

BRITISH MICROMOUNT SOCIETY



NEWSLETTER NO. 58 February 2001

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CONTENTS

Mineral Reactions	Alan Edwards	2
Minutes of the AGM - a correction	Editor	7
Branch News		7
Chemical Sleuth	Max Wirth	8
Miarolitic Minerals from Central Skye	Steve Rust	8
Historical Note	Paul Monk	10

MINERAL REACTIONS - A TALK AT THE BMS SYMPOSIUM 1999

A. Edwards

(This is the second and final part of Alan's talk - part 1 was in issue number 57. - Editor)

Many of you know what supergene minerals are and some of you may hear the word, and think it is a term used for super special minerals only found by the super experts. Some of which are sitting in this room.

Well it is in a way, but let us look at what it actually means. Supergene is a word suggesting an origin literally "from above". It is used almost exclusively for processes involving water, with or without dissolved minerals, percolating down from the surface.

Secondary (Supergene) Enrichment is a term used especially of ore deposits. It is applied to parts of the ore body in which the metal content of the ore has been increased, as a result of a downward percolation of waters carrying minerals in solution.

This enhancement takes place underground, mainly in the top portion of an ore body, a long time in the past without any intervention by man. Before erosion or earth movement exposed it.

The additional material may;

- (a) be deposited as a separate new mineral
- (b) be deposited as a further deposition of the existing ore mineral, or
- (c) replace the original ore mineral by one richer in valuable constituent.

As an example, a vein containing chalcopyrite may be enriched either:

by deposition of more chalcopyrite,	CuFeS_2	(35%Cu)
by deposition of bornite	Cu_3FeS_4	(63%Cu)
or by conversion of the chalcopyrite to chalcocite	Cu_2S	(80%Cu)

The percent of Cu is calculated by adding together the Relative Atomic Mass number for each mineral in the equation, then making a simple percent calculation. The atomic mass of copper is 64, Iron 56 and sulphur 32

Taking chalcocite as an example: $64 \times 2 = 128 + 32 = 160$, $128/160 = 80\%$

The chemistry for this will be explained further down.

The "Dictionary of Geology", by DGA Whitten with JRV Brooks, published by Penguin gives a diagram and description of secondary enrichment, as follows:

The gossan (or iron hat) near the surface, consists essentially of a mass of hydrated iron oxides from which copper (and any other metals) and sulphur have been removed by downward percolating water.

In the leached zone the sulphides are oxidised to sulphates and transported in solution. Copper can be oxidized to copper sulphate, which is water soluble, and the copper is therefore able to be carried down in a solution. Zinc can be oxidised to goslarite, which is also water soluble.

In the zone of oxidized enrichment, the reaction of the sulphate solution with the original ore in an oxygen-rich environment (Carbon dioxide is also present) results in the formation of carbonates and oxides, native metals, and (rarely) silicates.

Below the water table, secondary SULPHIDE enrichment occurs in an oxygen-free environment. The main contributing agent to this process seems to be HYDROGEN SULPHIDE. (rotten eggs smell).

Hydrogen sulphide (H₂S) is acid. By the combination of an acid and a base, the hydrogen of the acid is replaced by the metal of the base, and the result is the formation of a salt. The salt formed by sulphurated hydrogen is a sulphide and examples are chalcocite and bornite.

The area below the secondary enrichment is called the protore. This is an area containing ore material of low concentration which may not be economic to mine, though some are.

Mine owners loved to find these secondary enrichment zones. It saved them a lot of unprofitable work, by moving the sparse mineral content of the upper layers downwards and concentrating the mineral in one place for easy removal. Bear in mind that the present water table has not been constant and, over time it can have moved up or down

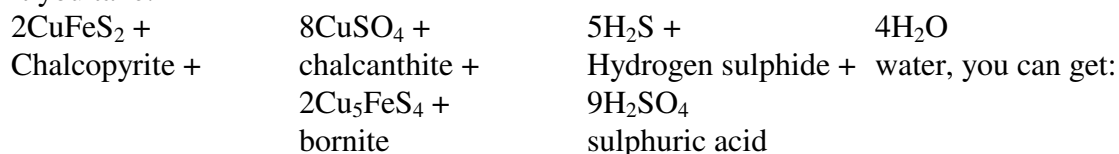
Tests on the South end of the vein at the New Glencrieff mine, showed the oxidized zone extending to 365 feet (112m) below the surface. It is concluded that the district had undergone a period of low water table at some time in the past. Today it is much closer to the surface.

First let us look at the reactions taking place, below the water table, in the secondary sulphide enrichment zone in an oxygen-free environment.

The thermodynamics underlying these reactions are complicated. I do not profess to understand them, so cannot explain them, but I can show the algebra, as they seem to take the form illustrated here.

Chalcopyrite (34%Cu) to bornite (63%Cu).

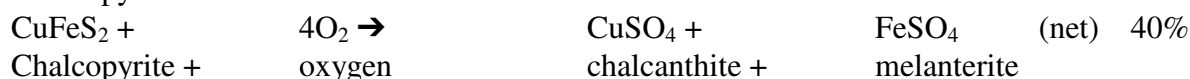
It you take:



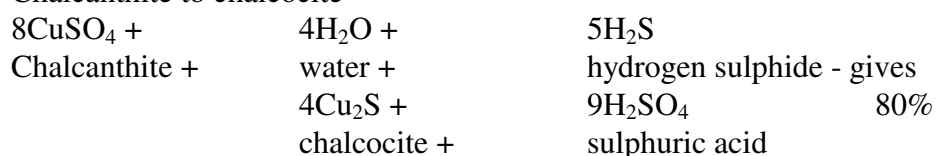
Where does the hydrogen sulphide come from? Possibly by putrefaction of organic substances containing sulphur, or by destructive distillation of coal, taking place underground.

Where did the Chalcantite come from, it was in solution, formed in the leached zone as copper sulphate, and was carried down below the water table in a solution of percolating water:

Chalcopyrite to chalcantite:



Chalcantite to chalcocite



The miners boots then get another clobbering.

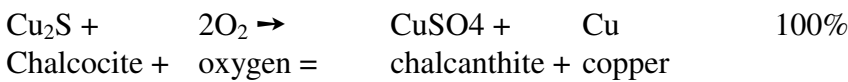
This shows that the copper content of the ore can rise from some 34% in chalcopyrite, to 63% in bornite and to 80% in chalcocite, without any outside help and by a series of natural mineral reactions.

If you are interested in the algebra, the first reaction to bornite involves 10 copper, 2 iron, 17 sulphur, 36 oxygen and 18 hydrogen on both sides, and is in balance.

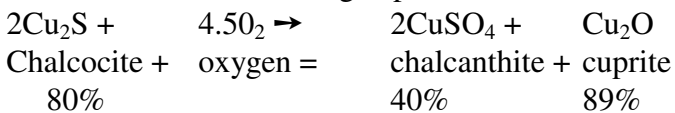
The second reaction to chalcocite, involves 8 copper, 13 sulphur, 36 oxygen and 18 hydrogen on each side, and is also in balance.

Time and erosion are liable to bring the sulphide Zone of Supergene Enrichment above the Water Table - The minerals are then exposed to air and oxidizing agents. For example:

If conditions are not very acidic and not highly oxidizing, copper can form as follows from the chalcocite:



with a little more oxidizing cuprite can form instead



Over time minor changes in O₂ levels can cause the deposition to Flip/Flop. In both cases the by-product of the reaction is chalcantinite (Copper sulphate).

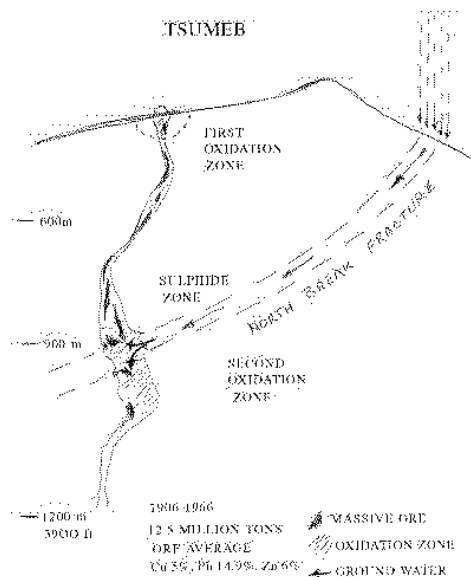
These subsequent changes can give rich pickings for miners.

I am indebted to the Mineralogical Record for some of the Tsumeb information given here. Most of the rest comes from "The Mineral Resources of Namibia", 1992 Geological Survey.

This famous mine in Namibia has several unique features. The most extraordinary of these is the lower or second oxidation zone, which was in two parts, and which was the product of a plumbing accident of nature. The north break fracture carried large volumes of surface water down to the ore vein, at some 800m deep. It also carried water through a karst-fissure to the ore vein at 1350 metres, then on down to the 48th level where mining operations terminated in 1996 at about 1690 metres. (some 5,400 feet)

The lower oxidation zones were the most mineralogically interesting feature of the deposit. The unique geo-chemical aspect profoundly influenced the mineralogy. The result was super supergene enrichment. Some 226 minerals are attributed to this mine, of which 40 have only been found here.

Massive sulphide bodies had contained as much as 60% metal. One large mass contained 26.7% lead, 12.4% zinc and 3.6% copper, a mineral content of 42.7% Throughout the pipe, tennantite, a grey copper sulphide of copper, iron, arsenic, and sulphur, was the most persistent primary copper mineral, and lead the dominant metal.



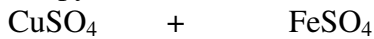
[Note for information only.

During the 90 years from 1906, 26 million tons were processed, with an average ore content of 5% copper, 14% lead, and 6% zinc.]

Sadly it is now all over. Sue and I have been to Tsumeb and photographed the main shaft headgear, which is just off Tsumeb Main Street, and through the bars of the security gate. That was as close as we could get. Whilst we were in Tsumeb we did manage to track down Tony Pitsch, via the bakery, to his house in Zincstrassr, and buy a few of his last remaining specimens.

To return to the reactions that take place in the oxidation zone, above the water table, where many of the well known copper secondary minerals are formed, the following takes place.

Chalcopyrite - CuFeS_2 - reacts to oxidation as we have already seen, to produce:



Copper sulphate and melanterite

(The cuprian variety of melanterite is known as pisanite) melanterites has the general formula of $\text{A} + \text{SO}_4$, where A can be iron, copper or zinc. With plenty of air, and in an acid environment, the melanterite, will oxidize further by the reaction we have already seen for pyrite, producing kornelite and water, and then goethite and sulphuric acid.

The copper sulphate, CuSO_4 , which is produced by this oxidation, can be the main building block for copper secondaries as chalcantite - $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

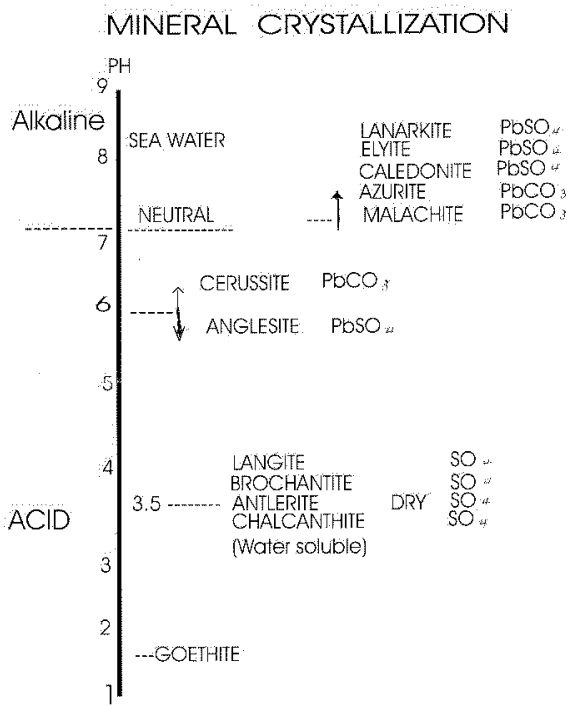
In dry and acid conditions it is stable, but it is soluble in water, so it can easily percolate downwards in ground water. The presence of dissolved calcium carbonate and water enables the copper sulphate to complete the reactions necessary to produce the secondary minerals.

The requirements for the formation of these secondaries are:

<i>Copper Sulphate</i> (CuSO_4)	<i>Calcium Carbonate</i> (CaCO_3)	<i>Water</i>
Take 4	3	3 and you get
Brochantite	$\text{Cu}_4\text{SO}_4(\text{OH})_6$	
Langite	$\text{Cu}_4(\text{SO}_4)(\text{OH})$	
Take 3	3	1 and add CO_2 and you get
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$	
Azurite needs a high concentration of free CO_2 in the environment.		
Take 2	2	2 and you get
Malachite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	
Take 3	2	2 and you get
Antlerite	$\text{Cu}_3(\text{SO}_4)(\text{OH})_4$	

This shows that a few common minerals make up the constituent parts of a number of secondary minerals, and a change in the mix results in the formation of a different mineral. There is also another factor which sets them apart, and that is the pH level of the environment in which they are created.

The pH control in a mineral vein is usually the result of a balance between free sulphuric acid from oxidizing pyrite and dissolved calcium carbonate.



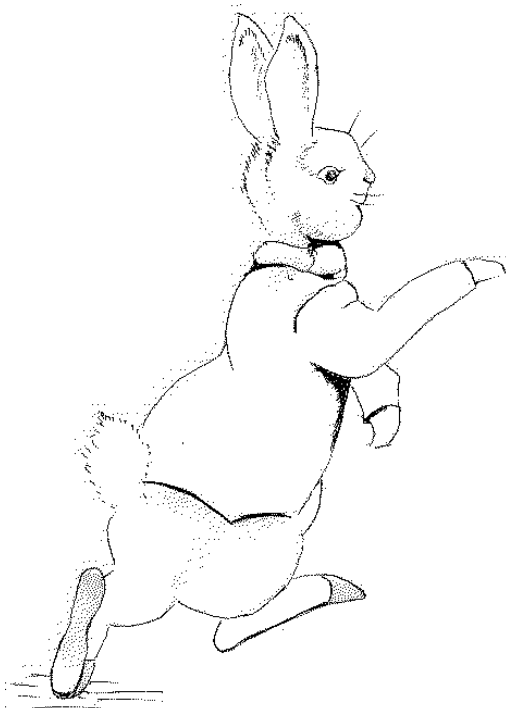
Minerals crystallize at different pH levels. So it is not all plain sailing, minerals are very picky about their environment. At the bottom you find goethite then work upwards to elyite. Sea level, which is mild alkaline from the calcium carbonate dissolved in it. Below pH 6, anglesite may crystallise out, above 6, cerussite forms instead. There is usually enough calcium carbonate in the ore body environment to raise the pH above 6, which is why anglesite is not abundant.

The conveyor belt of secondary copper mineralisation can be the copper sulphate chalcantite, as shown above. This conveyor belt starts from the oxidation of chalcopyrite, as copper sulphate in solution, percolates downwards into the oxidation zone and helps to form the secondary mineralisation of brochantite, langite, azurite and malachite, amongst others.

It also moves on down into the sulphide enrichment zone to help form bornite and chalcocite, with the presence of hydrogen sulphide, or it can be formed directly from chalcantite by reacting with sphalerite.

Then, if the chalcocite is subsequently exposed to oxidation, pure native copper and cuprite can form. In this process the chalcantite is once more released into the new oxide zone to carry on its good work all over again.

I therefore make the Peter Rabbit Mineral Award to chalcantite. It is constantly popping up and being re-produced. If anything should be labeled a supergene mineral, my money is on chalcantite. The one with the real supergenes.



MINUTES OF THE AGM - A CORRECTION

Paul Monk has pointed out an error which crept into the published version of the minutes and which was not in Shirley's original. Paul writes:

Roy's Chairman's report on page 3 has an inconsistency.

"The 1st edition listed the following 33 people, of whom 20 (printed in bold) are still members today."

Only 11 people are highlighted in bold and I am one who is not! I hope I am still a member!!!!

Could you check this paragraph and maybe put a correction in the next Newsletter?

With sincere apologies to the nine members who were not highlighted in the minutes which appeared in issue 57, Roy's list should read as follows:

Mike Bayley
Graham Bell
Richard Belson
Peter Braithwaite
Trevor Bridges
Michael Burt
Mike Gough
John Hall
Roger Harker
Audrey Hatt
Colin Horstman

Neil Hubbard
Alun Jones
Mike Leppington
David Middleton
Jim Miller
Paul Monk
John Nowak
Eric Otty
Pam Pearce
Peter Reynolds
Alan Pringle

Mike Rothwell
John Sheppard
John Slater
Mike Smith
Keith Snell
Roy Starkey
Martin Stolworthy
Ron Weaver
Bob Weatherall
Franz Werner
Trevor Wolloxall

BRANCH NEWS

SOUTH-EAST BRANCH

Austin Lockwood reports some uncertainty over the Branch venue following problems gaining access at the agreed time. Perhaps you could try appealing to a *Higher* authority, Austin. (*The attendees at the prayer meeting preceding the Branch meeting are sometimes late finishing.*)

The latest newsletter reports interesting Cornish minerals being shown at the November meeting and includes an appeal to members of this the largest Branch to begin preparing for the *Micromount* competition in good time for the Symposium. (*Other members might also wish to take heed of this appeal - Ed.*)

Meetings for the rest of 2001 will be held on 13 May, 12 August and 18 November.

(Other branch secretaries are reminded that the editor welcomes news from around the regions.)

CHEMICAL SLEUTH

Max Wirth

Looking through some old specimens, I came across one labeled 'Pyromorphite?'. Actually a foreign piece bought from Sam Weller, source Tsumeb. There were fairly large cerussite crystals and a lot of green aggregates (pyromorphite can be green!) as well as tiny calcite rhombohedra. I tried optical properties on the green material, but the crystals were too small and confused. The only answer was to try a few simple chemical tests. I managed to tease out some of the green, get rid of some colourless grains with a needle and divide the remainder into two piles. To one pile I added a drop of hydrochloric acid, to the other a drop of nitric acid.

Hydrochloric acid coated the grains in white lead chloride and removed the green colour. The green solution eventually dried leaving sprays of blue needles which had to be copper chloride, as well as a faint solid crust.

Nitric acid dissolved the specimen quite slowly, transforming it into beautiful 'diamonds' of lead nitrate and also leaving a solid crust, tinted a faint blue owing to the copper nitrate (hygroscopic).

Well there was lead and copper, therefore it was NOT pyromorphite. Scanning my database for lead/copper/something, it had to be a phosphate (tsumebite) or an arsenate (bayldonite or duftite). I prepared some solid silver nitrate by dissolving a grain of silver filing in a drop of nitric acid and letting it evaporate. Then I added a drop of water to the dried out nitric acid solution of the specimen (all this to ensure neutrality). When a slither of the solid silver nitrate was pushed into this neutral solution, little deep red grains of silver arsenate formed. If it had been a phosphate (tsumebite), the grains would have been yellow.

Now, looking at the original specimen again, I noted that the green colour was much paler and yellower than any bayldonite I had seen. This makes sense since duftite contains three times less copper than bayldonite. I have now renamed my specimen 'duftite'.

I hope that this account may encourage more members to do a bit of chemical detective work.

MIAROLITIC MINERALS FROM LOCH AINORT, CENTRAL SKYE

Steve Rust

These notes bring to light microminerals which can be collected from granite outcrops mostly along the south of Loch Ainort.

The Loch Ainort and Glas Bheinn Mhor granites are two of fifteen or so small acid intrusions on Skye. The granites form a U-shape around the Loch. Similar to some other intrusions, they are particularly rich in miarolitic cavities, mostly to around 5mm. Toward the top of the granites cavities to 6cm have been found.

Collecting has produced over 25 euhedral species. These have been collected from fresh blocks of granite from nearby road-cuts and from various outcrops from west to east.

1. Loch Ainort granite - zircon/clinochlore rich from Bruach nam Bò around the Moll road junction.
2. Loch Ainort and Glas Bheinn Mhor granite contact - rich in hedenbergite around the Moll road junction.
3. Glas Bheinn Mhor granite - moderately rich in zeolites east of the Moll road junction.
4. Undefined intrusion with "large" black crystals of hedenbergite on Sròn Ard a Mhullaich.

Minerals

Adularia	Very small colourless to pale beige prismatic crystals to 0.3mm. Adularia is quite a late stage mineral forming on calcite. SEM
Allanite	Unconfirmed but may be the small flat tabular brown crystals sometimes found to 0.5mm.
Anatase	Extremely rare as sparse typically black elongated bipyramids to 0.3mm on, or partly enclosed by, biotite.
Apatite	Tentatively identified on one specimen as a single whitish hexagonal prism. In material collected from Sròn Ard a Mhullaich.
Apophyllite	Found in a few specimens as colourless single crystals to 0.75mm and showing a long prism with complex steep pyramidal faces.
Biotite	Forms very dark green to black rounded crystal blocks to 5mm long.
Calcite	Common in some specimens as white thin platy hexagonal crystals to 1cm. Rare in prismatic forms to 1mm long.
Chabazite	Only found so far in Glas Bheinn Mhor granite as colourless to more common orange pseudo-cubic crystals to 2mm plus.
Clinochlore	Common as brown to green druzey coatings on minerals that have formed before calcite.
Epidote	Yellow green single crystals and sub-parallel groups on feldspar and quartz. Also found encrusting hedenbergite and coated by prehnite.
Hedenbergite	Common in some specimens as green to rare brown prismatic crystals to 2mm. Crystals to 10mm have been found on Sròn Ard a Mhullaich.
Feldspar group minerals	As a common crystalline lining to all cavities.
Fluorite	Not uncommon as octahedral colourless to pale purple crystals to 1.5mm. Rarely found as prismatic crystals to 2mm long, also with curls and twists.
Gadolinite-Y	Extremely rare as thickened bladed greyish-green crystals to 1.5mm long, as single crystals and sub-parallel groups. SEM & XRD
Hornblende	As dark brown and black prismatic crystals to 2mm long. SEM & XRD
Heulandite	Rare as colourless coffin shaped crystals to 3mm.
Ilmenite	Tentatively identified as bright metallic like crystals to 0.3mm with rounded form.

Kainosite-Y	The first occurrence in the United Kingdom, having been found in two forms which are both very rare. The first is from Loch Ainort as white tabular rhombic to pseudo-hexagonal crystals to 0.75mm. The second and much less common habit is as colourless thickened bladed crystals to 1.5mm long. SEM & XRD
Laumontite	Very rarely found as typical prismatic crystals to 1mm long.
Magnetite	Rare as octahedral crystals to 0.6mm.
Prehnite	So far only found in the Glas Bheinn Mhor granite as small platy crystals to 0.15mm, rarely as greyish radial groups to 3mm.
Pyrite	Rare as striated cubic crystals to 1mm.
Pyrrhotite	Maybe as single "hexagonal" crystal 0.2mm.
Quartz	Common as colourless crystals to 2cm but mostly to 2mm. Rare as pale smokey crystals.
Stilbite (and Stilbite-K)	At least some of the stilbite has shown little or no detectable Na or Ca but with major K, Si and Al. XRD shows it has a stilbite pattern. The form for both is as colourless bladed to prismatic crystals to 4mm. SEM & XRD
Sphalerite	Extremely rare as light brown Fe oxide coated crystals to 2mm showing concentric stepped growth on the faces. XRD
Sulphur	Rarely found associated with sphalerite as minute rounded crystals to 0.2mm.
Titanite	As light buff to tinted pink prismatic to broad blade crystals to 1.5mm. XRD
Zircon	Common as gemmy pale yellow to orange pyramidal and prismatic crystals to 2.5mm. SEM
Unknown minerals	
A	Yellow druzy lath-like crystals with Ca, Al, Si. SEM
B	Dark brown tiny prismatic crystals which might be fergusonite.

(Note: The place name spellings are as they appear on OS Landranger sheet 32 edition 4 - Ed.)

AN HISTORICAL NOTE

To mark the publication of the new edition of the British Directory of Micromounters, an article written by Paul Monk and published in the May/June 1981 issue of GEMS, the British Lapidary & Mineral Magazine, is reproduced here in full. It gives an interesting insight into the early days of the Directory and an opportunity to compare it with the present edition some twenty years on.

Members are reminded that GEMS is no longer published and that this is an historical note - please do not write to Roy at the address given, the house number is the only thing which has remained unchanged! Paul's request in the final paragraph is probably no longer relevant!!

(This is one of a series of articles which Paul contributed to GEMS during 1980 and 1981 covering all aspects of micromounting. While much of Paul's work is covered by BMS Occasional Papers, Paul has given me copies and his permission to reproduce them as I see fit. This one is both relevant and timely. Thank you, Paul. Ed.)

MICROMOUNTING

by Paul K. Monk

THE BRITISH MICROMOUNTERS DIRECTORY

I have put off the article on gem-stones, gold and silver until next time. This is because something important has happened in the field of micromounting in Britain.

At the end of March 1981, at the Holiday Inn Hotel in Leicester, the British Mineral and Gem Show was held. Two individuals showed initiatives that will surely give the hobby of micromounting a boost Roger Harker (Lythe Minerals) had micromount boxes and specimens for sale and Roy Starkey was collecting names for a Directory of British Micromounters.

Roger Harker has 1" x 1" x 1" black based hinged boxes for sale. He also said that he would soon have available some boxes of 1" x 1" x ¾". These boxes have a shallower clear lid and in many ways are better for smaller specimens. Roger also had for sale dendritic gold specimens from Breckenridge Mine, Colorado, U.S.A. These were of micromount size and he supplied them with a micromount box. The gold was protected by the gelatine capsules that micromounters so often use to transport fragile specimens. He also had other specimens that would make fine micromounts.

Upstairs, away from the hustle of the dealers' stands, Roy Starkey was collecting names of people who were interested in micromounting. He was near to several members of the Russell Society who had stereoscopic microscopes and specimens available for people to view; indeed several people showed an interest who had no experience of micromounting. Roy had a photographic display showing how a micromount is made. His methods are similar to those described earlier in this series.

Roy had read a copy of the Baltimore Mineral Society's International Directory of Micromounters and was disappointed to see that only fifteen names from Britain were listed (several of whom do not now micromount) compared with over 200 for W. Germany. He felt that there must be more people interested in micromounting in Britain so he set out to compile a British Directory.

He believes that a directory would help British micromounters to contact each other, since it is so easy for people to be isolated. It should help to record and, to some extent, analyse the interest for micromounting across the country. This may be the initial impetus for a contact between micromounters that may develop into a micromounters newsletter and gatherings of micromounters for exchange and field collecting.

To quote Roy:

"Most of all the Directory will enable and encourage contact between like-minded individuals, hopefully providing a forum for the development of our hobby, particularly as larger specimens become more scarce, and the attractions of good micro material become more widely appreciated."

Roy is still compiling the Directory and realises that not everybody could get to the Leicester show. He still wants interested people to contact him, if you are a collector, intending to be a collector, can supply boxes, microscopes or specimens. The details are as follows:

- (1) Initial fee of £0.50 to cover initial production and distribution costs.
- (2) Enclose an S.A.E. for the return of the registration form.
- (3) The address is:

R. E. Starkey,
15 Whitehall Drive,
Dudley,
West Midlands, DY1 2RD.
Telephone: 0384 59983.

It is hoped that the Directory will be published late June 1981, and will be accompanied by a Newsletter/Discussion document.

I hope that this venture is a success, since this is the sort of initiative that has been needed to get things moving.

In a similar vein, if any reader of this micromounting series in Gems has any comments and/or suggestions to make about micromounting or the articles please address them to me c/o the Editor, and I will try to include any points in subsequent articles.

As a postscript to the British Directory, I have just found out that a group of Australian micromounters have produced an Australian Directory of Micromounters. I am at this moment trying to obtain a copy and when I do I will be writing more about it. Are there any other such directories in the world?

NEWSLETTER EDITOR

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Articles for future newsletters are now urgently needed. The last issue had some 20 pages but a substantial part of this was devoted to the minutes of the AGM. While quality is more important than quantity, this issue is thinner than I would wish. Please give some thought to articles which will be of general interest to members.

The deadline for articles for Newsletter 59 will be 1st June 2001. Please let me have contributions as soon as possible. Articles or reports on PC disc are particularly welcome. Articles sent by E-mail can either be "attached" or part of the body of the E-mail message. Clearly printed documents are acceptable and can be scanned and read into the PC.