyrite, from the South quarry in the 1960s. Similar material has been seen recently in the north face of the South quarry.

Adjacent to the current entrance to South quarry in Cockshead Lane, there is a large detached boulder of limestone, presumably from one of the quarries, containing a 2.5-cm wide calcite vein. The vein is banded red and pink at the margins to white at the centre, and has fissures lined with modified scalenohedra of calcite (2 mm) associated with sparse malachite.

CALEDONITE, $Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$

Only one specimen containing caledonite has been reported (S.A. Rust, *personal communication*): poorly formed prismatic microcrystals of caledonite were associated with minor linarite on colourless to white blocky crystals of anglesite. Remains of galena were also present.

CERUSSITE, $PbCO_3$

Microcrystals of cerussite are found coating almost every piece of galena except the veinlets in dolomitised limestone, and on crusts of malachite in sandstone. It is also present apparently cementing sandstone. Cerussite is represented in the Russell and King collections (see Appendix). Twinned crystals are occasionally found.

CHALCOCITE, Cu_2S

Specimens in the Russell Collection and elsewhere in the NHM, collected during the second period of mining, contain substantial pieces of massive chalcocite, which suggests that this mineral was an important part of the total copper ore. However, Russell (undated MS in NHM) stated that malachite was the principal copper ore and recorded only small masses of chalcocite, "sometimes". A specimen containing chalcocite in the King Collection originated from C.S. Garnett and was probably also collected during the second period of mining. Now only very occasional grey metallic blebs of chalcocite embedded in calcite or sandstone may be found; some rod-like structures of malachite may be pseudomorphs after chalcocite.

CHALCOPYRITE, $CuFeS_2$

Chalcopyrite is present as isolated, altered crystals up to 3–4 mm across embedded in calcareous sandstone; it is often totally oxidised to iron oxides. It is also present unaltered and associated with galena as disseminations in dolomitised limestone; lightly oxidised in coarse white sandstone; and associated with massive chalcocite. Chalcopyrite together with malachite pseudomorphous after chalcopyrite are present on a specimen in the King Collection (NMW).

CHRYSOCOLLA, $(Cu,Al)_2H_2Si_2O_5(OH).nH_2O$

This occurs as coatings and also as spherules (<2 mm), perhaps representing pseudomorphs after malachite.

COPPER, Cu

Small blebs of native copper, and very occasional dendrites in vughs, have been found, most often associated with cuprite. Copper also occurs as inclusions in calcite.

CUPRITE, Cu_2O

Cuprite occurs most often covering small areas on fractures in association with copper, and rarely as euhedral crystals (<2 mm). Pseudomorphs of malachite after cuprite(?) octahedra have been found on a joint face in brown sandstone.

DOLOMITE, $CaMg(CO_3)_2$

Bemrose (1904) reported dolomite crystals in partially dolomitised limestone from the South quarry.

FLUORITE, CaF_2

Fluorite was reported by Bemrose (1904) and Dewey and Eastwood (1925). Both R.J. King (see Appendix) and R.S.W. Braithwaite (*personal communication*) collected fluorite in 1960–62 from a vein in the north face of South quarry; the exposure is now obscured by infill. Fluorite has been found recently as colourless cubes (<8 mm) associated with baryte in weathered specimens from the east face of South quarry.

GALENA, PbS

Galena occurs as small nodules and fragments, nearly always encrusted with cerussite; largely unaltered, filling spaces between calcite scalenohedra; and unaltered, as thin veins, embedded crystals and disseminations in dolomitised limestone, calcite, and coarse white sandstone. Euhedral crystals (<1 mm) are found embedded in calcite crystals.

GOETHITE, FeO(OH)

Goethite is present as pseudomorphs after chalcopyrite and pyrite (q.v.). Braithwaite (*personal communication*) found good botryoidal goethite in 1960 in North quarry, and specimens in the NHM have thin veins of goethite in an earthy limonitic matrix.

GYPSUM, $CaSO_4.2H_2O$

Transparent flat plates of gypsum 1 mm across have been found recently in a sandstone matrix.

LIMONITE

Light-brown powdery limonitic coatings and stains are frequently found on joints and in vugs. See also under goethite.

LINARITE, $PbCuSO_4(OH)_2$

Acicular or flattened microcrystals (<2 mm) of linarite sometimes form extensive crusts on joint-faces and are usually associated with galena and cerussite. Linarite was first identified here in 1960 (R.S.W. Braithwaite, *personal communication*).

MALACHITE, $Cu_2CO_3(OH)_2$

A. Russell noted (undated MS in NHM): "The curious deposit of lead and copper ores here was originally worked in a quarry of Carboniferous Limestone. It was reopened as a mine from 1909 to 1918 when I had several opportunities of examining it. The ore body occupies a fault between Keuper Marl, consisting of red marl, shale and beds of sandstone, and dove-coloured Carboniferous Limestone. The copper ore consists principally of malachite impregnating the sandstone, open joints of which sometimes afforded beautiful specimens both of malachite and crystallized azurite, the former consisting of delicate mammilated drusy crusts of a dark green colour. There also occurred small masses of chalcocite in the sandstone and nodules of galena in the limestone, crystals of cerussite, chalcopyrite with pitchy copper ore, barytes in cockscombe form, and pseudomorphs of limonite after pyrite. My collection contains a series of specimens from here mostly obtained in 1917." Both the Russell and the King collections contain specimens of malachite.

Malachite is found as sprays of acicular microcrystals in small vugs in calcite, on joint-faces and in vugs in the host rocks, and coating chalcopyrite in a quartz matrix. Occasionally it forms bladed transparent crystals (<2 mm), and rarely rod-like pseudomorphs, probably after chalcocite, or octahedral pseudomorphs after cuprite(?).

MANGANESE OXIDES

Stains, dendrites and coatings of unidentified manganese oxides are common and often associated with, e.g., malachite or wulfenite. Botryoidal or massive manganese oxides are sometimes present in sandstone. Dewey and Eastwood (1925) reported the rare occurrence of 'wad'.

PYRITE, FeS_2

Pyrite was reported by D.I. Green (personal communication), and has been found recently altered to goethite and closely associated with baryte in South quarry.

QUARTZ, SiO_2

Quartz is found filling cavities and occasionally as small (<2 mm), drusy, euhedral crystals, often coated with iron or manganese oxides. Doubly-terminated, euhedral crystals are present cemented into the coarse sandstone, together with rounded grains and fragments of feldspar.

ROSASITE, $(Cu,Zn)_2CO_3(OH)_2$

Rosasite from Snelston was reported without details by King (*personal communication* in Braithwaite and Ryback, 1963) and by Ford and Sarjeant (1964). Braithwaite (*personal communication*) found rosasite as apple-green globules on sandstone in 1960 and confirmed the identification by wet chemical methods.

SPHALERITE, ZnS

D.I. Green (*personal communication*), has noted that sphalerite occurs at Snelston.

WULFENITE, $PbMoO_4$

Wulfenite was first collected from Snelston mine in 1980 (see Appendix) and reported in 1986 (Green, 1986). It occurs as transparent to opaque microcrystals of various colours (colorless, vivid yellow, pale brown and brown) and habits (tabular, bipyramidal, or intermediate between these), on limonitic coatings associated with malachite and galena in calcite, dolomitised limestone, or sandstone; manganese oxides are nearly always present on such specimens. Rothwell and Mason (1992) record colour zoning of crystals. Almost cube-shaped crystals have been reported (G.W. Fletcher, *personal communication*). D.I. Green (*personal comminication*) has observed twinning on the c-axis. Wulfenite crystals are of small size (usually <0.5 mm, but exceptionally 1.5 mm for tabular crystals), very rare, and usually occur singly or in small groups of scattered crystals.

DISCUSSION

Dolomitisation of the Carboniferous limestone at Snelston is thought to have reduced its permeability to mineralising solutions percolating down through the Trias. This resulted in an accumulation of copper and lead minerals (with some manganese, molybdenum and zinc) above the unconformable junction, and to a lesser extent in both the fissure-fill material and the limestone below the junction. There are numerous examples of similar patterns of mineralisation elsewhere in the South Pennines, e.g.:

a) Alderley Edge and Mottram St Andrew, Cheshire, where Cu and Pb minerals (with Mn, Co, V and Mo) are found mineralising faults and cementing the more porous facies in otherwise resistant sandstones overlying barren clayey sandstones and clays (Warrington, 1965; Braithwaite, 1994).

b) Tickow Lane mine, Leicestershire, where galena and cerussite (with wulfenite and manganese oxides) are present in Lower 'Keuper' (Mercia Mudstone Group) sandstone (King and Ludlam, 1969; King, 1983). No unconformity is recorded here, but thin beds of red clay may have acted as impermeable barriers.

c) Localities in Charnwood Forest, Leicestershire, where the Trias unconformably overlies Precambrian plutonic rocks and is in places intensely mineralised at and just above the junction with copper minerals, minor galena, and traces of V and Mo minerals. The mineralisation can spread into the Precambrian along joints and fissures. Typical localities are at Bardon Hill, Cliffe Hill and Newhurst quarries (King, 1968).

c) Along the limestone outcrop between Nottingham and Mansfield, Nottinghamshire, and extending to near Doncaster in South Yorkshire, where galena and wulfenite were found in the thin dolomitised top layer of the Lower Magnesian Limestone underlying the Middle Permian Marl (Deans, 1961).

e) Manystones quarry and Ticknall, Derbyshire, where galena and baryte line solution cavities in dolomitised limestone under Permo-Triassic deposits (King and Ford, 1969). Galena is also reported from caverns in Breedon and Cloud Hill quarries, Leicestershire (King, 1991).

Examples outside the Midlands area include localities near Bristol described by Alabaster (1989).

Wulfenite occurs in small amounts at most of the localities mentioned above, indicating that molybdenum was widely present in Permo-Triassic deposits. The close association of manganese oxides with wulfenite at Snelston mine suggests that, as in the Bristol area (Alabaster, 1989), the molybdenum was originally present in manganese oxide gels, but as these crystallised it was liberated and reacted with galena or its oxidation products to form wulfenite.

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APPENDIX: LIST OF SPECIMENS IN PUBLIC COLLECTIONS

NATURAL HISTORY MUSEUM, LONDON

i) Russell Collection, BM 1964,R7071. Massive chalcocite with minor calcareous sandstone matrix, drusy azurite, altered malachite, and a few cerussite crystals. The sequence is cerussite crystals on crystalline azurite on matted malachite on massive chalcocite. Collected by A. Russell, 1917, from Snelston Copper Mine.

ii) Russell Collection, BM 1964,R7072 Two small hand-sized specimens: drusy azurite on malachite on calcareous sandstone matrix. One area shows small bright azurite crystals on cerussite on the matrix. Collected by A. Russell, 1917, from Snelston Copper Mine.

iii) BM 1928,415. A 4-cm rose of white iron-stained or red marl-stained lamellar baryte crystals (<25 mm) on Triassic marl. Presented by T. Wooddisse, 1928. From Birchwood Park, Snelston.

iv) BM 1951,174. Four chips of massive chalcocite, tarnished blue in places. From the Garnett Collection, purchased from Gregory, Bottley & Co., 1951; originally from C. Pattinson. Snelston Copper Mine.

v) BM 1982,343. Wulfenite, orange-yellow microcrystals in vugs in a limestone breccia with sandstone and calcite infilling; very minor massive galena, malachite crystals, and manganese oxide staining in small patches. Collected in 1980 by T.F. Bridges from "Isolation Mine."

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All are in the King Collection (K number given), and all except (iii) are registered as from Isolation Mine.

i) NMW 83.41G.M920; K 4017. Galena, disseminated crystals in purple sandstone. From the Garnett Collection.

ii) NMW 83.41G.M921; K 4015. Galena, disseminated crystals, with malachite, in sandstone. From the Garnett Collection.

iii) NMW 83.41G.M4296; K 2357. Fluorite, colourless to pale green cubes (not fluorescent in LW or SW UV light), on dolomitised limestone. Collected in 1962 from the South quarry.

iv) NMW 83.41G.M4720; K 3103. Malachite with azurite on joint or bedding surface in grey mudstone mottled red.

v) NMW 83.41G.M4723; K 4012. Malachite coating (4 × 5 cm) on joint(?) in feldspathic 'quartzite'. From the Garnett Collection.

vi) NMW 83.41G.M4724; K 4013. Malachite, rosette of crystals (<1 mm) on 'quartzite'. From the Garnett Collection.

vii) NMW 83.41G.M4725; K 4014. Malachite after chalcopyrite, with chalcopyrite and chalcocite, in a thin vein in 'quartzite' From the Garnett Collection.

viii) NMW 83.41G.M5659; K 4016. Cerussite in pale sandstone. From the Garnett Collection.

ix) NMW 83.41G.M8786; K 2356. Baryte with fluorite, galena and pyrite, forming a vein; no matrix. Collected in 1962.

x) NMW 83.41G.M9021; K 8408. Anglesite with galena; no matrix. Collected from the dumps, 1980.

xi) NMW 83.41G.M9119; K 7962. Wulfenite on dolomitised limestone. Collected in 1980.

xii) NMW 83.41G.M9122; K 7961. Wulfenite on galena with cerussite; no matrix. Collected in 1980.

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CALCIAN GOYAZITE AND FLORENCITE–(Ce) FROM GUNHEATH CHINA CLAY PIT, ST AUSTELL, CORNWALL

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Calcian goyazite and florencite-(Ce) have been identified at Gunheath china clay pit, St Austell, Cornwall, occurring in granite pegmatite. Calcian goyazite forms colourless pseudocubic crystals. Cation proportions are $Ca_{0.35}Sr_{0.65}$ and unit cell parameters are consistent with this composition. Florencite-(Ce) occurs as modified acute rhombohedra. Analysis reveals a complex composition illustrating the extensive solid solution possible for minerals of the plumbogummite—florencite groups.

ALUNITE – JAROSITE MINERALS AT GUNHEATH PIT

The presence of crandallite, goyazite and waylandite was reported in phosphate-containing pegmatites in the Hensbarrow granite, without detail, by Hawkes *et al.* (1987). Specimens of euhedral goyazite and florencite-(Ce) have now been identified on pegmatite matrix from the Hensbarrow section of Gunheath china clay pit (National Grid Reference SX 005 571).

Goyazite is a member of the plumbogummite group, of general formula $AB_3(PO_4)(PO_3OH)(OH)_6$, where A = Ca, Sr, Ba or Pb, and B = Al or Fe. Florencite-(Ce) is a member of the florencite group with general formula $AB_3(PO_4)_2(OH)_6$, where A = Ce, La, Nd, Bi, Ca, Th or Pb, and B = Al or Fe. Minerals in both groups are isostructural with an alunite-type structure. A-site cations in the plumbogummite group are predominantly divalent, and charge balance is maintained through protonation. In the florencite group, the A-site cation is predominantly trivalent.

The plumbogummite and florencite groups are really subgroups of a much larger collection of isostructural minerals known as the alunite–jarosite family (Scott, 1987; Birch *et al.*, 1992; Pring *et al.*, 1995; see also Lengauer *et al.*, 1994). The general formula may be written $AB_3(XO_4)_2(OH)_6$, where the XO_4 group may be phosphate, arsenate or sulphate. Very extensive solid solution is possible within the whole alunite–jarosite family, with substitution on A, B and (XO_4) sites. Hendricks (1937) showed that the alunite structure is unusually tolerant of a wide variation in the radius of the A cation; substitution on this site is particularly well documented and is also well illustrated by the Gunheath specimens.

GOYAZITE

Goyazite occurs at Gunheath pit as pale-green to colourless pseudocubic $\{10\bar{1}2\}$ crystals up to 0.2 mm across. The crystals commonly possess a white turbid core surrounded by a transparent shell and many are striated as reported in the literature (e.g. Palache *et al.*, 1951). Goyazite fills a vug in massive quartz intimately associated with masses of thin acicular tourmaline crystals. Coarse bladed wolframite occurs embedded in the quartz matrix, while a little pale green chalcosiderite occurs with the goyazite.

Quantitative EDX analysis was carried out using a Link QX2000 analyser on a JEOL JSM 840 scanning electron microscope. The electron beam (5×10^{-10} A measured on the Faraday cage at 25 kV) was raster-scanned over an area of specimen approximately 10 μm × 10 μm. Synthetic standards were used. The results (Table I) show the mineral to be intermediate between goyazite and crandallite. Recalculation of analysis data on the basis of 14 oxygens gives $(Ca_{0.35}Sr_{0.65})_{\Sigma=1.00}Al_{2.88}(PO_4)_{1.99}(OH)_{7.4}$. Writing Gz for goyazite and Cr for crandallite, the composition may be expressed as $Gz_{65}Cr_{35}$. The mineral is therefore calcian goyazite.

In the analysis, water was determined by difference and the recalculated OH proportion is based upon this value. It is likely that a low analytical total has led to an overestimate of the wt % water, and hence an overestimate in the recalculated hydroxyl content. Both McKie (1962) and McConnell (1942) noted that analyses of goyazite and related minerals often give high H_2O. However, high H_2O is normally accompanied by low analyses for P_2O_5, and is attributed to a statistical deficiency of PO_4, with charge balanced by the inclusion of extra hydroxyl. There is no significant deficiency of phosphate in the Gunheath goyazite.

Samples of calcian goyazite were prepared for XRD by hand grinding with acetone in an agate pestle and mortar, followed by dispersion on an Mo foil. NIST SRM 675 fluorophlogopite was used as an internal *d*-spacing standard. Data were collected over the range 7–55° 2θ (Cu-Kα), using a 1° divergence slit, 0.1 mm receiving slit, and a graphite monochromator. It proved impossible to isolate pure goyazite, and the resulting XRD patterns include lines from schorl and minor quartz. After correction for systematic errors, the unit cell was refined on ten lines indexed unambiguously and free from overlaps. The refined cell data are shown in Table II. In naturally occurring members of the plumbogummite group, McKie (1962) showed that both *a* and *c* cell dimensions vary linearly with the average effective radius of the A cation. A study of synthetic

TABLE I. EDX analysis of goyazite from Gunheath pit. (Weight %)

	1	2	3
Al_2O_3	33.30 (32.5—33.9)	33.14	36.95
P_2O_5	32.05 (30.5—32.8)	30.76	34.29
CaO	4.35 (3.6—5.9)		13.55
SrO	15.20 (12.1—16.9)	22.45	
H_2O	15.10*	13.65	15.21
Total	100.00	100.00	100.00

*H_2O by difference.

1. Gunheath goyazite, average of 7 analyses, range in parentheses.
2. Theoretical goyazite, $SrAl_3(PO_4)_2(OH)_6$.
3. Theoretical crandallite, $CaAl_3(PO_4)_2(OH)_6$.

TABLE II. Unit cell data for goyazite from Gunheath pit. (Å)

	1	2	3
a	7.006(1)	7.007	7.013
b	16.468(4)	16.216	16.650

1. Calcian goyazite from Gunheath pit. Figures of merit M(10) = 59.8 (1.748, 24) and F(10) = 31.2 (0.0133, 24).
2. Data for synthetic crandallite (Gilkes and Palmer, 1983).
3. Data for synthetic goyazite (Gilkes and Palmer, 1983).

crandallite-goyazite phases by Gilkes and Palmer (1983) confirms this observation, but finds different slopes and different end-member cell dimensions. These differences are attributed to the limited compositional range of natural samples available to McKie (1962).

Gilkes and Palmer (1983) show that a is virtually independent of composition, while c varies with the molar proportion of Sr according to the equation $c = 16.216 + 0.434[\mathrm{Sr}/(\mathrm{Sr} + \mathrm{Ca})]$ Å. For $\mathrm{Sr}/(\mathrm{Sr} + \mathrm{Ca}) = 0.65$ as analysed in the Gunheath specimens, this equation gives $c = 16.500$ Å, in tolerable agreement with the measured value, 16.468(4) Å. McKie's prediction for the same composition is significantly lower, ~16.36 Å.

FLORENCITE-(Ce)

At Gunheath pit, florencite crystals were found on, and penetrating, fluorapatite crystals in a vug in granite pegmatite. The vug contains coarse quartz and feldspar with needles of schorl, blue prismatic fluorapatite up to 6 mm long, and equant, euhedral fluorite crystals of a complex and much modified habit. Both florencite and fluorapatite are frequently penetrated by tourmaline needles. A few green tabular crystals of torbernite are scattered amongst the tourmaline. Florencite occurs as rhombohedral crystals (≤ 3 mm long), principally $\{01\bar{1}1\}$, but with small modifying faces of the form $\{10\bar{1}2\}$ (Fig. 1). The crystals are translucent but inhomogeneous in colour, varying from pale brown through dark brown to almost black. Some of the crystals are dusted with a powdery white coating.

EDX analysis shows the florencite to have a rather complex composition (Table III, column 1). Repeat analyses showed considerable variation, as indicated by the ranges in Table III.

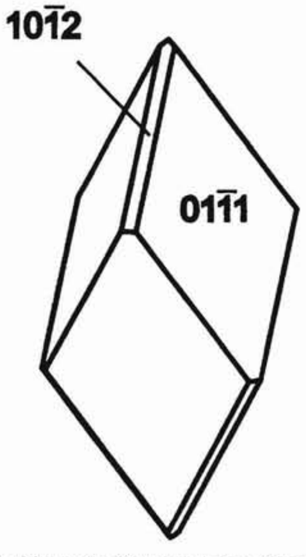

FIGURE 1. Habit of florencite-(Ce) crystals from Gunheath pit.

TABLE III. EDX analysis of florencite from Gunheath pit. (Weight %)

	1	2
Al_2O_3	26.13 (23.85–28.47)	29.81
P_2O_5	25.79 (22.90–28.22)	27.67
As_2O_5	2.15 (1.26–3.38)	
CaO	3.03 (1.53–3.99)	
SrO	3.43 (1.67–4.33)	
Ce_2O_3	10.34 (8.25–13.13)	32.00
La_2O_3	5.81 (5.11–7.74)	
Nd_2O_3	0.70 (0.00–1.51)	
PbO	2.10 (1.09–3.30)	
ThO_2	3.37 (2.33–4.50)	
H_2O	17.15*	10.52
Total	100.00	100.00

*H_2O by difference.
1. Gunheath florencite, average of 13 analyses, range in parentheses.
2. Theoretical florencite-(Ce), $CeAl_3PO_4)_2(OH)_6$.

Water was determined by difference and, as for the goyazite, is probably overestimated owing to low analytical totals. Because of the complexity of the mineral composition and resolution deficiencies of EDX analysis it is possible that minor amounts of some elements (e.g. sulphur) were present but not accounted for in the analysis. Recalculation of the data in Table III, column 1, on the basis of 14 oxygens gives

$$(Ca_{0.26}Sr_{0.16}Ce_{0.30}La_{0.17}Pb_{0.05}Th_{0.06})_{\Sigma=1.00}Al_{2.4}$$
$$(PO_4,AsO_4)_{1.8}(OH)_{9.1}.$$

It is noteworthy that there appears to be a deficiency of both Al and P. Writing Fc for florencite-(Ce), Fl for florencite-(La), and Ey for eylettersite, the composition may be expressed as $Fc_{30}Fl_{17}Cr_{26}Gz_{16}Ey_{11}$. According to naming conventions, the mineral may be called florencite-(Ce) but this belies its complexity, and the mineral is an excellent example of the extent of solid solution possible between minerals of the plumbogummite and florencite groups.

XRD data for the Gunheath florencite contains additional lines due to quartz. NIST SRM 675 fluorophlogopite was used as an internal standard. The unit cell was refined on the basis of 9 lines free from overlaps and unambiguously indexed for florencite; the results are given in Table IV. Both a and c cell dimensions are significantly larger than those for pure florencite-(Ce), as might be expected given the composition of the Gunheath mineral.

DISCUSSION

Plumbogummite and florencite group minerals are found at many localities worldwide in a variety of geological environments. The minerals occur in igneous pegmatitic rocks, in carbonatites, and also commonly as detrital minerals in sedi-

TABLE IV. Unit cell data for florencite-(Ce) (Å)

	1	2
a	7.018(4)	6.972(2)
c	16.338(9)	16.261(6)

1. Florencite-(Ce) from Gunheath pit. Figures of merit M(9) = 25.93 (1.893, 20) and F(9) = 15.20 (0.0296, 20).
2. Published data for florencite-(Ce) (Kato, 1990).

mentary rocks, soils and sands. These minerals can be a significant source of soil phosphate.

In the British Isles, goyazite has been recorded in the clay fraction of soils from the Culbokie area, Black Isle, Ross and Cromarty, Scotland (Livingstone and Macpherson, 1983). Calcian goyazite has been recorded in rims around chamosite ooids in rocks near Harston, Leicestershire (Harrison *et al.*, 1983). A mineral of the goyazite–woodhouseite group was found in clay from coal-bearing sequences in Durham and Scotland (Richardson and Francis, 1971), and florencite-(Ce) has been found in Ordovician mudstones in the Corris area, Gwynedd, Wales (Bevins, 1988). The occurrence of goyazite and florencite at Gunheath is noteworthy because the minerals were found as relatively large and euhedral crystals. It is also the first British occurrence in an igneous pegmatitic environment.

Paragenetic evidence suggests that the florencite is earlier than the fluorapatite and fluorite. Torbernite is the last-formed mineral in the pegmatite vug. All these minerals are of relatively late formation, as is the case in other deposits, both pegmatitic and carbonatitic (Mrose, 1953; Palache *et al.*, 1951; McKie, 1962). Gunheath goyazite is also a relatively late mineral.

In other occurrences, Ca and P in crandallite-type minerals commonly derives from the alteration of apatite. Aluminium may derive from various sources including alteration of clay minerals, alteration of pre-existing aluminium phosphates such as variscite or wavellite, or may be introduced from external sources (Blanchard, 1972; Palache *et al.*, 1951; McKie, 1962). Moreover, apatite often contains low levels of Sr and rare earth elements (REEs) (Roeder *et al.*, 1987). The alunite structure has a considerable capacity to concentrate Sr (Frondel, 1958), so it might be expected that Sr (and presumably REEs) liberated during decomposition of apatite would be readily incorporated into minerals of the alunite–jarosite family. Apatite is not a major source of REEs in the granites of SW England; most REEs tend to be concentrated in monazite (75% of light REEs in the Carnmenellis granite are contained in monazite, according to Jefferies (1985)). Apatite, monazite, zircon and xenotime commonly occur as microscopic inclusions in biotite (Stone *et al.*, 1988). Strontium is often contained within feldspars, but the levels tend to be low in SW England granites (Bradshaw, 1967).

Bristow (1993) describes a multi-stage process for the formation of china clay in the St Austell granite. Late-stage radiogenically driven convective circulation of meteoric water is thought to have produced the main kaolinisation by alteration of an earlier-formed illite–smectite assemblage. Some cross-course mineralisation of Fe and U may belong to this period (180 Ma to present) and it seems likely that the formation of late-stage pegmatite phosphates, including large euhedral fluorapatite, occurred during this phase. Earlier, and contemporary, stages of mineralisation could have liberated the Al (from clay minerals), Sr (from feldspars), and Ca, REEs and P (from pre-existing apatite, monazite, and associated species) necessary for the formation of calcian goyazite and florencite.

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EPISTILBITE FROM THE ISLE OF SKYE, SCOTLAND

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Epistilbite was first recorded in the British Isles in the mid-nineteenth century and has subsequently been reported at a handful of other localities. All occurrences which lie outside the Scottish Tertiary Igneous Province are now considered either doubtful or erroneous. Even Scottish specimens are very rare: only two, both from Talisker Bay, appear to be represented in major public collections. Epistilbite has recently been collected at Sgùrr nam Boc and Talisker Bay on the Isle of Skye. The occurrence at Sgùrr nam Boc is typical of others worldwide, epistilbite crystallising at the beginning of the zeolite sequence in association with silica-rich zeolites and quartz. Although epistilbite appears to have crystallised early at Talisker Bay the occurrence is atypical in that quartz and silica-rich zeolites are absent.

INTRODUCTION

Epistilbite, $CaAl_2Si_6O_{16}.5H_2O$, is an uncommon zeolite, which typically forms in amygdaloidal basalts at the beginning of zeolite crystallisation sequences when the pH and silica content of the fluids are high (Tschernich, 1992). The few undoubted British localities are restricted to the Tertiary amygdaloidal basalts of western Scotland. Epistilbite is recorded from Talisker Bay and from the shore below Beal, both on the Isle of Skye; and from Dearg Sgeir on the Island of Mull (Heddle, 1901). It has also been identified at a quarry beside Loch Sligachan on the Isle of Skye, in association with calcite and quartz (King, 1976).

All other reports from the British Isles are either doubtful or erroneous. Epistilbite discovered in vesicular basalt used to build a road near Castle Eden, Durham, is believed to have been imported as ship's ballast (Tschernich, 1992). A specimen from Park Brow quarry, Cumbria, in the National Museum of Wales (noted by Young, 1987) has since been shown to be laumontite (Richard Bevins, *personal communication*, 1996). Nineteeenth century reports of epistilbite from Rathlin and Portrush, County Antrim (e.g. Bryce, 1833; Brooke and Miller, 1852) were doubted by Nawaz (1988) and probably refer to flat-topped stilbite (Tschernich, 1992).

Only two authentic British epistilbite specimens, collected in 1852 at Talisker Bay by James Russell, appear to have survived in major public collections. In 1858, when the *Manual of the Mineralogy of Great Britain and Ireland* was published, both specimens were in the collection of R.P. Greg. The crystal drawing which accompanies the description in Greg and Lettsom (1858, p. 164) leaves no doubt that epistilbite was correctly identified. A report of a Mineralogical Society field meeting on the Isle of Skye (*Mineralogical Magazine*, **4**, ix (1880)) records that one of Russell's original specimens was in the British Museum, while the other was in Heddle's collection. The specimen in the Heddle collection at the Royal Museum of Scotland (accession number NMS G:440.1) displays colourless crystals up to 4 mm in size (Alec Livingstone, *personal communication*, 1995). The Natural History Museum has the second specimen (BM 95640) in its systematic mineral display.

Recent fieldwork on the Isle of Skye has resulted in the discovery of a new epistilbite locality at Sgùrr nam Boc, and the collection of further specimens at Talisker Bay. Exposures at Dearg Sgeir on the Island of Mull, and near Beal and at Loch Sligachan on the Isle of Skye, have also been examined, but no epistilbite was found.

The minerals described below, including all of the different epistilbite habits, and representative examples of the accompanying minerals (aragonite, clinochlore, calcite, heulandite, mordenite and stilbite), were identified by X-ray diffraction, to eliminate the possibility of confusion with morphologically similar species.

SGÙRR NAM BOC

The cliffs of Sgùrr nam Boc rise to a height of 230 m on the west coast of the Isle of Skye between Loch Brittle and Loch Eynort. They have provided some of the finest British specimens of apophyllite, heulandite and stilbite (Heddle, 1901; Pearce and Pearce, 1989). Epistilbite specimens were collected on the shore below the cliffs, mostly from two large basalt boulders. No occurrences were located *in situ* despite a thorough search.

Nearly spherical vesicles, usually less than 1 cm in diameter, containing epistilbite crystals in one of two distinct habits occur in a large boulder at National Grid Reference NG 3594 2090. Euhedral, equant to prismatic, pseudo-orthorhombic crystals (≤ 1.5 mm) are most common (Fig. 1). These are twinned on (100), with a well developed prismatic {110} form terminated by chisel-shaped {001} and $\{10\bar{1}\}$ forms (Fig. 2). Fan-shaped crystal aggregates, exceptionally up to 3 mm across, are much rarer (Fig. 3).

Irregular elongated vesicles, usually less than 2 cm long, containing epistilbite in several different crystal habits, occur

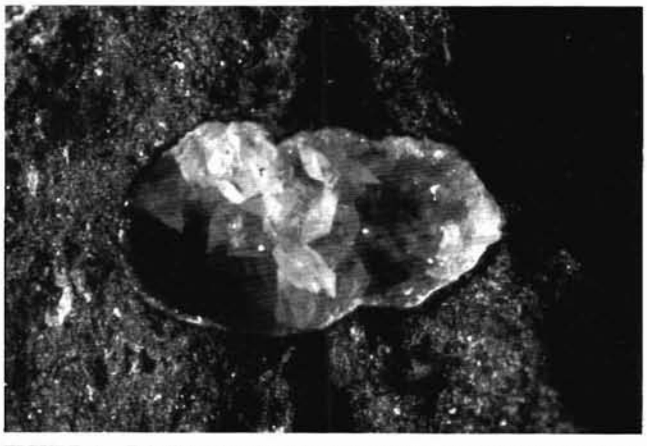

FIGURE 1. Epistilbite, blocky pseudo-orthorhombic crystals (≤ 1.4 mm), with slightly frosted chisel-shaped terminations, from boulder at NG 3594 2090, Sgùrr nam Boc.

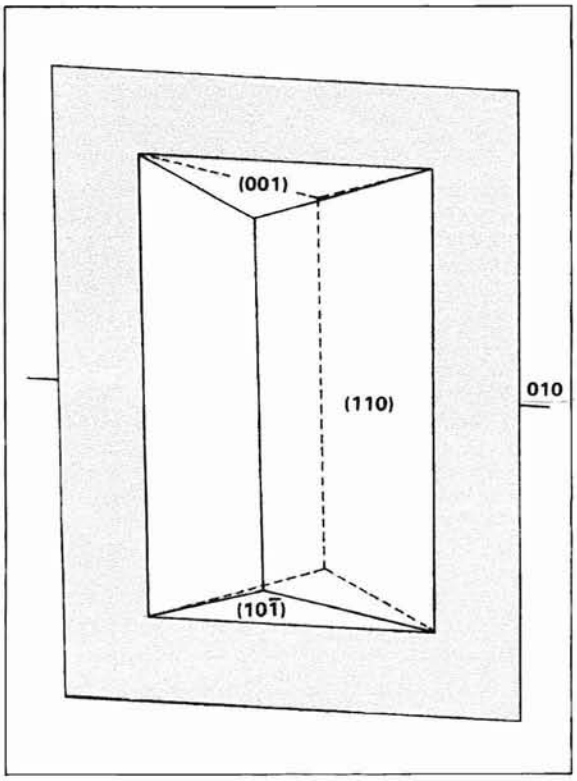

FIGURE 2. The classic pseudo-orthorhombic epistilbite crystal habit, produced by twinning on (100), showing a well developed prismatic {110} form with chisel-shaped terminations. The twin plane is stippled. Rotation of individual crystallites about 010 produces fan-shaped crystal aggregates.

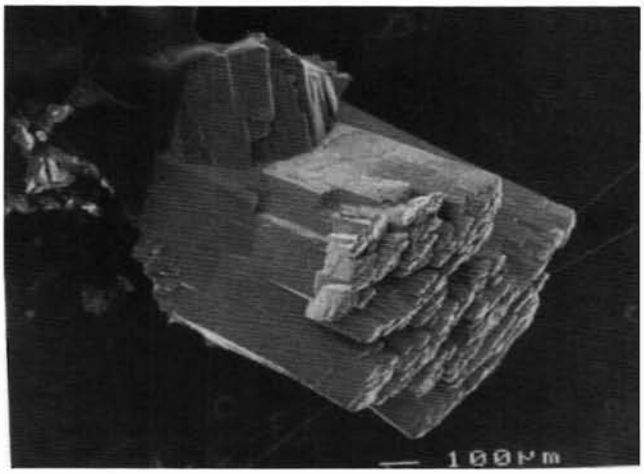

FIGURE 3. Epistilbite, SEM photograph of fan-shaped crystals from Sgùrr nam Boc. Scale bar 0.1 mm.

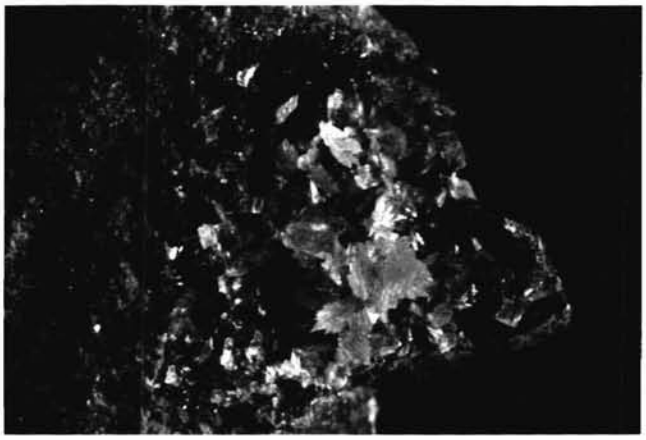

FIGURE 4. Epistilbite, fan-shaped crystal aggregates (≤ 1.2 mm), collected from boulder at NG 3577 2121, Sgùrr nam Boc.

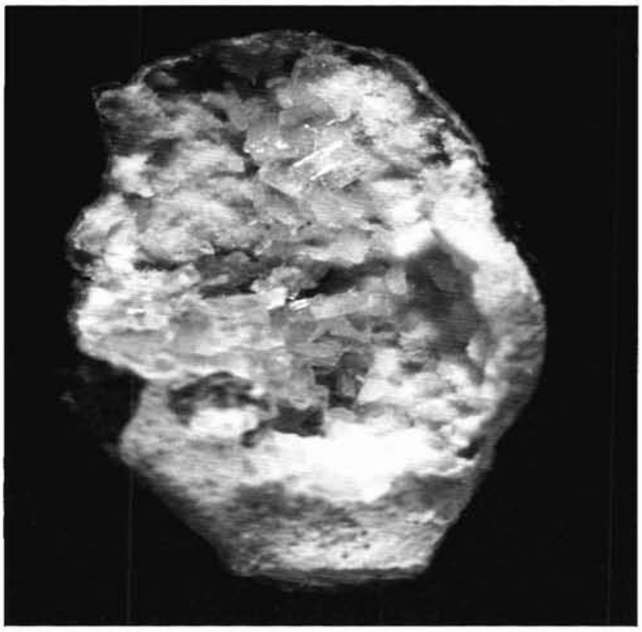

FIGURE 5. Epistilbite, tabular crystals (≤ 5.4 mm), in a 19 × 33 mm vesicle, from boulder at NG 3577 2121, Sgùrr nam Boc.

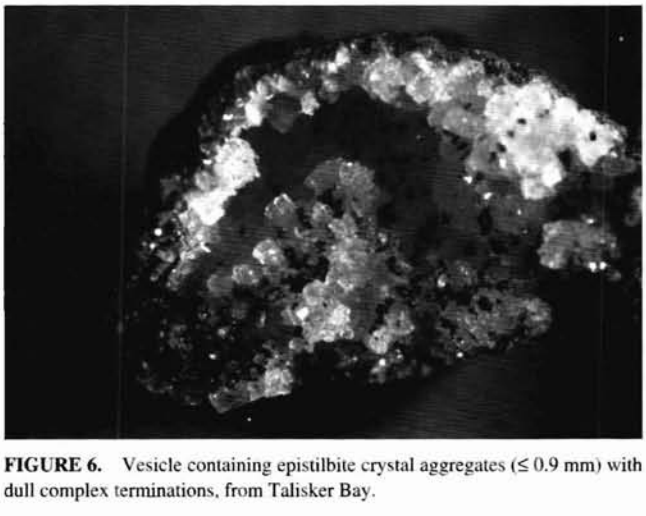

FIGURE 6. Vesicle containing epistilbite crystal aggregates (≤ 0.9 mm) with dull complex terminations, from Talisker Bay.

in a second boulder at NG 3577 2121. Fan-shaped crystal aggregates, exceptionally up to 5 mm in size, are most common (Fig. 4). This crystal habit is produced by subparallel growth of individual crystals with well developed {110} faces and dull flat terminations. Occasional minute perfect prismatic crystals accompany the fan-shaped crystals. Very rarely, tabular crystals up to 6 mm across are also found (Fig. 5).

In most cases epistilbite is the only zeolite occupant of the cavities although it is commonly associated with clinochlore and sometimes with quartz. Observation of the few specimens on which epistilbite is associated with other zeolites leads to a crystallisation sequence which begins with quartz, is followed by clinochlore, epistilbite, other zeolite species (stilbite, heulandite and very rarely chabazite) and ends with calcite or, in one case, aragonite.

Epistilbite specimens from the two boulders described above are accessioned in Manchester Museum (MANCH:N12812 to N12820). Representative specimens of the other zeolite species, including chabazite, heulandite, mordenite and stilbite, which occur in nearby vesicles in the same boulders, are also accessioned.

TALISKER BAY

Epistilbite occurs rarely in boulders of dark green olivine basalt about 200 m south of the sea stack at Talisker Point (NG 312 297). Aggregates of elongated prismatic crystals up to 1 mm long with dull flat terminations occur on dark green to black clinochlore in small spherical vesicles (Fig. 6). Rarely, vesicles filled with massive pinkish epistilbite which contains small cavities lined with drusy crystals are also found. The crystals are typically twinned on (100), producing the characteristic pseudo-orthorhombic habit dominated by {110}; they have complex terminations which are difficult to index. Rarely repeated twinning on (110) produces tabular crystals.

Epistilbite is usually the only zeolite in the vesicles, although it is occasionally accompanied by analcime, and in one case by stilbite. Nearby vesicles commonly contain chabazite, analcime and stilbite. Specimens from Talisker Bay are preserved in Manchester Museum (MANCH:N12638 and N12811).

DISCUSSION

Epistilbite usually occurs in olivine basalt associated with quartz and silica-rich zeolites; it typically crystallises at the beginning of a zeolite crystallisation sequence when the silica content and pH are high. At Sgùrr nam Boc, epistilbite is commonly associated with quartz, and the silica-rich zeolites heulandite, mordenite and stilbite are abundant in surrounding cavities; where associated with other zeolites it crystallised early in the sequence, before chabazite, heulandite and stilbite. The associations and crystallisation sequence at Sgùrr nam Boc are, therefore, typical of other localities worldwide.

The fan-shaped epistilbite crystal aggregates, which are common at Sgùrr nam Boc, are unusual. This crystal habit is relatively common in the related zeolite goosecreekite (Tschernich, 1992) but is not usually reported for epistilbite.

The mineral assemblage at Talisker Bay is unusual: quartz is absent, as are conspicuous quantities of the silica-rich zeolites. In common with other worldwide localities, however, epistilbite from Talisker Bay crystallised early in the zeolite sequence before analcime and stilbite. This suggests a silica-rich mineralising fluid was present early in the zeolite crystallisation sequence.

Epistilbite may be more common in western Scotland than previously supposed: both Sgùrr nam Boc and Talisker Bay are well known to collectors, and the apparent rarity of specimens possibly reflects the small size of the crystals and the difficulty of distinguishing them from other zeolites. Good specimens are difficult to find nonetheless and most require a stereomicroscope for identification.

ACKNOWLEDGEMENTS

Thanks to Dr Alec Livingstone of the Royal Museum of Scotland for information on epistilbite in the Heddle collection, to Dr Oneta Wilson for assistance in reviewing the British occurrence of the mineral, and to Dr George Ryback for historical information on British epistilbite.

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ZEOLITE OCCURRENCES IN BASALTIC DYKES ON THE WESTERN ISLES OF SCOTLAND

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Natural zeolite localities are well known on Skye and Mull but the rest of the Western Isles have received little attention since the work of Heddle (1901). British Geological Survey maps record many basaltic dykes (of suggested Tertiary origin) in the Western Isles, and we have studied dykes on Arran, Islay, Jura, Colonsay, Harris and Lewis as localities for natural zeolites. X-ray powder diffraction and differential thermogravimetry were used to identify the phases present. Gobbinsite was recorded for the first time in Scotland, and other dykes contained gismondine, gonnardite, and barium-rich phillipsite ('wellsite'), uncommon in the British Isles.

INTRODUCTION

The geology of the Western Isles (Fig. 1) varies from island to island. The islands have their own distinctive geological history and variety of rock types. These range through the geological time-scale from the Lewisian gneiss of the Precambrian to recent glacial and alluvial deposits. The zeolites which occur on the islands, however, are likely to have a common genesis. They occur in the amygdales and veins present in basalt and dolerite dykes and sills. These dykes and sills are most likely to be connected with the Mull and Arran centres of Tertiary activity.

The islands of Skye and Mull in the Western Isles of Scotland are well known and visited as sites for natural zeolites. Detailed records of their occurrences were reviewed by Heddle (1901) and more recently by Gottardi and Galli (1985). Attention to zeolite occurrences on the other Western Isles has been much more sporadic. Arran serves as a typical example because, although it must be one of the most frequently studied of all Scottish localities, few zeolite occurrences are mentioned. Exceptions are zeolites in the Dippin Sill (Dickin *et al.*, 1984) and the record of mordenite as an alteration product in one of Judd's Dykes on the foreshore at Tomore (Harris and Brindley, 1954).

Relatively modern references to zeolites on other Western Isles are sparse. An unaccredited mention of "zeolites" occurs in a current Islay tourist booklet – perhaps picked up from the record of analcime at Cnoc Rhaonastil (Walker and Patterson, 1959) – and some information relates to Lewis and Harris. Part of this is published: Stevens (1912) describes analcime and scolecite as interstitial minerals in a crinanite from a dyke located in a Tertiary alkali basalt at Stornaway, Lewis; and gismondine is said to occur at Roneval, South Harris (Witty, 1975). The other information comes from the National Museums of Scotland (NMS) mineral collection, which contains heulandite and phillipsite from Caryshader, Uig, on Lewis, and stilbite from a quarry at the south end of Loch Strandavat, near Arivraich, Loch Seaforth, also on Lewis.

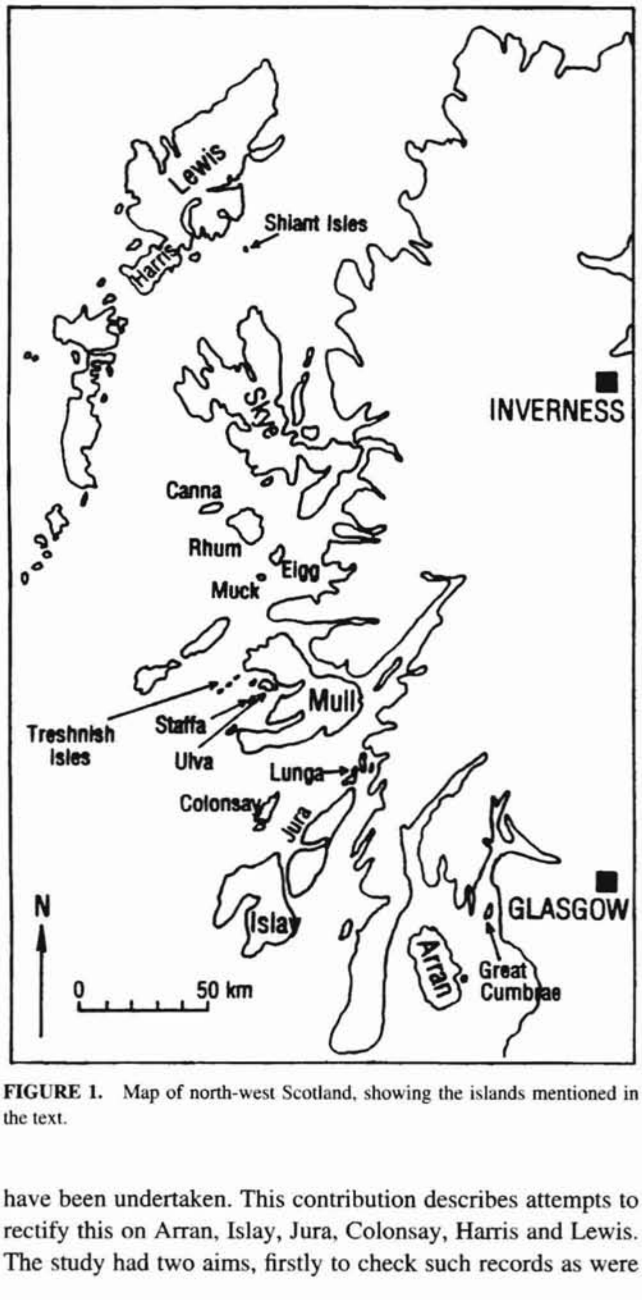

FIGURE 1. Map of north-west Scotland, showing the islands mentioned in the text.

Much older information has been collected by Heddle (1901) who reports zeolites on the following islands: Canna, Eig, Muck, Staffa, Ulva, Lunga, Treshnish, Great Cumbrae, and the Shiant Isles. Recourse to British Geological Survey (BGS) maps shows many basaltic dykes on the Western Isles but, Skye and Mull apart, no systematic study of these seems to have been undertaken. This contribution describes attempts to rectify this on Arran, Islay, Jura, Colonsay, Harris and Lewis. The study had two aims, firstly to check such records as were

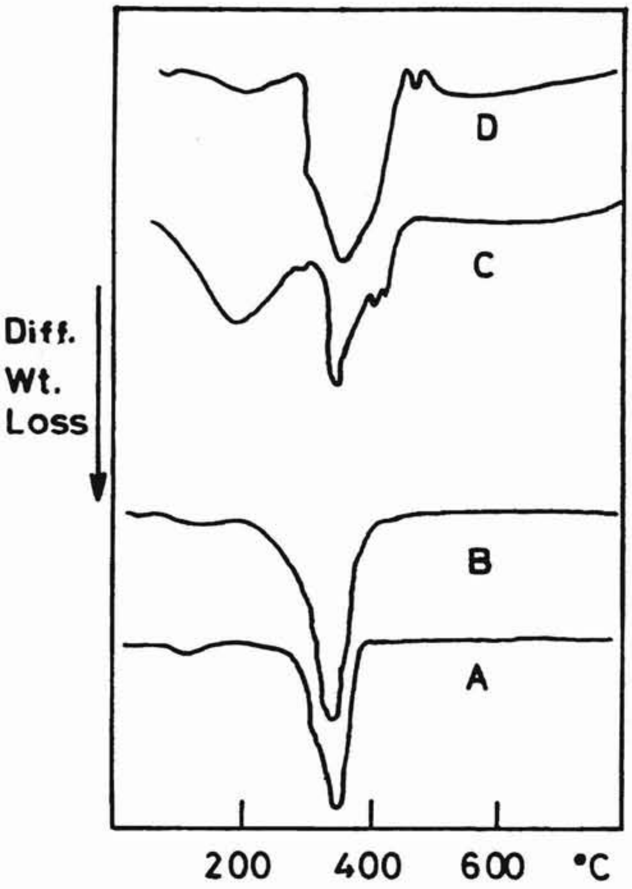

FIGURE 2. Examples of differential thermograms recording the water lost over a temperature span: our results compared with published thermograms (Gottardi and Galli, 1985). (**A**) Natrolite, Bunnahabhainn (Islay). (**B**) Natrolite, Tierno, Trento (Italy). (**C**) Thomsonite, Kildalton Cross (Islay). (**D**) Thomsonite, Savona (Italy). Heating rates: A & C, 15°C/min; B & D, 20°C/min.

available, as described above, and secondly to examine all the dykes marked on the geological maps as being of likely Tertiary age.

METHODS

Several vesicular dykes were noted including some smaller ones not shown on the BGS maps. Samples (~2 g) were obtained, allocated a grid reference, and stored in polythene bags. Identifications were made by X-ray powder diffraction (Philips PW1710 diffractometer with MicroVax search-match software) at the University of Wolverhampton and differential thermal gravimetry (DTG) (Mettler 3000) at the University of Salford. Most amygdaloidal materials collected were small samples (~10 mg). The minerals were suspended in ethanol and slurried over a disc of fused silicon for XRD investigation. The samples were then reclaimed for DTG analyses which were carried out with heating rates of 15°C per minute.

RESULTS AND DISCUSSION

DTG proved to be a useful, rapid method for confirming XRD identifications, as shown by Wilson (1994). The technique records weight loss from a small sample (20 mg) of the powdered mineral, heated at a fixed rate, on an automatically recording balance. Changes in weight (mass) are recorded as differential curves which are generally characteristic for each zeolite (Fig. 2).

For ease of assimilation the results have been presented in tabular form (Tables I, II, III).

ARRAN (Table I)

Previous work had identified analcime, natrolite and a conjectured laumontite in drill cores from the Dippin Sill (Dickin et al., 1984). This report is concerned with samples from surface localities on the sill (Table I, Whiting Bay). Analcime was abundant, and three sill sites yielded thomsonite, but no natrolite or laumontite was collected. Other dykes on Arran contained thomsonite and analcime and one (Bennan Head) contained phillipsite. It is only recently that phillipsite has been properly identified in Scotland, at Oisgill Bay on Skye (N. Hubbard, *personal communication*, 1993). The sample described by Heddle (1901) as phillipsite, and kept at the NMS, proved to be harmotome when subjected to modern analysis (A. Livingstone, *personal communication*, 1985).

Chabazite and scolecite were found in a boulder at Kingscross Point but this may not have been *in situ*. The occurrences of gismodine in a lopolith at Clauchland's Bay (north of Lamlash) and of gmelinite in a dyke at Breadlebane are interesting. The only other record of gismondine in the British Isles, apart from the well-known Northern Ireland localities, is that on Harris mentioned earlier. A.P. Walker identified gmelinite in a sample collected by Heddle from Quiraing, Skye (NMS Register No. 448.3), and Heddle (1901) describes it at Talisker Bay, Skye, although it is possible that the material from Talisker might have been phacolitic chabazite, as good samples of this can be collected from the sea stack at Talisker. The term 'phacolite' refers to a crystal habit which is lens-shaped, rather than the normal cubic chabazite habit. It arises from twinning around the *c*-axis (Tschernich, 1992, pp. 87–94).

TABLE I. Zeolites from Arran.

Locality	Grid Ref.	Phases identified	Comment
Kingscross Point	NS 056 284	Thomsonite, chabazite, scolecite	In boulder
Whiting Bay	NS 047 268	Thomsonite	McGregor's locality 5*
Whiting Bay	NS 048 252	Analcime	McGregor's locality 5*
Whiting Bay	NS 047 225 a	Thomsonite, analcime	Vug in Dippin Sill
Whiting Bay	NS 047 225 b	Thomsonite	Different vug
Bennan Head	NR 983 201	Phillipsite, thomsonite, analcime	Large dyke
Breadlebane	NS 031 206	Amalcime	Dyke
Breadlebane	NS 024 208	Gmelinite, thomsonite	Dyke
Breadlebane	NS 025 208	Thomsonite	Dyke
Torrylin Shore	NR 954 206	Analcime	Dyke
Clauchland's Point	NS 053 329	Gismondine	Lopolith near gun emplacement

*From McDonald and Herriott (1983).

TABLE II. Zeolites from Islay, Jura and Colonsay.

Locality	Grid Ref.	Phases identified	Comments
ISLAY			
Bunnahabhainn	NR 424 732	Thomsonite, gobbinsite, natrolite, analcime	Dyke near wrecked ship W of distillery
Kildalton Cross	NR 468 509	Thomsonite	Dyke – exposure near beach
JURA			
Ard Fernal	NR 564 713	Natrolite, mesolite (55%) + scolecite (45%), gonnardite	Various vugs in dyke
Glas Eilean*	NR 447 652	'Wellsite' (63%) + harmotome (37%)	Dyke on beach
COLONSAY			
Uragaig, Kiloran Bay	NR 389 984	Thomsonite	Beach exposure – dyke

*An islet off the SW coast of Jura

TABLE III. Zeolites from Harris.

Locality	Grid Ref.	Phases identified	Comments
Hushinish, North Harris	NA 992 125	Chabazite, stilbite	Dyke on shoreline of Caolas an Scarp

ISLAY, JURA, COLONSAY (Table II)

On Islay zeolites were found at Kildalton Cross and on the foreshore near the Bunnahabhainn Distillery. At the latter locality the rare zeolite gobbinsite was identified for the first time as a Scottish mineral. The localities on Jura and Colonsay represent the first records of zeolites on these islands. The occurrences of mesolite and scolecite at Ard Fernal, and of the so-called 'wellsite' on Glas Eilean, are noteworthy. Wellsite was described as a new zeolite from North Carolina by Pratt and Foote (1897), but is now regarded as an intermediate member of the phillipsite–harmotome substitution series. Gottardi and Galli (1985, p. 141) describe wellsite as a barian phillipsite, based on analyses of several samples which showed Na, K and Ba. Sheppard and Gude (1971) suggest that 'sodic harmotome' equally well describes the material. Phillipsite, 'wellsite' and harmotome give distinguishable XRD patterns, and quantitative XRD showed that the Glas Eilean sample was an intergrowth of 63 wt % of 'wellsite' and 37 wt % harmotome. The presence of gonnardite at Ard Fernal adds to the relatively few records of this zeolite. This apparent rarity may be misleading however because Alberti et al. (1995) have shown that there is a very close structural relationship between tetranatrolite and gonnardite, so it is possible that some previous records of tetranatrolite may well refer to gonnardite.

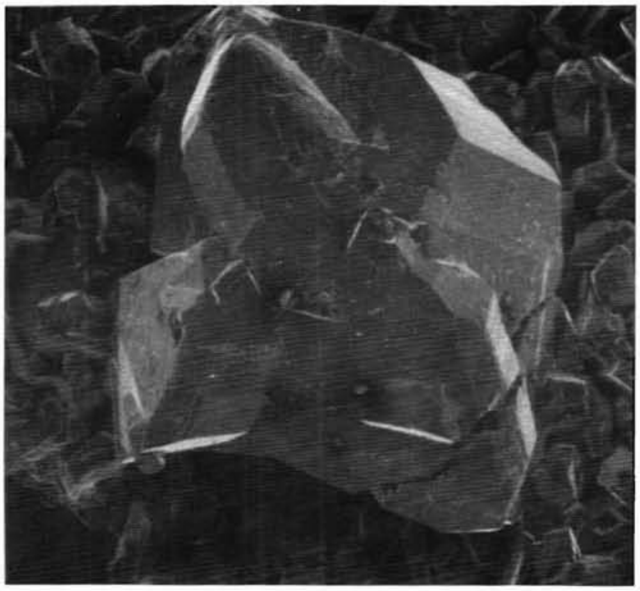

FIGURE 3. Phacolitic chabazite from dyke on shoreline of Caolas an Scarp, North Harris, SEM photograph. Field width 5.5 mm.

HARRIS AND LEWIS (Table III)

We were unable to confirm the zeolites at the sites on Harris and Lewis mentioned in the Introduction. However, good samples of stilbite and chabazite were identified as a surface coating on a dyke ~50 m north of the slipway on the shore of Caolas an Scarp, Hushinish, North Harris. The chabazite was of the phacolitic habit (Fig. 3).

ACKNOWLEDGEMENTS

D. Jones is thanked for suggesting the Bunnahabhainn site. Access to the mineral collection of the NMS, courtesy of Dr Alec Livingstone, is gratefully acknowledged.

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ROMANESQUE AND GOTHIC WALL PAINTINGS IN WINCHESTER CATHEDRAL: AN UNUSUAL USE AND ALTERATION OF VIVIANITE

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Detailed study of the original materials used in medieval wall paintings at Winchester Cathedral reveals that vivianite was extensively used as a blue pigment apparently in preference to more commonly used mineral pigments. The use of vivianite as a pigment in wall paintings has not hitherto been reported in Britain.

The exquisite Romanesque and Gothic wall paintings in the Holy Sepulchre Chapel at Winchester Cathedral constitute what is arguably the finest medieval painted interior in England. The most striking area of late 12th-century painting is on the east wall of the Chapel, comprising a *Deposition* in the upper register and, below the dividing geometric border, an *Entombment* with the *Maries at the Sepulchre* and the *Harrowing of Hell* (Fig. 1). A Gothic painting which originally overlay that on the east wall was detached and replaced on an artificial support on the west wall in the 1960s. It approximately mirrors the subject matter of the Romanesque scheme. Dating from *c.* 1175 and *c.* 1220, respectively, the iconography and style of the two paintings have been discussed exhaustively by Park (1983). From the technical point of view they provide a fascinating insight into the execution of two schemes of exceptionally high quality, separated in date by scarcely 40 years, but painted in very different techniques (for which see Howard, 1995).

The inclusion of vivianite, $Fe^{2+}_3(PO_4)_2.8H_2O$, in the palette of both schemes is particularly surprising, not only since this pigment has not previously been identified in English medieval painting, but also since it was clearly selected for its distinctive colouristic qualities, rather than as an economic alternative to other mineral blues. Ultramarine (powdered impure lazurite) was the mineral blue normally employed in Romanesque wall paintings (H. Howard, *unpublished work*), though azurite has been identified at Kempley, Gloucestershire (Rickerby, 1990) and Mårslet, Denmark (Graebe *et al.*, 1986).

At Winchester, the characteristic deep 'indigo' blue of vivianite was used extensively in both paintings, for the blue portion of the panelled backgrounds (Table I, samples 3, 15, 34, 44) and for numerous details, such as the central detail in the vair lining of Nicodemus' cloak in the *Deposition*, where it was played against a pale blue of natural ultramarine combined with lime white (sample 26). In several cases (samples 34, 36) it has been applied over a dark grey or black ground which would decrease the light scatter from the lime plaster substrate and thereby increase the covering power of the mineral blue pigment.

Initial identification of vivianite by polarised light microscopy – typified by blue to yellow pleochroism (Faye *et al.*, 1968) – was confirmed by XRD at the Mineralogy Department of the Natural History Museum, London. In recent years, vivianite has been identified in medieval painting in Germany, as on the Romanesque lectern at Freudenstädter of *c.* 1150 where it was applied over a grey ground of lead white combined with carbon black (Richter, 1988), and on the late 14th-century ceiling of Jakobuskircherl, Urschalling, where the patchy blue-brown appearance of the 14th-century decoration is thought to be due to an alteration of the mineral (analysis by H. Kühn: M. Alof, *personal communication*, 1988). In the context of English medieval polychromy, a preliminary identification of vivianite has been made on an Anglo-Saxon stone sculpture fragment from York (J. Darrah, *personal communication*, 1987).

Vivianite occurs naturally in oxidised portions of some metalliferous ore deposits, such as at Wheal Jane near Truro and mines around St Agnes, Cornwall, where it generally appears as dark indigo-blue to blackish green crystals (Collins, 1892; Rudler, 1905; Embrey and Symes, 1987). The mineral is generally stable although it may be colourless when initially brought to the surface (Watson, 1918). Vivianite is also found in an earthy form, frequently associated with bones or decaying wood and in other organic, phosphate-rich environments (Palache *et al.*, 1951). It is interesting to note that as early as the 18th century Delaval (1777) noted the association of iron and peat in blue earthy deposits, which were presumably vivianite.

It seems likely that vivianite was used as a pigment only where the mineral was found locally in the medieval period, and it is interesting in this respect that its use in medieval polychromy has been confirmed in Germany and England where mineral deposits are well known. Numerous occurrences of vivianite in England have been reported, most recently by Birley and Young (1993), Smith (1994), and Atkins (1995). The mineral has been found as small crystals at Whale Chine on the Isle of Wight, and in its earthy form at Fordingbridge, both close to Winchester (P. Tandy, *personal communication*, 1994). Either of these could conceivably be the local source used by the painters of the Holy Sepulchre Chapel, and of the wall paintings of *c.* 1230 in the Guardian Angels Chapel, Winchester Cathedral, where vivianite has also recently been identified by the author. However, even if these sources were known to the medieval craftsmen they are unlikely to have been substantial enough to yield an abundant, lasting supply of the pigment. It is perhaps more likely that a local source of vivianite came to light fortuitously at around the time the painting was executed, and that this material was found to be eminently suitable for the intended purpose.

Since vivianite is known to be generally stable in its blue form, it is significant that in the Holy Sepulchre Chapel paintings the particles have partially altered to a yellow colour, thus producing an overall green appearance to areas, such as the backgrounds, which would originally have been blue. The colour change of the mineral on initial exposure – from colourless to blue – is due to increased concentrations of Fe^{3+}, and it has been established that mechanical grinding of the colourless crystals, heating in air, storage in a vacuum, or chemical treatment of samples can produce a more rapid conversion from Fe^{2+} to Fe^{3+} and so to a blue colour (Hanzel *et al.*, 1990). It is therefore interesting to speculate whether grinding of the blue mineral to a particle size suitable for use as a pigment (or a chemical treatment used during conservation)

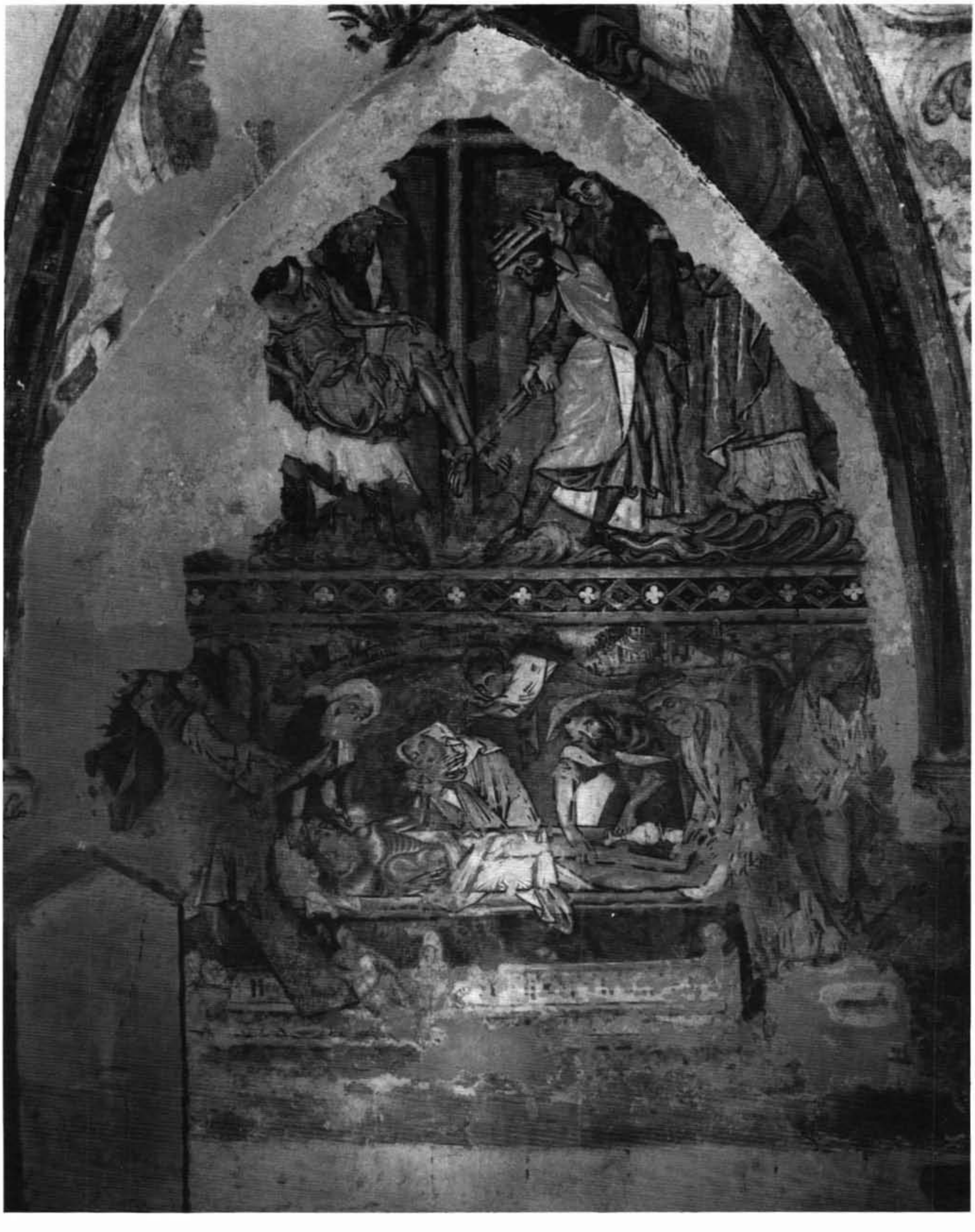

FIGURE 1. Holy Sepulchre Chapel, Winchester Cathedral. Wall painting of *c.* 1175 on the east wall depicting the *Deposition, Entombment, Maries at the Sepulchre, and the Harrowing of Hell.* Approx. 250 cm × 300 cm. Photograph courtesy of the Conservation of Wall Painting Department, Courtauld Institute of Art, London.

TABLE I. Selected samples from the Holy Sepulchre Chapel, Winchester Cathedral: Sample No. (with Courtauld archive accesion No.), location, and stratigraphy of the various layers from the top layer down.

Sample No:	Location & Description	Original Polychromy	Pigment Alterations & Added Materials
3/1071	E. wall, upper tier, S. side, olive green background to left of Nicodemus' foot.	● viviante 20 μm ● natural ultramarine 30 μm ● lime plaster with charcoal black inclusions 400 μm	● vivianite has partially altered from blue to yellow
26/1094	E. wall, upper tier, Nicodemus' cloak, blue and white vair lining, green area over blue	● vivianite in calcium carbonate matrix 90 μm ● natural ultramarine in lime matrix 100 μm ● plaster substrate 300 μm	● vivianite has partially altered from blue to yellow
34/1102	W. wall, upper tier, N. side, green background colour below white scroll	● vivianite 100 μm ● charcoal black 80 μm ● lime plaster substrate 60 μm	● beeswax coating containing calcium carbonate and calcium sulphate 20 μm ● proteinaceous coating 30 μm ● vivianite has partially altered from blue to yellow
36/1104	W. wall, upper tier, S. side, (left as viewed) leg of Joseph of Aramathea, dark green linear detail on back of calf.	● vivianite 150 μm ● charcoal black and lime white 40 μm ● lime plaster substrate 100 μm ● trace of red pigment from 12th century scheme 20 μm	● beeswax (trace) ● proteinaceous coating ● vivianite has partially altered from blue to yellow
12/1080	N. wall, E. arch, chamfer on S. side, E. end, 6th ashlar block from apex, yellow over green on plaster.	● yellow earth pigment in lead white matrix (100 μm) ● vivianite in lead white matrix (60 μm) ● lime white ground (trace)	● proteinaceous coating ● proteinaceous material is indicated in both paint layers ● vivianite has partially altered from blue to yellow
14/1082	N. wall, E. arch, soffit, E. side, lower figure, thick beige coating over green paint of drapery.	● vivianite in lead white matrix (120 μm)	● beeswax ● proteinaceous coating ● thick lead white layer ● vivianite has partially altered from blue to yellow
15/1083	Vault, E. bay, E. segment, under left proper hand of Christ, 'pea' green background of mandorla.	● vivianite 75 μm	● beeswax ● proteinaceous coating ● vivianite has partially altered from blue to yellow
44/1112	Vault, E. bay, E. segment, S. side, green background below Christ's hand, white decorative spot over green.	● lead white 90 μm ● vivianite 55 μm	● proteinaceous coating 5 μm

may have contributed to an additional increase in Fe^{3+} concentration and ultimately to a further colour alteration from blue to yellow. It is significant that the pigment has retained its blue colour (Table I, sample 44) only where it has been protected from environmental factors and from various conservation treatments undertaken in the past which include, for the 13th-century scheme, waxing, solvent cleaning, facing for detachment with a proteinaceous adhesive and subsequent cleaning; and for both 12th- and 13th-century schemes, consolidation with lime water.

Examination of polished thin-sections of paint samples at 1000 × magnification indicates that it is the largest particles (19 × 7 μm) which have remained blue. Although yellow particles of similar dimensions (15 × 5 μm) are present, there are clear divisions along cleavage planes within these particles, allowing more oxidation to occur. At high magnification it is also possible to see that a yellow halo surrounds some of the large blue particles, and that cleavage planes within the crystal are marked by a yellow line.

Identification of the yellow oxidation product of vivianite by XRD has proved extremely difficult since the minute samples taken from the wall painting contain not only a high proportion of calcite, but also a mixture of vivianite with the yellow alteration product. In one sample, however, XRD analysis indicated that metavivianite, a polymorph of vivianite, may be present. The nature of the yellow alteration product is the subject of further investigation by the author.

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NOTES

CORONADITE FROM THE NORTHERN PENNINE OREFIELD, ENGLAND

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Although manganese is commonly present in the limonite ores which are widespread in the Northern Pennine Orefield in the oxidised zone of primary siderite and ankerite ores, records of separate manganese oxide minerals are very few. Dunham (1990, p. 90) notes that manganese contents of between 3 and 5 per cent are normal in these ores, with exceptional levels of up to 13.6 per cent manganese recorded locally. The manganese may be present as psilomelane or pyrolusite though to date these minerals have been specifically mentioned only from old workings on the Remmington's veins on Great Dunn Fell (Dunham, 1990, p. 91). Manganese oxide contents in the primary minerals from which these oxidised ores are derived varies from up to about 2.5 per cent in ankerites to up to about 3.5 per cent in siderites.

Examination by X-ray diffraction powder photography (BGS X-ray Nos XE849, XE875) has revealed the presence of coronadite, $(Mn^{4+},Mn^{2+})_8O_{16}$, in oxidised veinstone from shallow workings on Sedling vein at High Sedling mine, Cowshill, Weardale, Co. Durham (National Grid Reference NY 8698 4076). Sedling vein was formerly an important source of both galena and fluorite. Other primary minerals noted by Dunham (1990, p. 208) are quartz, sphalerite, marcasite and chalcopyrite.

Coronadite is common in the spoil as blocks, up to 20 cm across, composed of compact, closely spaced aggregates of small-scale mamillated crusts. Freshly broken surfaces are homogeneous with a smooth or locally sub-conchoidal fracture, a dark steel-grey colour, and a rather faint sub-metallic lustre. In many blocks coronadite is unaccompanied by any other mineral though in other blocks it encrusts and cements broken fragments of pale purple fluorite or quartz. Also present on this dump are blocks of cellular dark brown goethite with pockets of orange-brown ochreous limonite. A little goethite locally accompanies the coronadite. None of this material has been seen *in situ* though the small area of dumps from which these specimens were obtained appears to have been derived from opencast or shallow underground workings in Sedling vein in the Coalcleugh Beds sandstone. A few blocks of exactly similar coronadite-bearing veinstone occur scattered through the abundant spoil within the gully which marks the course of Sedling vein between High Sedling mine and Sedling Burn to the west. These may have been derived from a rich concentration of the mineral at High Sedling, or the mineral may be present more widely within the oxidised outcrop of Sedling vein.

At Sedling coronadite is clearly of supergene origin and presumably results from the oxidation of manganese-rich ankerite or siderite in the presence of galena. Although Dunham (1990) mentions neither ankerite nor siderite from Sedling vein these minerals are almost universally present in fluorite-bearing veins in this part of the orefield.

The first British record of coronadite was by Hartley (1960) who described the mineral from Dry Gill mine, Caldbeck Fells, Cumbria, where it occurs in a similar paragenesis to that at Sedling. Its presence within the suite of manganese oxide minerals which accompany mendipite and other rare oxychloride minerals at Merehead quarry, Mendip Hills, Somerset, has been suggested by Embrey (1978) but apparently not confirmed. Nicholson (1986) noted the presence of coronadite in a complex manganese ore of supergene origin at Arndilly, Banffshire. The apparent rarity of this mineral may in part reflect the lack of precise identification of many black manganese oxide minerals commonly referred to as "psilomelane". X-ray powder photography of a sample from the only recorded Northern Pennine occurrence of "psilomelane", Remmington's veins on Great Dunn Fell, revealed that the mineral was romanèchite, $BaMn^{2+}Mn^{4+}{}_8O_{16}(OH)_4$ (BGS X-ray No. XE879).

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A FURTHER OCCURRENCE OF WIDENMANNITE IN CORNWALL, ENGLAND

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Widenmannite, $Pb_2UO_2(CO_3)_3$, is previously reported from Michael mine, Weiler, near Lahr in the Black Forest, Germany (Walenta and Wimmenauer, 1961; Walenta, 1976) and Loe Warren zawn, St Just, Cornwall (Elton and Hooper, 1995a, 1995b). Further specimens of widenmannite have been found recently at North Zawn (National Grid Reference SW 355 326), some 800 m SW of Loe Warren. Identification was by XRD and EDX spectroscopy. Although North Zawn is close to the original Cornish locality for widenmannite, the paragenesis at the two localities is quite different.

North Zawn is a narrow, steep-sided cove produced by marine erosion of a mineralised lode. A short drive leads inland (SE) from the back of the zawn on its northern side along the line of the lode. Widenmannite was found in detached quartz–calcite–sulphide boulders lying near the top of the beach. The matrix is composed chiefly of massive quartz and spherulitic pyrite with minor chalcopyrite. The pyrite often gives the impression of having incompletely filled cavities in the rock with radial growth. Calcite, in the form of small imperfect scalenohedra often occurs on the surface of the pyrite, partially or completely filling the remainder of the space formed by intersecting surfaces of the pyrite spherulites. Gypsum is also occasionally found in these cavities.

The matrix also contains considerable amounts of colourless, white, or pale yellowish calcite in the form of small rhombohedral crystals. The cores of the pyrite spherulites typically contain granular calcite and other sulphides, notably galena in the form of scattered grains, and sphalerite as larger blackish grains or as yellowish crusts. The galena is significantly altered, and the surrounding matrix contains many open spaces amongst etched calcite, allowing the development of small crystals of cerussite and anglesite. Widenmannite occurs sparingly in patches, usually close to the areas of altered galena. The appearance of the widenmannite is very similar to that at Loe Warren zawn, viz. soft white flaky anhedral mats and groups of minute colourless euhedral lath-like crystals 10-20 µm long. Widenmannite is not associated particularly with any other supergene species.

Small crusts and blobs of bright yellow microcrystalline sodium-zippeite also occur sparingly in or near areas of altered galena. On a few specimens, sodium-zippeite occurs very close to widenmannite; both are evidently late-formed minerals, but their relative ages cannot be determined. Both uranium species appear to post-date cerussite and anglesite. In the SEM, the sodium-zippeite shows a flaky petaline habit similar to certain habits observed at Geevor mine (Elton and Hooper, 1993), but the crystals are very minute (about 10 µm across). Rare platy torbernite is observed scattered over the matrix on a few specimens.

The quartz and spherulitic-pyrite matrix is highly characteristic and rock of a similar appearance can be found *in situ* a short distance along the drive towards the back of North Zawn. This observation suggests that the widenmannite-containing boulders originated from the North Zawn lode. Specimens of matrix collected *in situ* show alteration of pyrite with crusts of iron oxide and iron sulphate, but no evidence of secondary uranium species. The top of the beach at North Zawn lies well above high tide, but certainly in reach of sea spray at rough high tides. Similar conditions prevail at Loe Warren zawn. It is suggested that widenmannite and sodium-zippeite have formed in boulders on the beach at North Zawn by the action of sea spray and rain water on pyrite, calcite and galena in the matrix. The source of uranium ions is probably minute grains of uraninite associated with the galena, although this has not been confirmed. The associations at North Zawn contrast with those at Loe Warren zawn in most respects, the only common elements being the undoubted presence of Pb and U and CO3 ions and the coastal environment. Representative specimens of widenmannite and sodium-zippeite have been deposited at the University Museum, Oxford.

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DIABOLEITE FROM GUNVER HEAD, CORNWALL, ENGLAND

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Diaboleite, $Pb_2CuCl_2(OH)_4$, is well known as a British mineral, but almost exclusively from manganiferous pods in the limestone of the Mendip Hills, in close association with mendipite and other lead minerals. It has been reported in these pods from a number of localities (Spencer and Mountain, 1923; Kingsbury, 1941; Alabaster, 1976, 1990; Symes and Embrey, 1977), and was first described from one of these, its type locality being the old mine at Higher Pitts Farm, St Cuthbert Out, Somerset (Spencer and Mountain, 1923). A number of occurrences of lead and copper hydroxychlorides have been reported from coastal sites in south-west England in recent years, but at only one has diaboleite been reported. This is a find by R.E. Starkey in 1985, *in situ* at Daymer Bay, Polzeath (National Grid Reference SW 927 777), checked by X-ray powder diffraction at the Natural History Museum, London, and reported in the *British Micromount Society Newsletter* for November, 1987.

In March 1994 one of us (M.G.H.M.) collected material from a cliff exposure at SW 894 770 at Gunver Head, in the area of Padstow Consols (Cuddrabridge) mine, bearing phosgenite, cerussite, anglesite and native sulphur crystals in addition to small blue crystals of cumengeite, in an oxidised quartz–galena veinlet. Some of this material displays small patches of a blue fibrous mineral in association with the cumengeite, which on investigation proved to be diaboleite. It forms sky-blue needles up to ~0.4 mm long, in matted crusts and scattered crystals, on a matrix of quartz–galena–sphalerite–chalcopyrite veinstuff interspersed with grey slaty killas, and closely associated with bipyramidal cumengeite crystals up to 0.1 mm in size.

A Fourier Transform infrared spectrum was obtained of the blue needles from Gunver Head (Nujol mull between KBr plates; Philips Analytical PU9600 spectrometer). It was similar to those of diaboleites from Mammoth mine, Arizona, U.S.A.; Mina Caracoles, Sierra Gorda, Chile; and Chah Khouni mine, Anarak, Iran; in addition it showed absorptions due to contamination with quartz and other impurities. Absorption maxima for the Gunver Head sample are compared in Table I with those for Mammoth mine diaboleite, with the probable assignments also given. Which of the metal–O–H and metal–O absorptions listed are assignable to Pb–O–H and which to Cu–O–H vibrations is uncertain; taking, for example, the 442 and 470 cm^{-1} bands, litharge (PbO) has a Pb–O stretching absorption at 465 cm^{-1} (White and Roy, 1964), but tenorite (CuO) displays a Cu–O stretching absorption at 475 cm^{-1}.

TABLE I. Infrared absorption maxima of diaboleite.

Absorption maxima, cm^{-1}		Assignments
1	2	
3455 m	3455 m	
3433 s, sp	3432 s, sp	O–H stretch
~3330 sh	~3330 sh	
1081 m		Quartz
935 m		Unidentified impurity
856 m	855 m	Metal–O–H bend
798 mw		Quartz
779 mw		Quartz
679 vs, sp	678 vs, sp	Metal–O–H bend
665 m, sp		Unidentified impurity
509 w		Quartz
470 fw	470 fw	Metal–O
442 s, sp	442 s, sp	Metal–O

1. Blue needles, Gunver Head (small, impure sample), off RSWB 94–70.
2. Diaboleite, Mammoth mine, Arizona, off RSWB 73–302.

sp = sharp; sh = shoulder; s = strong; m = medium; w = weak; f = fairly; v = very.

The association of diaboleite with cumengeite at this locality is not surprising as diaboleite and cumengeite form under similar pH conditions, diaboleite being formed preferentially when the activity (i.e. the effective concentration) of chloride ions is lowered somewhat (Turgoose and Williams, 1981).

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TALMESSITE, WITH RAUENTHALITE OR PHAUNOUXITE, FROM IVY TOR MINE, DEVON, ENGLAND

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Ivy (or Ivey) Tor mine, Belstone, Devon, on the south bank of the River Taw, at National Grid Reference SX 627 932, was worked intermittently for copper ore from the late 1840s to about the turn of the century, in the metamorphic aureole of the Dartmoor granite (Dines, 1956; Harris, 1968; Edmonds *et al.*, 1968). It has yielded an interesting range of minerals, including chalcopyrite, arsenopyrite, bismuthinite, marcasite and axinite (Collins, 1871); scheelite (Kingsbury, 1964); native bismuth and quartz (R.W. Barstow, Sale Catalogue, July–August 1982); a massive brown garnet (G. Ryback, *personal communication*, 1960); a chlorite (P. Golley, *Russell Society Newsletter* 1992, No.23, p.9); and a little cobalt ore (Edmonds *et al.*, 1968).

In 1994 one of us (M.G.H.M.) broke up a lump of veinstone from the dump, revealing a cavity lined with white radiating spherules on a silvery primary ore, with a pinkish gangue mineral. Further study, using microchemical, infrared and powder XRD techniques, showed the spherules to be mainly talmessite, sometimes mixed with rauenthalite or phaunouxite, the primary ore to be löllingite, and the gangue mineral to be dolomite. This is the first reported locality for talmessite in the British Isles, but the rauenthalite–phaunouxite system has been reported from Muckross, Killarney, Co. Kerry, in the Irish Republic (Ryback and Moreton, 1993).

Talmessite from Ivy Tor forms silky white radiating spheroidal aggregates (up to ~0.5 mm across) of blades; some is of a more waxy white appearance, forming more confused, coarse-grained aggregates up to ~1 mm across, and this latter type is sometimes contaminated with rauenthalite. The aggregates show up well, being perched on a blackish-grey matrix of löllingite forming islands within a pinkish, compact, coarsely crystallised gangue of dolomite.

Fourier Transform infrared spectroscopy, using powdered samples in Nujol mulls between KBr plates, gave spectra similar to those of talmessite from Criss Creek, British Columbia, Canada, and from Bou Azzer, Morocco. The spectra display a very strong, broad O–H stretching absorption centred near 3000 cm^{-1}, indicating strong hydrogen bonding, its profile suggesting at least three overlapping bands. Together with the medium weak H–O–H 'scissor' deformation vibrations at 1645 and 1550 cm^{-1}, this provides strong evidence for the presence of water molecules in the structure, as suggested by the normally quoted chemical formula $Ca_2Mg(AsO_4)_2.2H_2O$ (e.g. Fleischer and Mandarino, 1995) rather than the alternative formulation $H_2Ca_2Mg(AsO_4)_2(OH)_2$ suggested by Sturman and Dunn (1980). Other absorption bands include very strong overlapping bands at 798, 848, and ~807 cm^{-1} due to arsenate stretching vibrations, a medium strength band at 972 cm^{-1}, probably due to a metal–H_2O libration, and a strong band at 430 cm^{-1}, probably a metal–O vibration. The identification was confirmed by X-ray powder diffraction, which also indicated the presence of rauenthalite, $Ca_3(AsO_4)_2.10H_2O$, in one sample. However, rauenthalite can arise by the reversible dehydration at room temperature of phaunouxite, depending upon the humidity of the surrounding air (P. Davidson, *personal communication*, 1996), so the 'original' phase could have been either of these species.

The dark grey to silvery compact massive ore mineral, resembling arsenopyrite, has a blackish streak. An infrared spectrum shows no absorption bands in the 4000–400 cm^{-1} range, whereas arsenopyrite has a metal–S absorption at 435 cm^{-1}. An open tube heating test gave a sublimate indicating the presence of arsenic, and an oxide residue containing ferric iron, but no smell of SO_2 could be detected. These results match those expected for löllingite.

The infrared spectrum of the pinkish gangue mineral is similar to published spectra of dolomites (Farmer and Warne, 1978; Jones and Jackson, 1993), displaying a very strong, broad absorption centred near 1440 cm^{-1} due to the asymmetric stretch ($\nu3$) of the carbonate ion, and strong, sharp asymmetric deformation absorptions at 881 ($\nu2$) and 729 ($\nu4$) cm^{-1}, with a weak $\nu2$ absorption at 852 cm^{-1}.

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STALACTITIC GALENA IN THE MENDIP HILLS, SOMERSET, ENGLAND: ANOTHER 17th CENTURY REFERENCE

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A recent note (Cowdry, 1995) mentions some 17th century descriptions of nodular or stalactitic galena occurring in the Mendip Hills. A further reference to stalactites of galena is found in a letter written in 1676 by John Beaumont, a gentleman who lived at Ston Easton, not far from Lamb Leer Cavern, Lamb Bottom (Beaumont, 1676).

In the 17th century it was believed that cave formations were derived from 'steams' (which referred to cold as well as hot waters), or grew like plants from earth and clays, and the various stalactites, helictites, cave pearls, etc. were thought to originate from live matter which turned to a stony consistency. In his letter Beaumont suggested ways in which these 'rock plants' formed, and even gave an early description of a dyke or fissure fill of rubble, typical of the Mendip orefield. He went on to report that the spar hangs from the roof (of caverns) like icicles, "Lead-oar [*sic*] often growing in the same manner". This passage is reproduced by Hill and Forti (1986) but with those few words on lead ore omitted. There is no mention of Lamb Leer on this particular page (734) of Beamont's letter, but on the following two pages he was certainly describing the formation in that cavern, and it seems likely that the preceeding descriptions are from his own observations in a very local context.

Beamont had descended Lamb Leer Cavern only a short time before 1676, and in 1681 he gave a full account of his adventure, in which he said "Our miners digging daily meet with these caverns, which are different widenesses, some being very large; but the most considerable vault in a hill call'd Lamb" (Beaumont, 1681).

ACKNOWLEDGEMENT

I am most grateful to Dr Peter Burr for pointing out the overlooked passage in Beaumont's letter.

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BOOK REVIEWS

Robinson, G.W., *Minerals: an Illustrated Exploration of the Dynamic World of Minerals and their Properties*. Weidenfeld and Nicholson, London, 1994. 208 pp., 140 colour photographs. Price £19.99. ISBN 297 83329 4.

This beautifully illustrated book presents many of the most photogenic minerals in the Canadian Museum of Nature, *via* full-colour photographs and a carefully interwoven text. In the introduction, the reader is introduced to a geologist's way of thinking, the plate tectonic theory, the nature of minerals and the geological cycle. The tone of the text is authoritative yet simple and 'down to earth'; thus if a temperature of 1500°C is needed to synthesise a mineral in the laboratory, then looking for that mineral in rocks that form at lower temperature would make little sense. And again, "minerals are like people, they like to be comfortable in their surroundings; just as we respond to changes in our environment, so do minerals".

The later sections deal in turn with minerals from molten rocks, minerals and water, chemical alteration, and recrystallization, each section being illustrated by excellent colour photographs, by J.A. Scovil, of choice specimens from the Museum collection. The narrative continues in the refreshingly lucid style. It is explained briefly why olivine can accept iron partly substituting for magnesium but how other elements such as potassium or beryllium do not fit easily into the olivine structure and therefore remain in the magma to form different minerals later on at lower temperatures. This theme is followed up in the chapter on granitic pegmatites, illustrated with photographs of tourmaline, topaz, euclase, albite and columbite. The section on chemical alteration includes the concept of equilibrium and chemical reactions, including hydration-dehydration, oxidation-reduction, the formation of secondary minerals, and replacement deposits; we are reminded that no mineral is immune to alteration given the right physical and chemical conditions. The changes due to heat and pressure are dealt with comprehensively, and in the final section the concept that more than one geological process may have been required to produce such relatively rare occurrences as the emerald deposits of Colombia or the massive volcanogenic sulphide deposits in the so-called black smokers.

Throughout the book, in addition to the colour photographs of well-crystallized mineral specimens and the equally illuminating text, there is a sprinkling of a dozen or so coloured diagrams illustrating some of the various geological processes involved. The size of all the specimens photographed is stated; most are somewhat magnified, but the overall result is to make this a very desirable book and one which will surely appeal to all members of the Russell Society, particularly at the very reasonable price.

R.A. Howie

Dunn, P.J., *Franklin and Sterling Hill, New Jersey: the World's Most Magnificent Mineral Deposits*. Franklin-Ogdensburg Mineralogical Society (P.O. Box 146, Franklin, New Jersey 07416, U.S.A.), 1995. xxiv + 755 pp., 420 photographs, 300 maps, sections and line-drawings. Published in five parts at $30.00 per part or $150.00 for the entire work (plus surface shipping and handling of $5.00 per part or $15.00 for the entire work).

This five-part *tour de force* attempts to outline the history, geology, mining development and above all the mineralogy of these famous deposits, now worked out, but which were particularly rich in zinc, manganese and iron. They have been known for some 300 years and yielded over 33 million tons of ore. Approximately 10% of all known mineral species were to be found here; more valid new mineral species (69) have been described from here than from any other locality, and some 10% of the minerals are unique to Franklin and Sterling Hill.

The work opens with an extensive bibliography of some 1600 items, and Part 1 continues with chapters presenting historical perspectives of the local iron mining and processing, which was under way in the 1740s (including the attempts at working the enigmatic franklinite which resembled magnetite but did not react in smelting as magnetite did), and local zinc mining which was first developed in the late nineteenth century. It is interesting to learn that Sterling Hill was purchased at a Sheriff's sale for £40. Part 2 deals with the quarries in the Franklin Marble, which is the host to all the ores, the beneficiation of the zinc ores, the regional and local geology of the area and, in particular, the geology and structure of the zinc deposits. The ores are Precambrian in age and it is considered that the metal content of the protores was in place in sediments before the complex later history of igneous intrusions (granites and pegmatites) and several episodes of regional metamorphism to the sillimanite grade (upper amphibolite to granulite facies).Various genetic theories for these orebodies are reviewed but no comprehensive solution to the various problems posed is yet available. This part of the work continues with details of the geochemistry of the orebodies and the distribution of the elements between the numerous host minerals; as noted earlier by Frondel and Baum (1974) there is a close correspondence between the suite of trace elements found in these deposits and those typical of marine and hot-spring deposits of manganese oxides. The discovery early in the twentieth century that electric arcs from switchgear caused fluorescence in nearby minerals led to the recognition of more than 80 fluorescent mineral species in this area. The paragenetic and textural aspects of the various mineral assemblages in the zinc ore units are considered; silicates are much more common in these ores than might be surmised from the literature.

The remaining three parts are concerned with the descriptive mineralogy of the deposit, starting with the silicates, which include over forty manganese silicates and some twenty zinc silicates, in addition to numerous silicates of calcium, magnesium and iron. In many cases, earlier data on morphology and physical properties are supplemented by some new microprobe analyses, and by hand specimen photographs and numerous photomicrographs, together with details on the occurrence and paragenesis for all the major species represented. This style is followed also in giving the descriptive details of native elements, sulphides, arsenides, antimonides, sulphosalts, oxides, halides, carbonates, sulphates, borates, tungstates, molybdates, arsenates, arsenites, phosphates and vanadates, together with brief descriptions of eight unnamed species. The work concludes with appendices on obscure mineral names, a glossary of local terms (e.g. 'Cousin-Jack', a name for Cornish miners, many of whom were brought over to do underground mining), and a description by the mine management of the operations of the Sterling mine in 1966, followed by fairly full subject and mineral indexes.

This is the most important work on these deposits and their minerals since the classic U.S. Geological Survey Professional

Paper 180, by Palache in 1935 (*The Minerals of Franklin and Sterling Hill, Sussex County, New Jersey*) and represents over twenty years of research by the author and cooperation with other geologists, miners and mineralogists interested in Franklin and Sterling Hill. The photographs incorporated in the text are black-and-white, and the reproduction of these is good, though some of the older but informative views of Franklin and of the underground mining operations are somewhat lacking in contrast but are nevertheless of considerable interest; the numerous maps and cross-sections are clear and helpful. These famous deposits have yielded some magnificent specimens to be seen in mineral museums all over the world and it is exciting to have an up to date record of all the mineralogical data pertaining to the many rare species represented in this unique assemblage. Libraries and others fortunate enough to possess a copy of Professional Paper 180, will certainly need to obtain this latest production to supplement and expand the record of this classic locality. The Franklin mine closed in 1954 and the Sterling mine closed in 1986, but the Franklin Mineral Museum prospers and has been designated as a New Jersey Historical Site.

R.A. Howie

Cairncross, B. and Dixon, R., *Minerals of South Africa*. Johannesburgh (Geological Society of South Africa, P.O. Box 44283, Linden 2104, South Africa), 1995. xix + 296 pp., numerous coloured maps & photographs. Standard Edition (ISBN 0-620-19324-7), U.S. $115; Luxury leather-bound collectors' Edition (ISBN 0-620-19325-5), U.S. $300.

This volume, which deals exclusively with minerals found in South Africa, combines mineral photographs in colour with descriptions of the minerals, together with their geological settings; historical information and abundant locality maps are also given, as well as a coloured geological map showing the simplified geology of the whole country.

The main section of the book takes a chronostratigraphic approach, from the Archaean (Monarch cinnabar mine, the asbestos deposits of the Barberton greenstone belt, the gold deposits of the Witwatersrand Basin, the Messina copper and Pafuri nickel deposits), on to the Proterozoic, and the Phanerozoic, concluding with the carbonates and phosphates of cave deposits. Most of the individual mines and deposits are shown on clear locality maps, which are just one of the strengths of this work; for many of the mining areas, alphabetical lists of minerals occurring there are presented.

The text is absorbing and both geologically and mineralogically authoritative. A typical section on the Archaean deposits gives details of the Bon Accord nickel deposit, with a geological sketch-map and a list of rare nickel minerals, for many of which this is the type locality. The discovery of the Witwatersrand gold deposits is summarized; this basin has already produced over 40 000 tons of gold and in 1972 was producing more than 66% of the world's gold, though this proportion has now declined. In the section on the Proterozoic, detailed descriptions are given of the Kalahari manganese field to the west of Kuruman in the Northern Cape Province; of around 150 species recorded here, 10 have to date been found only in the Kalahari Mn field. Then we come to the Bushveld complex, which with three large suites of igneous rocks occupying an area of 65 000 km^2 is the largest layered complex in the world. This has provided type specimens for 14 platinum group minerals as well as being rich in chromite; it also has some zeolites. The Phalaborwa carbonatite complex, about 550 km NE of Johannesbug in the Northern Transvaal, has been developed to become one of the largest open pit copper mines in the world; magnetite, uraninite-thorianite and baddeleyite are subsidiary products (a photograph shows a 10 cm baddeleyite crystal), and fine zeolites occur associated with cross-cutting dolerite dykes in the open pit. The Namaqua–Natal Province icludes the 3000 km^2 Okiep copper district with well-crystallized chalcopyrite and chalcocite, and granitic pegmatites are widely distributed in the NW part of the Northern Cape Province, yielding crystals of tantalite, libethenite, beryl, native bismuth, bismoclite, etc. Polymetallic deposits in this province include the Aggeneys Pb–Zn deposits (Gamsberg Zn deposit, Broken Hill with Pb, Zn, Cu and Ag), various small tungsten deposits and a high-grade monazite deposit.

The Phanerozoic era was characterized by the deposition of sediments in two large basins (the Cape supergroup and the Karoo supergroup) and at least two periods of volcanism. The Karoo lavas that form the Drakensberg Mountains have a maximum thickness of 1400 m in North Lesotho and were erupted from the early Jurassic to the early Cretaceous; their associated dolerite dykes contain abundant secondary minerals, ranging from amethyst and agate to calcite, prehnite, apophyllite and numerous zeolites. Pipes and dykes of Phanerozoic age include kimberlite, the primary source of diamonds; a brief account is given of the development of the diamond mines and of the indicator minerals used to locate kimberlites.

This geologically integrated section of this book is followed by a 75-page alphabetical compilation of South African minerals, again well illustrated, and giving brief historical and locality details. The minerals mentioned earlier in the text are included, but there are descriptions here of many more, ranging from 3 mm crystals of erythrite, to mozartite, poldervaartite and werdingite. We learn that prehnite was the first mineral to be described from South Africa (from the Karoo dolerites) and was also the first mineral to bear the name of a person. There follows a glossary of terms, a list of Museum and institutional collections in South Africa, a stratigraphically arranged bibliography of some 540 items and a comprehensive index.

We may all be familiar with some aspects of the geology and mineralogy of such areas as the Witwatersrand, Kimberley, the Bushveld complex, and the Karoo lavas, but as one reads this book the immense mineral wealth of South Africa (in both financial and intrinsic terms) come to be realised. This beautifully produced volume tells not only of gold, platinum and diamonds, but also of an exceptional variety of pristine mineral specimens frequently associated with the major mineral deposits. It also manages to give some impression of the harsh and uncongenial conditions often confronting the early prospectors. This book is strongly recommended for all interested in fine minerals, to which the high-quality photography does full justice. The authors and photographers are to be congratulated, as are the Geological Society of South Africa who have published the work as part of their Centennial Congress celebrations. Their slogan was "South Africa – land of Geological Superlatives" and this sumptuous production appropriately puts on record their bountiful mineral heritage. For such excellent and informative production, the price is eminently reasonable.

R.A. Howie

Craig, J.R. and Vaughan D.J., *Ore Microscopy and Ore Petrography*, 2nd edition. John Wiley & Sons, Inc., New York & Toronto, 1994. xiv + 434 pp. Price £18.95, paperback. ISBN 0-471-11599-1.

This book is now the standard student text for those interested in ore mineralogical studies as part of their course whether it be at undergraduate or postgraduate level. Wisely, the authors have taken the opportunity to update and revise the first edition to take account of new technical developments, new data, and advances in theory.

The first chapters concern the ore microscope and specimen polishing techniques, the latter generally more of an art than science! Qualitative and quantitative ore mineralogy is then dealt with at some length. Following a brief chapter on microindentation hardness testing (still used to characterise minerals but rarely used as a diagnostic tool), is a chapter on ore mineral textures. Both primary and secondary (replacement) textures are illustrated here together with their interpretation. Further interpretation of the sequence of mineral deposition, or paragenesis, follows and details of how to apply phase equilibria and fluid inclusion geothermometry. The largest chapter is one on ore mineral assemblages. Applications of ore microscopy in mineral technology is the final chapter. Three appendices are provided: the first, a table of diagnostic properties of the common ore minerals; next come the characteristics of common ore minerals (reflectance at 546 nm and Vickers microhardness; finally, a list of ancillary techniques which includes notes on everything from X-ray diffraction to atomic force microscopy.

In short, a valuable text for students. The specialist will use the more advanced texts. I would guess that more than a few Russell Society members would find the contents of interest even if not of immediate relevance.

C.J. Stanley

Tomlinson, J.M. (with geological appendices by T.D. Ford), *Derbyshire Black Marble*. Special Publication No. 4, Peak District Mines Historical Society, Matlock Bath, 1996. 95 pp. Price £9.95. ISBN 0-904-33404-X.

This work gives a beautifully illustrated account of the black marble from Ashford-in-the-Water, near Bakewell in Derbyshire, and the inlay work carried out in it, using such materials as Blue John, malachite, baryte and various coloured marbles. The Ashford marble is a very fine-grained, dark, bituminous limestone of Carboniferous age; this was mined from around 1750 until 1905. Both smaller items such as brooches, pendants, paperweights and candlesticks, and larger tabletops and urns are now collectors' items. There are numerous colour plates and also black-and-white photographs of the workshops; in an appendix photographs are given of some of White Watson's geological tablets showing cross-sections of Derbyshire strata.

R.A. Howie

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BACK COVER: Parkinsonite, prismatic crystals in a polished section, showing the red colour where the surface is chipped, and associated with wulfenite. Merehead quarry, Somerset, England. See R.F. Symes *et al.*, *Mineralogical Magazine*, **58**, 59–68 (1994). Reflected light photomicrograph in oil by C.J. Stanley. Field width ~0.5 mm.