Commission of the European Communities

environment and quality of life

Selected papers arising from the EEC primary raw materials programme (1978-81)

Report
EUR 8617 EN-FR

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Directorate-General
Science, Research and Development

1984

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Published by the
COMMISSION OF THE EUROPEAN COMMUNITIES

Directorate-General
Information Market and Innovation

Bâtiment Jean Monnet
LUXEMBOURG

Cataloguing data can be found at the end of this publication

Luxembourg, Office for Official Publications of the European Communities, 1984

ISBN 92-825-4086-3
Catalogue number: CD-NO-83-037-2A-C

reprinted from *Mineralium Deposita*

Mineral.Deposita 18, 301 (1983)

MINERALIUM
DEPOSITA

Foreword

This special issue of *Mineralium Deposita* is devoted to certain aspects of the 1978-1981 Research and Development programme of the European Communities in the field of "Primary Raw Materials". A major aim of this programme was to increase the E.C. potential for self-supply of a number of mineral raw materials, principally non-ferrous metals. The main research areas were: (1) Exploration, with emphasis both on economic geology and on the improvement of geochemical, geophysical and remote sensing techniques; (2) ore processing, and (3) mining technology.

In keeping with the orientation of this journal, the papers presented here concern the geology and geochemistry of ore-bearing formations, problems of ore genesis and potential applications to prospecting. Although they do not cover the entire range of research activities that have been sponsored by the E.C. in these particular fields, they do highlight a number of topics of great interest to economic geologists:

- Investigations on fluid inclusions in granites and other rocks
- Stable isotope studies
- Geochemical proximity indicators for massive sulphide deposits
- Trace element patterns in black shales and carbonates
- The origin of base-metal vein-type deposits in carbonates
- A statistical multivariable approach to regional prospecting
- Diagenesis in red beds and its bearing on mineralizing processes

More papers on these and other themes may follow in subsequent regular issues of the journal.

On behalf of the Commission, I wish to thank the president of the Society for Geology Applied to Mineral Deposits as well as the editors of *Mineralium Deposita* for their invaluable assistance in preparing this special issue. May I also express the hope that this is but a first step, a first experiment which will be continued and perhaps amplified upon the completion of the new Raw Materials programme sponsored by the E.C. for the period 1982-1985.

J. Boissonnas
Commission of the European Communities
Directorate General for Science, Research
and Development

Mineral.Deposita 18, 303-313 (1983)

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Thallium, Nickel, Cobalt and Other Trace Elements in Iron Sulfides from Belgian Lead-Zinc Vein Deposits

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Fe-sulfides associated with Belgian Pb-Zn vein deposits have been analysed by DC arc spectrometry and XRF for Tl, Ni, Co, Mn, Zn, Pb, Ge, Cd, and As. They show high Tl contents (from > 30 ppm upt to 6800 ppm) and Co:Ni ratios < 1. These features permit to distinguish them from Fe-sulfides of sedimentary and high temperature occurrences. The Tl distribution in a botryoidal marcasite of Vedrin (average Tl content of 0.68%) has been investigated by ion microprobe. It displays a pattern similar to colloform texture. Principal component analysis shows that the behaviour of Tl is partly controlled by a factor opposing Tl to all other elements. This is interpreted as reflecting the influence of sorption mechanisms by contrast with direct precipitation. Tl and the other elements are not considered of magmatic origin because no acidic magmatism is known during or after Variscan times. Extraction from sedimentary rocks by hydrothermal brines is favoured.

INTRODUCTION

A systematic study of the trace element geochemistry of pyrite and marcasite has been undertaken in order to characterized iron sulfides associated with Pb-Zn vein deposits, and to examine whether trace elements could help to understand the conditions of formation of the ore, and thus facilitate the detection of hidden deposits. A preliminary study by Duchesne (1964) showed the presence of relatively large amounts of thallium in marcasite from the Vedrin ore deposit (Belgium) and pointed to the similarities with Pb-Zn deposits from the Cevennes border in France. The purely syngenetic origin of these latter deposits proposed by Bernard (1961) was questioned on this basis (Duchesne, 1964), and discussed (Bernard, 1965; Duchesne, 1965). The present study corroborates these first results with the help of more powerful analytical techniques and statistical methods of interpretation.

ANALYTICAL METHODS

As a general rule, the specimens were carefully investigated under the reflected light microscope to select the homogeneous Fe-sulfide parts of the ore. The purity of the sampled parts was checked under the binocular after reduction to small fragments. When necessary hand-picking of impurities was further done and remains of calcite removed by a brief HCl 2N attack. Though greatest care was exercised in the operation, the method - like any other separation method - cannot however warrant the absolute purity of the analysed aliquots of the samples. This fact was taken into consideration in the interpretation of data by means of statistical methods (see below). The use of Clerici's solution (Tl formate and malonate) as a density liquid has been prohibited to avoid contamination by Tl. The final grinding to about -150 mesh was done in agate mortars.

Three different analytical methods are used:

1. DC arc spectrography
2. X-ray fluorescence spectrometry
3. Ion microprobe analysis (SIMS)

1. DC arc spectrography is used to determine Co, Ni, Mn, Cd, Ge, Sb, Bi, Sn, Cr as well as low contents of Tl, Pb and As. The method is inspired from Hegemann and Leybold (1954). The powdered sample is mixed with 2 parts of "specpure" graphite, and loaded in the conical cavity of a graphite electrode (SCHRIBNER type - National Carbide L4024). A 3 mm diam-rod (Le Carbone-Lorraine type 207) is used as an upper electrode. A drop of Elvacite 2044 diluted in toluene is placed on the loaded electrode and dried in order to form a cake. This procedure prevents loss of material during the first seconds of arcing and regularizes burning. An optimum reproductibility (± 5%) can thus be obtained.

A stabilized DC arc of 6.5 A and 220 V from a PHILIPS Multisource is used to burn the sample (anode) during 30 sec. All analyses are duplicated. The spectrograph is a FUESS 110 H (4 prisms) equivalent to the HILGER large spectrograph. The densitometer is mod C 1285 from FUESS. The spectra are recorded on KODAK plates (type) SA 1 in the range of 2760 Å to 3480 Å. The analytical lines (Å) are the following: Co 3044; Ni 3051; Mn 2933; Zn 3822; Cd 3261; Cu 3274; Ge 3039; Sb 3878; Bi 3068; Sn 2840; Cr 3015; Tl 2768; As 2780; Fe 3053 is used as an internal standard. Four international standard samples of pyrite: PS-1 (Schrön et al., 1975), P-1 and P-2 (Robinson and Walshe, 1977) and ASK-3 (Christie, 1975) are used for calibration of Co, Ni, Mn, Zn, Cu. The four standards provide excellent working curves for Co, Ni, Mn and Zn, and a good one for Cu. Only one standard out of the four available can be used for Cd, Ag, Sb, Bi, Sn and Cr. Therefore, 45° slope working curves, passing through the standard values, in log-log coordinates, are used for these elements (Ahrens and Taylor, 1961). For Ge synthetic standards obtained by mixing Ge to a Fe_2O_3 matrix are used. Tl, Pb and As are calibrated with values measured by X-ray fluorescence. The detection limits are: 0.2 ppm Ag; 1 ppm Pb, Mn, Cu, Ge; 5 ppm Co, Ni, Sb, Bi, Sn, Cr; 10 ppm Tl; 15 ppm As, Cd.

2. X-ray fluorescence analysis is used for the determination of relatively high contents of Tl, Pb and As. A CGR alpha 2020 semi-automatic spectrometer working with a Mo-tube at 50 kV and 50 mA and a LiF100 analysing crystal is used. Analytical lines are Tl $L\beta_1$, As $K\beta_1$ and Pb $L\beta_1$. Standard samples ASK-3 and PS-1 are used to calibrate the method for Pb and As. Synthetic samples made by mixing various amounts of Tl_2O_3 to a pyritic matrix are used for Tl. It must be noted that the Tl content of 100 ppm, given by Schrön et al. (1975) for PS-1, is highly overestimated. No Tl is detected by DC arc spectrography, which means that the Tl content is lower than 10 ppm. Inspection of the most sensitive line at 5350 Å with ICP spectrography also reveals no Tl. The limits of detection (LD), following Currie (1968), are 30 ppm Tl and Pb and 45 ppm As.

3. Secondary ion mass spectrometry (SIMS) in the ion microscope mode is used to study the distribution pattern of Tl through polished sections of about 1 cm in diameter, with a spatial resolution of 1-10 µm. Quantitative analyses with a spatial resolution of 250 µm is possible for e.g. Mn, Co, Ni, Cu and Tl. The instrument used is a Cameca IMS-300 ion microscope, and a 6 KeV Ar^+ primary beam is used with a current density of 12 A/mm^2. For quantitative analyses an electrostatic sector is used to select 140-160 eV ions for Mn, Co, Ni and Cu, and 60-80 eV ions for Tl. The analysed surface is 250 µm in diameter.

For calibration of Mn, Co and Cu the four already mentioned reference samples are used in the form of pellets, as described by Dillen and Gijbels (1981). No certified standards being available for quantitative Tl analyses, a sample from Vedrin, which has been examined by SIMS and found virtually homogeneous at the 250 µm-scale (standard deviation for 14 different measuring sites of 250 µm diameter each: 11%), is used as a reference sample after determination of its Tl content by ICP-AES, in nitric acid solution, using the 5350 Å Tl-line. The instrument is calibrated by Tl-solutions containing the same amount of iron and acids. A concentration of 6800 ppm is found by that method for the Vedrin sample. A massive part of the specimen is used to determine a sensitivity factor for SIMS, with ^{32}S as an internal standard.

SAMPLING

84 samples belonging to 36 occurrences of marcasite or pyrite have been anal-

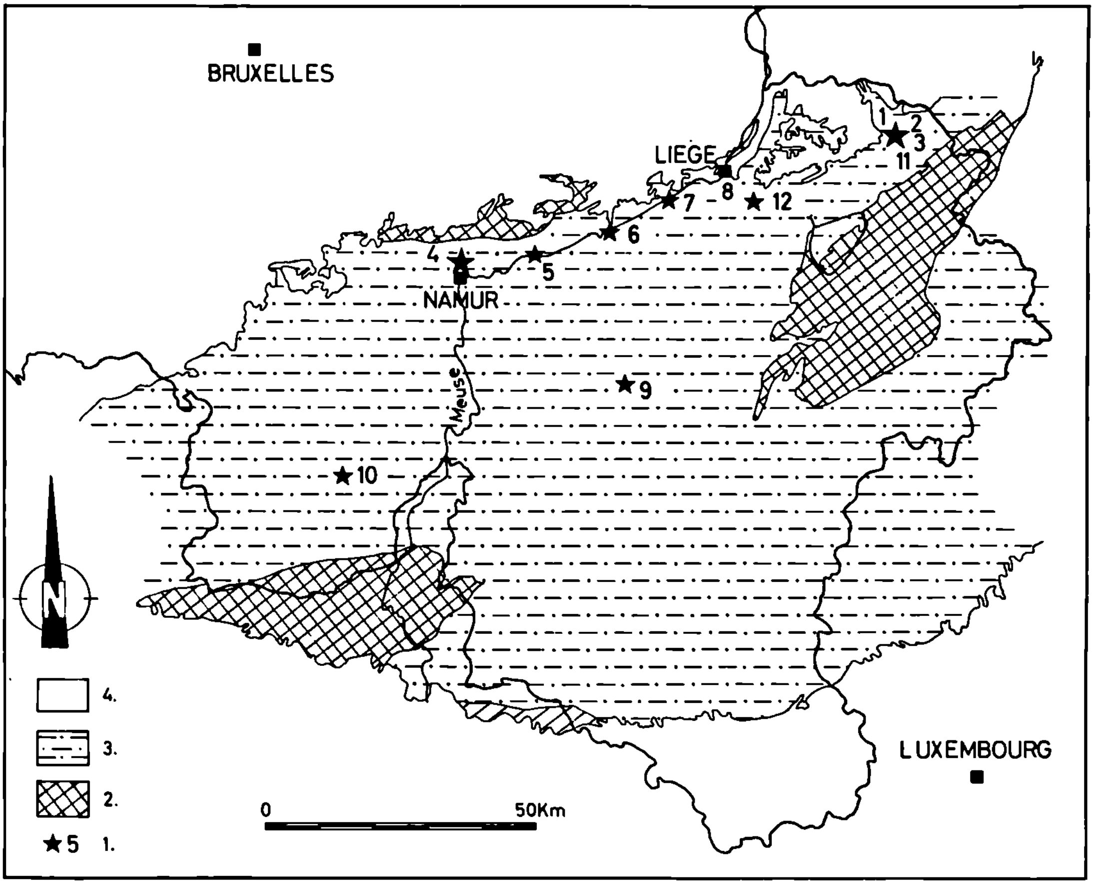

Fig. 1. Geological sketch map of South Belgium showing the provenance of the various iron sulfide samples from Pb-Zn vein deposits. 4. Post-Variscan terrains; 3. Devonian and Carboniferous terrains; 2. Cambrian and Silurian terrains; 1. Numbered stars refer to the investigated occurrences: 1, 2, 3 and 11: Poppelsberg, Stuck, Lontzen and Moresnet, respectively; 4: Vedrin; 5: Hayes-Monet; 6: Corphalie; 7: Engis; 8: Angleur; 9: Heure; 10: Villers-en-Fagnes; 12: Chaudfontaine

ysed. The main occurrences come from East Belgium (Fig. 1): Poppelsberg (11 samples) and Stuck (2 samples) are small post-Variscan Pb-Zn vein deposits cutting across Dinantian carbonate rocks and Famennian rocks of the Vesdre Massif. They were recently drilled by the Union Minière Company. Lontzen (15 samples) also belongs to the same type of mineralization and comes from the same area, but is entirely situated in siltic to pelitic rocks of Famennian age.

Another well documented site - the Vedrin Mine, near Namur - has also been investigated. It is a vein deposit in Dinantian carbonate rocks of the Namur synclinorium (Evrard, 1943). Two types of sulfides are studied. The first and most common one is the vein type (12 samples): a fibro-radiated marcasite associated with some blende and galena in a calcite gangue. The second type (5 samples) is a marcasite, filling small veins and veinlets of a brecciated dolostone, at a distance of 10-20 m from the main vein.

Other Belgian Pb-Zn occurrences have also been included: Hayes-Monet, Corphalie, Engis and Angleur (2 samples) from the Namur synclinorium; Heure and Villers-en-Fagnes in Devonian strata from the Dinant synclinorium; Moresnet and Chaudfontaine in the Vesdre Massif, the latter is a cubic pyrite associated with a baryte stratiform deposit (Dejonghe, 1979) in Devonian strata.

Two occurrences from the Cévennes border - Soulier and St Félix de Pallière - previously studied by Duchesne (1964) have also been reinvestigated.

Moreover, 12 occurrences from sedimentary rocks, mainly pyrite cubes from shales, have been included for the sake of comparison (Rochelinval, Bayehon, Deville, Grand-Halleux, Longfaye, Huccorgne, Ronquière, Grufflingen, Bouxharmont, Visé, Gris-Nez - France, Ballachullish - Scotland) as well as pyrites formed at high temperature (Agrokipia-Cyprus, Calamita and Rio Marine - I. Elba, Pamour-Canada, Luzenac-France and Buranga-Ruanda).

The results of the analysis are summarized in Table 1 which gives the average and the range of variation of each trace element in each occurrence.

DISCUSSION

The results usually show a wide dispersion in the various Pb-Zn occurrence They can however be summarized as follows:

1. The Co content is low - usually clos to or below 5 ppm - in the Belgian Pb-Zn type and contrasts with the sedimentary and high temperatures occurrences, which show averages of 332 ppm and 2180 ppm respectively. The Ni content of the Pb-Zn type is higher than the Co and can be compared to the sedimentary or high temperature sulfides. Therefore, the Co:Ni ratio is <1 in the Pb-Zn type. According to classical interpretations (see e.g. the reviews by Loftus-Hills and Solomon, 1967 and Bralia et al., 1979) this would indicate a sedimentary origin. However, the various authors usually consider that this criterion is poorly significant when used alone. The present data on sedimentary occurrences also confirm that the Co/Ni ratio has to be used with caution. Indeed, 5 out of 12 sedimentary occurrences which are studied here show Co:Ni >1, an inverse relation to what should be expected since they all concern typical cubic pyrites in black shales or slates. It is likely that recrystallization due to incipient metamorphism can lead to an enrichment of C with respect to Ni, in such a way that an original Co:Ni <1 might be modified to a Co:Ni >1.

It can be concluded that, in Pb-Zn deposits, the Co:Ni ratio in iron sulfides has no genetic significance since the observed relation (<1) is not in agreement with the geological evidence. It must however be noted that the low Co content of the Pb-Zn occurrences appears to be a feature restricted to this type of deposits and is likely to have a promising genetic meaning.

2. Thallium is always present (from >30 ppm up to 6800 ppm) in the Belgian Pb-Zn type, whatever the geological uni to which they belong (Dinant or Namur synclinoria, Vesdre Massif) or the age of the enclosing rocks (Dinantian or Devonian). It is also present in the Cevennes border (Duchesne, 1964) where Aubagne and Leleu (1981) have recently

Table 1. Trace element contents (ppm) of iron sulfides

		POPPELSBERG	STUCK	LONTZEN	VENDRIN		OTHER BELGIAN OCCURRENCES	CEVENNES OCCURRENCES	SEDIMENTARY OCCURRENCES	HIGH TEMP OCCURRENCES
					MAIN VEIN	BRECCIA				
Number of samples		11	2	15	12	5	9	3	12	7
Tl	$\bar{x}$	235	90	83	517	78	229	806	<10	<10
	range	30-1600	30-150	30-190	73-6800	54-88	55-650	460-1080		
Co	$\bar{x}$	? (7)(1)	? (1)	36	<5	<5	? (6)	<5	332	2180
	range	<5-90	<5-48	8-98			<5-220		<5-1470	47-6600
Ni	$\bar{x}$	370	300	448	17	10	200	5	374	145
	range	45-1650	10-600	42-1010	<5-42	5-17	<5-620	<5-6	8-2050	8-440
Co/Ni	$\bar{x}$	<0.04-0.14	<0.1-0.5	0.05-0.15	<0.1-0.5	<0.3-<1		<1	0.08-14	2.4-30
Pb	$\bar{x}$	3760	3680	2590	4050	4160	4170	1555	123	? (4)
	range	15-7500	3500-3850	1100-4750	15-12600	2720-7050	25-12000	325-3700	18-485	<1-10
Zn	$\bar{x}$	460	?	1123	445	29	925	293	108	79
	range	40-2250	400-15000	40-9000	20-2200	20-42	30-5400(2)	95-650	20-610	10-420
Mn	$\bar{x}$	23	7	22	245	2	73	113	310	35
	range	1-125	3-11	3-290	1-1000	<1-3	1-620	15-310	<1-3400	<1-125
Cu	$\bar{x}$	163	150	397	6	3	18	34	146	470
	range	4-360	3-310	115-1010	1-25	2-4	1-65	10-65	10-790	3-2200
Ag	$\bar{x}$	15	55	44	7	3	4	45	16	5
	range	2-50	4-105	18-105	2-34	2-4	1-7	18-85	1-140	1-16
Cd	$\bar{x}$	? (8)	? (1)	? (8)	? (7)	21	? (4)	<15	<15	<15
	range	<15-30	<15-1900	<15-95	<15-55	15-25	<15-185			
Ge	$\bar{x}$	23	? (1)	? (7)	19	5	30	<1	<1	<1
	range	<1-65	<1-470	<1-95	<1-80	0	<1-95			
As	$\bar{x}$	383	2500	472	? (11)	<15	100	2720	283	273
	range	<10-2450	500-4500	50-1010	<10-40		<10-310	1300-5000	20-625	<10-850
Sb	$\bar{x}$	19		54	<5	<5	? (7)	310	27	? (6)
	range	<5-65	10-100	15-150			<5-25	20-660	<5-180	<5-10
Bi	$\bar{x}$	<5	<5	<5	<5	<5	<5	<5	? (8)	
	range								<5-35	(50)
Cr	range	<5	<5	<5	<5	<5	<5	<5	<5-250	(350)

(1) average not significant: the figure into brackets gives the number of values below the detection limit
(2) with two additional values > 50000 ppm
Detailed data can be obtained from the authors

mentioned Tl-rich (0,5 to 1%) melnikovites and marcasites in Pallière.

On the other hand, Tl is absent (< 10 ppm) from all sedimentary and high temperature occurrences. According to Ivanov et al. (1960), Tl is commonly found in numerous varieties of polymetallic deposits. It is usually more enriched in sphalerite or galena than in iron sulfides, e.g. from some Caucasus deposits. Shaw (1952) and Albuquerque and Shaw (1972) also report high Tl content in marcasite from several localities (Japan, Caucasus, Central Asia, etc...). In Western Europe, since Stoiber (1940), Tl is mentioned in Pb-Zn deposits of Belgium, Westphalia, and Silesia. Except for the data of Thein (1975) on the Meggen deposit (see below), no modern analyses have been made available on sulfides and this hampers the study of the chalcophile behaviour of Tl.

In the Belgian Pb-Zn occurrences the maximum Tl content in iron sulfides is found in a radiated botryoidal marcasite from the Vedrin mine (0,68%). The distribution of Tl, as revealed under the ion microprobe, is shown on Plate 1. Tl is not incorporated as independent phases larger than 1 µm (the resolution power of the ion microprobe) and can thus be considered regularly distributed troughout the marcasite phase. At a larger scale thin alternating bands (from 1 to 50 µm) of contrasting Tl contents are disposed perpendicular to the radiating directions of the texture. The overall picture is quite similar to the so-called colloform texture and can be put together with the fact that Tl is notably enriched in colloform varieties of iron sulfides (Ivanov et al., 1960). In a second specimen from Vedrin an inclusion of a Tl and Pb bearing mineral-possibly hutchinsonite $(Pb, Tl)_2(Cu, Ag)As_5S_{10}$ - was also found, thus indicating that trace minerals can also control the distribution of Tl.

3. Some variations can be observed between the different Belgian deposits or even within the same deposit. The Vedrin marcasites are low in Co, Ni, As, Sb, Cu, Ag compared to the East Belgium occurrences. The Tl, Zn, Mn, Cu and Ag contents in the Vedrin marcasite from the brecciated dolostone are lower than in the main vein occurrences; they also display less dispersed values. In Lontzen, almost all trace elements are enriched relative to the Poppelsberg-Stuck type. Since the deposits all belong to the same fault system, it is likely that this difference is due to the siltic to pelitic nature of the Famennian enclosing rocks at Lontzen as compared to the carbonate rocks at Poppelsberg and Stuck.

4. In addition to the variations between the different occurrences, the trace elements display large intervals of variation within the different deposits. In order to investigate these variations in detail, the statistical method of principal component analysis has been applied to the Pb-Zn type. The computing has been performed by the Fortran IV program of Davis (1973) adapted for a Heathkit Z89 microcompute with a memory of 64 K of RAM and two 5.25 inch floppy discs.

Fig. 2 summarizes the results obtained on 40 samples from Pb-Zn deposits, representing the whole population of this type except the samples from the Vedrin mine. Bi and Cr which are absent from the Pb-Zn type were not considered. The reason for discarding the Vedrin samples is that the contents in Co, Cd, As and Sb are currently below the limit of detection of the method. A large number of data below the detection limit can indeed artificially modify the true correlation between the elements.

Four factors can explain 72 % of the variance of the population. They can be interpreted as follows.

Factor 1 opposes Tl to a group of several elements which comprises elements such as Ni, Co, Zn, Cu and Ge which have an ionic radius close to that of Fe and therefore are compatible with their entering in the crystallizing iron sulfide by isomorphism. On the other hand, the opposite sign of the Tl factor loading can indicate a different controlling mechanism, possibly related to the higher value of the ionic radius (Tl^+ = 1.40 Å) (Sahl, 1974). As already mentioned, Tl is enriched in minerals presenting a collo-

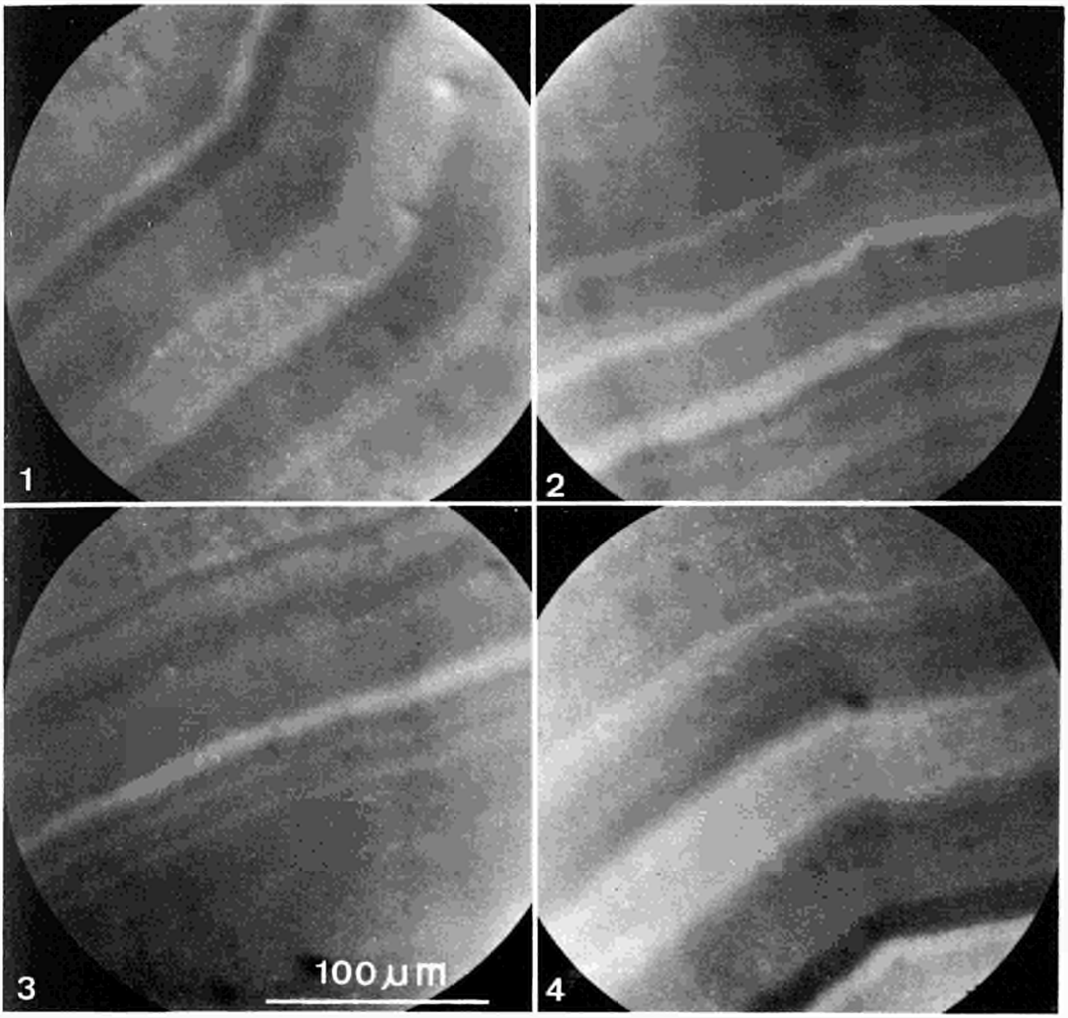

Plate 1. Tl distribution in a botryoidal marcasite from the Vedrin mine (Namur, Belgium) as revealed by secondary ion mass spectrometry (ion microprobe). Thin alternating bands (1 to 50 µm) of contrasting Tl contents – the higher the content, the darker the intensity – are perpendicular to the radiating directions (well displayed in photo 2) of the texture in a pattern similar to colloform texture

form structure, such as Schalenblende or in various "gel"-like or amorphous minerals, such as melnikovite (see Ivanov et al., 1960). Moreover, its size and chemical similarity with large alkali ions is consistent with its extraction from solutions by adsorption processes (Albuquerque and Shaw, 1972).

The similarities between the picture of the Tl distribution which is obtained under the ion microprobe and colloform texture is striking and strongly suggests that adsorption on colloids is the mechanism which controls the behaviour of Tl. This is not in agreement with Roedder's view (1968), in which colloform texture cannot be formed by material in a colloidal state when deposited, but by direct crystallization from a fluid. We however believe that

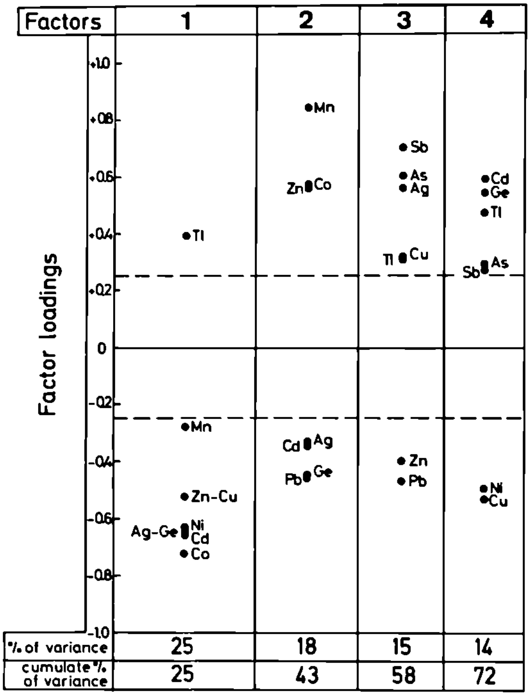

Fig. 2. Graphical representation of the principal component analysis of the trace element contents of iron sulfides from Pb-Zn vein deposits. Factor loadings less than 0.22, below the level of significance following Harman (1967), are not represented

our factor 1 is an indication that two different mechanisms play a role in the deposition of the iron sulfides and that, all things being equal, the Tl content of a sample is a measure of the relative importance of sorption effects in the process of formation of the particular sample.

Factor 3 groups together S-As-Ag and is also loaded with Cu and Tl. We interpret this as due to inclusion of trace minerals of sulfosalts, some of them containing Tl, which is known to have geochemical affinities with Sb and As (Jankovic and Le Bel, 1976).

Factor 2 is positively loaded with Mn and Zn and negatively with Pb-Ag-Cd-Ge. Factor 4 groups Tl with Cd-Ge which are opposed to Ni-Cu, and might indicate the influence of inclusions of blende which can be rich in Tl (Evrard, 1945) and in Ge-Cd.

Factor 2 is difficult to interpret. It probably results from the combination of several mechanisms. Mn might come from inclusions of blende. It is however hard to understand why Mn, which could easily substitute for Fe, is mainly controlled here by its substitution with Zn and also why Cd-Ge, classically diadochic of Zn (see factor 4) appears here with factor loadings of sign different from Zn. The grouping of Pb with Ag is classical in galena and might also indicate inclusions of trace amounts of this mineral.

Though some points are still somewhat obscure, principal component analysis clearly shows that several possible mechanisms can account for the presence of Tl in the population: sorption phenomena and inclusions of sulfosalts and also possibly of blende. This is in agreement with the modes of occurrences of Tl observed under the ion microprobe and in conformity with what is known of its chalcophilic behaviour.

SOURCE OF THALLIUM: AN OPEN QUESTION

Polymetallic deposits which show the highest amount of Tl are related to acidic magmatism either volcanic or plutonic such as in the classical region of Caucasus (Ivanov et al., 1960) or in Turkey (Jankovic and Le Bel, 1976). The enrichment of Tl in the late stages of the magmatic differentiation is well in agreement with its similarity of behaviour with K.

The source of Tl in Pb-Zn deposits in carbonate environment is however a debatable question. In the Meggen deposit (Westphalia), the distribution of Tl in and around the stratiform ore body is considered to be due to the exhalative origin of the elements (Thei 1975; Gwosdz and Krebs, 1977) and can thus be linked to a syn-sedimentary event. In Belgium however, except for some thin K-bentonites of Dinantian age (Thorez and Pirlet, 1979), volcanic rocks are not known interbedded in the Variscan sedimentary pile. In the area, acidic plutonism is restricted to the small granitoids of La Helle and Lammersdorf (Germany) (Corin, 1965). They are situated far away from important deposits, such as the Vedrin Mine, and since they have suffered a deformation of Variscan or Caledonian age, they are certainly older than the post-Variscan tectonic event which controls the emplacement of the veins. The presence of a granitic batholith at depth under the Ardennes has been surmised by Fourmarier (in Dewez and Lespineux, 1947) to account for the distribution of the Belgian ore deposits. But no evidence in favour of such an hypothesis has ever been put forward.

Tl, if not magmatic, must find its source in sedimentary rocks from which it was scavenged by hydrothermal brines. When taking the data of Heinrichs et al. (1980) on sedimentary rocks, it is noted that the Tl content (average: 0.41 ppm; black shales: 2.5 ppm) is high relative to the Pb content (average: 16.7 ppm, black shales: 82 ppm). The Tl/Pb ratio varies between 1/50 and 1/30, values which are higher than those commonly found in sulfides from Pb-Zn deposits. Therefore it is not unlikely that any process which would extract and concentrate Pb would also be active for Tl.

CONCLUSIONS

Distribution of trace elements in various occurrences of iron sulfides indicates:

1. The iron sulfides related to Belgian Pb-Zn vein deposits, mainly in carbonate environment, belonging to different geological units (Namur Synclinorium, Dinant Synclinorium, Vesdre Massif) or situated in Devonian or Dinantian strata, form a group along with two occurrences from the Cévennes border; this group can be distinguished from iron sulfides of various origins by their Ni, Co and Tl contents. Their Co:Ni ratio (< 1) can be compared with sedimentary occurrences but is distinctly lower than in high temperature occurrences (Co:Ni > 1). Their Tl content (> 30 ppm up to 0,6%) permits to distinguish them from all other occurrences (Tl < 10 ppm). The Co content is lower than in sedimentary occurrences.

2. The mode of occurrence of Tl in iron sulfides is either in the form of trace minerals or is dispersed in the iron sulfide phase according to a zoned and recurrent pattern, similar to a colloform texture. Several lines of evidence indicate that sorption phenomena and inclusions of sulfo-salts can account for most of the behaviour of this element in the deposition of the iron sulfides.

3. The paucity of acidic magmatism in Belgium during Devonian and Carboniferous sedimentation or in post-Variscan times makes the hypothesis of a magmatic source for the Tl difficult to accept. The hypothesis that Tl together with other elements was scavenged from sedimentary rocks by hydrothermal solutions is favoured.

Acknowledgements. The present investigation is part of a research program supported by the EEC (111-79-7-MPPB) and the Belgian SIPS (MP-CE-5) (Project Leaders: P. Evrard and J. Belliere). The authors wish to express their gratitude to the Union Minière, for giving access to drilled samples of Poppelsberg, Stuck and Lontzen; to L. Dejonghe, A.M. Fransolet and F. Dimanche for donating various samples; and to R. Gijbels for the use of the SIMS instrument and for interesting discussions.

REFERENCES

Ahrens, L.H., Taylor, S.R.: Spectrochemical analysis (2nd Ed) Addison-Wesley, 454 p (1961)

Albuquerque de, C.A.R., Shaw, D.M.: Thallium. In: "Handbook of Geochemistry". Wedepohl, K.H. (ed) Springer, Berlin. Vol. II-5 section 81, 1972

Aubagne, M., Leleu, M.: Recherche de guides de prospection pour les gites Pb-Zn liés aux strates en environnement carbonaté. Deuxième phase: Le gite de la Croix de Pallières (Bordure Cevenole, Gard), B.R.G.M.Compte rendu de fin d'étude, 1981

Bernard, A.: Contribution à l'étude de la province métallifère sous-Cévenole. Sci. Terre, 7, 3-4, 123-403 (1961)

Bernard, A.: Comments on "Présence de thallium dans les sulfures de fer de la mine de Pallière (Gard, France)" by J.C. Duchesne. Ann. Soc. Geol. Belgique 88, 151-152 (1965)

Bralia, A., Sabatini, G., Troja, F.: A reevaluation of the Co/Ni ratio in pyrite as geochemical tool in ore genesis problems. Miner. Deposita, 14, 353-374 (1979)

Christie, O.H.J.: Three trace element geological materials certified as a result of a cooperative investigation. Talanta, 22, 1048-1050 (1975)

Corin, F.: Atlas des roches éruptives de Belgique. Mém.Expl.Cartes Géol. et Min. de Belgique, no 4, 190 p, 1965

Currie, L.A.: Limits for qualitative and quantitative determination. Anal. Chemistry, 40, 586-592 (1968)

Davis, J.C.: Statistics and data analysis in Geology. John Wiley, 420 p, 1973

Dejonghe, L.: Discovery of a sedimentary Ba (Fe, Zn, Pb) ore body of Frasnian age at Chaudfontaine, Province of Liège, Belgium. Mineral. Deposita, 14, 15-20 (1979)

Dewez, L., Lespineux, G.: Les minerais du sol belge. In: "Centenaire de l'A.I.Lg - Congrès 1947 Section Géologie". Ed. AILg, Liège, 73-120 (1947)

Dillen, H., Gijbels, R.: Etude de quelques éléments en traces dans la pyrite par analyseur ionique. J. Microsc. Spectrosc. Electron., 6, 179-194 (1981)

Duchesne, J.C.: Présence de thallium dans les sulfures de fer de la mine de Pallière (France). Ann. Soc. Géol. Belgique, 87, 1-7 (1964)

Duchesne, J.C.: A reply to A. Bernard's comments on "Présence de thallium dans les sulfures de fer de la mine de Pallière (Gard, France)". Ann. Soc. Géol. Belgique, 88, 153-155 (1965)

Evrard, P.: La minéralisation de Vedrin (Province de Namur, Belgique). Ann. Soc. Géol. Belgique, 66, M181-202 (1943)

Evrard, P.: Minor elements in sphalerites from Belgium. Econ. Geol. 40, 568-574 (1945)

Gwosdz, W., Krebs, W.: Manganese halo surrounding Meggen ore deposit, Germany. Trans. Inst. Min. Metal., sect. B, 86, 73-77 (1977)

Harman, H.H.: Modern factor analysis (2nd ed) University of Chicago Press, 1967

Hegemann, F., Leybold, C.: Eine Methode zur quantitativen spektrochemischen Analyse von Pyrit. Zeitschr. Erzbergbau u. Metallhüttenwesen, v. 7, 108-113 (1954)

Heinrichs, H., Schulz-Dobrick, B., Wedepohl, K.H.: Terrestrial geochemistry of Cd, Bi, Tl, Zn and Rb. Geochim. Cosmochim. Acta 44, 1519-1533 (1980)

Ivanov, V.V., Volgin, V.Y., Krasnov, A.A., Lizunov, N.V.: Thallium: Basic geochemical and mineralogical properties, genetic types of deposits and geochemical provinces (in Russian), Moscow Academy of Sciences, Transl. International Geology Review, Booksection. Published by the American Geological Institute, 1960

Jankovic, S., Le Bel, L.: Le thallium dans le minerai de Bözcukur près Kitahya, Turquie. Bull.Suisse Minéral. Pétrol. 56, 69-77 (1976)

Loftus-Hills, G., Solomon, M.: Cobalt, Nickel and Selenium in sulfides as indicators of ore genesis. Mineral. Deposita, 2, 228-242 (1967)

Robinson, P., Walshe, J.L.: Trace-element analysis of pyrite - an interlaboratory survey. Trans. Inst. Min. Metal. 5, B216-218 (1977)

Roedder, E.: The noncolloidal origin of "colloform" textures in sphalerite ores. Econ. Geol. 63, 451-471 (1968)

Shal, K.: Thallium. In: Handbook of Geochemistry. Wedepohl, K.J. (ed) vol. II-5 section 81A. Springer, Berlin, Heidelberg, New York, 1974

Schrön, W., Rossler, H.J.: Drei neue geochemisch-mineralogische Komplexstandards Galenit GF-1, Sphalerit SF-1 and Pyrit PS-1. Z. Angewandte Geologie, 21, 17-25 (1975)

Shaw, D.M.: The geochemistry of thallium. Geochim. Cosmochim. Acta, 2, 118-154 (1952)

Stoiber, R.E.: Minor elements in sphalerites. Econ. Geol. 35, 501-519 (1940)

Thein, J.: Geochemische Untersuchungen im Sulfiderz im Nebengestein und in den Böden der Lagerstätte Meggen-Westfalen. Doctorate thesis - Rheinische Friedrich-Wilhelms-Universität zu Bonn, 70 p (unpublished), 1975

Thorez, J., Pirlet, H.: Petrology of K-Bentonite beds in the carbonate series of the Visean and Tournaisian stages of Belgium. In: "Intern. Clay Conference 1978", Mortland & Farmer (eds), Elsevier, 323-332 (1979)

Received: October 7, 1982
Accepted: January 4, 1983

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Mineral.Deposita 18, 315-333 (1983)

MINERALIUM
DEPOSITA

Scheelite Mineralization in Central East Greenland

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Numerous scheelite-mineralized areas have been located in the Caledonian fold belt of Central East Greenland (70° - 74 1/2° N). The fold belt comprises Archaean and Proterozoic metamorphic complexes flanked by Late Proterozoic and Lower Palaeozoic sediments, and intruded by Upper Proterozoic and Caledonian granitic rocks. Scheelite mineralization occurs in: marble-skarns in Upper Proterozoic metasediments often spatially associated with Caledonian or older granitic intrusives; skarns and quartz veins in Late Proterozoic sediments (Lower EBG quartzite) up to 7 km from outcropping Caledonian granites; veins in fault zones cutting late Proterozoic sediments (Upper EBG limestones). In this paper, the three types are described with emphasis on structural setting, mineralogy and trace-element chemistry. It is concluded that most scheelite mineralization is associated with Caledonian igneous activity, either at or near granite contacts or as mineralization distal to granites at depth. Of the various types described, the scheelite veins in Late Proterozoic limestone are considered to be of the best economic potential.

INTRODUCTION

The work of this paper formed part of the project "Study of Scheelite Mineralization in Central East Greenland" which was supported by "The program for Research and Development of the European Community in the Field of Primary Raw Materials". The project was initiated in 1979 and completed early in 1982.

Minor scheelite mineralization in float and outcrop was known in the area prior to the start of the project (Hintsteiner, 1977). Scheelite had also been observed in the area during a regional survey in 1974-1975 as part of the International Geological Correlation Program by Ghisler et al. (1980). They described scattered scheelite grains of detrital origin in quartzitic sediments. Furthermore, tungsten as wolframite occurs at the Malmbjerg porphyry molybdenum (Kirchner, 1964) (Fig. 1).

Geochemical exploration during the course of the project (Hallenstein et al., 1981) enabled the finding of numerous scheelite-mineralized areas which are described and discussed in this paper.

The East Greenland project area lies between 70°00'N and 74°30'N and is bounded to the west by the Greenland ice cap, and to the east by the Greenland Sea (Fig. 1). The physiography is dominated

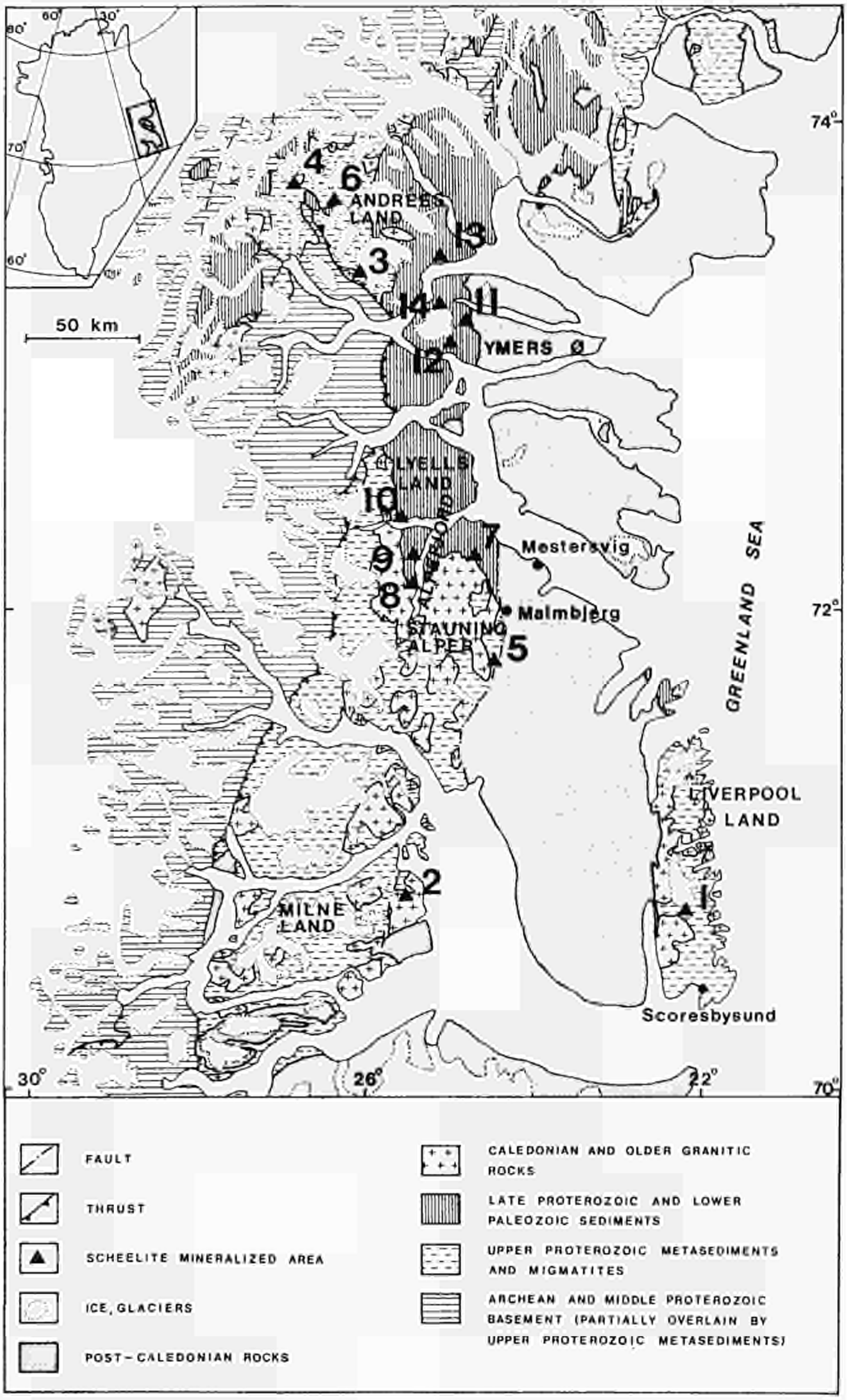

Fig. 1. Geological map of Central East Greenland showing scheelite-mineralized areas. 1. Kalkdal, 2. East Milne Land, 3. Knivbjergdal, 4. Gemmedal, 5. Roslin Gletscher, 6. Eremitdal, 7. Bersaerkerbrae and Skjoldungebrae, 8. Trekantgletscher, 9. Galenadal and Scheelitdal, 10. Randenaes, 11. North Margeries Dal, 12. South Margeries Dal, 13. Panoramafjeld and Eleonores Bugt and 14. Noa Dal

by mountainous terrain, varying from glacier-dissected alpine regions with peaks nearing 3000 m above sea level, to less rugged mountains, often topped by plateaus with an elevation of 1000 to 2000 m, and cut by deep U-shaped valleys. Numerous, long, deep fjords dissect the entire area.

The climate of the area is arctic, with average yearly precipitation of 400 mm, and average temperatures for Juli and January of 5°C and -20°C respectively.

GEOLOGY

The Caledonian fold belt occupies most of the investigated area (Fig. 1). It comprises Archaean and Proterozoic crystalline rocks, flanked by Late Proterozoic and Lower Palaeozoic sediments. Proterozoic and Caledonian granitic rocks intrude the fold belt (Henriksen and Higgins, 1976, and Higgins et al., 1981). Post-Caledonian rocks include Devonian to Lower Permian molasse sediments, Upper Permian to Cretaceous mostly marine sediments, and Tertiary plutonic and volcanic rocks (Haller, 1971).

Archaean and Proterozoic Metamorphic Complexes

Archaean and Middle Proterozoic high-grade-metamorphic basement complexes occupy the western-most parts of the area (Fig. 1). Isotopic age determinations have yielded dates of 2935 to 2300 m.y. and 1980 to 1705 m.y. for the basement complexes (Steiger et al., 1979; Rex et al., 1976; Rex and Gledhill, 1981).

The basement complexes are overlain and bordered to the east by Upper Proterozoic metasediments and migmatites (Fig. 1). These rocks consist of quartzites, mica schists and some marbles, and were metamorphosed 1100 m.y. ago (Hansen et al., 1978; Rex and Gledhill, 1981). They were subjected to a stage of migmatization and granitic intrusion around 1000 m.y. ago (Steiger et al., 1979). Upper Proterozoic granitic rocks have been identified in West Milne Land, South Stauning Alper and in West Andrées Land. They comprise foliated augen and muscovite granites.

Late Proterozoic and Lower Palaeozoic Sediments

The metamorphic complexes are flanked by Late Proterozoic sediments of the Eleonore Bay Group (EBG) and Tillite Group, and by Cambro-Ordovician sediments (Fig. 1). The main belt of these sediments stretches from Alpefjord to northeast of Andrées Land.

The oldest sediments are the Lower EBG, which is sub-divided into the Arenaceous-Argillaceous "series", the Calc-Argillaceous "series", and the Argillaceous-Arenaceous "series". The Lower EBG is best known in the Alpefjord region, and exceeds 8000 m in thickness. The sediments comprise quartzites, siltstones and minor carbonate horizons. The overlying Upper EBG is about 4000 m thick, and has been divided into three "series", the 2000 m thick Quartzite "series", which is overlain by the 1000 m thick Multicoloured "series" and the over 1000 m thick Limestone-Dolomite "series". The Quartzite "series" consists of red and white quartzites and black to green quartzitic shales. The Multicoloured "series" comprises up to 100 m thick, dark limestone units and interbedded yellow, red and green dolomitic and quartzitic shales and light-coloured dolomites. The Limestone-Dolomite "series" is a 1200 m thick sequence of white to black dolomites and limestones. Fossil studies have indicated a very late Riphean or Vendian age for the Upper EBG (i.e., 700 to 600 m.y. old) (Vidal, 1979). The Upper EBG is slightly unconformably overlain by Tillite Group tillites and dolomitic shales, and Cambro-Ordovician limestones and dolomites. These are the youngest sediments which were deposited prior to Caledonian deformation.

Caledonian Orogenesis and Granitic Intrusion

During the Caledonian orogeny, metamorphism was widespread but variable throughout the fold belt. Amphibolite facies was reached in some of the Upper Proterozoic metasediments, and the western-most EBG sediments of the Alpefjord-Andrées Land belt have been weakly metamorphosed in the greenschist facies (Thyrsted, 1978).

Caledonian deformation occurred mostly as broad, N-S trending fold structures. Both the metasedimentary complexes and the EBG sediments have been affected by the folding. The folding is interpreted as having formed as a result of vertical forces accompanying the updoming of crystalline rocks (Haller, 1971; Higgins et al., 1981). The fold axes exhibit alternating culminations and depressions.

Normal faulting along N-S, E-W and NW-SE trends also developed during the deformation (Eha, 1953). The largest displacements are associated with the E-W and NW-SE faults, and may exceed 1000 m.

Caledonian granitic rocks occur in East Milne Land, the Stauning Alper, West Andrées Land and Liverpool Land. They span a wide range of ages and compositions (Steiger et al., 1979; Rex and Gledhill, 1981). The oldest Caledonian granitics, with ages from 560-475 m.y. have the compositions granodiorite, monzonite, and two-mica granite. The intrusions which accompanied the peak of the orogenesis, from 455-430 m.y. ago also have compositions from granodiorite to muscovite granite. The latest phases of Caledonian activity resulted in late to post orogenic intrusions with an age of 420-375 m.y. These dated rocks comprise biotite granite, aplite and pegmatite.

DESCRIPTION OF SCHEELITE MINERALIZATION

Numerous scheelite-mineralized areas have been found in a 350 km long belt in Central East Greenland. Outcropping scheelite mineralization is known in 12 areas, which vary from 1 to 20 km^2 in size, and scheelite-bearing boulders have been located in a further two areas. The location of all areas is indicated on Fig. 1. It is possible to divide the scheelite-mineralized areas into three groups on account of their geological setting. The groups and their respective areas are as follows:

- Scheelite mineralization in Upper Proterozoic metasediments, often spatially associated with Caledonian or older granitic intrusions. The areas assigned to this group are Kalkdal, East Milne Land, Knivbjergdal, Gemmedal Roslin Gletscher and Eremitdal.

- Scheelite mineralization in the Lower EBG sediments, up to 7 km from outcropping Caledonian granites. The areas of this group comprise Bersaerkerbrae, Skjoldungebrae, Trekantgletscher, Galenadal, Scheelitdal and Randenaes.

- Scheelite mineralization in fault zones in Upper EBG sediments without spatial relation to granitic rocks. The areas of this group comprise North and South Margeries Dal, Panorama Fjeld, Eleonores Bugt and Noa Dal.

Work in the areas has included geological mapping at scales from 1:10,000 to 1:500 and systematic sampling. Samples have been subjected to petrographic and chemical studies. Unless otherwise specified, chemical analyses of tungsten, antimony and arsenic were by XRF and of other elements by semi-quantitative emission spectroscopy The results of this work are summarized in the following descriptions of the mineralized areas of each group.

Mineralization in Upper Proterozoic Metasediments

Kalkdal

Kalkdal is an E-W trending valley in Liverpool Land, and scheelite mineralization occurs at several localities within a 20 km^2 area of the valley (Fig. 2).

The geology of Kalkdal comprises ESE-striking metasediments intruded by pinkish biotite granite in the west an grey foliated granodiorite in the east The granite has been dated at 434 m.y. (Hansen and Steiger, 1971) and the met

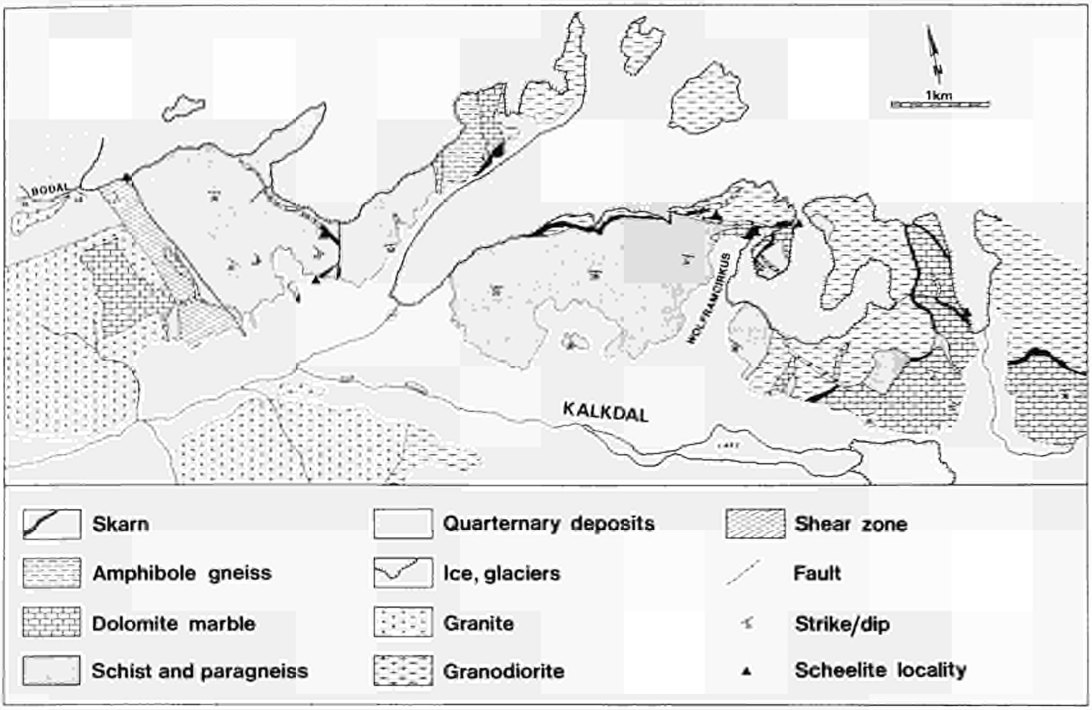

Fig. 2. Geological and scheelite-mineralization map of Kalkdal

sediments at 1183 m.y. (Hansen et al., 1973). The metasediments are dominated by biotite-hornblende-garnet schist and paragneiss, with some dolomitic marble beds and amphibole gneiss. Skarn has developed in marble when in contact with granodiorite and in a marble horizon several kilometres from outcropping intrusive rocks. Skarn does not occur at granite-marble contacts.

Scheelite mineralization in Kalkdal has been located in the skarns (Fig. 2) and in a few pegmatite and quartz veins which cut the skarns.

The skarns at the granodiorite contact are from a few centimetres to several metres thick, and can be grouped into four principal assemblages:

- green diopside skarn, which is formed from forsterite marble and also contains plagioclase and scapolite
- dark green actinolite skarn, which forms as a replacement of diopside skarn;
- grass-green epidote skarn, which alternates with the diopside and actinolite skarns, and also contains diopside, actinolite, plagioclase and scapolite;
- reddish-green garnet skarn, which is a subordinate type and is irregularly distributed. It contains epidote, augite, quartz, humite and fluorite in addition to garnet.

Only the actinolite and garnet skarns contain scheelite. Tungsten contents in hand-sized samples may reach 1%, but the overall content of the skarns is less than 100 ppm. The scheelite is molybdeniferous.

In the marble horizon which is distal to the granodiorite, skarn has developed where the horizon is cut by small faults. Both diopside and actinolite skarns occur, and they are intersected by plagioclase-scapolite veinlets. Lenses of molybdenum-free scheelite mineralization, up to several metres long, occur in these skarns, and are accompanied by sericitization of plagioclase and scapolite. The lenses contain up to 2% W, but the tungsten content of the entire skarn is less than 500 ppm. The scheelite-bearing skarns are enriched in lithium (up to 100 ppm) and beryllium (up to 100 ppm).

East Milne Land

Scheelite mineralization is known in a 2 km long zone at the northern contact of an over 100 km^2 granodiorite-dominated intrusive complex in East Milne Land (Fig. 1).

The geological setting of East Milne Land is similar to that of Kalkdal. E-W striking metasediments, comprising marble, quartzite and mica schist, are intruded by a plutonic complex. The oldest, and principal intrusive phase, was granodiorite, which has a radiometric age of 453 m.y. (Hansen and Tembusch, 1979). The next phase was mafic quartz syenite and the youngest was biotite granite. Biotite granite has been dated at 386 and 373 m.y. (Hansen and Tembusch, 1979).

Scheelite-bearing skarns have formed at contacts between granodiorite and marble. The skarns occur either as lenses, up to 2 m wide and 10 m long, in dolomitic marble within 50 m of the granodiorite or as a continuous band at the granodiorite-marble contact. The band has been traced for 150 m, is 40 cm thick, and is scheelite-bearing in the 20 cm closest to the marble. The scheelite-bearing skarn consists of tremolite, idocrase, quartz and calcite, together with minor biotite, diopside, chlorite and native bismuth. Diopside, tremolite and scheelite are early minerals of the assemblage. Idocrase represents an intermediate stage, and quartz and calcite fill the final interstices. Hand samples of skarn may contain up to 3% W, 0.5% Bi, 200 ppm Sn and 30 ppm Mo. The average tungsten content of the skarn lenses is about 500 ppm, and of the skarn band about 0.5%.

It is evident from field relationships that the formation of the skarn postdates the intrusion of the granodiorite. Pegmatite veins in the granodiorite do not continue into the skarn or marble, which indicates a pre-skarn truncation of the veins.

Knivbjergdal

Mineralization has been located in an area of a few square kilometre in Knivbjergdal, West Andrées Land (Fig. 1).

The geology of the area consists of Upper Proterozoic metasediments which are dominated by quartzites, with an interbedded, 100 to 200 m thick horizon of schists and marbles. The metasediments have been intruded by granite, and the schists now occur in the top of the granite as large lenses up to 1000 m long and 100 m thick (Fig. 3). The schists comprise biotite, quartz and plagioclase with accessory sphene and apatite. They are calcareous in places and may contain diopside, tremolite and clinozoisite. The marbles are calcitic and often bituminous. The main granite intrusion is a grey two-mica granite, although a red, potassium-rich granite also occurs. Pegmatites crosscut the entire area. The granites have not been dated. Two types of skarn - a pale brown zoisite-clinozoisite skarn and a green diopside skarn - have formed in the marble near the contact to the granite. The zoisite skarn envelopes the diopside skarn.

Scheelite mineralization occurs in both the schist and marble lenses at the top of the granite (Fig. 3). In mineralized schist, scheelite occurs in clinozoisite-rich layers, in crosscutting shear zones and disseminated in biotite-rich schistose layers. Mineralization is typically restricted to centimetre-thick bands in the schist with up to 0.3% W. The overall tungsten content of the schist is less than 100 ppm. Studies of the schist mineralization have revealed that the more intense scheelite mineralization is accompanied by increasing contents of fluorite (up to 10% by vol.) and apatite (up to 2% by vol.), by bleaching of the biotite, and by enrichment in tin (200 ppm) and beryllium (70 ppm).

In the marbles, scheelite mineralizations has developed with zoisite-clinozoisite skarn. The skarn also contains minor diopside, quartz, plagioclase, fluorite, calcite and apatite. This type has only been observed in boulders. The boulders contain skarn bands up to 20 cm wide, in which the

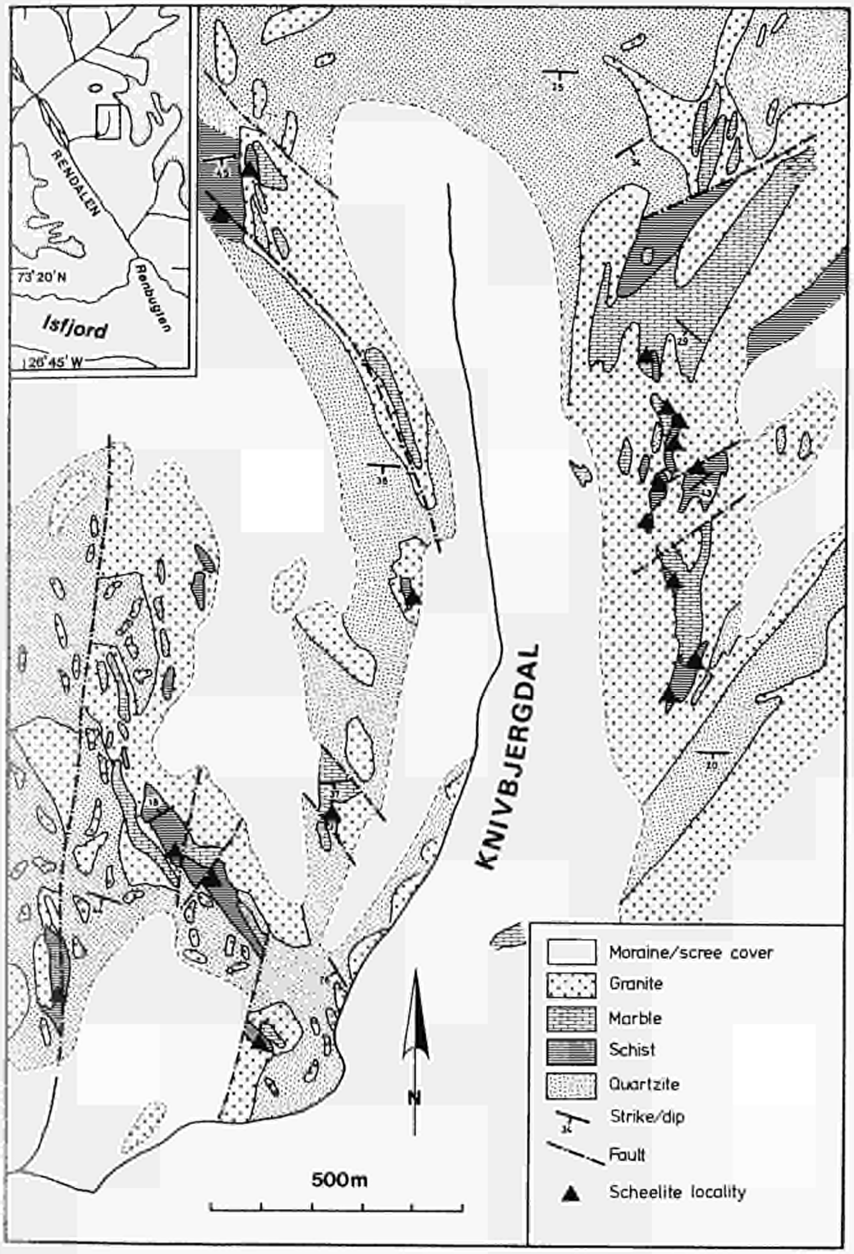

Fig. 3. Geological and scheelite-mineralization map of Knivbjergdal

tungsten content is about 1%, and which are also enriched in copper (150 ppm), lead (150 ppm), tin (400 ppm), beryllium (70 ppm), lithium (700 ppm) and bismuth (50 ppm).

Other Areas

Scheelite mineralization in Upper Proterozoic metasediments is also known from Gemmedal, Eremitdal and Roslin

Gletscher (Fig. 1). Outcropping marble/calc-silicate lenses with minor scheelite occur in biotite-muscovite schist at Gemmedal. The calc silicates comprise diopside, clinozoisite, idocrase and garnet. As well as containing up to 3.4% W in hand samples, the calc-silicate rocks are enriched with up to 400 ppm Sn and 200 ppm Bi. The metasediments have been intruded by garnet and tourmaline-bearing, two-mica granite veins, and have been subjected to post-mineralization deformation.

Boulders of forsterite marble, with scheelite in dark green, massive skarn have been found at Roslin Gletscher. They stem from the migmatized metasediments of the area. The skarn is composed of diopside, plagioclase, scapolite and scheelite. Post-mineralization deformation of the skarn is evident. A hand sample of skarn contained 2% W and minor tin (80 ppm) and beryllium (200 ppm).

The Eremitdal mineralization is also known only in skarn boulders. The boulders are of marble cut by veins of tourmaline-bearing, two-mica granite. A scheelite-bearing, up to 0.5 m thick calc-silicate assemblage has developed at the granite-marble contact. The calc-silicate rock comprises diopside, garnet and idocrase, with minor clinozoisite, sphene, plagioclase, muscovite, actinolite, quartz, calcite, apatite, fluorite and scheelite. The skarn has a low tungsten content (< 100 ppm), and is enriched in tin (300 ppm).

Mineralization in the Lower EBG Sediments

Alpefjord

Scattered scheelite mineralization has been located along 15 km of the west coast of Alpefjord. The geological setting of this area comprises quartzitic sediments of the Arenaceous-Argillaceous "series" (Fränkl, 1951) and Caledonian intrusive granites (Fig. 1).

Scheelite mineralization has been studied at three localities - Trekantgletscher at the contact of the lowermost-preserved sediments of the Lower EBG and granite in the south of the area, and at Scheelitdal and Galenadal which respectively are 1 km and 3 km stratigraphically higher than the sediments at Trekantgletscher, and which are 5 to 7 km east of the outcropping granite (Fig. 1).

At Trekantgletscher, scheelite occurs in centimetre to metre dimensione lenses of contact metamorphosed calcareous quartzite - the skarnoid rocks. The lenses are often zoned, with an approximately 1 cm thick, greenish hor blende-diopside-clinozoisite rim and a calcareous core usually dominated by garnet-hornblende skarnoid. The garnet hornblende skarnoid comprises quartz, grossularite, diopside, hornblende, clinozoisite, plagioclase, scapolite and calcite. Fluorite and scheelite occur in minor amounts, and sphene, apatite and opaque minerals are accessories. In some cases, a zone of garnet-idocrase skarnoid occurs within the garnet-hornblende skarnoid. The garnet idocrase skarnoid comprises quartz, grossularite, idocrase, fluorite, calcite, diopside and clinozoisite. Scheelite, sphene and opaque minerals are accessories. Most scheelite occurs in the garnet-hornblende skarnoid. Tungsten contents of hand samples vary from 0.1 to 0.8% W. The average conten of an entire skarnoid lens is only a few hundred ppm tungsten. The skarnoid are also enriched in beryllium (300 pp tin (200 ppm) and bismuth (100 ppm).

At Scheelitdal, scheelite is associated with concordant quartz veins. The veins are from fifty to several hundre metres apart, are up to 3 m thick, and can be followed for up to 500 m. In addition to coarse-grained quartz, the veins contain coarse-grained arsenopyrite and rare scheelite as centimetr large idiomorphic crystals. The scheelite occur near the contact to the wal rocks.

In an approximately 5 km^2 area sout of Galenadal, quartz veins and fractur zones are mineralized with arsenopyrit and scheelite. The mineralized veins and fracture zones occupy 1 to 2% of the volume of the sediments. At one locality, more intense scheelite mineralization has been located in 2 to 6 m wide, E-W striking quartz-vein swarms (Fig. 4). The swarms are not co

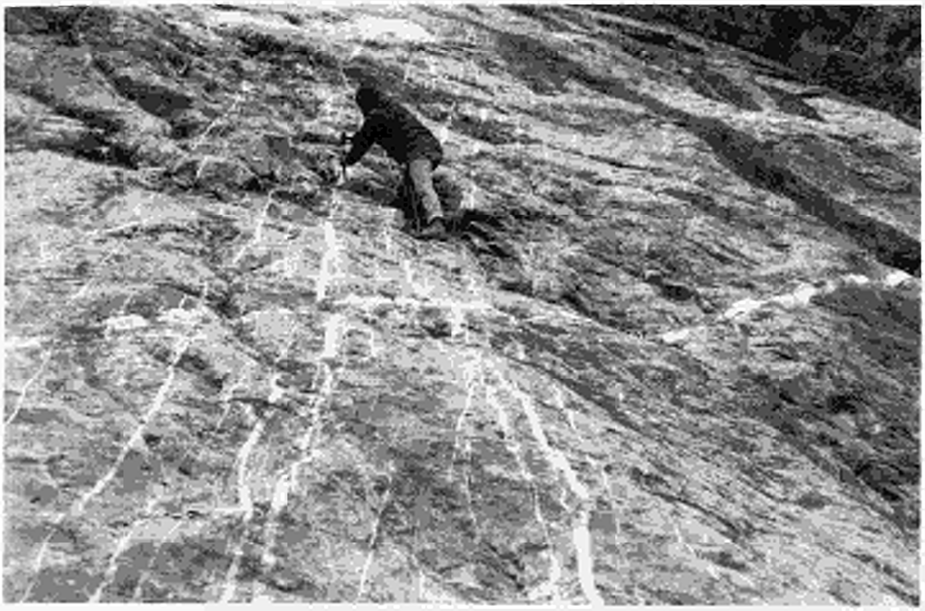

Fig. 4. Quartz-vein swarm, Galenadal

tinuously exposed, but it appears as if one continues for 800 m along its strike. Detailed field observations in the swarms have revealed the existence of several generations of quartz veins. The oldest veins contain most of the scheelite, whereas arsenopyrite, galena, chalcopyrite, pyrrhotite and bismuthinite occur in the youngest veins.

Systematic sampling of the vein swarms indicates an average content of 0.1% W and 0.2% As. The contents of other elements in sulphide-rich samples are 1500 ppm Pb, 200 ppm Bi, 15 ppm Ag, 12 ppm Sb, 50 ppm Cu, 25 ppm Zn and 0.1 ppm Au (Stendal, 1982).

Bersaerkerbrae and Skjoldungebrae

Scheelite mineralization has been found at these two localities in the North Stauning Alper, some 10 km from each other. Both are near the contact between Lower EBG sediments and Caledonian granite (Fig. 1).

The geology of both areas consists of grey quartzites of the Arenaceous-Argillaceous "series", overlain by alternating limestones and shales of the 150 m thick Calc-Argillaceous "series", and the rusty shaly quartzites of the Argillaceous-Arenaceous series (Fränkl, 1953). Large-scale folding has resulted in tilting of the sediments at about 50° to the northeast. The granites have intruded to a level about 500 m below the Calc-Argillaceous "series". Some calc-silicate minerals have developed in calcareous rocks during contact metamorphism.

The principal scheelite mineralization at both localites is associated with quartz veins. Minor mineralization in calc-silicate rocks has also been seen, but only in boulders.

At Bersaerkerbrae, 0.5 to 5 cm thick veins occur in the Calc-Argillaceous "series". The centre of the veins consists of muscovite with accessory fluorite, apatite and cassiterite, and is enveloped by an up to 1 cm thick zone of fluorite, muscovite, quartz, plagioclase and minor scheelite. In the Arenaceous-Argillaceous "series", sub-concordant quartz veins from 0.2 to 1 m thick and up to several hundred metres long are mineralized. Mineralization is principally in an up to 5 cm thick, greisen-like, muscovite-rich selvage of the veins, which comprises cassiterite, apatite, fluorite and scheelite. The quartz core of the veins contains accessoric bornite, chalcopyrite, cassiterite, hematite, galena, bismuthinite and stannite. The average tungsten content of the veins is less than 100 ppm, but the muscovite selvage contains on average about 0.5% Sn.

Scheelite mineralization at Skjoldungebrae occurs in a few, up to 2 cm thick quartz-muscovite-fluorite veins, and in more frequent, up to 1 m thick quartz-fluorite-carbonate veins. Tungsten contents of the veins average less than 100 ppm.

Randenaes

Randenaes is situated on the south coast of Lyells Land just east of the contact zone between Proterozoic metasediments and Lower EBG sediments (Fig. 1). The contact zone is intruded by Caledonian two-mica granites and by pegmatites. The oldest pegmatites are sub-concordant to the easterly dipping Lower EBG sediments, and are rimmed by millimetre to centimetre-thick muscovite greisen. Younger pegmatites are sub-vertical and without associated greisen. The metasediments are contact metamorphosed and comprise interbedded quartzite, biotite schist and garnet-biotite schist, with some metre-sized lenses of calc-silicate (skarnoid) rocks.

Most of the scheelite mineralization of the area is associated with the greisen rims of the oldest pegmatites. The greisen may also contain cassiterite, arsenopyrite, tourmaline and fluorite. The greisen contains up to 3000 ppm W, 800 ppm Sn and enhanced contents of lithium (200 ppm) and beryllium (50 ppm) Traces of scheelite also occurs in joints in the wall rocks of mineralized pegmatites and in lenses of skarnoid rocks.

Mineralization in the Upper EBG Sediments

North and South Margeries Dal

Margeries Dal is a 20 km long, NNE-striking valley on West Ymers Ø. Scheelite mineralization is known in two areas about 12 km from each other - North and South Margeries Dal (Fig. 1)

In Margeries Dal, Upper EBG sediments are cut by large E-W striking faults, over 10 km long and with throw of 100 to 1000 m (Fig. 6). The norther blocks are generally downthrown. Many second-order faults, up to a few hundred metres long, branch off the main faults (Fig. 5). The throws of the second-order faults are up to 100 m, but diminish on going away from the main faults. The sediments of Margerie Dal form part of the easterly dipping flank of an open anticline. On the structural contour map (Fig. 6), it ca be seen that the anticline forms a dom culmination in West Ymers Ø. Lamprophy dykes intrude the sediments and contai fragments of quartzite and granite.

Mineralization in North and South Margeries Dal occurs in the 100 m thic lowermost limestone unit of the Upper EBG as veins in second-order structure At North Margeries Dal (Fig. 5) the largest vein contains both scheelite and stibnite in a breccia zone striking 080° and dipping 75°N. Stibnite predominates in the 65 m of the breccia zone nearest the main fault. It occurs as decimetre-thick massive vein and as thin veinlets in the hanging wall of the breccia zone in the limestone. Scheelite has been observed in the brecciated limestone of this 65 m long zone, but only as scattered grain

West of the stibnite-dominated zone the brecciated limestone is mineralize along strike for 110 m, mostly with scheelite, but also with stibnite. Scheelite occurs as irregularly distributed fillings in the 1-2 m thick breccia zone. Stibnite occurs in a few millimetre to decimetre-thick veins in both the footwall and hanging wall of the breccia zone. Sampling of the entire 110 m long zone indicates content of 0.8% W and 2.4% Sb with a thickness averaging 3 m. Dolomitization and silicification of the limestone is also present in the breccia zone. Magnesia contents are up to 5% and silica from 10 to 60%, compared with < 1% MgO and 1-5% SiO_2 in unmineralized limestone. There are slight enrichments in bismuth (up to 10 ppm), mercury (up to

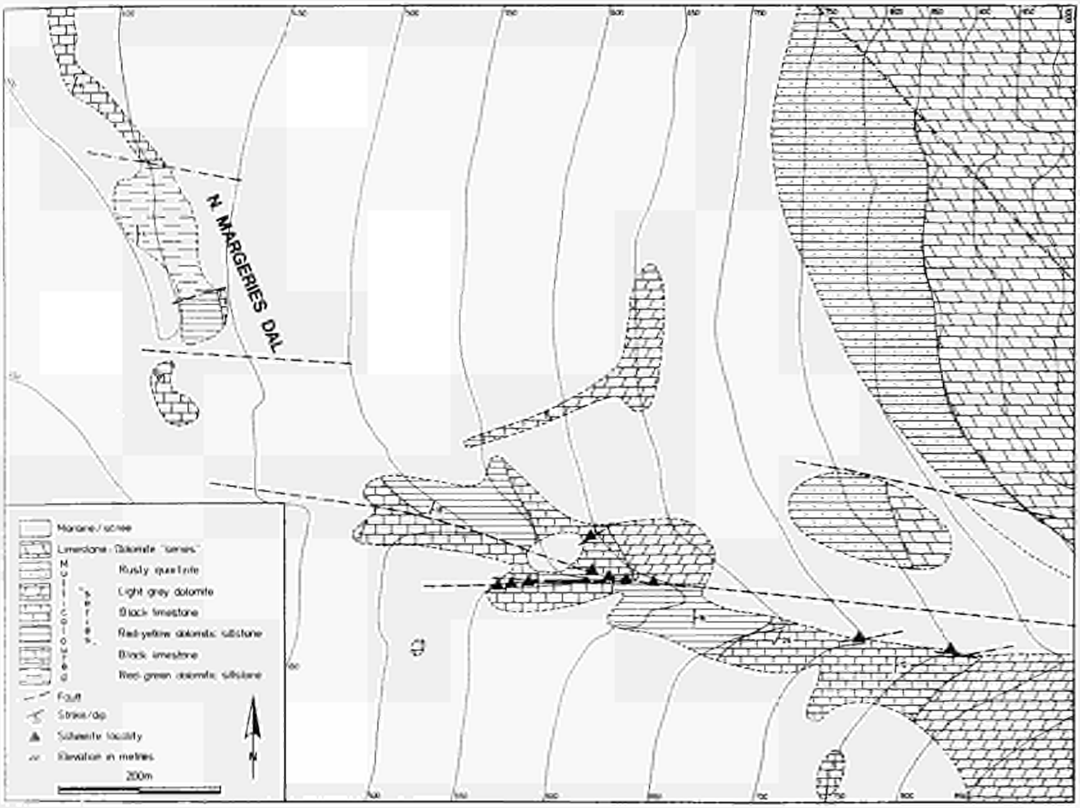

Fig. 5. Geological and scheelite-mineralization map, North Margeries Dal

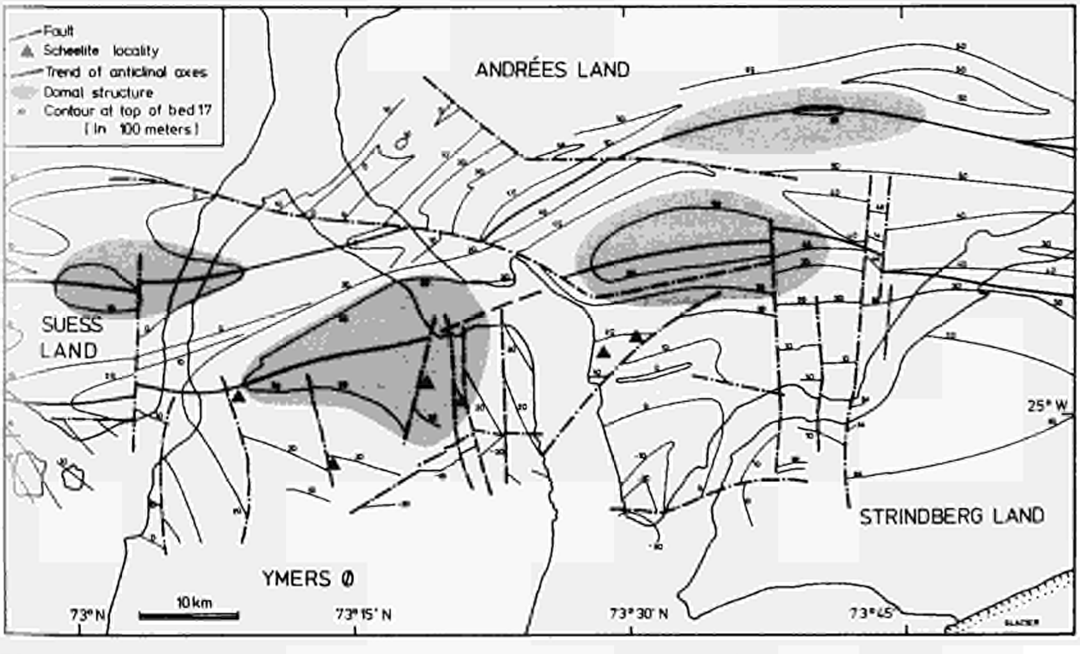

Fig. 6. Structural contour map of the Upper EBG, Andrées Land and Ymers Ø (after Haller, 1971)

greisen-like, muscovite-rich selvage of the veins, which comprises cassiterite, apatite, fluorite and scheelite. The quartz core of the veins contains accessoric bornite, chalcopyrite, cassiterite, hematite, galena, bismuthinite and stannite. The average tungsten content of the veins is less than 100 ppm, but the muscovite selvage contains on average about 0.5% Sn.

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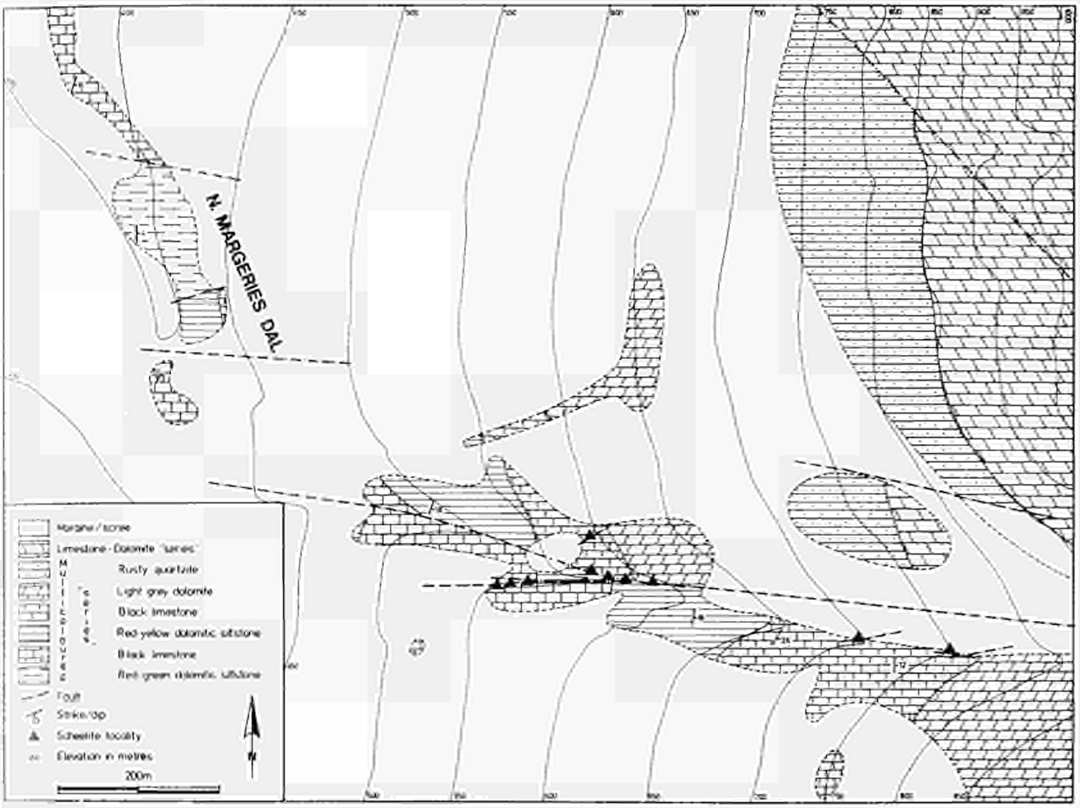

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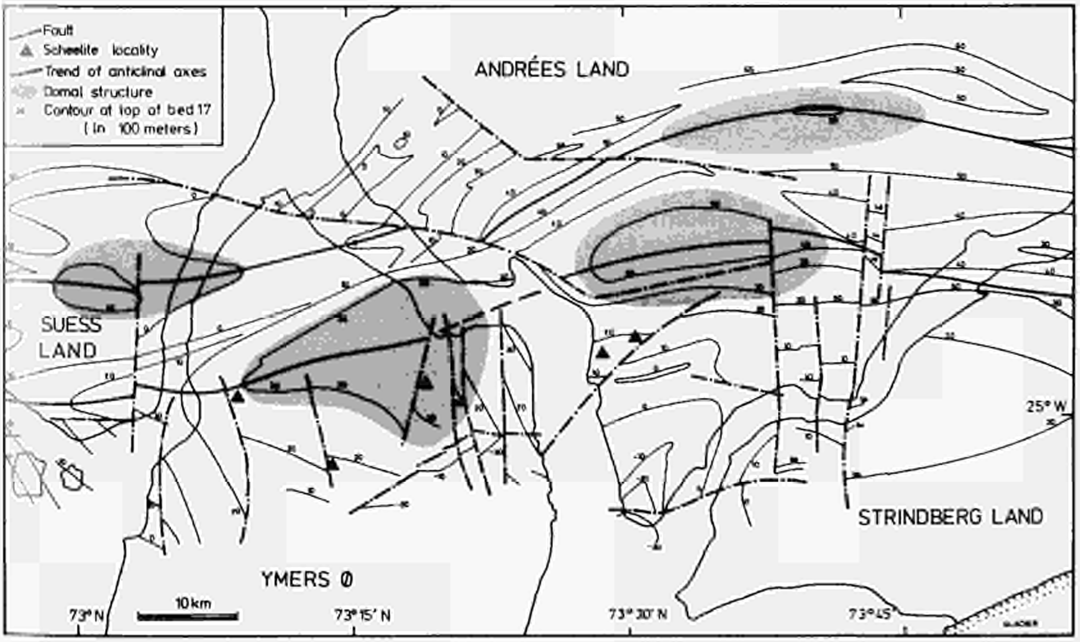

Fig. 6. Structural contour map of the Upper EBG, Andrées Land and Ymers Ø (after Haller, 1971)

3 ppm), silver (up to 2 ppm) and gold (up to 0.15 ppm). Gold analysis was by fire assay, other elements were analyzed by atomic absorption.

The breccia zone can be traced for a further 50 m to the west. It is 0.5-1 m wide with no visible scheelite or stibnite, but the contents of tungsten and antimony are still elevated with 4-100 ppm W and 2-100 ppm Sb.

Several other mineralized lenses occur in an overlying limestone unit up to 40 m north of the main fault (Fig. 5). They are up to 1 m thick, 10 to 15 m long, contain about 1% W but no antimony. The tungsten, as scheelite, occurs as breccia fillings in second-order fault structures. Similar small scheelite-mineralized lenses have been located in second-order structures in the overlying limestone approximately 200 m east of the main mineralization (Fig. 5).

The main mineralization of South Margeries Dal is a vein in a breccia zone, striking ENE, dipping 80°N, and without any appreciable amount of displacement. The zone is up to 3 m wide and can be followed from the bottom to the top of the 100 m thick, lowermost limestone unit. Scheelite occurs as breccia fillings in the limestone (Fig. 7), and is particularly concentrated in the breccia zone in the lower half of the unit. The tungsten content averages nearly 3% over an average width of 2.5 m. Dolomitization and silicification are pronounced and correlate well with the distribution of scheelite. Stibnite has not been observed, but antimony can be detected as a trace element (up to 19 ppm Sb).

Petrographic studies of the North and south Margeries Dal veins have enabled the description of the textural and mineralogical development during vein formation in the limestone. After cataclastic deformation of the limestone, very fine-grained quartz, dolomite and scheelite replaced calcite in the fractured limestone. During progressive replacement, large subhedral scheelite grains formed. Fine-grained quartz occurs as inclusions in the rims of the scheelite grains. At a late stage, calcite and stibnite (if present) precipitated in the centre of veins. Post-mineralization deformation has caused deformation twinning and fracturing of the scheelite grains, and shearing of stibnite into very fine-grained aggregates.

Fig. 7. Scheelite-mineralized limeston breccia, South Margeries Dal. Photo in UV-light with scheelite shining white

Other Areas

Minor scheelite mineralization as thin veinlets in joint planes in Upper EBG sediments is known at several other localities (Fig. 1.). At Panorama Fjel the veinlets occur in the lowermost limestone unit of the Upper EBG and ar associated with a major, SE-striking, normal fault zone. The mineralization is antimony free, and was accompanied by silicification and dolomitization o the limestone. At Eleonore Bugt, dolomites underlying the lowermost limestone unit host the few scheelite veinlets. They occur a few hundred metres east of a SE-striking fault. The veinlets of Noa Dal occur in calcareous quartzite beds of the Upper EBG Quartzite "series", and are associated with an E-W striking fault. Panorama Fjeld and Eleonore Bugt occur on the east flank of a domal culmination in East Andrées Land, and Noa Dal on the east flank of the West Ymers Ø culmination (Fig. 6).

DISCUSSION

Mineralization in Upper Proterozoic Metasediments

Relationship between mineralization and granitic rocks

The mineralization in Upper Proterozoic metasediments is typically associated with calcareous units in the metasediments, and is often spatially associated with granitic intrusion. The scheelite-bearing skarns of Kalkdal, Milne Land and Eremitdal all occur at the contacts of intrusive rocks - granodiorite for the first two and granite for the last. However, the skarn of Milne Land is clearly post granodiorite, whereas those of Kalkdal and Eremitdal were formed at the same time as the intrusion of the igneous rocks with which they are in contact.

The relationship between mineralization and granitic intrusion in Knivbjergdal is uncertain. No signs of skarn or scheelite have been observed at the exact metasediment-granite contacts, but there is a general spatial relationship between granite and mineralization.

The scheelite-bearing calc-silicate rocks of Gemmedal and Roslin Gletscher are not clearly associated with granitic rocks although the metasediments of each area are characterized by granite veining and migmatization respectively.

Skarn Formation

The calc-silicate assemblages of Kalkdal, Milne Land, Gemmedal, Eremitdal and Roslin Gletscher have been formed in dolomitic marble, and are dominated by magnesian minerals. Those of Knivbjergdal, however, have been formed in calcic-carbonate rocks and are magnesium poor. Furthermore, the calc silicates of all areas are generally iron poor.

The calc-silicate assemblages which have developed in dolomitic marble all contain diopside. Some diopside, as well as forsterite, have been observed in unaltered marble, but most diopside developed as a first stage of the skarn-forming process. The scheelite of Roslin Gletscher occurs in a diopside skarn, which has not been subjected to further skarn or hydrothermal processes. The Kalkdal and Milne Land skarns are also characterized by the early formation of diopside, but without accompanying scheelite. Under a continuing skarn-forming process, the diopside of these areas was replaced by actinolite or tremolite or epidote or idocrase. Actinolite, tremolite and idocrase may be accompanied by minor scheelite, whereas scheelite has not been observed with epidote. In Kalkdal, a final hydrothermal phase occurred, with sericitization of plagioclase and the precipitation of significant scheelite. The scheelite-bearing skarns of Gemmedal and Eremitdal contain garnet and idocrase in addition to diopside, but a paragenetic sequence of calc-silicate minerals is not apparent.

The Knivbjergdal calc-silicate assemblage is principally zoisite, clinozoisite and diopside,and was accompanied by scheelite. In a second, and apparently subsequent phase, the formation of diopside predominated. It is probable that the mineralization in schists developed during the phase of zoisite-skarn formation.

There are also several features evident in the trace-element chemistry of the various skarns. The scheelite of the diopside skarn of Roslin Gletscher, the tremolite skarn on Milne Land, and the actinolite skarn in Kalkdal is always molydeniferous. Enhanced contents of tin occur in the skarns of all areas except Kalkdal. Bismuth, lithium and beryllium are enhanced in the skarns of many of the areas.

Age of Mineralization

There are no clear dates for the formation of the various skarns. The best age information exists for the Kalkdal and Milne Land areas. The Kalkdal mineralization postdates the metamorphism of its host sediments (1183 m.y.: Hansen et al., 1973), is associated with the intrusion of granodiorite which has not been dated, and predates the intrusion of the granite (434 m.y.: Hansen and Steiger, 1971). The Milne Land skarn postdates the intrusion of the granodiorite with which it is in contact, and is thus younger than 453 m.y.

(date from Hansen and Tembusch, 1979). The intrusive history of Kalkdal and East Milne Land is similar, there being an early granodiorite phase which was subsequently intruded by granite. If the Kalkdal granodiorite is of similar age to the Milne Land granodiorite, the skarns which formed at the contacts of the Kalkdal granodiorite would be of an age corresponding to the peak of Caledonian orogenesis (455-430 m.y.). If it is presumed that the Milne Land granodiorite and the post-granodiorite skarns were derived from a common magmatic parent, an age corresponding to the main Caledonian orogenesis may also be attributable to the Milne Land skarns.

The scheelite occurrences of Knivbjergdal, Gemmedal, Eremitdal and Roslin Gletscher occur in Upper Proterozoic metasediments intruded by Upper Proterozoic and Caledonian granites. It is thus possible that the occurrences are of Upper Proterozoic and/or Caledonian age. The post-mineralization deformation which is evident in Gemmedal and Roslin Gletscher suggests that the mineralization of these two areas may be older than that of the other areas.

Mineralization in Lower EBG Sediments

The Lower EBG sediments of the Alpefjord and North Stauning Alper region are intruded by Caledonian two-mica granites. Scheelite or other mineralization has not been observed at the actual granite-sediment contacts, even when the granites cut the thick limestone beds of the Calc-Argillaceous "series". There is, however, a clear zoning of the scheelite-mineralization type from within a few hundred metres of the contact to up to 7 km from the contact.

One type of mineralization generally occurs within 1 km of the granite contact, and is associated with muscovite-greisen formation at the borders of pegmatite and quartz veins. This situation is known at Randenaes and Bersaerkerbrae.

The second mineralization type also occurs within 1 km of the granite contact. It is restricted to skarnoid developments in lenses of calcareous quartzites. This type is known at Bersaerkerbrae, Skjoldungebrae, Trekantgletscher and Randenaes. The zoned skarnoid assemblages are interpreted as having been formed by a combination of metamorphism and metasomatism. The calc-silicates grossularite, diopside and hornblende developed during metamorphism. Idocrase, scapolite, fluorit and scheelite were formed during later reaction with skarn-forming fluids.

The third mineralization type occur either in quartz veins as at Randenaes and Galenadal, or in quartz-fluorite veins, as at Bersaerkerbrae and Skjoldungebrae. Mineralized veins have been observed up to seven kilometres from the granite contact.

All three mineralization types are enhanced in bismuth. Tin is associated with the greisen type, and arsenic wit the quartz-vein type.

It is assumed that all scheelite mineralization in the area is of similar age. Direct age evidence does not exist, but the intrusion of the granites, which appear to have controlled the mineralization, was during the main Caledonian orogeny (455-430 m.y.) A granite intruding the Lower EBG sout of Randenaes has been dated at 445 m.y (Rex et al., 1976).

Mineralization in Fault Zones in Upper EBG Sediments

The mineralization of this group occur as veins in fault and breccia zones in folded Upper EBG sediments, and in particular in the lowermost limestone uni of the Upper EBG. The development of the folds and of culminations along anticlinal axes are believed to be a function of granitic upwellings at depth. The presence of granite stocks is supported by the occurrence of granite xenoliths in the lamprophyre dykes of the domal areas. Anticlinal culminations occur in West Ymers Ø and in Eas Andrées Land (Fig. 6). All the known fault-associated scheelite mineralization occurs on the flanks of these two domal structures within 20 km of the apices of the domes. In addition to updoming and faulting the sediments, the granitic stocks are considered to have been the source of epithermal solutions, from which the mineralization was precipitated.

Most of the mineralization occurs in the lowermost limestone unit of the Upper EBG, which is of obvious potential as a chemical trap for ascending solutions. The unit is furthermore physically competent, and production of open fracture, fault and breccia zones, i.e. suitable physical traps, is thus possible in the limestone. Similar chemical and physical conditions exist in overlying limestone units, and some scheelite-mineralizing fluids have reached overlying units in North Margeries Dal. Minor occurrences of scheelite have been observed in quartzites and dolomites below and above the lowermost limestone unit (Noa Dal, Eleonores Bugt and North Margeries Dal).

In North Margeries Dal, the mineralization occurs in second-order structures up to 150 m from the main fault structure, and generally becomes less intense on going away from the main fault. Stibnite, which is also present in North Margeries Dal, occurs only in the zone nearest the main fault. Trace contents of tungsten and antimony are detectable as a halo in the breccia zone for 50 m beyond the visible mineralization. Movement of ore-forming fluids along the main fault and into second-order structures is thus implied.

Petrographic studies have indicated that the first stage of vein development involved replacement of calcite in limestone by quartz and dolomite. As replacement progressed, scheelite, and finally calcite and stibnite (if present) were precipitated. Petrographic and chemical studies have confirmed

Table 1. Comparison of East Greenland tungsten occurrences with a world-scale classification of tungsten occurrences

CLASSIFICATION OF TUNGSTEN OCCURRENCES (Burnol et al. 1978)	OCCURRENCES IN EAST GREENLAND
I DEPOSITS ASSOCIATED WITH THE PLUTONIC ENVIRONMENT	
A Skarn	Milne Land, Kalkdal, Knivbjergdal etc.
B Pegmatites	Randenæs
C Vein type	
1 STOCKWORK MINERALIZATION	
JUST ABOVE AN INTRUSION	
WITH NO APPARENT RELATION TO AN INTRUSION	
2 DISSEMINATION IN PLUTONIC CUPOLAS	Malmbjerg
3 INDIVIDUAL VEINS OUTSIDE OR WITHIN A PLUTONIC INTRUSION	
QUARTZ VEINS WITH WOLFRAMITE	
QUARTZ VEINS WITH CASSITERITE AND WOLFRAMITE	
QUARTZ VEINS WITH SCHEELITE	Galenadal and North Stauning Alper
QUARTZ VEINS WITH SCHEELITE AND GOLD	
4 PIPE MINERALIZATION	
II DEPOSITS ASSOCIATED WITH THE SUBVOLCANIC ENVIRONMENT	
A Tungsten and tin together	
1 TUNGSTEN-TIN-BEARING POLYMETALLIC VEINS RICH IN SULPHIDES	
2 TUNGSTEN-TIN MINERALS DISSEMINATED IN RHYOLITE	
B Tungsten without tin	
1 QUARTZ VEINS WITH HUEBNERITE AND SULPHIDES	
2 QUARTZ VEINS WITH FERBERITE OR SCHEELITE, AND STIBNITE	North and South Margeries Dal
3 QUARTZ VEINS WITH FERBERITE	
III TUNGSTEN ASSOCIATED WITH MANGANESE OXIDES	
IV STRATABOUND TUNGSTEN DEPOSITS	
V PLACER DEPOSITS WITH TUNGSTEN	

that silica, tungsten, antimony, sulphur and magnesium have been introduced during the mineralization process. Some post-mineralization faulting has affected the veins, resulting in fracturing of scheelite grains, shearing of stibnite, and recrystallization of calcite.

The metallogenetic model which is proposed above for this mineralization type invokes a main Caledonian orogeny age. The post-mineralization deformation which has occurred is attributed to fault reactivation in post-Devonian times.

THE EAST GREENLAND OCCURRENCES COMPARED WITH A WORLD-SCALE CLASSIFICATION OF TUNGSTEN DEPOSITS

In the past, tungsten deposits have been divided into vein deposits, often together with tin, and skarn deposits. However, during the last 20 years, the finding of new types and new areas of tungsten mineralization has resulted in the need for a more detailed and comprehensive classification scheme. Such a scheme for tungsten occurrences has been proposed by Denisenko (1975), and revised by Burnol et al. (1978). This revised scheme is summarized in Table 1. It has been possible to classify the East Greenland scheelite occurrences in accordance with this scheme, into the categories skarns, pegmatites and quartz veins in the plutonic environment, and into scheelite plus stibnite veins in the subvolcanic environment (Table 1). This categorization of East Greenland scheelite is discussed below. The wolframite-bearing porphyry molybdenum deposit at Malmbjerg is furhtermore classifiable into the category of dissemination in a plutonic cupola.

Skarns

In their comprehensive review of skarn deposits, Einaudi et al. (1981) have characterized tungsten skarns according to associated plutonic rocks, host rocks and skarn mineralogy. Tungsten skarns are typically associated with plutonic rocks of granodiorite to quartz monzonite composition, and of Middle Palaeozoic to Upper Cretaceous ages. They occur in carbonate rocks, which for most exploitable tungsten deposits are calcitic and not dolomitic limestones. The skarn mineralogy is typified by early-stage, magnesium-aluminium-rich, iron-poor calc-silicates (diopside, grossularite, idocrase), by middle-stage iron rich calc-silicates (hedenbergite, andradite, almandine), and by late-stage hydrous assemblages (tremolite, actinolite, hornblende, epidote). The early stage is generally tungsten-poor, whereas the middle, and particularly the late stages are generally tungsten rich.

The skarn occurrences of East Greenland exhibit some, but not all of the above-mentioned characteristics. Granodiorite is associated with the skarns of Kalkdal and Milne Land, whereas the other occurrences either are associated with granite or are without obvious plutonic association. The intrusion of most of the granodiorites and granites is believed to have accompanied the main Caledonian orogeny (455-430 m.y.) - the end of the Lower Palaeozoic. Only the skarn of Knivbjergdal has developed in calcitic marble. The other skarns of the Upper Proterozoic metasediments have developed in dolomitic marbles, and the skarns in the Lower EBG of Alpefjord and the North Stauning Alper are in calcareous quartzites. The East Greenland skarns generally exhibit an early, diopside-rich phase, which was often followed by a stage of hydrous-mineral development (amphiboles, idocrase, epidote). The hydrous phase was typically accompanied by minor scheelite mineralization. A final stage of more intense alteration and rich scheelite mineralization occurred locally in Kalkdal, but not at any of the other known skarn occurrences. None of the East Greenland skarns exhibit an iron-rich stage of calc-silicate development.

Pegmatites

Burnol et al (1978) point out that scheelite or wolframite-bearing pegmatites are a relatively unimportant source of tungsten. Such pegmatites are characterized by enrichment in the elements beryllium, lithium, niobium and tantalum and by the minerals topaz, tourmaline, beryl, apatite, etc. The scheelite and cassiterite-bearing pegmatites at Randenaes are quite comparable with this characterization.

Quartz Veins with Scheelite

Tungsten-bearing quartz veins are the source of 70-75% of the worlds tungsten (Burnol et al., 1978). Most of these veins occur in argillaceous and arenaceous sediments (or metasediments) and contain wolframite. However, scheelite - often with gold - occurs in quartz veins in more calcareous host rocks, or even in granitic host rocks. The tungsten deposit of Barruecopardo in Spain comprises scheelite-bearing quartz veins in granites (Arribas, 1979). The veins are from 1 to 50 cm thick, and are traceable over several hundred metres. Arsenopyrite accompanies the scheelite. The tungsteniferous quartz veins of East Greenland (in the Alpefjord and North Stauning Alper areas) occur in argillaceous and arenaceous sediments with a minor calcareous component. However, scheelite is the only tungsten mineral which has been observed in the veins. Arsenopyrite and base metals accompany the scheelite. The quartz-vein swarm of Galenadal is of similar dimensions and mineralogy to the veins of Barruecopardo.

Quartz-Scheelite-Stibnite Veins

Quartz veins of the subvolcanic environment with scheelite, ferberite and stibnite are an important source of tungsten in Bolivia. The veins typically occur in fault and fracture zones, contain small lenses which are rich in tungsten, and are not accompanied by any obvious magmatic source (Burnol et al., 1978). Arribas (1978) has described a similar scheelite-stibnite vein deposit - that of the Codosera mine in Spain. This vein occurs in a breccia zone in limestone, and is also without direct association with magmatism. The East Greenland scheelite-stibnite veins (Margeries Dal) are quite comparable with these examples, as they occur in fracture/breccia zones in limestone, contain small lenses of rich mineralization, and are without direct association with magmatism.

CONCLUSIONS

Numerous scheelite occurrences have been discovered in a 350 km long belt of Central East Greenland. It has been possible to group the occurrences into three main geological settings:

- scheelite in Upper Proterozoic metasediments, often associated with granodiorite or granite intrusion;
- scheelite in Lower EBG sediments, associated with granite, pegmatite and quartz-vein intrusion;
- scheelite in Upper EBG sediments, without direct magmatic association.

Metallogenetic models have been constructed for the groups, and Caledonian magmatic activity is a common factor in each of the models. The geological environment of the first group is considered to represent a deeper level of Caledonian magmatic activity. Several of the scheelite occurrences suggest that minor tungsten mineralization may have been present in the Upper Proterozoic rocks prior to the Caledonian orogeny. The second geological environment represents an upper level of Caledonian magmatism, whereas the third environment is considered to be distal to Caledonian granite at depth.

The metallogenetic models are of use as exploration aids:

- The contact zones of granodioritic intrusives and marble-bearing metasediments are the best targets in the Upper Proterozoic metasedimentary belts. The scheelite-bearing skarns of the Upper Proterozoic metasediments contain enhanced contents of tin, bismuth, lithium and beryllium, which also may be useful as exploration aids.
- Exploration for scheelite in the contact zones of Caledonian granites and the Lower EBG sediments should take into account the zoning of mineralization type from skarn and greisen type nearest the granites to quartz-vein type up to several kilometres from the granites, as well as the minor element contents - bismuth in all types, tin nearest the granites and arsenic furthest from the granites.

- The metallogenetic model for the third group involves mineralization in the lowermost limestone unit of the Upper EBG when cut by E-W trending fault zones, and on the flanks of anticlinal culminations. Exploration in such potential areas could furthermore utilize the tungsten and antimony haloes in the fault zones around the mineralization.

It is also possible to draw some conclusions about the economic potential of the various mineralization types in East Greenland based on the comparison with the world-scale classification of tungsten deposits:

- The skarn-type occurrences on East Greenland are probably not of great economic potential because: they are generally of limited extent and relatively low tungsten content, they mostly are developed in dolomitic marble, and they lack the iron-rich formation phase which normally accompanies economically viable scheelite-skarn deposits.

- The scheelite-bearing quartz veins in the plutonic environment are rather extensive in East Greenland, but are of overall low tungsten content. They are comparable with tungsten deposits in other parts of the world which have been mined, but appear to be too low grade for exploitation in East Greenland.

- The scheelite-stibnite-quartz veins of the subvolcanic environment of East Greenland contain small but rich concentrations of tungsten, similar to exploitable deposits in other parts of the world. These veins are probably of economic potential.

Acknowledgements. The support of the European Economic Community under contract 077-79-1 MPP DK is gratefully acknowledged. We wish to thank Mogens Lind, Svend Karup Møller, Jes Pedersen and Henrik Stendal for their participation in the field work of the project. Thanks are also due to Asker Geyti, Henrik Stendal and Bjørn Thomassen for reading and improving the manuscript, and to Jørgen Geyti for draughting the figures.

REFERENCES

Arribas, A.: Mineral paragenesis in th Variscan metallogeny of Spain. Stvdia Geologica 14, 223-260 (1978)

Arribas, A.: Le gisement de tungstène de Barruecopardo (60°31'W et 41°08' Chronique Recherche Minière, FRA 450 42-49 (1979)

Burnol, L., Geffroy, J., Soler, P.: Le tungstène, ses principaux types de gisement. Chronique Recherche Minière, FRA 441, 27-43, et n° 443, 27-44 (1978)

Denisenko, V.K.: Classification des gisements de tungstène à des fins prévisionnelles. Zap. Vses. min. obshch. 104, vyp 5, 526-538 (in Russian). (Translation B.R.G.M. 5, 493) (1975)

Eha, S.: The pre-Devonian sediments of Ymers Ø, Suess Land and Ella Ø (East Greenland) and their tectonics. Medd Grønland 111, 2, 105 pp (1953)

Einaudi, M.T., Meinert, L.D., Newberry R.J.: Skarn deposits. Econ. Geol. 75th Anniversary Volume, 317-391 (1981)

Fränkl, E.: Die untere Eleonore Bay Formation im Alpefjord. Meddr. Grønland 151, 6, 15 pp (1951)

Fränkl, E.: Die Geologische Karte von Nord-Scoresby Land (NE-Grønland). Meddr. Grønland 113, 6, 56 pp (1953)

Ghisler, M., Jensen, Aa., Stendal, H., Urban, H.: Stratabound scheelite, arsenopyrite, and copper sulphide mineralization in the late Precambri Caledonides. Geol. Surv. Irl. Specia Paper 5, 19-24 (1980)

Hallenstein, C.P., Pedersen, J.L., Stendal, H.: Exploration for scheelite in East Greenland. - A case study. J. Geochem. Explor. 15, 381-392 (1981)

Haller, J.: Geology of the East Greenland Caledonides. 413 pp. New York: Interscience Publishers 1971

Hansen, B.T., Steiger, R.H.: The geochronology of the Scoresby Sund area 1: Rb/Sr mineral ages. Rapp. Grønlan geol. Unders. 37, 55-57 (1971)

Hansen, B.T., Tembusch, H.: Rb-Sr isochron ages from east Milne Land, Scoresby Sund, East Greenland. Rapp. Grønlands geol. Unders. 95, 96-101 (1979)

Hansen, B.T., Frick, U. Steiger, R.H.: The geochronology of the Scoresby Sund area. 5: K/Ar mineral ages. Rapp. Grønlands geol. Unders. 58, 59-61 (1973)

Hansen, B.T., Higgins, A.K., Bär, M.-T.: Rb-Sr and U-Pb age patterns in polymetamorphic sediments from the southern part of the East Greenland Caledonides. Bull. geol. Soc. Denmark 27, 55-62 (1978)

Henriksen, N., Higgins, A.K.: East Greenland Caledonian Fold Belt. In: Geology of Greenland, Escher, A., Watt, W.S., (eds) pp 182-246, Copenhagen: Geol. Surv. Greenland 1976

Higgins, A.K., Friderichsen, J.D., Thyrsted, T.: Precambrian metamorphic complexes in the East Greenland Caledonides (72°-74°N) - their relationships to the Eleonore Bay Group, and Caledonian Orogenesis. Rapp. Grønlands geol. Unders. 104, 5-46 (1981)

Hintsteiner, E.A.: Scheelitprospektion in Ostgrönland. Berg-Hüttenmänn. Monatsh. 122, 2a, 31-35 (1977)

Kirchner, G.: Die Molybdänlagerstätte des Erzberges bei Mesters Vig, Ostgrönland. Berg- Hüttenmänn. Monatsh. 109, 162-173 (1964)

Rex, D.C., Gledhill, A.R.: Isotopic studies in the East Greenland Caledonides (72°-74°N) - Precambrian and Caledonian ages. Rapp. Grønlands geol. Unders. 104, 47-72 (1981)

Rex, D.C., Gledhill, A.R., Higgins, A.K.: Progress report on geochronological investigations in the crystalline complexes of the East Greenland Caledonian fold belt between 72° and 74°N. Rapp. Grønlands geol. Unders. 80, 127-133 (1976)

Steiger, R.H., Hansen, B.T., Schuler, Ch., Bär, M.T., Henriksen, N.: Polyorogenic nature of the Southern Caledonian fold belt in East Greenland. An isotopic study. J. Geol. 87, 474-495 (1979)

Stendal, H.: Geochemistry and genesis of arsenopyrite mineralization in late-Precambrian sediments in Central East Greenland. Trans. Instn. Min. Metall. (Sect. B: Appl. Earth. Sci.) 91, B187-B191 (1982)

Thyrsted, T.: Structural and metamorphic studies in the East Greenland Caledonides between 72° and 74° N. Rapp. Grønlands geol. Unders. 90, 94-99 (1978)

Vidal, G.: Acritarchs from the Upper Proterozoic and Lower Cambrian of East Greenland. Bull. Grønlands geol. Unders. 134, 55 pp (1979)

Received: June 15, 1982
Accepted: January 13, 1983

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Mineral.Deposita 18, 335-347 (1983)

MINERALIUM
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Fluid Inclusion Petrography of SW England Granites and its Potential in Mineral Exploration

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Fluid inclusions in granite quartz from SW England provide a record of the complex and protracted hydrothermal history of this important metallogenic province. Regional variations in terms of the different types of inclusions can be correlated on an inter-pluton scale with both the texture of the host granite and the extent to which it is mineralized. On an intra-granite scale those areas where mineralization is particularly pronounced show a higher overall inclusion abundance than areas where little or no mineralization is known to occur. The types of fluid inclusion most commonly related to Sn-W-Cu mineralization are halite-free, moderate temperature inclusions. Inclusions containing visible CO_2 at room temperature are restricted to two localities in SW England. Both of these contain stockwork/vein-swarm tungsten mineralization. These regional 'fluid inclusion anomalies' show that fluid inclusion petrography using a simple petrographic microscope has potential application in the field of mineral exploration.

INTRODUCTION

This paper reports on the distribution and abundance of fluid inclusions in quartz from mineralized granite of SW England with the primary aim of assessing the value of fluid inclusion petrography in regional mineral exploration in this area.

A number of accounts of fluid inclusions as tools in mineral exploration already exist in the Russian literature. These have recently been reviewed by Roedder (1977). Studies in the West are limited and with few exceptions are concerned either with porphyry copper deposits (Nash, 1976; Chivas and Wilkins, 1977; Evans et al., 1979) or vein deposits on a mine scale (Roedder, op. cit.).

The idea that fluid inclusion petrography might prove useful as a regional exploration tool in SW England was encouraged by Sorby's early observations (1858) which clearly demonstrated marked variations in the fluid inclusion assemblage in granite quartz. Several fluid inclusion studies have recently been undertaken in SW England on a local scale mostly on vein material (for summaries see Charoy, 1979; Jackson et al., 1982; Rankin et al., 1982; Rankin and Alderton, 1982).

There has been little interest since Sorby's early work in studying fluid inclusion populations in the granites themselves. Our own data, presented here, is only a beginning and should not be considered an exhaustive account. We have concentrated on methods which are simple and rapid to use and therefore potentially useful in exploration.

From Sorby's early description and from our own initial observations it is clear that most of the inclusions in granite quartz are secondary. These represent late-stage, post-consolidation fluids that have passed through and (sometimes) altered and mineralized the granites. Primary inclusions are rare but when present may either represent magmatic fluids generated from the early magma (in the case of magmatic quartz) or later fluids (in the case of hydrothermally recrystallised quartz).

In theory, it should be possible to study the fluid inclusion paragenesis and hence build up a picture of the progressive stages in the thermochemical evolution of hydrothermal fluids associated with these granites. In practice, magmatic and hydrothermal quartz are very difficult to distinguish. Matters are further complicated because samples from different plutons show marked differences in their fluid inclusion populations as do samples from different areas of the same pluton. Thus, even from a cursory examination it is apparent that hydrothermal activity, as recorded by the fluid inclusion assemblages in the granites themselves, was non-uniform in its distribution and episodic. This is entirely compatible with the complex nature and non-uniform distribution of alteration and ore mineralization as discussed below. The rationale behind the present study is to establish whether it is possible to relate differences in the fluid inclusion populations to different degrees or types of hydrothermal activity associated with the granites. The results for four of the five major plutons are presented here. The St. Austell pluton is associated with intensive kaolinisation. This process has, in many places, obscured the earlier hydrothermal events, and further complicated the fluid inclusion populations. Because of this we will not consider this pluton in the present paper. The results are published in detail elsewhere (Alderton and Rankin, 1983).

GRANITES AND MINERALIZATION OF SW ENGLAND

The geology has recently been reviewed by Charoy (1979) and Edmonds et al. (1975). Five main granite masses are intruded into a sequence of Devonian and Carboniferous sediments which were regionally metamorphosed to greenschist facies prior to granite intrusion.

Geophysical evidence suggests that the five main masses of granite are part of a larger batholith buried at depth. A series of minor granite intrusions also occur and these are presumed to be similarly connected at depth.

The granites were intruded towards the end of the Hercynian orogeny and have been dated at about 280 m.y. (for details see Jackson et al., 1982). Geochemically they show only minor variations and are *sensu stricto* biotite-muscovite granites. Textural variation are more pronounced (Dangerfield and Hawkes, 1981).

The main variations are in terms of:

i) overall grain size
ii) size of K-feldspar megacrysts

Regional variations also occur in the distributions and abundance of late-magmatic minor and trace minerals such as topaz, tourmaline and fluorite Fractures initiated by regional stresses before and during granite emplacement were exploited by subsequent hydrthermal and late-stage magmatic phenomena (Moore, 1975). The linear fractures are in general parallel to the axis of the batholith (Fig. 1), tending to occur on one particular margin of a pluton. Some portions of the granite are much more extensively mineralizd whilst others are almost barre of mineralization.

Ore mineralization occurs mostly in veins or vein swarms. The ore mineralogy is complex and variable but domina ed by cassiterite, wolframite and sulphides of Cu, Pb, Zn, As and Fe. Gang minerals and alteration products of th granite are dominated by quartz, tourmaline, fluorite, muscovite, chlorite, alkali-feldspar and kaolinite.

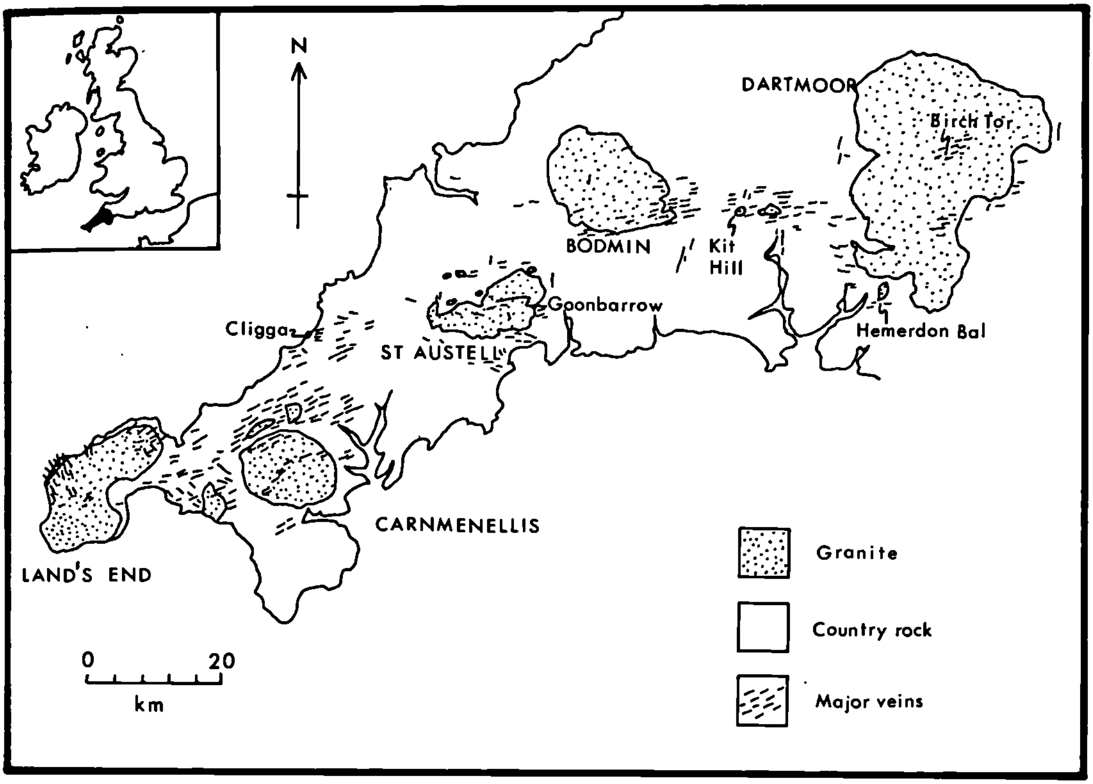

Fig. 1. Geological map of SW England (adapted from Alderton, 1976)

SW England is a classic example of temporal and spatial mineral zonation (Moore, 1982). The earliest mineralization, closest to the granite, is characterized by Sn-W-Cu veins. Later mineralization is dominated by Pb-Zn and tends to occur further away from the granites. Early mineralization has been dated about 270 m.y., which is very close to the age of granite emplacement (Jackson, et al., 1982). A number of later hydrothermal events have been postulated on isotopic evidence (op. cit.). Uranium mineralization and extensive kaolinisation are almost certainly related to these later events. Warm springs in underground workings (Alderton and Sheppard, 1977) and high heat flow (Tammemagi and Wheildon, 1974) show that even today the region is hydrothermally active. Thus a number of separate hydrothermal events have affected the areas from the time of emplacement of the granite to the present day.

Stable isotopic evidence (Sheppard, 1977; Jackson et al., 1982) indicates that the fluids involved in ore mineralization and hydrothermal alteration contained a large component of meteoric water. Simpson et al. (1979) and Moore (1982) have suggested that areas of intense mineralization are where convective hydrothermal cells, involving large volumes of meteoric water, were extensively developed.

The origin of the ore metals is the subject of much speculation. Leaching from the surrounding country rocks or consolidated granites is plausible, but a magmatic origin cannot be excluded on the basis of available evidence.

METHODOLOGY AND APPROACH

Normal petrographic thin sections were used to study the size, shape, abundance and types of inclusions present in quartz from samples of unaltered granite collected at about 1-3 km intervals from each of the four major plutons. Only the last two parameters showed significant variations and these were studied in detail. The usual size of the inclusions ranged from about 5 to 20 µm and shapes ranged from highly irregular through to rounded or negative crystal cavities. Fluid inclusions were also observed in feldspars, and certain accessory minerals (apatite, topaz, fluorite) within the granite, but were seldom as well-developed as in the quartz, and were therefore not considered further.

A limited amount of heating and freezing stage work on polished wafers was conducted during the initial stages of this research to determine the overall range of salinities and homogenisation temperatures (T_h) for the inclusion populations. Routine determination of T_h and salinity were not attempted for all samples because of the inordinate length of time required to accumulate data and the concommitant unlikelihood that this approach would find application as a rapid, routine exploration technique.

CLASSIFICATION OF INCLUSIONS IN SW ENGLAND GRANITES

Fluid inclusions may be classified in a number of ways. Most obvious is a genetic classification (P, PS, S) but this is very subjective and in granite quartz, as previously indicated, may be impossible. An alternative is to classify the inclusions according to gross composition. A six-fold classification scheme is proposed. The inclusions are classified according to the volumetric proportion of vapour and aqueous solution and whether the inclusions contain liquid CO_2 or chloride daughter minerals (halite) at room temperature. Solidified melt inclusions are included in this scheme. The subdivisions are somewhat arbitrary and considerable overlap can occur between each inclusion type in some samples. In general, however, the classification is useful and effective. The general features of each inclusion type are listed below.

Type 1

Monophase aqueous inclusions sometimes containing a small vapour bubble. Thes are highly irregular, usually flattene and occur in distinct planes. Their homogenisation temperatures range up to about 200°C.

Type 2

Aqueous inclusions containing a moderate to large vapour bubble. Generally, these inclusions are more regular in shape and show less of a tendency to occur in planar groupings. An arbitrar subdivision based on the proportion of vapour (2a, 2b) has sometimes been mad T_h range is from about 200°C to 600°C.

Type 3

Aqueous inclusions characterised by chloride daughter minerals (e.g. halite). The vapour bubble is variable in size but typically occupies between 10% and 30% of the inclusion volume. Vapour-liquid homogenisation temperatures are generally between 200°C and 350°C. Halite solution temperatures are variable but may be as high as 500°C.

Type 4

Gaseous inclusions, either totally filled with vapour or, more rarely, together with a small rim of liquid. The often occur in planes and are characteristically rounded or equant in shap Homogenisation is to the vapour phase but it is rarely possible to determine the exact temperature at which this occurs.

Type 5

CO_2-rich inclusions, containing a variable proportion of aqueous solution a characterised by a CO_2-rich phase ($CO_2\ell$ and/or CO_2v).

Type 6

Our final inclusion type is essentially crystalline or possibly glassy. A small amount of vapour is usually present and we tentatively identify these as trapped silicate melts.

DETERMINATIONS OF THE OVERALL ABUNDANCE OF INCLUSIONS

For total fluid inclusion abundance estimates, the most accurate (and time-consuming) method would be to actually count the number of inclusions in a representative volume of quartz. The other extreme would be to make a rapid visual estimate of the overall inclusion density. We have adopted an approach between these two extremes as a compromise between time and accuracy.

The use of petrographic sections of standard thickness (30 μm) meant that a standard volume of quartz was compared at each operation, and that samples in other collections could also be studied. In addition, the petrography of the rock could be assessed at the same time. Six standard charts were prepared illustrating the range of overall fluid inclusion abundances in quartz as seen under x 280 magnification. These were chosen for the ease in visually distinguishing the different abundances. The thin section was scanned at x 280 magnification, 100 to 150 half fields of view were observed at random, and the individual overall abundance score estimated each time by comparison with the standard charts. The mean abundance score was then calculated. This method became quite rapid with practice and soon took about 20 minutes per sample. Routine checks were made by comparing the counts obtained by estimation with the values obtained by absolute counting methods and the results compared favourably. One necessary factor to be considered is the size of the inclusions. Counting was restricted to those inclusions which were > 2 μm in size.

DETERMINATION OF THE RELATIVE PROPORTIONS OF DIFFERENT FLUID INCLUSION TYPES

At a fixed interval during the abundance estimates (depending on the abundance of inclusions) a count of the various inclusion types was made. About 100-150 inclusions were counted overall and the results expressed as percentages of the total population. The main problem with this procedure is that it is sometimes difficult to unambiguously classify an inclusion and this introduces a certain amount of subjectivity. Tests were however carried out to assess the within sample and operative variability. A variability of 10-15% is typical when assessing the overall abundance of inclusions. For the individual types the variability can be up to ± 30% in some samples, probably because about 100 inclusions are not truly representative of the sample. These variations could be reduced by increasing the number of observations. For our purposes, where we are only concerned with broad differences these numbers are considered sufficient.

RESULTS

The main results are summarised in Figure 2.

Type 1 Inclusions

These comprise about 10-20% of the total population for most samples. They show no systematic spatial relationship to mineralization but are especially abundant (up to 50%) in areas of intense kaolinisation, as already noted in the St. Austell mass (Rankin and Alderton, 1982; Alderton and Rankin, 1983).

Type 2 Inclusions (a and b)

They show a wide variation, between about 5% and 80%. They are especially common in the Carnmenellis granite and

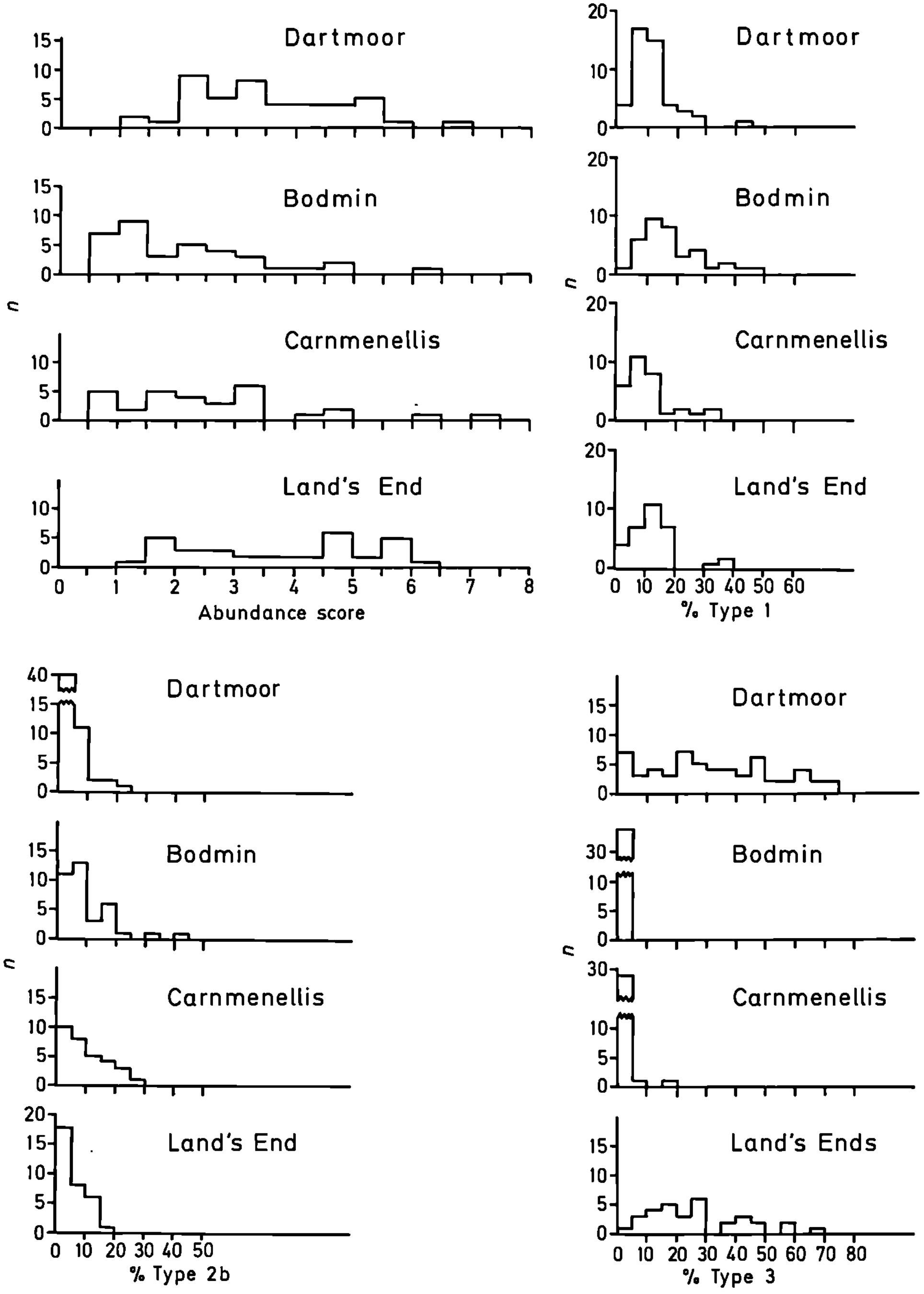

Fig. 2. Histograms of the distribution of inclusion types and overall abundance for four of the major plutons from SW England (n=number of separate granite sampl

least abundant in the Dartmoor granite. A high percentage of these inclusion types *sometimes* correlates with regions where extensive mineralization occurs (e.g. Land's End, Fig. 3c and the small mineralized stocks of Cligga and Kit Hill).

Type 3 Inclusions

These show the most marked variations of all inclusion types between the various plutons. The Dartmoor and Land's End populations contain up to 75% of this inclusion type whilst the Bodmin and Carnmenellis granites typically only show a trace (< 1%). A noteworthy exception is in the Carnmenellis granite where a small 'stock' of fine-grained granite within the main mass contains an enhancement (~20%) of this inclusion type. This enhancement is also noted in the normal, coarse granite close to this stock.

Type 4 Inclusions

These show a very wide spread between samples from the same granite and between granites. Large variations occur (5% to 80%) but no regional trends are apparent.

Type 5 Inclusions

These are exceptionally rare and have only been identified at two localities; Hemerdon Bal, to the south of Dartmoor, and Goonbarrow, in the kaolinised mass of St. Austell. Both these localities are host to sheeted vein systems containing W mineralization (Wolframite). However this relationship is not consistent; several other W-bearing localities (e.g. Cligga) contain no CO_2-bearing inclusions.

Type 6 Inclusions

These are very difficult to identify but have been recorded tentatively from all the granites.

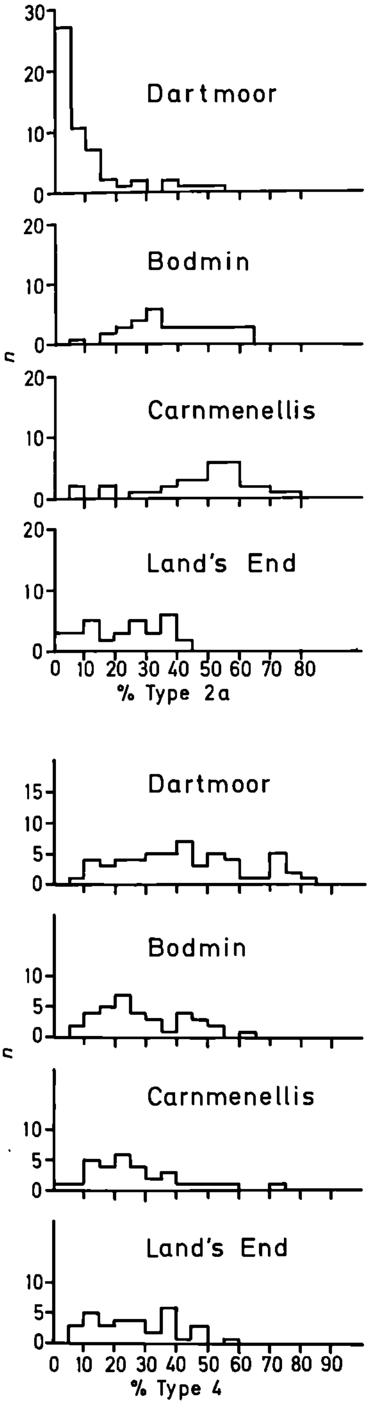

Fig.2

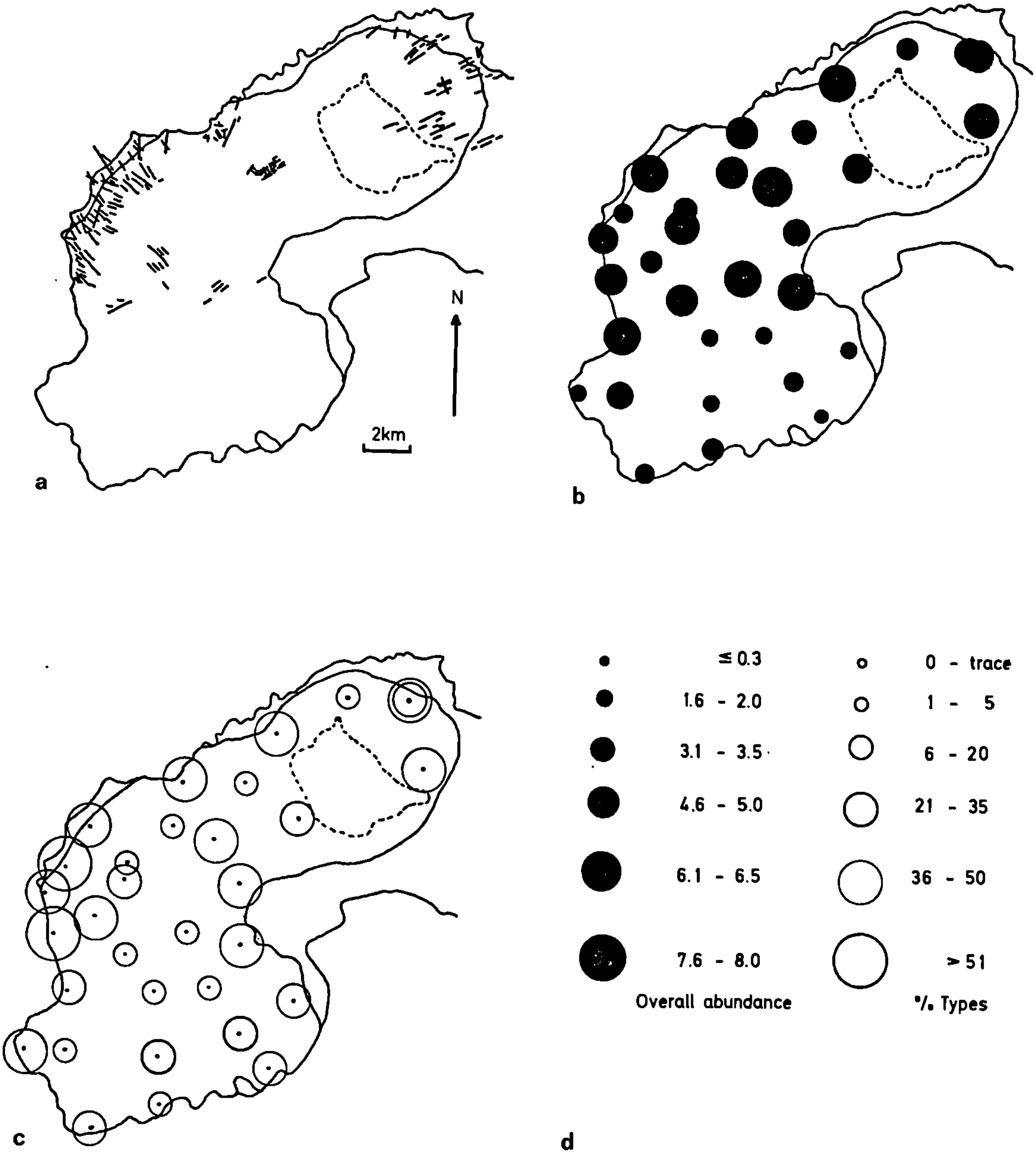

Fig. 3a-c. Distribution of veins (a), fluid inclusion abundances (b) and Type 2a inclusions (c), Land's End granite. Key for figures 3 to 6 (d)

Overall Inclusion Abundance (Figs. 3-6)

This parameter is perhaps the best for distinguishing broad areas in the granite where mineralization is known to occur. High inclusion abundances generally typify these areas in the Bodmin, Land's End, and Carnmenellis granites. In these granites the regions of high abundance extend away from the areas of known mineralization but do follow the overall trend of the vein systems
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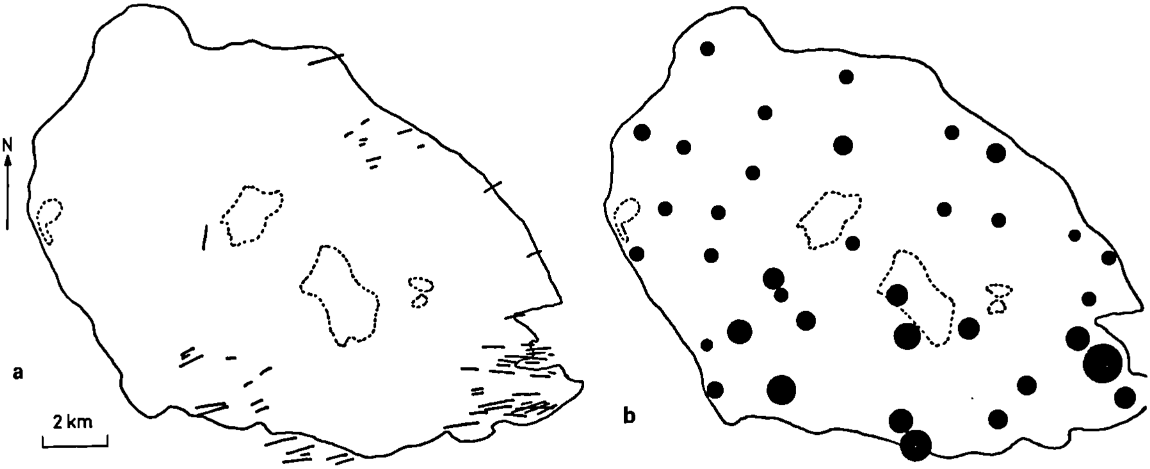

Fig. 4a and b. Distribution of veins (a) and fluid inclusion abundances (b), Bodmin Moor granite

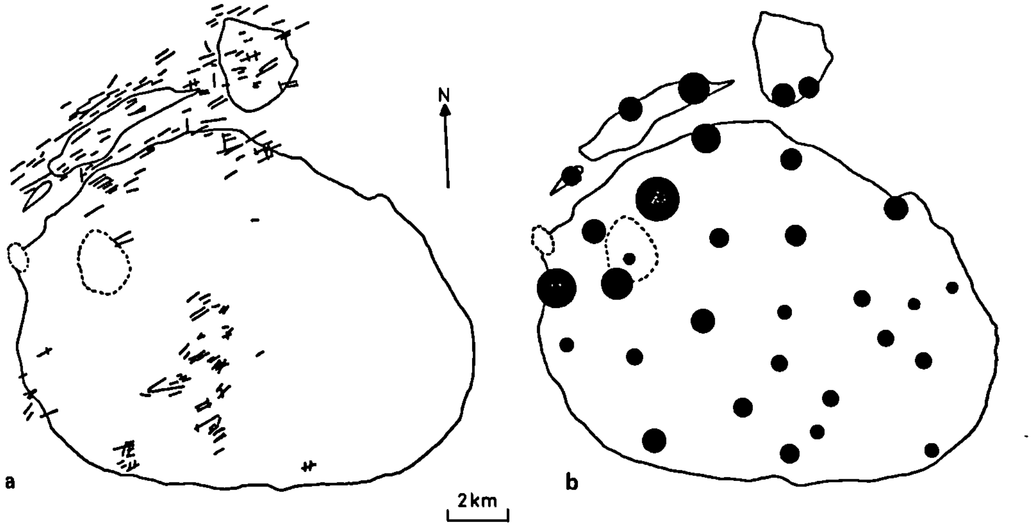

Fig. 5a and b. Distribution of veins (a) and fluid inclusion abundances (b), Carnmenellis granite

(Figs. 3, 4). This could indicate concealed mineralization or could represent broad zones of fluid migration.

We are surprised by the lack of correlation between high abundances and *all* the mineralized areas in the Dartmoor granite (e.g. around Birch Tor). There is however the possibility that the style of this mineralization is different to that in most of the other areas.

Although mineralized areas within a granite may show increased fluid inclusion abundances, such differences may not occur between a mineralized and a non-mineralized granite. In fact the Dartmoor granite (least mineralized) probably contains the highest overall fluid inclusion abundances in SW England. These abundances are presumably related to factors concerned with the granites crystallisation and evolution.

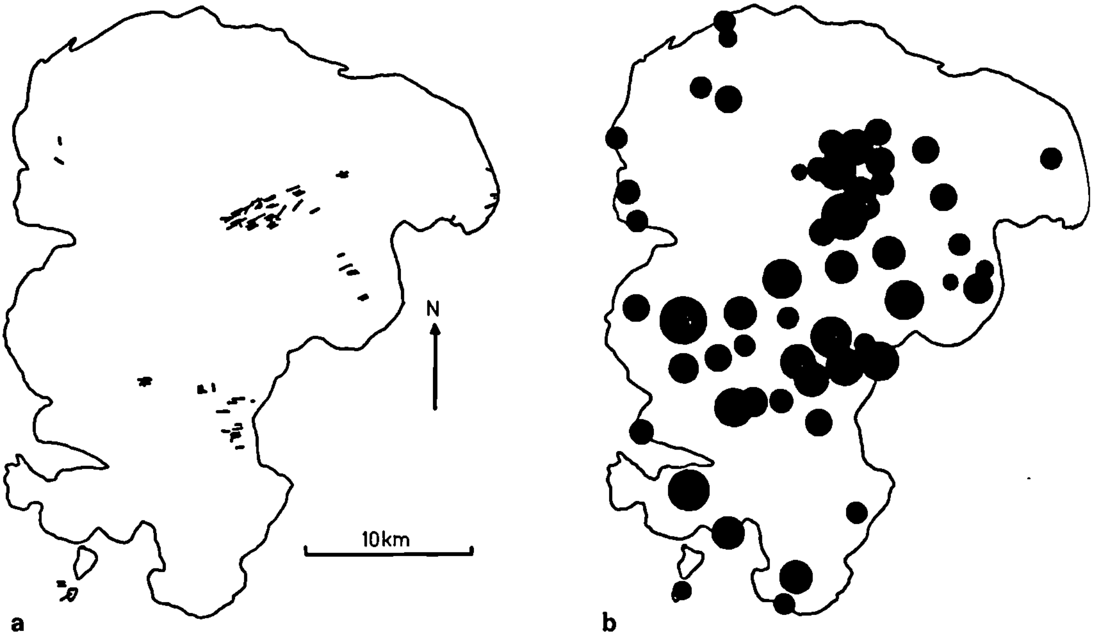

Fig. 6a and b. Distribution of veins (a) and fluid inclusion abundances (b), Dartmoor granite

DISCUSSION

The approach used in this study has been simple and empirical. We have not concerned ourselves with comprehensive heating and freezing stage studies nor with establishing a detailed chronology for the fluids in different areas of the SW England granites. This is purposeful because if fluid inclusion studies are to be used routinely in regional mineral exploration, the techniques need to be relatively inexpensive, rapid and cheap to use by persons who are perhaps unfamiliar with established fluid inclusion methods. The parameters of abundance and distribution of inclusion types have been chosen to fulfill these requirements. They can be determined routinely during normal petrographic microscopy.

In granite the distinction between P, PS and S inclusions is usually very difficult and subjective. This is why we have chosen not to consider it in too much detail. As a generalization, however, most of the inclusions have the appearance of S or PS types (i.e. they occur in planar groupings or arrays).

Several generations are generally present but age relationships are almo impossible to establish, except for Type 1 inclusions. These clearly postdate all others and represent the fina phase of hydrothermal activity in the region. These general observations are compatible with the conclusions from isotopic and age dating studies (Jackson et al., 1982) that hydrothermal ac tivity in SW England was a complex, protracted process made up of a number of separate events.

It is also clear from the overall distribution of inclusions (Fig. 2) that different plutions developed different types of fluids. This is shown by variations in the proportions of Type 2a and Type 3 inclusions. Type 3 halite-bearing inclusions seem to correlate with the texture of the granite Based on the classification of Dangerfields and Hawkes (1981) those with large K-feldspar megacrysts (Dartmoor and Land's End) contain a high proportion of halite-bearing inclusions, whereas those with smaller megacrysts

(Bodmin and Carnmenellis) have little or no halite-bearing inclusions.

Previous ore production figures (Dines, 1956) for each granite may be taken as a guide to their degree of mineralization (Sn-W-Cu). Carnmenellis has by far the most mineralization, Bodmin and Land's End have intermediate amounts and Dartmoor the least. Halite-bearing inclusions show no relationship to mineralization, but Type 2a inclusions do. They are most abundant in the Carnmenellis granites and least abundant in Dartmoor. This is consistent with published fluid inclusion data for vein quartz and cassiterite referred to in the Introduction; the fluids responsible for main-stage mineralization generally have the character of a Type 2a inclusion.

It therefore seems probable that, although the chemistry of the granites is very similar, their associated fluids varied during their final stages of evolution. The generation of saline fluids was *not* associated with extensive Sn-W-Cu mineralization. At present it is not clear whether these fluids represent the same stages of evolution in the separate granites or for instance whether the less saline assemblages in the Bodmin and Carnmenellis granites are indicative of later influx of dilute (perhaps meteoric) fluids. However it is clear that those granites with a dominant assemblage of Type 2a inclusions are more favourable as regards Sn-W-Cu mineralization.

The other major feature emerging from our data is that within these granites areas of higher *total* inclusion abundance can often be correlated with areas of mineralization. In addition these areas of increased fluid inclusion abundance are often more extensive than the actual areas of mineralization. This could indicate that the fluids responsible for hydrothermal mineralization were able to penetrate the granite well beyond the confines of the visible mineralization. Yermakov (1966) has formulated the concept of the 'steam aureole' or 'steaming-through aureole', whereby fluids causing mineralization are able to migrate away from the channelway and pervade the surrounding, solid rock. These fluids presumably migrate via microfractures and may be trapped as fluid inclusions. They may well be unable to alter the host rock (e.g. granite) but may form distinctive fluid inclusion assemblages beyond the visible lithological or geochemical anomalies in the rocks. This is presumably what is seen in the SW England granites.

The rare occurrence of inclusions containing liquid CO_2 at two localities in SW England is especially relevant in the context of mineral exploration because at both localities extensive vein swarms carrying tungsten mineralization are known to occur. The origin of these CO_2-bearing fluids is unknown but the association of such fluids and tungsten mineralization elsewhere in the world is well established (Higgins, 1980). It is, however, emphasised that Type 5, CO_2-liquid bearing are not always associated with tungsten deposits in SW England. Fluid inclusions associated with the Cligga Sn-W-Cu deposit, for example, have been extensively studied by Jackson et al. (1977) and Charoy (1979) neither of whom were able to detect CO_2 in the inclusions even during cooling studies.

SUMMARY AND CONCLUSIONS

Fluid inclusion populations in SW England granites provide a record of the complexity and episodic nature of hydrothermal events in the area.

Low temperature, Type 1 inclusions represent the final phase of hydrothermal activity, related to kaolinisation of the granite. On a broad, inter-pluton scale the proportion of moderate to high temperature Type 2 inclusions correlates with the extent to which each pluton is mineralized. ·

Halite-bearing, Type 3 inclusions are unrelated to mineralization but overall show a distinct relationship to the texture of the granite. The land's End and Dartmoor granite can be distinguished from the Bodmin and Carnmenellis granites on this basis, though the reasons for this distribution are unclear. Perhaps they represent two separate though petrochemically similar phases of intrusion with different hydrothermal systems associated with them.

Type 4 gas-rich inclusions show no variation between plutons, but do demonstrate that the hydrothermal phase did in fact boil at stages during its evolution.

Type 5 CO_2-bearing fluid inclusions are only found associated with two W-bearing vein swarm deposits. In view of the known association with tungsten deposits elsewhere in the world, and their extremely rare occurrence in SW England it is recommended that future finds be viewed with interest as indicators of the proximity of potential ore deposits of tungsten.

Thus fluid inclusion petrography does hold some promise as a tool in mineral exploration in this region. The overall abundance of the fluid inclusion population is often effective at distinguishing areas within a particular pluton where hydrothermal activity is pronounced. However, it is not possible to compare abundances between different plutons because each probably developed its own particular hydrothermal system.

It is believed that routine fluid inclusion petrography and abundance determinations could become part of general exploration strategy for Sn-W-Cu deposits in granitic areas elsewhere in the world especially during the reconnaissance and target selection stages of exploration. The methods are simple and rapid to use and should be considered a routine part of normal petrographic examination of granite samples.

Acknowledgements. This work was jointly funded by European Economic Communities as part of their R & D programme on Primary Raw Materials and by the Natural Environment Research Council. DHMA gratefully acknowledges the support provided by these organizations during the tenure of a post-doctoral research assistantship at Imperial College.

REFERENCES

Alderton, D.H.M.: The geochemistry of mineralisation at Pendarves, and other Cornish areas. Unpubl. PhD thesis, University of London (1976)

Alderton, D.H.M., Rankin, A.H.: Fluid inclusion studies in the St. Austell granite. (Jl. Geol. Soc. Lond., 140, 297-310 (1983)

Alderton, D.H.M., Sheppard, S.M.F.: Chemistry and origin of thermal water from southwest England. Trans. Instn. Min. Metall. (sect. B: Appl. earth Sci.) 86, B191-194 (1977)

Charoy, B.: Definition et importance des phenomènes deuteriques et des fluides associes dans les granites, consequences metallogeniques. Science Terre, Nancy, Mem. 37, 364 (1979)

Chivas, A.T., Wilkins, R.W.T.: Fluid inclusion studies in relation to hydrothermal alteration and mineralization at Koloula porphyry copper prospect. Guadalcanal. Econ. Geol. 72, 153-169 (1977)

Dangerfield, J., Hawkes, J.R.: The Variscan granites of south-west England: additional information. Proc. Ussher Soc. 5(2), 116-120 (1981

Dines, H.G.: The metalliferous mining region of southwest England. Mem. Geol. Surv. U.K. 2 vols, HMSO (1956)

Edmonds, E.A., McKeown, M.C., Williams, M.: British regional geology: southwest England (fourth edition). HMSO, London (1975)

Evans, A.M., Haslam, H.W., Shaw, R.P.: Porphyry style copper-molybdenum mineralisation in the Ballachulish igneous complex, Argyllshire, with special reference to the fluid inclusions. Proc. Geol. Ass. 91, (1 & 2), 47-51 (1979)

Higgins, N.C.: Fluid inclusion evidence for the transport of tungsten by carbonate complexes in hydrothermal solutions. Can. J. Earth Sci. 17, 823-830 (1980)

Jackson, N.J., Moore, J.McM., Rankin, A.H.: Fluid inclusions and mineralization at Cligga Head, Cornwall, England. Jl. geol. Soc. Lond. 134, 343-349 (1977)

Jackson, N.J., Halliday, A.N., Sheppard S.M.F., Mitchell, J.G.: Hydrothermal activity in the St Just mining district, Cornwall. In: Metallization associated with acid magmatism, Evans, A.M. (ed) John Wiley and Sons, New York, 385, 137-179 (1982)

Moore, J.McM.: Mineral zonation near the granite batholiths of south-west and northern England and some geothermal analogues. In: Metallization associated with acid magmatism. Evans, A.M. (ed) John Wiley and Sons, New York, 385, 229-241 (1982)

Rankin, A.H., Alderton, D.H.M.: Fluid inclusion studies on mineralized granites of the British Isles: an assessment of their use in the exploration for mineral deposits associated with granitic rocks. Final Report, Contract 041 MPP UK 168 p. EEC R & D programme on 'Primary Raw Materials' (1982)

Rankin, A.H., Alderton, D.H.M., Thompson, M., Goulter, J.E.: Determination of uranium: carbon ratios in fluid inclusion decrepitates by inductively-coupled plasma emission spectroscopy. Miner. Mag. 46, 179-186 (1982)

Roedder, E.: Fluid inclusions as tools in mineral exploration. Econ. Geol. 72, 503-525 (SEG distinguished lecture in scientific research) (1977)

Sheppard, S.M.F.: The Cornubian batholith, SW England: D/H and $^{18}O/^{16}O$ studies of kaolinite and other alteration minerals. Jl. geol. Soc. Lond. 133, 573-591 (1977)

Simpson, P.R., Brown, G.C., Plant, J., Ostle, D.: Uranium mineralization and granite magmatism in the British Isles. Phil. Trans. R. Soc. Lond. A291, 385-412 (1979)

Sorby, H.C.: On the microscopical structure of crystals, indicating the origin of minerals and rocks. Q. J. geol. Soc. London 14, 453-500 (1858)

Yermakov, N.P.: Use of gas-liquid inclusions in prospecting and exploration for postmagmatic ore deposits and blind ore bodies. Sovetskaya Geologiya 9, 77-90 (in Russian, translated in International Geology Review 9 (7), 947-956, listed as P P Ermakov) (1966)

Received: August 30, 1982
Accepted: February 16, 1983

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Mineral.Deposita 18, 349-363 (1983)

MINERALIUM
DEPOSITA

Caractère Epigénétique-Etranger des Gîtes Filoniens Pb-Zn (Ba-F) du District du Bord Sud du Synclinorium de Dinant (Belgique)

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Numerous vein mineralizations occur in the carbonate series of the Middle and Upper Devonian located in the Pb-Zn (F-Ba) metalliferous district of the South border of the Dinant Synclinorium. A regional lithogeochemical study (major and trace elements) of the Givetian limestones reveal the low potential of heavy metals in these platform sediments. These results are confirmed by the distribution of 13 elements present in a vein mineralization and its close surrounding. Finally, the comparison of the isotopic composition of the lead in the galenas of the vein mineralization and the traces of lead in the host rocks add decisive important arguments. These results seem to be sufficient to reject the hypothesis of the origin of the metals by lateral secretion and are in favor of an "epigenetic-foreign" character for these mineralizations.

De nombreux indices et anciennes exploitations de faible tonnage pour Pb-Zn-Ba-F s'observent dans les séries carbonatées du Dévonien moyen et supérieur du SW du Synclinorium de Dinant où elles délimitent un district métallifère. Une étude lithogéochimique régionale des calcaires givétiens montre le faible potentiel métallifère de ces sédiments de plateforme. Ces résultats sont confirmés par l'étude de la distribution de 13 éléments présents dans un filon et son encaissant immédiat. Enfin la comparaison des compositions isotopiques du Pb des galènes du filon et du Pb en trace dans les calcaires encaissants apporte des arguments décisifs. Ces résultats sont suffisants pour rejeter l'hypothèse de l'origine des métaux par sécrétion latérale et militent en faveur du caractère "épigénétique-étranger" de ces minéralisations.

I. INTRODUCTION

Les relations systématiques généralement observées entre les concentrations métallifères et les milieux rocheux au sens large constituent des guides logiques en exploration et les bases de toutes typologies. Au delà de ces relations figées, les processus génétiques peuvent cependant être reconstitués.

L'élaboration de modèles génétiques cohérents, but ultime de la métallogénie, comporte la reconstitution des différentes étapes qui, de l'aval vers l'amont, sont le milieu de dépôt, le transport et la source des métaux. De cette trilogie, c'est le problème de la source qui est le plus difficile à aborder car le plus éloigné des manifestations du dépôt (Routhier, 1967).

A ce sujet, la connaissance du degré de familiarité (Routhier, 1969, 1980) du contenu des minéralisations par rapport à leurs terrains encaissants constitue un guide majeur dans la recherche de la source des éléments présents dans le corps minéralisé.

La présente étude a pour principal objectif d'envisager certains aspects de ce problème, et d'établir les relations entre les minéralisations filoniennes du bord sud du Synclinorium de Dinant et l'ensemble des terrains sédimentaires formant leur cadre géologique.

L'évaluation du degré de familiarité de ces minéralisations par rapport aux roches encaissantes s'appuiera d'abord sur l'étude régionale de la distribution des éléments majeurs et en traces dans ces dernières. Une étude des profils de distribution des mêmes éléments présents dans un filon plombo-zincifère et son encaissant immédiat permettra ensuite d'écarter l'hypothèse d'une origine des métaux par sécrétion latérale sensu stricto. Une étude isotopique comparative du plomb des galènes du filon et du plomb en traces dans les sédiments situés à proximité immédiate confirmera les observations précédentes et permettra, vu la convergence des arguments, de conclure au caractère étranger du contenu du corps minéralisé.

La comparaison de ces résultats isotopiques avec ceux déjà publiés (Cauet et al., 1982; Herbosch et al., 1983) permettra enfin d'étendre cette conclusion à l'ensemble des minéralisations filoniennes du bord sud du Synclinorium de Dinant.

II. CONTEXTE GEOLOGIQUE ET METALLOGENIQUE

De nombreux indices et anciennes exploitations de faible tonnage en Pb-Zn-Ba-F sont connus depuis longtemps et délimitent au sud-ouest du Synclinorium de Dinant un district métallifère (de Magnée, 1967; Bartholomé et al., 1979) d'axe est-ouest s'étendant sur une centaine de kilomètres en longueur et une dizaine de kilomètres en largeur, depuis Beaumont à l'ouest jusqu'à Bomal à l'est (Fig.1). On y observe deux types de minéralisations:

- des amas et disséminations d'apparence stratiforme liés aux phénomènes de dolomitisation des récifs frasniens appartenent aux dômes anticlinoriaux de la partie médiane du Synclinorium de Dinant (Massifs de Beaumont et de Philippeville). Des filons sont également présents et semblent liés à ces amas. Ces minéralisations n'ont, à ce jour, encore jamais fait l'objet d'études métallogéniques détaillées;
- des filons transverses recoupant les séries carbonatées du Givétien et du Frasnien, plus rarement du Couvinien. Ces derniers, également peu étudiés jusqu'ici, recoupent soit la bordure méridionale du Synclinorium de Dinant, soit les brachyanticlinaux secondaires à noyaux de calcaire givétien qui accidentent sa partie centrale.

Ce sont ces dernières minéralisations de type épigénétique qui font l'objet du présent travail.

Il s'agit de minéralisations discordantes liées à un grand nombre de petites failles transversales et quasi verticales de direction moyenne NNW-SSE. Les filons, de faible épaisseur (0,1-0,9 m), sont le plus fréquemment associés aux calcaires givétiens situé de part et d'autre de la localité de Givet (Fig.1). La paragenèse est simple: marcasite, galène, sphalérite, barytine, fluorine, calcite, dolomite, quartz. L'ensemble de ces minéralisations se distingue par l'absence de structures collomorphes à rubanées à schalenblende et de minéraux accessoires de nickel, bien connus dans l'important district de Bleiberg-Moresnet situé au nord-est de la Belgique (de Magnée, 1967). Par contre, la barytine est localement abondante (Vierves, Ave et Auffe). Les bandes calcaires de la partie centrale du district recèlent également des gîtes à fluorine exclusive (Calembert et Van Leckwijck, 1942 dont les liens avec les concentrations plombo-zincifères sont inconnus.

Malgré leurs nombreux caractères géologiques communs, ces minéralisations ne sont pas similaires du point de vue de la composition isotopique du

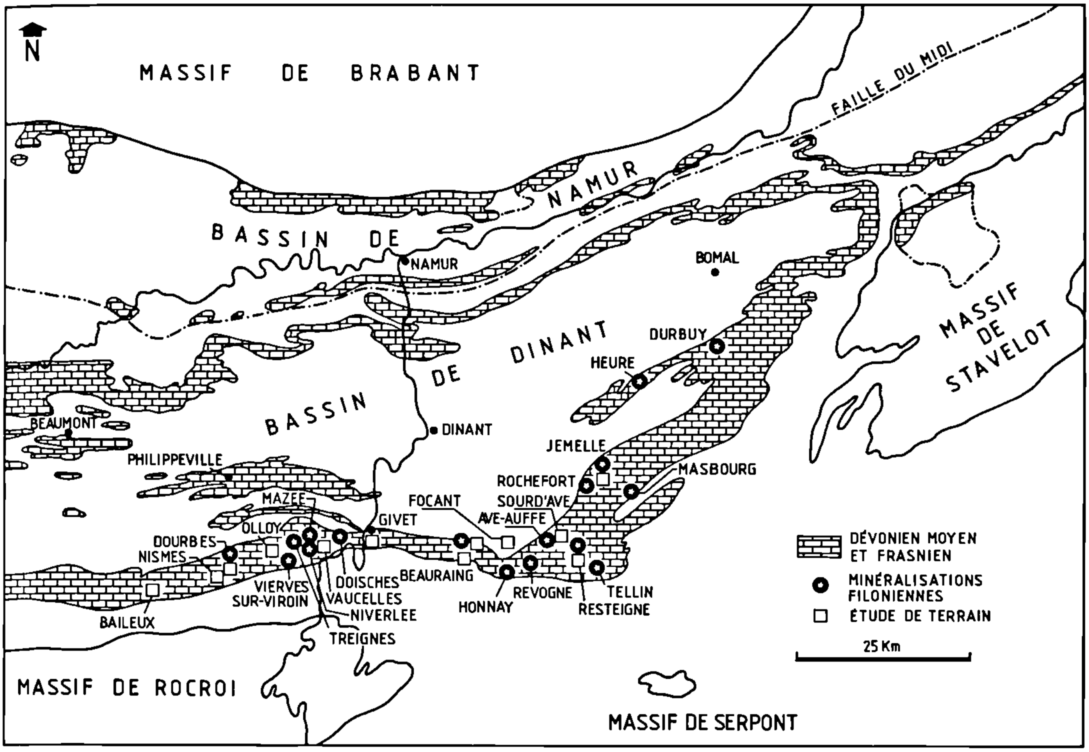

Fig.1. Localisation des principales minéralisations filonienne plombo-zincifères du bord sud du Synclinorium de Dinant

plomb des galènes: Cauet et al.,(1982) ont montré qu'une partie de ces dernières (Beauraing, Revogne, Resteigne, Tellin, Jemelle au "Bois de Lamsoule", Masbourg) présentent des compositions isotopiques similaires et significativement différentes des autres minéralisations filoniennes du district (Fig.1). Elles définissent un petit groupe homogène, à la fois isotopiquement (groupe 2 de la Fig.2) et géographiquement (est de Givet, Fig.1).

C'est dans cette région que le Givétien, épais d'environ 500 mètres, a été divisé sur base lithostratigraphique en trois formations: Formation de Trois-Fontaines à la base, Formation du Mont d'Haurs et enfin Formation de Fromelennes au sommet (Errera et al., 1972). Chacune de ces Formations correspond à la répétition d'un phénomène simple se déroulant en quatre phases, avec prédominance d'une phase à sédimentation essentiellement lagunaire et continentale ou de sebkha (Errera,1975).

L'importance prise par cette dernière phase dans l'ensemble de la sédimentation carbonatée, tout particulièrement dans la Formation de Fromelennes, a généralement conduit à l'idée que cette Formation pourrait constituer la source des métaux pour les minéralisations de la région. Dans ce contexte, les phénomènes de compaction et de diagenèse seraient à l'origine de l'expulsion physique et chimique de l'eau intersticielle présente dans les systèmes poreux de ces sédiments et constitueraient ainsi le principal facteur responsable de la migration des fluides. Ces derniers peuvent alors être piégés dans des formations perméables relativement proches ou lorsque celles-ci n'existent pas ou sont inaccessibles, rester associés sous forme d'un aquifère lié aux sédiments d'origine. Dans le détail, ces mécanismes sont évidemment très complexes et concernent également les circulations des eaux météoriques, des eaux de compac-

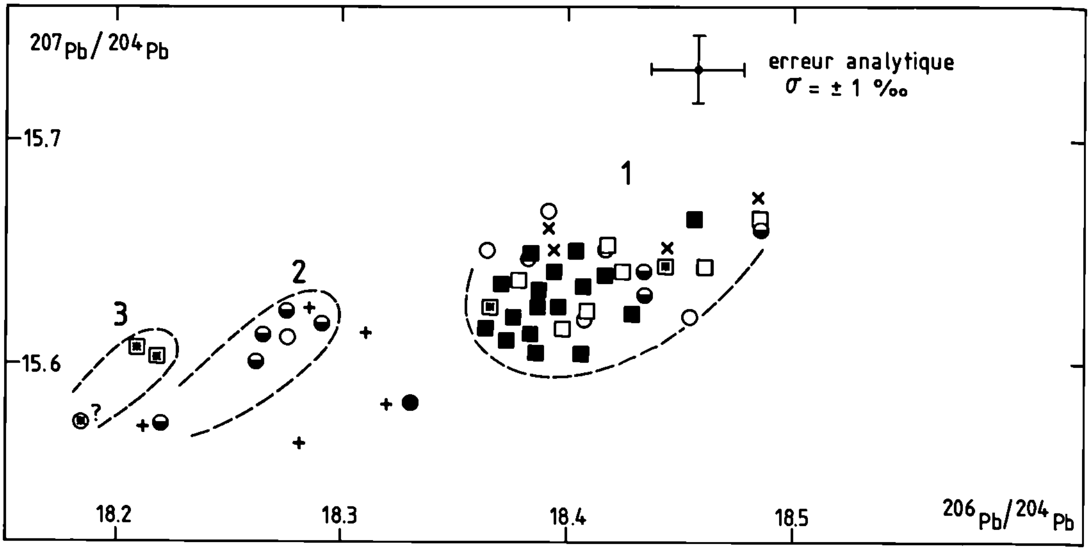

Fig.2. Diagramme $^{207}Pb/^{204}Pb$ - $^{206}Pb/^{204}Pb$ pour les galènes des minéralisations. In Cauet et al., 1982

tion expulsées par tassement des formations argileuses suivant des circuits paléohydrologiques dont il manque encore de nombreuses données pour leur reconstitution (de Magnée, 1967; Bartholomé et Gérard, 1976).

De tels modèles génétiques faisant soit appel au blocage rapide des métaux sur une bordure littorale et dans des conditions climatiques particulières (développement d'une sebkha ou d'une plaine supratidale en climat tropical), ou bien faisant appel à des circulations paléohydrologiques de saumures ont déjà été invoqués de nombreuses fois pour expliquer certains gisements d'origine sédimentaire (Bush, 1970; Dozy, 1970; Renfro, 1974; Lagny, 1975; Routhier, 1980; etc. ...).

La découverte, il y a une dizaine d'années, d'un niveau d'anhydrite dans la Formation de Fromelennes au sondage de Focant (Graulich et al., 1967) effectué à proximité immédiate de la zone étudiée (Fig.1), ne pouvait que renforcer cette hypothèse et rendre compte du caractère sursalé des fluides évoluant à partir d'eaux marines connées par filtration osmotique (Dunham, 1970) ou à partir d'eaux météoriques par dissolution des évaporites. D'autres faciès évaporitiques ont également été reconnus au Givétien mais sont localisés dans la prolongation septentrionale du Bassin de Namur (Van Tassel, 1960); Legrand, 1962; Coen-Aubert et al., 1980). Il faut également noter l'association d'indices de galène avec des faciès récifaux et lagunaires du Frasnien (Pel et Monseur, 1979).

En conclusion, les sédiments givétiens de la région étudiée se sont déposés en climat tropical sur une plate-forme carbonatée peu profonde et subsidente essentiellement dominée par des environnements lagunaires et de sebkhas évaporitiques ayant pu constituer un métallotecte pour certains métaux lourds dont le Pb et le Zn.

Dans le but de vérifier ces hypothèses, une série de coupes situées dans l'axe du district (Fig.1) ont été étudiées du point de vue sédimentologique et géochimique.

III. ETUDE SEDIMENTOLOGIQUE ET LITHOGEOCHIMIQUE

III.I *Sédimentologie*

L'analyse sédimentologique fine permet de définir pétrographiquement plus de 20 microfaciès essentiellement carbonatés caractérisant des milieux de dépôts comparables à ceux que l'on rencontre aujourd'hui dans les plateformes carbonatées (Purser, 1980).

Ces différents paléomilieux de sédimentation permettent de définir un profil paléogéographique théorique; ils s'étendent du domaine marin ouvert le plus externe et subtidal avec développement d'épisodes récifaux, puis dans les domaines intertidaux caractérisés par plusieurs hauts-fonds oolitiques et les domaines subtidaux internes essentiellement lagunaires, et enfin dans les zones les plus internes du domaine supratidal où se développent de nombreux platiers algaires accompagnés de dépôts parfois émergés de laminites ayant subi une diagenèse dans les eaux phréatiques ou vadoses.

En tenant compte de la succession des différents microfaciès ainsi que de la position des différentes coupes étudiées, on constate que la sédimentation carbonatée du Givétien s'est effectuée dans un domaine peu profond relativement limité sur la partie interne de la plateforme en relation directe avec la mer ouverte. L'environnement le plus représentatif est celui d'un lagon (Préat et Boulvain, 1982). Dans ce milieu, pouvant être particulièrement abrité, les eaux sont alors confinées et au niveau du fond les sédiments sont réducteurs. L'extension des faciès supratidaux y est relativement faible et leur isolement de l'influence marine jamais suffisamment durable pour que de véritables précipités salins s'y développent. En conséquence, aucun faciès évaporitique franc, ni même aucune dolomie primaire n'ont pu être mis en évidence lors de cette étude sédimentologique.

Tableau 1. Teneurs moyennes des calcaires givétiens

	GROUPE DE GIVET				
	FORMATION TROIS-FONTAINES			FORMATION FROMELENNES	
	RESTEIGNE* N=99	VAUCELLES N=75	OLLOY N=83	S. D'AVE N=40	DOURBES N=87
(%)					
CaO	45.3±8.5	50.3±3.0	51.3±4.0	51.7±4.5	55.0±3.0
MgO	2.1±1.6	2.0±0.7	1.7±0.5	0.8±0.2	1.2±1.0
K_2O	1.0±0.8	0.4±0.3	0.5±0.6	0.5±0.4	0.2±0.3
Al_2O_3	2.4±2.4	1.2±0.7	1.2±1.0	1.1±1.2	0.6±0.7
SiO_2	8.0±7.2	4.3±2.0	3.9±2.7	4.5±4.1	2.0±2.1
Fe_2O_3	1.0±0.7	0.5±0.3	0.5±0.4	0.5±0.4	0.3±0.6
(ppm)					
Mn	378±350	170±122	275±149	180±140	160±154
Sr	298±67	250±92	244±90	308±49	240±54
S	4269±2714	-	-	1607±1286	-
Pb	17±17	20±30	-	8±4	-
Zn	22±47	11±19	21±26	17±33	8±7

* Formation de Trois-Fontaines et du Mont d'Haurs pro-parte

Tableau 2. Comparaison des teneurs moyennes en Pb et en Zn de différentes roches carbonatées

	Pb	Zn
CLARKE : calcaires de plateforme (TUREKIAN et WEDEPOHL, 1961)	9	20
"world" average limestone (WOLF et al, 1967, table II)	8	26
MASSIF SCHISTEUX RHENAN : roches carbonatées dévono-carbonifère (HEINRICH et al, 1980)	11	50
SYNCLINORIUM DE DINANT :		
- Formation de Trois-Fontaines, Givétien, Resteigne, (cette étude) n = 99 (1)	17	22
- Formation de Fromelennes, Givétien, Sourd d'Ave, (cette étude) n = 40 (1)	8	17
- Roches carbonatées Tn3-VA Salet - Pont-de-Bonne - Martinrive (VAN ORSMAEL et al, 1980) (2) n = 236	2	17
- calcaires n = 153	2	22
- dolomies n = 56	1	14
BASSINS DE LA VESDRE ET NAMUR		
- Calcaires de Schmalgraf Carbonifère (SWENNEN et al, 1981) n = 21 (2)	10	77
- Calcaires de Plombières Carbonifère (SWENNEN et al, 1981) n = 101 (2)	3	44
- Dolomies (type Sovet) Carbonifère (VAN ORSMAEL et al, 1980) (2)		
- bassin Vesdre	16	146
- bassin Namur	28	213
- Calcaires frasniens (FRIEDRICH et SCHEPS, 1981) (1)		
- récifaux n = 110	7	65
- noduleux n = 43	20	98

(1) analyses sur roches totales

(2) analyses de la phase soluble à l'acide

III.2. *Lithogéochimie*

Plus de 300 échantillons calcaires appartenant aux coupes étudiées (Resteigne, Sourd d'Ave, Olloy, Vaucelles, Nismes, Dourbes, Fig.1) ont été analysés en roche totale pour 13 éléments majeurs, mineurs et en traces: SiO_2, Al_2O_3, Fe_2O_3 total, MgO, CaO, Na_2O, K_2O, Mn, Sr, S, P, Pb et Zn (Tableau I Tous ces éléments ont été analysés par spectrofluorescence des rayons X, par calibration linéaire sur cru pour les éléments majeurs (Leake et al., 1969) et par une méthode mathématique de correction des effets de matrice pour les traces (Vie Lesage et al., 1979). L'étalonnage est basé dans les deux cas sur des standards internationaux.

Ces analyses correspondent à un échantillonnage particulièrement dense de l'ordre du mètre, à raison d'un échantillon tous les 3 ou 4 bancs environ, ce qui est suffisant pour définir un fond continu régional et mettre en évidence d'éventuels niveaux porteurs d'anomalies en métaux lourds.

L'ensemble des résultats (Tableau I) révèle d'une manière générale l'homogénéité géochimique des sédiments étudiés, qui se marque par l'absence de variations importantes des teneurs au sein de chacune des Formations, aussi bien pour les éléments majeurs que ceux en traces. On notera également la très grande pureté de ces calcaires dont les teneurs moyennes en CaO dépassent souvent 50%. En ce qui concerne le Pb et le Zn, on remarque immédiatement les faibles teneurs moyennes, la faible amplitude de leurs variations:

σ_{Pb} = 17 ppm, σ_{Zn} = 47 ppm pour la coupe de Resteigne

σ_{Pb} = 4 ppm, σ_{Zn} = 33 ppm pour la coupe du Sourd d'Ave

ainsi que l'absence d'anomalies notables, les valeurs maximales ne dépassant pas 100 ppm pour le Pb et 200 ppm pour le Zn. Les teneurs en soufre, assez élevées pour des calcaires, sont nettement plus fortes dans la Formation de Trois-Fontaines ($\bar{x}$ = 4270 ppm) ce qui s'explique par des teneurs en S systématiquement plus élevées dans les faciès lagon qui y représentent l'essentiel de la sédimentation.

On constate donc qu'en ce qui concerne les métaux lourds, leurs teneurs moyennes sont faibles dans l'ensemble des coupes étudiées: elles sont inférieures au Clarke pour le Zn, égales ou légèrement supérieures au Clarke pour le Pb (Tableau II). Il en est de même si on les compare aux valeurs extrêmement bien documentées concernant les calcaires du Massif Schisteux Rhénan (Heinrich et al., 1980; Tableau II), dont les Ardennes constituent le prolongement occidental. Malgré les approches analytiques différentes, la comparaison des teneurs observées dans les calcaires givétiens (analyse sur roche totale) avec celle des roches carbonatées du Dinantien (analyse de la phase soluble à l'acide) et du Frasnien (analyse sur roche totale) met en évidence le faible fond géochimique en Pb et en Zn du Synclinorium de Dinant et en particulier du Givétien de son bord sud.

Ces observations, purement descriptives, permettent déjà de conclure au faible potentiel métallogénique des roches givétiennes du bord sud du Synclinorium de Dinant.

Une analyse factorielle en mode R a été effectuée sur les données des deux coupes-types de Resteigne (Fig.3) et du Sourd d'Ave dans le but d'élucider les processus géologiques fondamentaux qui contrôlent la distribution des éléments dans ces calcaires. Les résultats, assez semblables pour les deux coupes, montrent que le comportement géochimique du Pb et du Zn ne semble pas obéir à des lois simples, leurs communautés assez faibles ($h^2 < 0.6$) témoignent de l'importance des phénomènes aléatoires parmi les processus qui contrôlent leur distribution. Ces faits s'expliquent et par les très faibles teneurs observées et par l'absence de variations importantes.

Néanmoins dans la Formation de Trois-Fontaines (Fig.3), le Pb co-varie systématiquement avec le Mn et plus faiblement avec le Zn (facteur III). Dans la Formation de Fromelennes, ces trois éléments sont regroupés au sein d'un même facteur s'opposant fortement au Mg, traduisant leur expulsion lors des phénomènes de dolomitisation qui existent localement.

L'opposition avec le S (facteur III), ainsi que la présence d'un facteur IV s'identifiant avec la diagenèse des sulfures en milieu réducteur conduisant à la seule formation de pyrite, sont révélatrices de la pauvreté en métaux lourds de l'environnement sédimentaire.

L'interprétation de l'analyse factorielle montre clairement que si les conditions nécessaires au "piégeage" des métaux lourds existaient (milieu anaérobique à sédimentation ralentie), par contre la disponibilité en Pb et en Zn sous forme d'ions en solution n'existait pas.

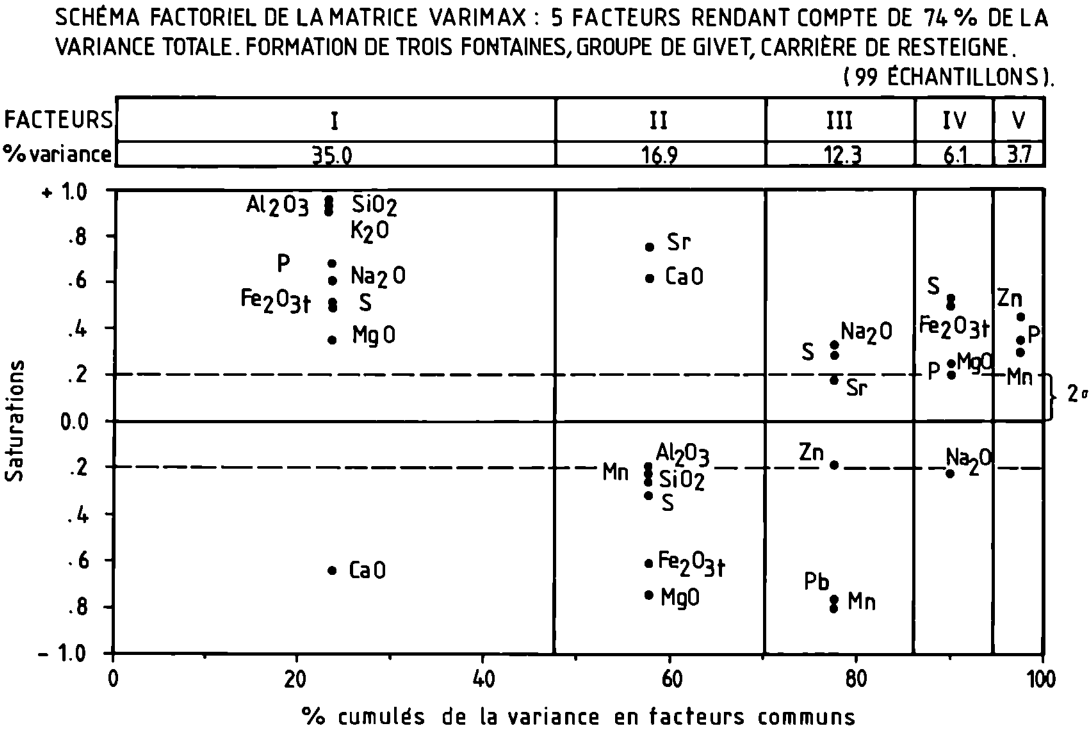

Fig.3. Schéma factoriel de la matrice varimax. Formation de Trois-Fontaines, Resteigne

IV. ETUDE GEOCHIMIQUE ET ISOTOPIQUE D'UN FILON

Il s'agit d'un filon de faible épaisseur (10 à 20 cm), visible sur une quinzaine de mètres dans les deux niveaux supérieurs de la carrière de Resteigne, où il présente une direction générale N45°E et un pendage 45°SE nettement sécant par rapport aux calcaires de la Formation de Trois-Fontaines en succession normale. I est essentiellement constitué d'hydroxydes de fer et de manganèse et on y observe localement des rognons et mouchetures de galène.

IV. I. Etude géochimique d'un profil filon-encaissant

Les profils de distribution de 13 éléments ont été établis pour le filon et son encaissant carbonaté immédiat sur une longueur voisine de 15 mètres et dans un même banc recoupé par le filon. Les figures 4 et 5 représentent en ordonnée la gamme des teneurs observées pour chacun des éléments analysés le long du profil filon-encaissant, ainsi que la moyenne arithmétique des teneurs ($\bar{x}$) pour l'ensemble des calcaires analysés dans la coupe de Resteigne (Tableau 2). Cette moyenne définit ainsi pour chacun de ces éléments son fond continu.

L'examen de ces figures montre immédiatement que la longueur du profil est bien suffisante, aussi bien vers l'ouest que vers l'est, puisqu'on retrouve à quelques mètres seulement les fonds continus de tous les éléments analysés. De plus, une série d'anomalies positives apparaît très nettement pour les éléments suivant

- le Pb et le Zn présentent une migration du filon vers l'encaissant, les pics étant surtout localisés dans les premiers mètres au-delà desquels on retrouve immédiatement les fonds continus

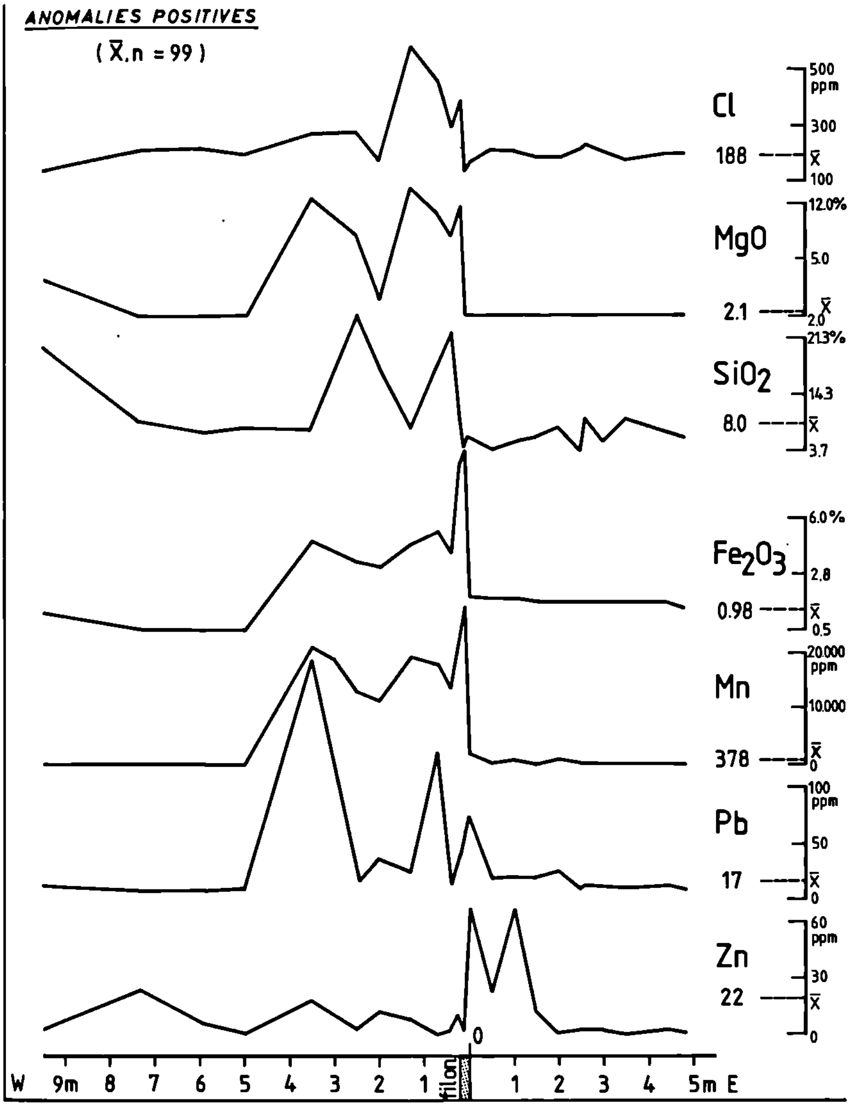

Fig.4. Profils de distribution du Zn, Mn, Fe_2O_3, SiO_2, MgO et Cl dans les calcaires encaissant le filon de Resteigne

- le Fe, Mn, Mg, Si et Cl présentent le même type de variations et délimitent ainsi sur plusieurs mètres de véritables halos accompagnant le filon. En ce qui concerne le Mn, les rapports pics sur fonds continus sont très élevés de sorte que cet élément pourrait représenter un excellent indicateur de minéralisation. Des anomalies négatives, indiquant un appauvrissement du filon et de son encaissant, s'observent pour le Ca, le Sr et le S. En ce qui concerne les deux premiers, leurs comportement s'explique facilement par des phénomènes de dolomitisation hydrothermale, par contre pour le soufre aucune explication n'a pu être trouvée. Les profils de distribution de K_2O, Al_2O_3 et P sont très semblables et ne montrent pas de relations évidentes avec ceux des éléments précédents. Remarquons également que les halos observés sont essentiellement développés à l'ouest du filon et sont donc dissymétriques. Malgré la localisation de cette partie ouest en

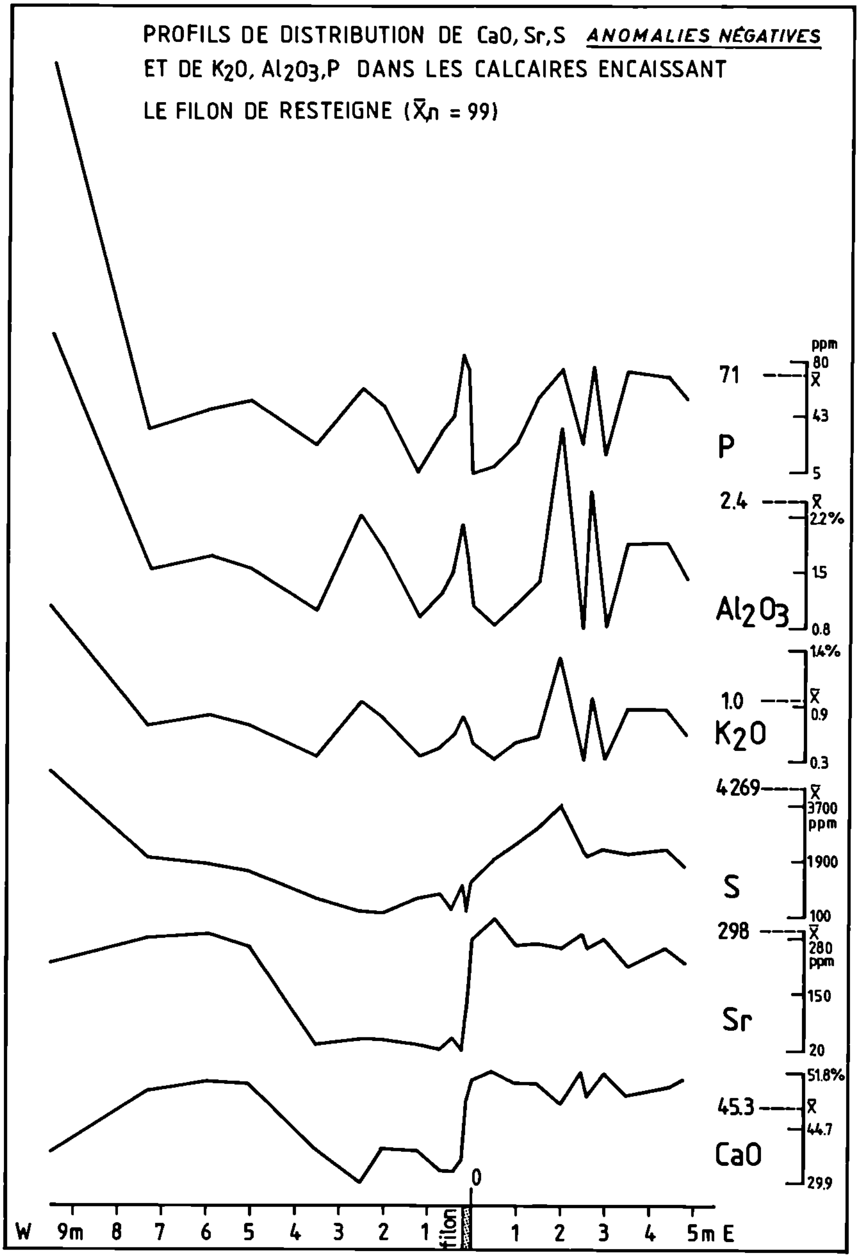

Fig.5. Profils de distribution de CaO, Sr, S, K_2O, Al_2O_3 et P dans les calcaires encaissant le filon de Resteigne

aval pendage et la possibilité d'altération météorique avec percolation des éléments les plus solubles, il nous semble que cette dissymétrie est primaire vu sa remarquable régularité pour tous les éléments y compris la silice (insoluble dans les conditions superficielles).

Une analyse factorielle effectuée sur ces données (malgré le faible nombre d'échantillons) fait apparaître quatre facteurs (Fig.6): le premier rend compte manifestement des phénomènes hydrothermaux tandis que les trois suivants sont identiques à ceux déjà identifiés sur la coupe de Res-

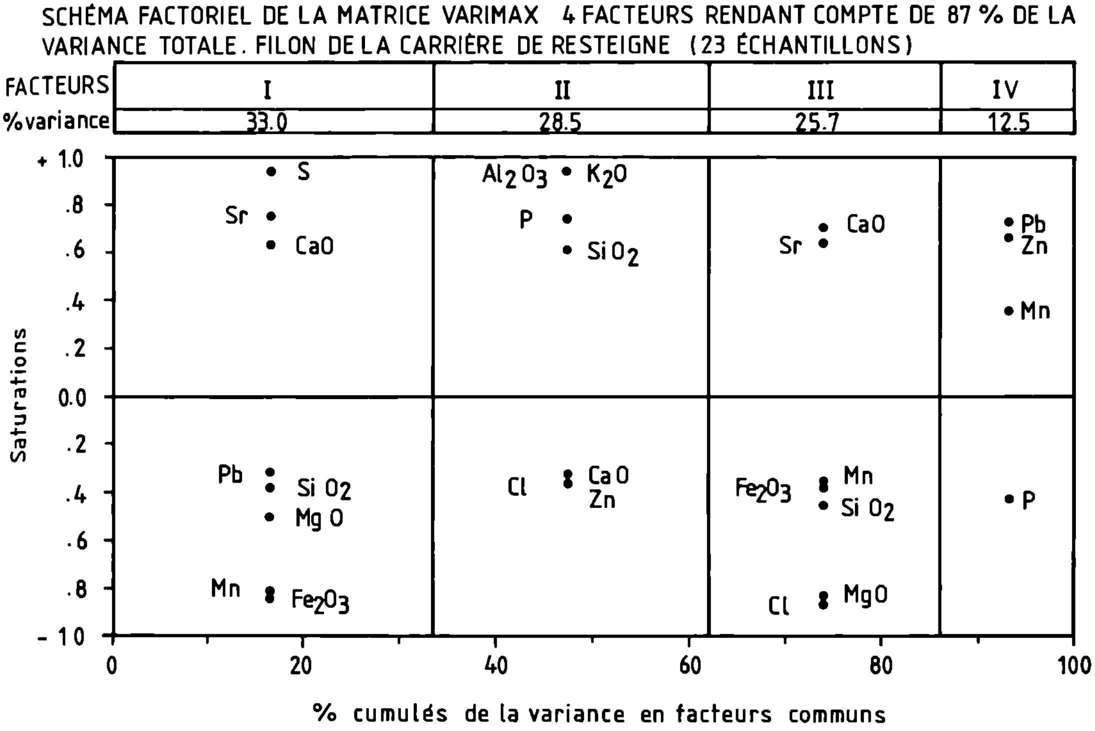

Fig.6. Schéma factoriel de la matrice varimax. Filon de Resteigne

teigne (facteurs I, II et III de la Fig.3) et correspondent à la roche saine. Le premier facteur, représentant 33 % de la variance totale, oppose les éléments fortements appauvris (CaO, Sr, S) dans le filon et son halo aux éléments enrichis (Pb, SiO_2, MgO, Fe_2O_3, Mn).

En conclusion, l'allure des profils et en particulier l'absence de zone de drainage (dépression par rapport au fond continu) à l'approche du filon semble exclure l'origine des métaux par sécrétion latérale sensu stricto.

IV. 2. *Géochimie isotopique du Pb*

L'évaluation du degré de familiarité de la minéralisation par rapport aux sédiments hôtes a également été approchée par une étude isotopique comparative du Pb des galènes de la minéralisation et du Pb en trace au sein des sédiments.

La mesure des compositions isotopiques du Pb de trois galènes du filon met en évidence son homogénéité isotopique (Fig.7). Les compositions isotopiques du Pb en roches totales ont également été mesurées sur trois échantillons lithologiquement représentatifs de l'encaissant du filon.

A la différence des galènes, une roche ne peut être considérée comme un système fermé vis-à-vis du Pb, sa composition isotopique évolue après sa formation suite à la désintégration de l'uranium présent in situ. Afin de mettre en évidence d'éventuelles filiations entre le Pb de la minéralisation et celui des roches, il convient dès lors d'effectuer des corrections afin de connaître leur composition isotopique au moment de leur formation. Ces corrections, fonction des teneurs en U, Pb des échantillons, sont cependant difficiles car ces éléments peuvent avoir migré, en particulier l'uranium qui est très mobile lors des phénomènes d'altération. Ces corrections, et par conséquent l'incertitude associée, ont beaucoup d'influence sur le rapport $^{206}Pb/^{204}Pb$ et extrêmement peu sur le rapport $^{207}Pb/^{204}Pb$.

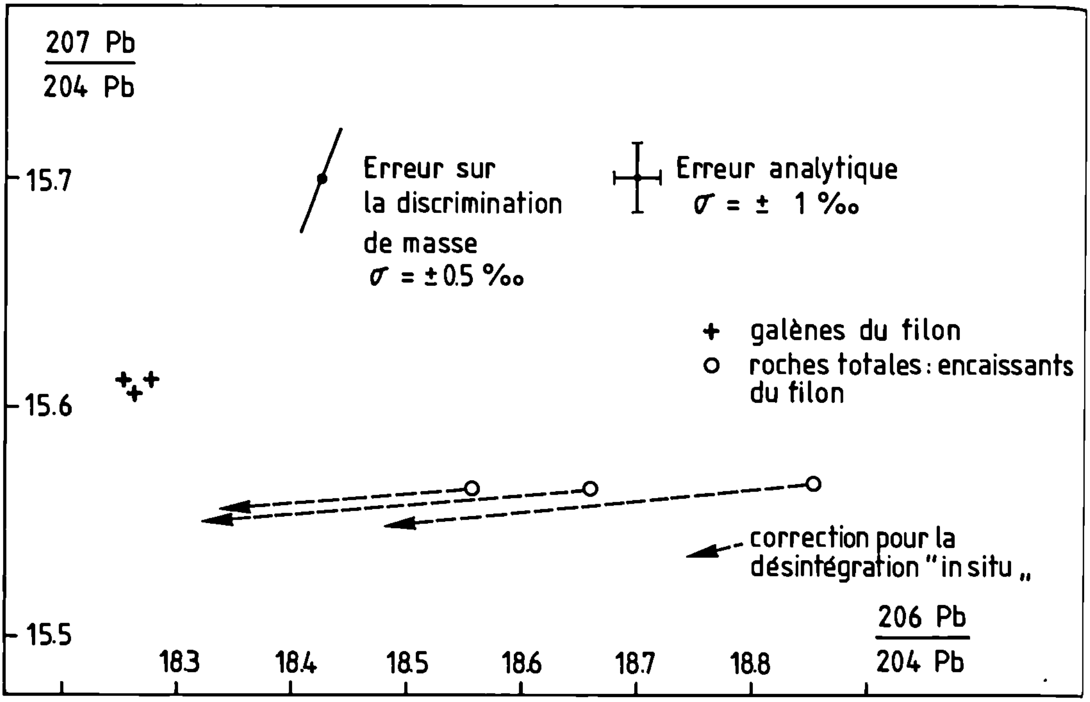

Fig.7. Géochimie isotopique de Pb du filon de Resteigne et de son encaissant

Relativement aux rapports $^{206}Pb/^{204}Pb$ de la minéralisation, les rapports $^{206}Pb/^{204}Pb$ des sédiments sont nettement plus élevés (Fig.7). Malgré l'incertitude sur la correction, il est fort probable que les rapports $^{206}Pb/^{204}Pb$ de ces sédiments devaient être plus élevés que ceux de la minéralisation à l'époque permo-triasique. L'hypothèse d'une sécrétion latérale à cette époque ou plus tard est donc exclue car dans ce cas les compositions isotopiques des galènes de la minéralisation devraient obligatoirement être plus radiogéniques. Bien plus, le fait d'avoir des rapport $^{207}Pb/^{204}Pb$ significativement différents entre minéralisation et sédiments hôtes rend impossible toute idée de filiation.

La source principale du Pb de la minéralisation de Resteigne ne se trouve certainement pas dans les sédiments encaissants (Formations de Trois-Fontaines et du Mont d'Haurs), ce qui exclut la possibilité de sécrétion latérale sensu lato.

IV. 3. Conclusions

L'allure des profils de distribution de 13 éléments dans un filon et son encaissant immédiat, ainsi que la comparaison des compositions isotopiques du Pb des galènes du filon et du Pb en trace dans les calcaires encaissants, permettent d'écarter l'hypothèse d'une origine des métaux du filon par sécrétion latérale, ce qui milite en faveur du caractère épigénétique-étranger de la minéralisation du filon de Resteigne

Vu les caractères minéralogiques et structuraux très semblables des autres filons présents dans ce district (Fig.1 ainsi que le très faible potentiel métallifère de l'encaissant carbonaté givétien (Tableaux 1 et 2), il nous semble possible de généraliser cette conclusion à tous les filons du district du bord sud du Synclinorium du Dinant.

V. CONCLUSIONS GENERALES

V.1. Résultats

L'étude sédimentologique montre que malgré la présence importante des environnements confinés et supratidaux, aucun faciès évaporitique n'est présent dans le Givétien des coupes étudiées. De plus, les phénomènes de dolomitisation y sont mineurs et secondaires.

L'analyse des éléments majeurs et en traces permet de conclure d'une part à la très grande pureté (CaO > 50%) et homogénéité de ces roches carbonatées et, d'autre part à leur faible potentiel métallogénique: les teneurs moyennes en Pb et Zn sont très proches, si pas inférieures à leurs Clarkes respectifs et les variations autour de leurs moyennes très faibles.

L'étude des facteurs contrôlant la distribution des éléments dans ces calcaires, effectuée par analyse factorielle en mode R, permet en outre de montrer quantitativement et objectivement que si les conditions nécessaires au piégeage des métaux lourds existaient (milieux lagunaires réducteurs à sédimentation ralentie), par contre la disponibilité en métaux lourds faisait défaut.

Compte tenu de la convergence de ces résultats, il apparaît fort peu probable que les calcaires givétiens du bord sud du Synclinorium de Dinant aient pu constituer la source des métaux des gisements filoniens qui leur sont cependant préférentiellement associés.

L'étude géochimique et isotopique des relations entre un filon minéralisé en galène et son encaissant calcaire permet d'écarter définitivement l'hypothèse d'une origine des métaux par sécrétion latérale. L'argument isotopique révèle, en particulier, l'impossibilité d'une filiation entre le Pb en trace dans les roches et celui des galènes, dont la composition isotopique moins radiogénique traduit nécessairement une autre provenance.

L'ensemble de tous ces résultats permet d'infirmer l'hypothèse de départ, à savoir les sédiments givêtiens en tant que métallotecte-source, et traduit le caractère épigénétique-étranger des minéralisations filoniennes affectant le Givétien du district du bord sud du Synclinorium de Dinant.

V. 2. Perspectives

Dans ce contexte, un modèle épigénétique-étranger peut être envisagé non seulement pour le Givétien mais d'une façon plus générale pour le Dévonien moyen et supérieur du bord sud du Synclinorium de Dinant qui s'est déposé sur la bordure méridionale d'une large plateforme s'étendant depuis le bord sud du Massif du Brabant jusqu'au moins Givet. Les sédiments de cette localité appartenaient probablement dès le Givétien et beaucoup plus certainement dès le Frasnien au talus continental assurant la transition entre les faciès de plateforme et ceux de bassin.

Dans ce cas, la présence d'évaporites à Focant pourrait présenter un intérêt particulier par sa position paléogéographique de bassin qui, si elle se confirme par l'étude sédimentologique en cours, rendrait compte de l'origine des saumures sur la bordure de la plateforme. Entraînés à de grandes profondeurs par les mouvements de subsidence, ces fluides pourraient alors migrer le long du talus en système relativement fermé sous forme d'aquifères longeant les discontinuités sédimentaires structurellement liées à l'évolution de la marge continentale. Ce sont les mouvements orogéniques qui, en rompant les conditions d'équilibre lithostatique établies au cours de la phase précédente, permettent l'ouverture du système et la remontée des fluides qui peuvent alors précipiter leurs métaux.

Un modèle basé sur une activité volcanique dévonienne peut également être envisagé pour expliquer l'origine d'une partie des minéralisations filoniennes du bord sud du Synclinorium de Dinant, celui-ci étant effectivement coupé de ses racines par un charriage important de 40 à 100 km suivant une direction septentrionale (Bless et al., 1980). La présence plus au sud et à l'est (Nord du Massif Armoricain, Massif Schisteux Rhénan) d'un volcanisme alcalin intra-plaque connu dès le Dévonien inférieur (Bebien et al.,1980) pourrait étayer cette hypothèse. Ceci permettrait également de rendre compte de la similitude des compositions isotopiques du Pb d'une partie des minérations de la région étudiée et de celles du Dévonien inférieur (Fig.2).

Afin de tester la validité de ces modèles, desétudes sédimentologiques et paléogéographiques devraient s'assurer que le sud de la région étudiée soit un équivalent possible de la zone rhéno-hercynienne bien connue plus à l'est dans la région de Marburg en Allemagne (Franke et al., 1978).

Remerciements. Cette étude a pu être réalisée grâce à l'aide financière de la C.E.E. (contrat n° 110-79-7 MPPB) et des Services Interministériels de la Politiques Scientifique (contrat MP/CE/6). Une partie des analyses ont été réalisées sur l'installation de Fluorescence X appartenant au Collectif Interuniversitaire de Géochimie Instrumentale, subventionné par le F.R.F.C. (convention n° 2.4521.76). L'un de nous (Cauet S.) bénéficie d'une bourse de recherche du F.N.R.S. Nos plus vifs remerciements à F. Boulvain, G. Ceuleneer et F. Alderson pour leur participation à l'étude de terrain.

BIBLIOGRAPHIE

Bartholomé, P., Ek, C., Batacchi, A., Catalono, M., Pellegrini, L.: Dossiers II. Lead and Zinc. Commission of the European Communities DGXII, vol. 1, 492 p., 1979

Bartholomé, P., Gérard, E.: Les gisements plombo-zincifères d'Engis, province de Liège, Belgique. Annales des Mines de Belgique, 11e livraison: 901-917 (1976)

Bebien, J., Gagny, Cl., Rocci, G.: La place du volcanisme dévono-dinantien dans l'évolution magmatique et structurale de l'Europe moyenne varisque au Paléozoïque. Mémoire du BRGM, 108, 213-225 (1980)

Bless, M.J.M., Bouckaert, J., Paproth, E.: Environmental aspects of some Pre-Permian deposits in N.W.Europe. Meded. Rijks. Geol.Dienst, 32-1, 3-13 (1980)

Bush, P.R.: Chlorid-rich brines from sabkha sediments and their possible role in ore formation. Trans. Inst. Min. Metal..(sect. B), 79, 137-144 (1970)

Calembert, L., Van Leckwijck, W.: Les gisements de fluorine belges et français, du bord méridional de Synclinorium de Dinant. Bull.Soc. Géol de Belgique, 65, 64-75 (1942)

Cauet, S., Herbosch, A., Weis, D.: Genetic study of belgian lead-zinc mineralizations in carbonate environments through lead isotopic geochemistry. Actes du Symposium sur les gîtes filoniens Pb, Zn, Ba, F du domaine varisque. Bull.BRGM (2 II, 329-341 (1982)

Coen-Aubert, M., Groessens, E., Legran R.: Les formations paléozoïques des sondages de Tournai et de Leuze. Bull.Soc.belge Géol. Paléont. Hydro 89, 241-275 (1980)

Dozy, J.J.: A geological model for the genesis of the lead-zinc ores of th Mississippi Valley, U.S.A. Trans. Inst. Min. Metall.(sect. B), 79, 163-170 (1980)

Dunham, K.C.: Mineralization by deep formation waters: a review. Trans. Inst. Min. Metall. (sect.B), 79, B127-136 (1970)

Errera, M.: La séquostratigraphie: développement théorique et applicatio au Givétien franco-belge. Thèse de doctorat. Université Libre de Bruxelles, 401 p. 1975

Errera, M., Mamet, B., Sartenaer, P.: Le Calcaire de Givet et le Givétien à Givet. Bull. Inst. Roy. Sci. Nat. Belgique, 48, 1-59 (1972)

Franke, W., Eder, W., Engel, W., Langestrassen, F.: Main aspects of geosyclinal sedimentation in the Rhenohecynian zone. Z.dt.Geol. Ges. 129, 201-216 (1978)

Friedrich, G., Scheps: Prospection of stratabound sulfide mineralization in the western part of the Rhenish Schiefergebirge. Contact group "Geology of ore deposits and of their host rocks", Liège, discussions et communications personnelles, 1981

Graulich, J.M., Bouckaert,J., Delmer, A.: Le sondage n° 27 - Neuville (1967-1973) P. 185 W n° 407. Notes de débitage. Rapport Service Géologique de Belgique, 1967-1973

Heinrich, H., Schulz-Dobrick, B., Wedepohl, K.H.: Terrestrial geochem istry of Cd, Bi, Th, Pb, Zn and Rb. Geochim. Cosmochim. Acta 44, 1519-1533 (1980)

Herbosch, A., Cauet, S., Préat, A.: Recherche de métallotectes de nature géochimique pour la prospection de gîtes Pb-Zn belges. Prof.Paper, 197, Service Géologique de Belgique, 117p. 1983

Lagny, P.: Les gisements stratiformes associés aux évaporites: position dans le temps et place dans l'espace des bassins sédimentaires évaporitiques. Bull. Centre Rech. Expl. Pau 4, 445-476 (1975)

Leake, B.E., Hendry, G.L., Kemp, A., Plant, A.G., Harvey, P.K., Wilson, J.R., Coats, J.S., Aucott, J.W., Lünel, T., Howartz, R.J.: The chemical anaysis of rock powders by automatic X-ray fluorescence. Chem. Geol. 5, 7-86 (1969/1970)

Legrand, R.: Données nouvelles sur le Tournaisien grâce aux forages de Tournai et de Leuze. C.R.Acad.Sc. Paris 254, 3878-3880 (1962)

De Magnée,I.: Contribution à l'étude génétique des gisements belges de Pb, Zn et barytine. In: Genesis of stratiform lead-zinc barite fluorite deposits. Ed.J.S.Brown. Econ.Geol. Mon. 3, 255-266 (1967)

Pel, J., Monseur,G.: Minéralisations de galène et de pyrite dans le récif F_2h du Frasnien de Frasnes (Belgique). Annales Soc.Géol.de Belgique 101, 389-397 (1979)

Preat, A., Boulvain,F.: Etude sédimentologique des calcaires givétiens à Vaucelles (Bord sud du Synclinorium de Dinant). Ann. Soc. Géol. Belgique, 105, 273-282 (1982)

Purser, B.A.: Sédimentation et diagenèse des carbonates néritiques récents. Inst. Francais Pétr., Ed. Technip, 366 p. (1980)

Renfro, A.R.: Genesis of Evaporite - Associated Stratiform Metalliferous Deposits - A Sabkha Process. Econ. Geol. 69, 33-45 (1974)

Routhier, P.: Le modèle de genèse: quelques concepts fondamentaux en Pétrologie et Métallogénie. Modèle des théories métallogéniques. Chron. Mines et Rech. minière, 177-190 (1967)

Routhier, P.: Essai critique sur les méthodes de la géologie (de l'objet à la genèse) Paris, Masson (ed.), 202 p. 1969

Routhier, P.: Où sont les métaux pour l'avenir? Mémoire du BRGM, 105, 409 p. 1980

Swennen, R., Viaene, W.: Lithogeochemistry of some carbonate sections of the Dinantian in the Vesdre region (Belgium). Bull.Soc. Belge de Géologie 90, 65-80 (1981)

Turekian, I.K., Wedepohl, K.H.: Distribution of the elements in some major units of the Earth's crust. Bull. Geol. Soc. Amer. 72/2, 175-192 (1961)

Van Orsmael, J., Viaene, W., Bouckaert, J.: Lithogeochemistry of upper Tournaisian and lower Visean carbonate rocks in the Dinant basin. Meded. Rijks. Geol. Dinst, 32-12, 96-100 (1980)

Van Tassel, R.: Anhydrite, célestine et barytine du Givétien du sondage de Tournai. Bull.Soc. Belg. Géol. Paléont. Hydrol. 69, 351-361

Vie le Sage, R., Quisefit, J.P., Dejean de la Batie, R., Faucherre, J.: Utilisation du rayonnement primaire diffusé par l'échantillon pour une détermination rapide et précise des éléments traces dans les roches. X-Ray Spectrometry, 8-3, 181-184 (1979)

Wolf, K.H., Chilingar, G.V., Beales, F.W.: Elemental composition of carbonate skeletons, minerals and sediments. In: G.V.Chilingar, H.J.G.Bissell and R.W.Fairbridge (eds.), Carbonate rocks, physical and chemical aspects. (Developments in Sedimentology, 9B) Elsevier, Amsterdam, 413 p. 1967

Received: August 3, 1982
Accepted: February 16, 1983

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Mineral.Deposita 18, 365-377 (1983)

MINERALIUM
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Diagenetic Processes and the Mineralization in the Triassic of Central England

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Continental red beds are the host rocks of a characteristic style of mineralization which suggests a genetic link between red bed formation and ore formation. Samples of unmineralized and mineralized Triassic sediments from Central England have been studied sedimentologically, petrographically and geochemically with the aim of clarifying this link which may provide valuable guides for exploration. On the basis of sedimentological and petrographic observations it is suggested that these red beds were formed as a result of diagenetic alteration whereby detrital silicates and oxides are progressively dissolved and the iron released is deposited as hematite. A model for mineralization is proposed involving the release of trace metals from detrital minerals during diagenesis, their retention in saline interstitial solutions, migration to suitable sites of precipitation and deposition by reaction with trapped hydrocarbons or reduced sulphur.

INTRODUCTION

Continental red beds are the host rocks of a characteristic style of mineralization which is dominated by the metals copper, lead, zinc, uranium and vanadium, although not all these metals are necessarily present in any one deposit or region of mineralization (Stanton, 1972). This distinctive association suggests a genetic link between red bed formation and the processes of ore formation, a link which still remains to be properly explained and may provide valuable clues in the search for ore deposits of this type. Many of the mineralogical and textural features of red beds are a product of diagenesis and the relationships between mineralization and diagenesis may be a crucial aspect of ore formation in this environment. This aspect of red bed mineralization has not yet been investigated in detail. In this work, the mineralization in the Triassic rocks of Central England has been studied together with the petrology and geochemistry of the host rocks both adjacent to and distant from mineralization. The objectives of this preliminary survey have been to clarify the relationship between mineralization and diagenesis.

GEOLOGICAL SETTING

The Triassic of Britain was deposited in a number of fault-bounded, avolcanic, often deep sedimentary basins. A number of separate depositional basins can

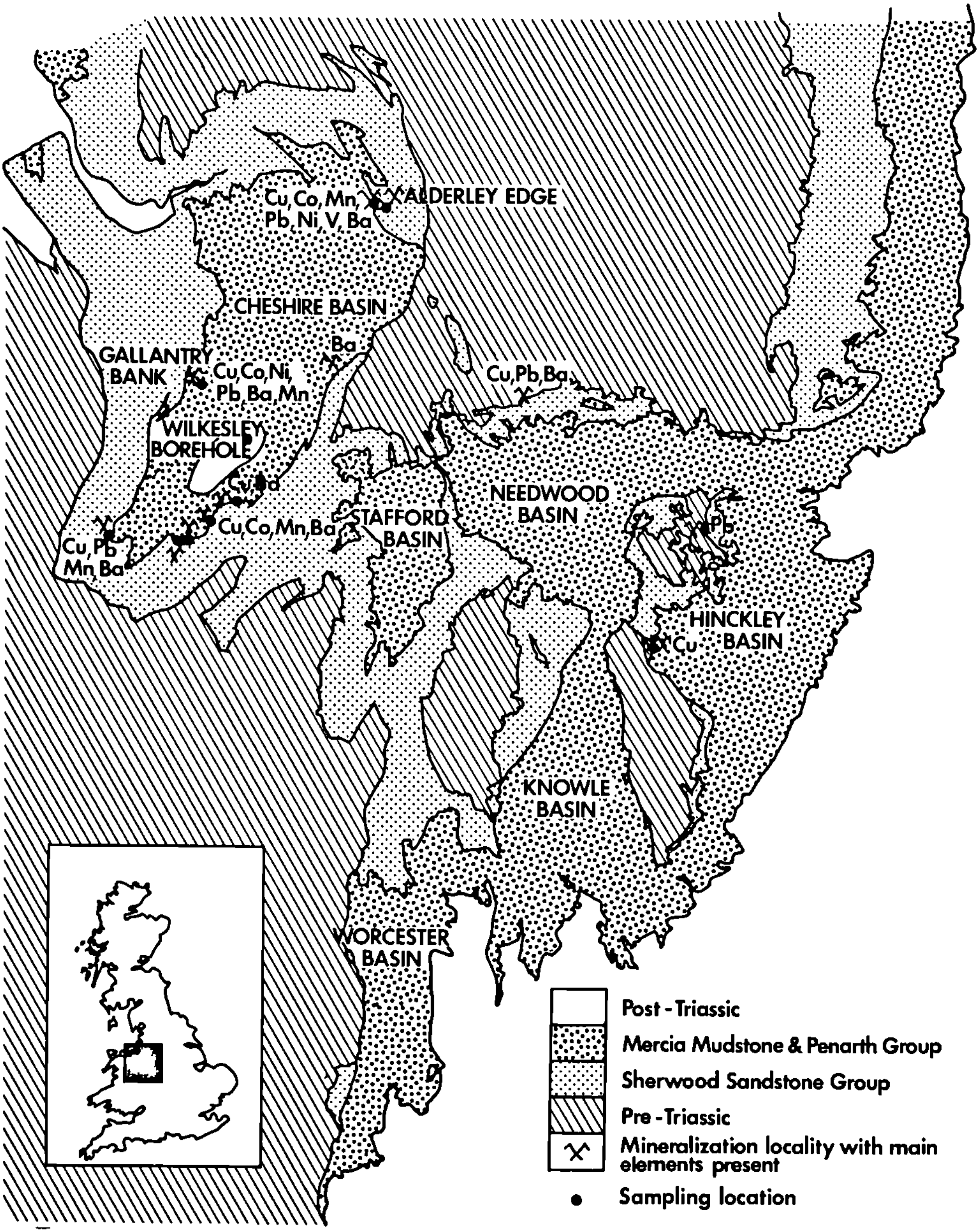

Fig. 1. Geological map of Central England showing the Triassic sedimentary basins. Areas in which mineralization has been exploited in the past are shown along with the major elements known to occur

be identified in Central England and these are shown in Fig. 1. These basins may be divided into two broader overall areas - Northwest Central England, including the Cheshire (-Shropshire) basin and the Central Midlands, comprising the Stafford, Needwood, Hinckley, Knowle and Worcester basins.

The stratigraphy of the British Triassic has been recently reviewed by Warrington et al. (1980) who recommend subdivision into three lithostratigraphic divisions - the Sherwood Sandstone Group, the Mercia Mudstone Group and the Penarth Group. In Northwest-Central England the Sherwood Sandstone Group is diachronously conformable with underlying dominantly argillaceous Permian strata, while in the Central Midlands this junction is unconformable. The junction between the Sherwood Sandstone Group and the Mercia Mudstone Group is conformable and diachronous. Both groups are of considerable thickness in Central England, as shown by the representative sections in Fig. 2. The overlying Penarth Group is seen in the Cheshire Basin and further south in the Midlands.

The Sherwood Sandstone Group is composed of a variety of conglomerates, pebbly sandstones and mudstones. The conglomerates and pebbly sandstones lower in the sequence are generally interpreted as the deposits of an alluvial fan/braided river system, whilst the overlying finer-grained sandstones represent alluvial deposits of low sinuosity stream channels (Audley-Charles, 1970). In addition, in the Helsby Sandstone Formation, Thompson (1969) identified aeolian dune deposits. In general,

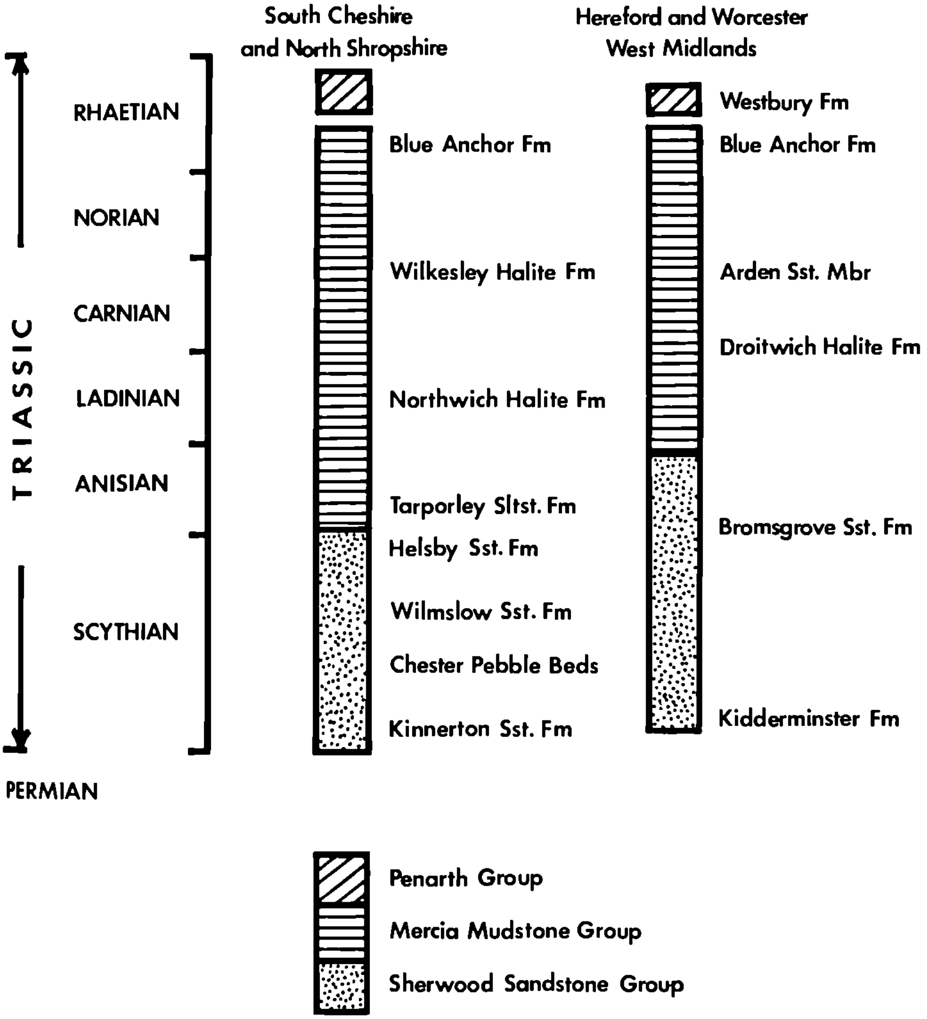

Fig. 2. Representative stratigraphic sections of the Triassic sediments of Central England

the grain size of the Sherwood Sandstone Group decreases in a northerly direction through Central England, which is the general direction of alluvial transport in the British area.

The Mercia Mudstone Group commences in Northwest-Central England with the Tarporley Siltstone Formation, which, with its lateral equivalents in the Central Midlands, represents deposition in intertidal conditions (Ireland et al., 1978). This is followed by a very thick succession comprising dominantly mudstones, but in places with very thick halite deposits. The origin of these deposits is controversial since carbonate and sulphate facies of comparable significance are absent. Detailed sedimentological study of parts of the Mercia Mudstone Group by Arthurton (1980) led to the conclusion that the layered halite and associated laminated mudstones were the result of marine flooding due to eustatic rise in sea level. The more blocky mudstones were considered to represent emergent conditions during periods of regression. At the top of the Mercia Mudstone Group, the Blue Anchor Formation appears to be transitional between the underlying mudstones and the marine Penarth Group and may be a marginal marine deposit.

Palaeogeographic reconstructions for the Triassic of Central England (Audley-Charles, 1970), show that the Sherwood Sandstone Group was laid down on a north-west sloping piedmont. Most of the sediment influx was thus from the Hercynian mountain chain of North Europe and Southwest England, although isolated upstanding blocks centred on Wales, the Lake District and the Pennines would have been important local sources. The source rocks were probably varied, including a mixture of sedimentary, low-grade metamorphic and igneous rocks. The unconformity at the base of the Helsby and Bromsgrove Sandstone Formation is thought by Warrington (1970) to be a possible equivalent of the Hardegsen discontinuity in Germany. This unconformity is followed by an increase in coarse-grained detritus and an increase in the content of perthitic feldspar and heavy minerals (particularly mica, apatite and garnet), possibly indicating source area uplift and an increase in igneous influences (Ali, 1982). During deposition of the Mercia Mudstone Group, local topography was apparently reduced to the extent that Central England was a low plain subject to variable marine influences, with limited detrital supply.

SAMPLE COLLECTION

Samples representative of unmineralized Triassic sediments were obtained from the core of the Wilkesley borehole stored by the Institute of Geological Sciences. Samples were also collected from exposures in Central England, mainly in the vicinity of known mineralization These samples were collected so as to represent both mineralized and unmineralized material. Sampling locations are shown in Figure 1.

PETROGRAPHY

Sediments from the Wilkesley borehole range in grain size from coarse sandstones to mudstones. They are dominantly red in colour, but occasionally grey or green. The sandstones frequently sho carbonate and sulphate cements, togethe with a varied suite of authigenic minerals including quartz, potash feldspar plagioclase feldspar, hematite and TiO_2 minerals (Fig.3). Sediments obtained from areas adjacent to mineralization range from mudstones to conglomerates. They may be red in colour but are frequently bleached. Sulphate and carbonate cements are absent, except in areas where barium mineralization is prevalent, when barite cements are common. Authigenic feldspar is not as common as in the unmineralized material, but authigenic quartz and hematite are widely distributed. Particularly in the sediments associated with mineralizatio but also in the unmineralized sediments iron and copper sulphides occur within quartz overgrowths, indicating their formation during diagenesis.

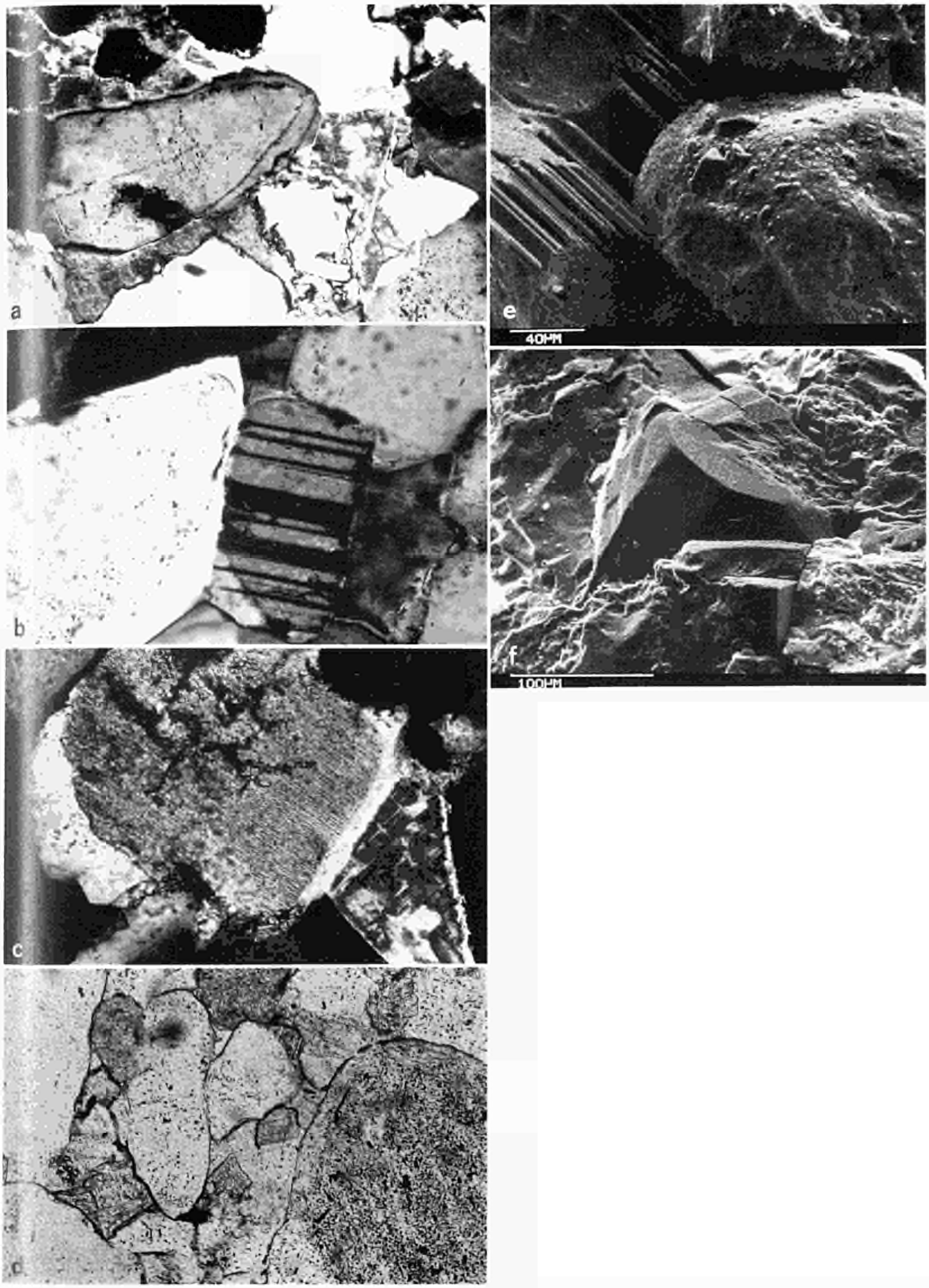

Fig. 3a-f. Photomicrographs of sediments from the Wilkesley borehole: (a) quartz grain showing an authigenic overgrowth of quartz and anhydrite pore-filling cement; (b) authigenic overgrowth of plagioclase feldspar showing twins in optical continuity and forming a triple junction with an authigenic overgrowth of quartz; (c) authigenic potash feldspar grain surrounded by anhydrite cement; (d) dolomite rhombs blocking pore connections; (e) scanning electron photomicrographs showing rounded quartz grain with barite cement; (f) scanning electron photomicrograph showing anhydrite cement

There is a general discrepancy in the petrological characteristics of surface exposures and subsurface drill cores in the Triassic of Central England. Carbonate and sulphate cements are often absent in surface and near-surface rocks and have presumably been dissolved in the present-day groundwater zone. Detrital and authigenic silicates, particularly K-feldspar, also show dissolution textures within this zone and kaolinite is frequently abundant, filling secondary pore spaces. This kaolinite may have been precipitated in equilibrium with the present groundwater which is usually mildly oxidizing and slightly acid to neutral.

Walker (1976) proposed that the formation of continental red beds was a result of diagenetic alteration. He considered that the Permo-Triassic red beds of Europe formed under similar conditions to those observed at the present time in south-western USA. There, due to the aridity of the area, unstable ferromagnesian silicates are not destroyed by surface weathering but are supplied to the depositional basin. These minerals are then progressively dissolved during diagenesis by oxygenated groundwater and the iron thus released is deposited as hematite, or precursor minerals to hematite. With time (possibly tens of millions of years) the unstable ferromagnesian minerals are completely destroyed, leaving no direct evidence for their former existence.

Walker's (1976) proposed mechanism for the genesis of red beds fits well with the data already outlined for the Triassic of Central England. The presence of aeolian dunes indicates that arid conditions were common, while the formation of authigenic quartz, feldspar and hematite would be expected to follow the dissolution of unstable ferromagnesian silicates. The formation of authigenic minerals is, of course, dependent upon the prevalence of suitable conditions of Eh and pH. Thus, for example, the occurrence of authigenic plagioclase and of sulphate cements in sediments from the upper part of the Sherwood Sandstone Group may indicate that interstitial conditions were more alkaline than at other horizons.

GEOCHEMISTRY

Samples have been analysed by a combination of X-ray fluorescence spectrometry, atomic absorption spectrophotometry and delayed neutron activation analysis. In Table 1 and 2 are listed results of the analysis of samples from the Wilkesley borehole. Analysis was by X-ray fluorescence spectrometry, with the exception of Cd and Co which were determined by atomic absorption spectrophotometry. Certain of the major element values are shown graphically in Figure 4. Major element contents will obviously reflect mineralogical changes in the succession and it can be seen from Figure 4 that while SiO_2 increases generally towards the base of the sequence, the other major elements show a broad decrease. This reflects the increasingly arenaceous character of the lower part of the succession. In more detail, whereas Al_2O_3 and Fe_2O_3 show a reasonably steady decrease down through the sequence, CaO and MgO show large fluctuations (Table 1) due to variations in the content of carbonate and sulphate cements. The alkalis, Na_2O and K_2O, show reasonably constant values through the sequence, except for high K_2O contents in the mudstones at the top of the sequence and in sample 9826 (which contains a large reduction spot) and a high Na_2O content in sample 9828, from within a halite bed.

The trace element contents in Table 2 show similar distributions to the major elements in that they are depleted in samples with the highest SiO_2 contents. Concentrations of most trace elements are similar to those reported from the analysis of sedimentary rocks, with the main exception of Cu, which in several samples is much higher than the published average values of ~30 ppm (Wedepohl, 1978). Ba and Sr show significant enrichment in two samples each, in the case of Sr this is probably due to Sr substitution in calcite and anhydrite.

In Table 3 are shown results of the analysis of samples from three mineralized areas - Alderley Edge, Gallantry Bank and Grinshill. All of these analyses were performed by atomic absorp-

Table 1. Geochemical analysis of samples from Wilkesley Borehole

Major elements as % weight

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	SO_3	Cl	L.O.I.	* Total
9355	41.54	12.58	5.81	8.77	9.48	1.03	4.26	0.53	0.09	0.12	0.05	N.D.	16.00	100.26
9356	44.15	11.99	5.61	7.72	9.77	1.12	3.70	0.60	0.11	0.14	0.03	N.D.	15.10	100.04
9361	45.10	13.59	3.84	13.19	5.68	1.31	2.92	0.67	0.10	0.14	0.04	N.D.	13.30	99.88
9369	53.46	13.88	4.13	7.44	4.21	1.63	3.83	0.73	0.09	0.13	0.20	0.04	10.10	99.86
9728	29.51	5.48	1.37	0.59	3.47	19.40	1.04	0.28	0.02	0.05	5.63	13.41	22.00	99.21
9770	43.89	13.98	6.49	8.31	6.82	2.41	3.36	0.60	0.06	0.13	2.36	0.09	11.80	100.28
9772	40.88	12.23	5.23	7.20	9.87	1.44	3.17	0.62	0.07	0.15	4.60	0.07	14.20	99.77
9776	46.19	10.61	4.12	9.45	8.53	0.95	2.46	0.54	0.07	0.12	2.71	0.01	14.40	100.15
9781	41.83	12.26	3.68	8.87	10.43	1.41	2.42	0.60	0.10	0.11	0.45	0.05	18.40	100.59
9782	45.22	10.76	3.39	7.84	10.89	1.43	2.50	0.66	0.08	0.12	0.76	N.D.	16.60	100.27
9792	69.84	3.35	0.94	1.78	8.84	0.52	1.07	0.25	0.04	0.06	5.37	N.D.	7.70	99.76
9792A	66.15	7.82	2.50	4.28	5.88	0.71	2.14	0.48	0.03	0.10	1.55	N.D.	8.60	100.24
9799	61.90	3.78	1.19	1.56	11.69	0.70	1.13	0.32	0.05	0.06	8.34	N.D.	9.00	99.72
9799A	61.27	4.00	1.97	3.52	10.57	0.75	1.08	0.38	0.11	0.08	4.48	N.D.	11.40	99.61
9803	74.15	2.16	0.32	0.17	8.99	0.25	1.13	0.05	0.02	0.02	7.22	N.D.	5.30	99.79
9807	86.65	6.40	1.20	0.60	0.38	1.37	2.55	0.35	0.02	0.09	0.11	0.01	0.90	100.63
9810	87.85	4.59	0.72	0.74	0.87	1.20	2.02	0.15	0.03	0.05	0.11	0.01	1.90	100.24
9815	87.28	4.77	0.99	0.76	1.05	1.01	1.94	0.20	0.03	0.06	0.00	N.D.	2.20	100.29
9817	87.00	5.25	0.92	0.71	0.54	1.18	2.08	0.22	0.03	0.07	0.11	0.01	1.50	99.62
9821	80.83	7.77	2.12	1.08	1.02	1.43	2.60	0.53	0.05	0.11	0.07	N.D.	1.80	99.41
9826	58.29	18.50	5.14	3.54	0.54	1.06	6.03	0.87	0.04	0.18	0.12	0.01	4.70	99.02
9828	72.03	8.15	2.60	1.86	4.17	1.19	2.57	0.55	0.06	0.11	0.42	N.D.	6.20	99.91
9831	50.81	13.86	5.76	5.94	6.22	0.74	4.63	0.65	0.13	0.12	0.16	0.01	10.70	99.73
9853	83.23	4.30	1.02	0.31	3.52	0.98	1.85	0.25	0.03	0.07	1.08	N.D.	3.70	100.34

L.O.I. = Loss on ignition

N.D. = Not determined

* Total corrected for O ≡ Cl

Table 2. Geochemical analysis of samples from Wilkesley Borehole

Trace elements in ppm

Sample	Ba	Sr	Rb	Zr	Cu	Co	Pb	Zn	Cd	Ni	Cr	V	Y	La
9355	292	213	158	121	157	29	14	46	3	45	87	85	24	29
9356	261	241	138	176	21	34	23	55	3	47	91	86	28	33
9361	364	172	135	180	17	33	15	122	2	47	94	118	30	39
9369	539	161			14	45	26	83	4	54	73	136		
9728	241	1325			5	19	22	25	3	22	32	40		
9770	251	321			6	48	33	92	3	86	112	124		
9772	257	456			4	47	35	71	4	65	88	110		
9776	316	344			9	31	27	66	2	38	60	94		
9781	317	120			21	43	32	57	3	44	71	118		
9782	115	231	107	274	122	28	13	46	4	33	53	49	30	23
9792	147	361	32	211	12	12	10	13	N.D.	31	29	18	14	10
9792A	221	289	77	259	5	25	12	54	1	35	65	57	20	19
9799	228	463	31	337	70	16	11	11	N.D.	26	31	20	18	12
9799A	1438	640	33	440	323	13	13	16	N.D.	36	40	34	24	19
9803	165	304	31	33	7	2	11	0	N.D.	36	7	5	5	3
9807	361	57			0	83	11	12	5	19	19	27		
9810	302	45			1	70	8	12	0	9	9	10		
9815	290	58	53	155	31	11	12	2	N.D.	78	22	16	11	14
9817	294				210	13	20	15	N.D.	82		18		
9821	321	77	73	348	25	23	12	15	N.D.	55	56	45	23	25
9826	438	59			3	77	20	74	8	74	97	177		
9828	284	158	75	370	120	23	13	21	N.D.	49	62	56	25	26
9831	314	100			5	53	21	58	3	56	77	121		
9853	212	172	40	265	24	6	10	3	N.D.	56	24	14	11	12

N.D. = Not determined

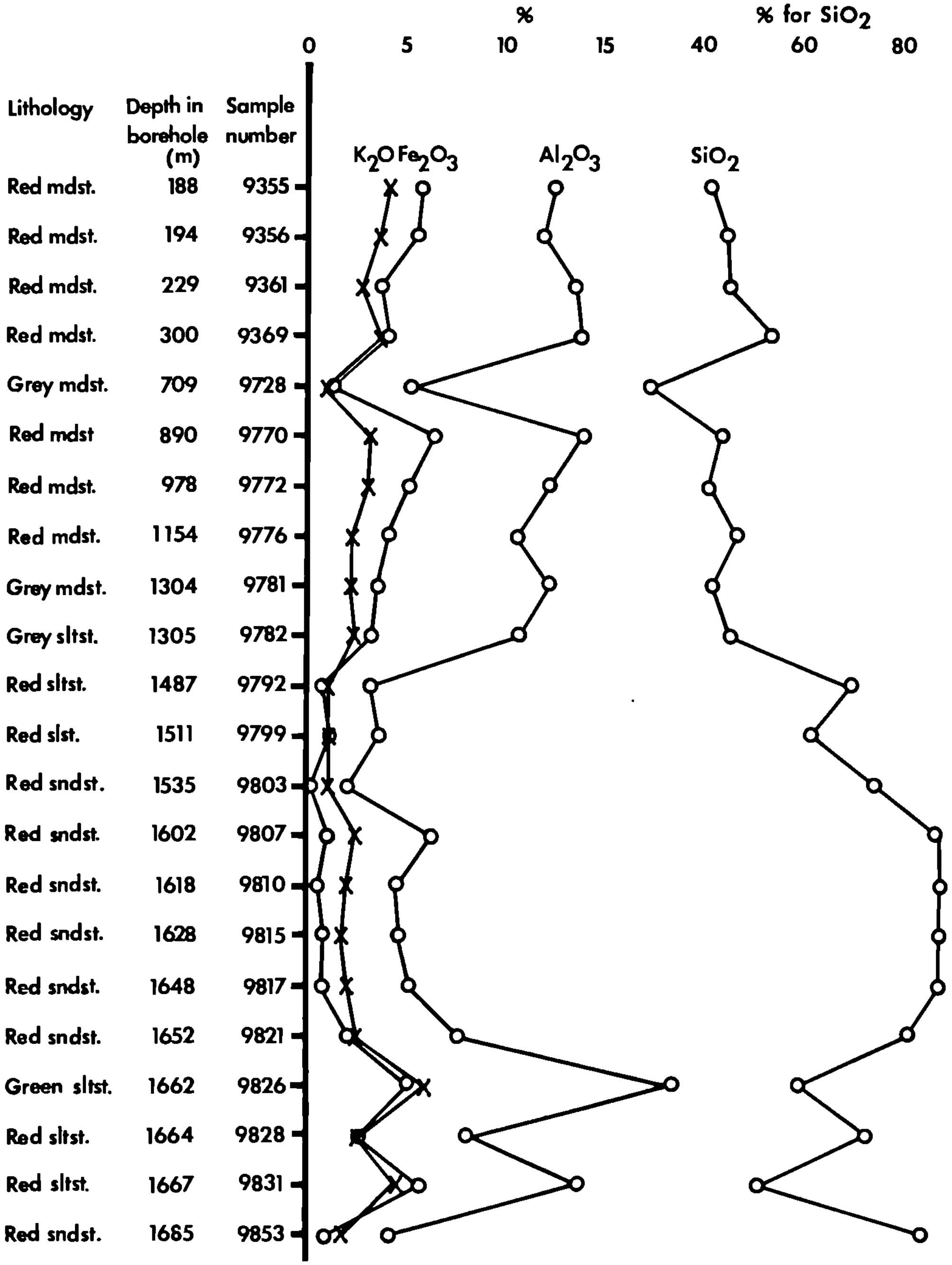

Fig. 4. Plot showing the variation in concentration (weight %) of certain major elements in samples from the Wilkesley borehole

Table 3. Geochemical analyses and descriptions of samples from mineralised areas

	Major elements as %						Trace elements in ppm						
Sample no.	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Mn	Cu	Co	Pb	Zn	Cd	Ni
G1	5.33	1.24	0.32	0.19	0.22	2.81	153	7	18	14	0	0	40
G3	2.42	0.20	0.08	0.03	0.34	1.58	54	60	6	23	20	1	65
GB1	2.66	0.36	0.11	0.28	0.23	1.80	100	11	9	14	0	0	40
GB3	3.14	0.63	0.12	0.07	0.22	1.72	55	14	9	9	4	0	37
GB4	2.42	0.18	0.09	0.06	0.17	1.41	38	11	5	9	4	1	1
AE1	18.27	7.42	1.64	0.39	0.61	6.05	266	1347	98	26	454	8	100
AE2	17.53	3.20	1.48	0.30	0.44	5.50	301	2595	177	916	345	8	80
AE31	1.04	0.17	0.05	0.16	0.09	0.42	168	356	50	6	355	4	40
AE32	2.25	0.26	0.10	0.75	0.44	1.21	172	4973	40	15	546	6	80
AE5	1.53	0.30	0.07	0.04	0.10	0.66	67	81	35	11	26	1	6
AE8	2.31	0.65	0.06	0.04	0.15	1.28	18	19617	104	31	1517	14	44
AE9	4.38	0.42	0.09	0.06	0.28	2.48	33	386	26	84	129	7	39
AE11	3.00	0.26	0.08	0.04	0.20	1.59	38	30	20	6	7	0	19
AE13	2.95	4.37	0.05	0.03	0.20	1.61	84	51822	248	9252	1380	47	456

G1	Red sandstone, Grinshill
G3	Indurated bleached sandstone, Grinshill
GB1	Red sandstone with barite, Gallantry Bank
GB3	Red sandstone, Gallantry Bank
GB4	Bleached sandstone, Gallantry Bank
AE1	Red mudstone, Alderley Edge
AE2	Green mudstone, Alderley Edge
AE31	Bleached sandstone, Alderley Edge
AE32	Bleached sandstone with malachite, Alderley Edge
AE5	Red sandstone with barite, Alderley Edge
AE8	Malachite stained conglomerate with barite, Alderley Edge
AE9	Light-brown pebbly sandstone, Alderley Edge
AE11	Light-brown sandstone, Alderley Edge
AE13	Vein material, Engine Vein Mine, Alderley Edge

tion spectrophotometry. It can be seen that the tabulated major element contents are generally lower than those for the Wilkesley samples. This is a reflection of the coarser-grained nature of the sediments and their correspondingly higher quartz contents. Especially notable are the low CaO and MgO contents, which reflect the almost complete absence of carbonate and sulphate cements (except for barite). The trace element values for the samples from Gallantry Bank and Grinshill are similar to those for the Wilkesley sediments, while those from Alderley Edge are frequently much higher, indicative of the more extensive mineralization occurring at Alderley Edge. The trace element contents of the Alderley Edge sample show the mineralization to be dominantly copper, with subsidiary enrichment in lead and zinc.

Analysis of samples for uranium from both Wilkesley and the mineralized areas by the delayed neutron activation method showed uniformly low U contents, commonly in the range 1-3 ppm, with a highest value of 5.5 ppm. U values tend to be slightly higher in the finer-grained sediments. Analysis of ore material from Alderley Edge similarly showed U contents below 3 ppm.

ASPECTS OF THE MINERALIZATION

Numerous examples of mineralized sediments occur in the Triassic rocks of Central England and the more significant occurrences are shown on Figure 1. The dominant mineralization appears to be of copper and barium, with more restricted lead and zinc occurrences. Cobalt and nickel also occur, as does manganese. Vanadium has been reported from a few localities but uranium has not been recorded to any great extent, although it has not been searched for systematically. Many of the areas of mineralization were mined on a small scale in the 18th and 19th centuries (Carlon, 1979, 1981).

Most of the metalliferous deposits in the Triassic of Central England have a broadly similar geological setting. The mineralization is commonly associated with a fairly major fault and is largely limited stratigraphically to the sediments of the upper part of the Sherwood Sandstone Group. In particular, the mineralization is more common in the porous conglomerates and coarse sandstones, especially where these underlie or are faulted against mudstone bands, to form stratigraphic traps. The mineralization tends to be better developed down-dip from the fault zone. Barite is far more widespread than the metalliferous mineralization, but in general follows the same form, being especially widespread in the more permeable horizons

The Alderley Edge deposit may be cited as an example of the ore mineral paragenesis of the deposits in the Triassic of Central England. This has been studied by Ixer and Vaughan (1982) who found the following sequence. Detrital opaque phases including iron-titanium oxides and pyrite in clastic grains are followed by iron and copper sulphides found in quartz overgrowths and therefore associated with the diagenesis of the sediments. The main phase of mineralization consists of sulphides cementing the clastic grains and forming in the order iron/nickel - copper - zinc - lead. This primary assemblage has undergone substantial alteration, resulting in the formation of secondary copper sulphides and carbonates and sulphates of copper, zinc and lead. Reactions within the present groundwater zone are probably responsible for this alteration.

DISCUSSION

The mineralisation occurring in red beds of the type found in Central England has clearly been deposited from solutions which have passed through permeable sandstone horizons and then deposited metals in suitable environments. Similar solutions are also responsible for the diagenesis of the sediments, suggesting that a link between mineralization and diagenesis may exist.

It has already been stated that the diagenetic history of the Central England Triassic sediments is thought to be similar to that shown by Walker (1976) for Tertiary red beds in south-western USA and north-western Mexico. The proposed sequence of diagenetic changes is shown in generalised form in Table 4. Detrital silicates, clays and oxides are subject to dissolution during early diagenesis and authigenic mineral grains or overgrowths are formed by later precipitation when these solutions meet suitable conditions. More complete cementation (and possibly mineralization) can be regarded as an extension of this process. The major element redistributions which may be expected to occur during this diageneti sequence are shown in Table 4.

As well as possibly releasing large amounts of major elements, the dissolution stage will also result in the release of the trace metals located in the detrital minerals. As an example of the trace metal contents to be expected copper averages 100 ppm in pyroxenes and biotites but may reach 1000 ppm and 11,600 ppm respectively (Wedepohl, 1978 These and other ranges of expected copper contents for detrital phases are shown on Table 4.

Walker (1976) has shown that during diagenesis and red bed formation, ferromagnesian silicates, feldspars and detrital oxides are often completely dissolved, thus releasing the major and minor element contents into solution. These elements will only remain in solution as long as the chemical conditions are suitable for them to do so, once conditions become unsuitable the element will precipitate. Taking again the example of copper, it has been shown that copper will be released into solution following the dissolution of detrital silicates and oxides. As the solubility of copper in normal terrestrial groundwater is less than 1 ppm at near neutral pH, it may be expected that either diagenetic solu

Table 4. Scheme for the main diagenetic reactions occurring in red bed formation

Detrital supply	Early diagenesis - dissolution	Authigenic precipitation	Cementation	Mineralization
Silicates				
Quartz		Quartz		Barite
K-feldspar (Cu $\bar{x}$ 5ppm; <20ppm)	K Al Si Ba Pb	K-feldspar		Galena
Plagioclase (Cu $\bar{x}$ 62ppm; <840ppm)	Ca Na Al Si	Plagioclase		Pyrite
Ferromagnesians (Cu $\bar{x}$ 100ppm;<11,600)	K Na Ca Fe Mg Al Si Cu U			Cu - sulphides
			Gypsum/Anhydrite	
			Calcite	
			Dolomite	
Clays				
Illite		Illite		
Smectite	Na Ca Al Fe Si	Chlorite		
Chlorite (Cu $\bar{x}$ 100ppm; <400ppm)	Fe Mg Al Si			
Kaolinite (Cu $\bar{x}$ 23ppm; <226ppm)				
Oxides				
Goethite		Hematite		
Titanomagnetite (Cu $\bar{x}$ 76ppm; <800ppm)	Fe Ti V Mn Co Cu Ni			Co, Ni, Fe -sulphides
TiO_2		Anatase		
	pH ≃7, Eh +ve		$CO_3^=$ $SO_4^=$	pH <7, Eh -ve
			↑ ↑	

tions would be extremely dilute with respect to copper or that copper would be quickly precipitated from solution.

Rose (1976), however, has shown that the solubility of copper is dramatically increased in saline waters, through the formation of $CuCl_2^-$ and $CuCl_3^{2-}$ complexes. He found solubilities of 100 ppm copper for approximately 10g/l dissolved chloride. Of more direct importance to red bed mineralization studies is that a complex such as $CuCl_3^{2-}$ is stable at a pH of about 7 and in the presence of hematite, conditions comparable to those prevailing during the diagenesis of red beds.

Having shown that possible mechanisms exist for the dissolution of trace metals during diagenesis and for their transportation and concentration in solution, it remains only to consider means for their precipitation from solution. Metals such as copper, lead and zinc are all precipitated from solution as sulphides, presumably in a reducing environment with the presence of dissolved sulphur. Such environments would occur if the metal-rich brine solutions encountered trapped hydrocarbons, hydrogen sulphide or sediments rich in sulphides such as pyrite.

As a modern analogue of the dissolution, transportation and concentration of trace metals in red beds, the example of the Cheleken Peninsula (USSR) may be considered. Lebedev (1972) reported that hot brines derived from the Neogene red beds of the Cheleken Peninsula commonly contain 2 ppm copper and lead and 4 ppm zinc in solution. In extreme cases the lead content ranges to 77 ppm and the copper content to 15 ppm. Lebedev et al. (1971) showed that the lead was mainly present in solutions as $PbCl_3^-$ and $PbCl_4^{2-}$ complexes. These brines produce on average 300 tons of lead, 50 tons of zinc and 30 tons of copper annually at the surface. This modern evidence supports the hypothesis of derivation of metalliferous solutions from red beds.

In the case of the Triassic rocks of Central England, there is abundant halite within the sedimentary sequence to produce saline interstitial waters capable of dissolving and transporting significant quantities of trace metals. It was shown in Table 2 that the copper contents of an unmineralized Triassic sequence showed several anomalously high values. This may well be an indicator that redistribution of trace metals, especially copper, has occurred during the diagenetic formation of the red bed sequence. The amounts of metal involved may be roughly estimated by making an assumption of the amount of the original copper content of the sediment removed during diagenesis. Considering the Sherwood Sandstone Group sediments in the Cheshire Basin, the area involved is approximately $3.4 \times 10^9 m^2$, in which the Sherwood Sandstone Group ranges up to 1000 m in thickness. Taking a thickness of only 100 m gives a rock volume of $3.4 \times 10^{11} m^3$. Assuming an average initial copper content of 30 ppm and removing from this during diagenetic alteration only 1 ppm produces 884,000 tons of copper metal. It is evident, therefore, that the potential exists for deriving substantial metalliferous deposits from the diagenetic processes involved in red bed formation. As a comparison with the above figure, the total tonnage of ore removed from Alderley Edge is estimated to have yielded approximately 5000 tons of copper metal.

Acknowledgements. The work described in this paper was supported by the Primary Raw Material Research and Development Programme of the Commission of the European Communities under Contract No. MPP. 155.81 UK(H).

The Director and Staff of the Institute of Geological Sciences, particularly Dr. A.A. Wilson, are thanked for providing access to samples and data from borehole material. Dr. R.J. King of Leicester University is thanked for his advice and the loan of samples from the East Midlands areas and Dr. C.J. Carlon for access to his unpublished Ph.D. thesis.

We thank Pam Minor for preparation of the typescript and Beverley Parker for drafting the diagrams.

REFERENCES

Ali, A.D.: Triassic stratigraphy and sedimentology in central England. Unpublished University of Aston Ph.D. thesis (1982)

Arthurton, R.S.: Rhythmic sedimentary sequences in the Triassic Keuper Marl (Mercia Mudstone Group) of Cheshire, northwest England. Geol. J. 15, 43-58 (1980)

Audley-Charles, M.G.: Triassic palaeogeography of the British Isles. Q.J. geol. Soc. Lond. 126, 49-89 (1970)

Carlon, C.J.: The Alderley Edge mines. J. Sherratt & Son, Altrincham 1979

Carlon, C.J.: The Gallantry Bank copper mine, Bickerton, Cheshire. British Mining No. 16, 1981

Ireland, R.J., Pollard, J.E., Steel, R.J., Thompson, D.B.: Intertidal sediments and trace fossils from the Waterstones (Scythian-Anisian?) at Foresbury, Cheshire. Proc. Yorks. geol. Soc. 41, 399-436 (1978)

Ixer, R.A., Vaughan, D.J.: The primary ore mineralogy of the Alderley Edge deposit, Cheshire. Min. Mag. 46, 485-492 (1982)

Lebedev, L.M.: Minerals of contemporary hydrotherms of Cheleken. Geochem. Int. 9, 485-504 (1972)

Lebedev, L.M., Baranova, N.N., Nikitina I.B., Vernadskiy, V.I.: On the forms of occurrence of lead and zinc in the Cheleken thermal brines. Geochem. Int 8, 511-516 (1971)

Rose, A.W.: The effect of cuprous chloride complexes in the origin of redbed copper and related deposits. Econ. Geol. 71, 1036-1048 (1976)

Stanton, R.L.: Ore Petrology. McGraw Hill, New York 1972

Thompson, T.B.: Dome shaped aeolian dunes in the Frodsham Member of the so-called "Keuper" Sandstone Formation (Scythian-?Anisian: Triassic) at Frodsham, Cheshire (England). Sed. Geol. 3, 263-289 (1969)

Walker, T.R.: Diagenetic origin of continental red beds. In: Falke, H. (ed.) The Continental Permian in Central, West and South Europe. D. Reidel Publishing Co., Dordrecht-Holland, p. 240-282 (1976)

Warrington, G.: The stratigraphy and palaeontology of the "Keuper" Series of the Central Midlands of England. Q.J. geol. Soc. Lond. 126, 183-223 (1970)

Warrington, G., Audley-Charles, M.G., Elliott, R.E., Evans, W.B., Ivimey-Cook, H.C., Kent, P.E., Robinson, P.L., Shotton, F.W., Taylor, F.M.: A correlation of Triassic rocks in the British Isles. Geol. Soc. Lond. Spec. Report No. 13, 78 p. (1980)

Wedepohl, K.H.: Handbook of Geochemistry. Springer, Berlin Heidelberg New York, 1978

Received: July 27, 1982
Accepted: April 5, 1983

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Mineral.Deposita 18, 379-386 (1983)

MINERALIUM
DEPOSITA

Inclusions Fluides dans les Calcites Associées à la Mineralisation Pb-Zn de Poppelsberg (Est de la Belgique)

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Les inclusions fluides des calcites prélevées dans un filon plombo-zincifère dans l'Est de la Belgique montrent une grande dispersion des températures d'homogénéisation Th (30°C à plus de 360°C) et sont caractérisées par deux types de températures de fin de fusion Tf_2(-14°C et -21°C). L'ébullition n'a pu être démontrée. En raison de la dispersion des températures d'homogénéisation non expliquée à ce jour, la profondeur de mise en place du gisement reste difficile à estimer. Toutefois, les propriétés thermométriques des inclusions fluides permettent de distinguer les calcites issues d'un site fertile (Poppelsberg) des calcites provenant d'un site stérile (Belle Roche, Th=150°C, Tf_2 variable avec un mode à -8°C):

Fluid inclusions in calcites sampled in a Pb-Zn mineralized vein in East Belgium are characterized by a large dispersion of filling temperatures Th (30°C to more than 360°C) and by two groups of freezing points Tf_2 (-14°C and -21°C). Boiling has not been proved. According to the still unexplained dispersion of the filling temperatures, this study does not permit an estimation of the depth of the ore formation. Nevertheless, fluid inclusions thermometric properties make possible the distinction between calcites associated with a mineralization (from the fertile locality of Poppelsberg) and calcites from sterile area (Belle Roche, Th=150°C, Tf_2 variable around a mode of -8°C).

SITUATION GEOLOGIQUE

Les minéralisations plombo-zincifères exploitées jadis (Moresnet, La Calamine, Schmalgraf...) se répartissent dans une bande de terrains carbonifères qui s'étend de Namur à l'ouest à Aachen à l'Est (Fig.1). Les gisements Pb-Zn de l'Est de la Belgique (massif de la Vesdre) se situent généralement au contact calcaire dinantien-schiste houiller, à l'intersection des coeurs synclinaux hercyniens et des failles transversales anté-crétacées (Timmerhans, 1905).

La minéralisation de Poppelsberg (Fig.1) jalonne une faille NNW-SSE redressée, transverse aux structures hercyniennes NE-SW (Fig.2). Le filon recoupe des couches aréno-pélitiques famenniennes et carbonatées dinantiennes.

La minéralisation se compose de galène, blende colloforme et marcasite en zonages disséminés dans une gangue calcitique. L'absence de dissolution majeure aux épontes de l'encaissant carbonaté indique que les solutions devaient être saturées en carbonates avant d'arriver sur le site du dépôt. La présence de calcites précoces par

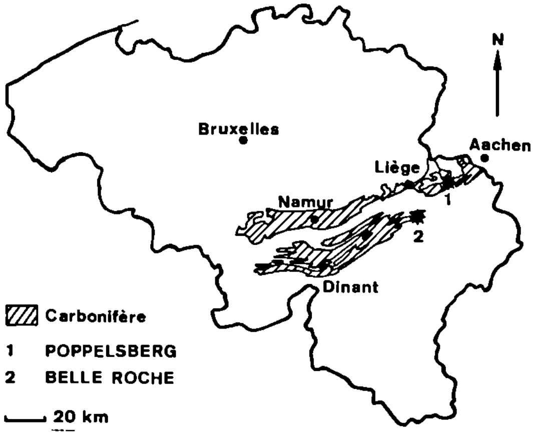

Fig.1. Position des niveaux carbonifères belges; localisation des sites de Poppelsberg et Belle Roche

rapport aux sulfures démontre la stabilité de la calcite pendant le transport du Plomb et du Zinc (Giordano and Barnes, 1981).

La calcite est le seul minéral transparent omniprésent sur le site. On la rencontre en gangue de la minéralisation (filon), en veines millimétriques à centimétriques (veines) et en remplissage de cavités dans certains niveaux dolomitiques (géodes).

La calcite du filon est rubannée transparente à opaque; la calcite des veines est microgrenue ou spathique souvent translucide; la calcite des géodes est présente sous forme de cristaux idiomorphes millimétriques à centimétriques transparents implantés sur une croûte de calcite microgrenue.

De façon à comparer les caractéristiques thermométriques des inclusions fluides des calcites prélevées dans le site fertile avec celles de calcites provenent d'un site stérile, des calcites ont été prélevées dans une région vierge de minéralisation plombo-zincifère connue et dans le même contexte lithologique et stratigraphique. Elles proviennent de la carrière de la Belle Roche, située le long de l'Amblève dans le synclinorium de Dinant (Fig.1). Il s'agit essentiellement de calcites en géodes dans des niveaux dolomitiques ou bréchiques; les veines sont rares.

MATERIELS ET METHODES D'INVESTIGATION

La calcite a été échantillonnée systématiquement en veines, filon et géodes dans les sondages et carrières de Poppelsberg (Fig.2); elle a été prélevée dans les niveaux dolomitiques ou bréchiques de la carrière de La Belle Roche.

Les calcites clivées en esquilles millimétriques, sont observées au moyen d'un microscope Leitz Ortholux polarisant muni d'une platine chauffante 350. Le principe et la méthode d'étalonnage correspondent à ceux de la platine Chaixmeca (Hollister L.S., 1981, p.293). L'intervalle de températures se situe entre -100°C et +350°C.

Toutes les inclusions biphasées observées (789 mesures) ont été chauffées. Certaines (146 mesures) ont été congelées. Des problèmes optiques ont souvent empêché de faire les lectures de températures d'homogénéisation et de fin de fusion sur la même inclusion.

Des calcites broyées et calibrées, diamètre compris entre 420 et 590 microns, ont été écrasées à la platine à écrasement de façon à apprécier le dégagement en CO_2. 19 d'entre elles ont été étudiées au spectromètre de masse par M.F.Miller et T.J.Shepherd de l'Institute of Geological Sciences, à Londres.

TYPES D'INCLUSIONS

A température ambiante, les inclusions fluides sont monophasées (liquide) ou biphasées (liquide-gaz). Aucune phase solide n'a été observée.

Les variétés morphologiques rencontrées peuvent se résumer en trois types (Fig.3):

I inclusions claires à contour géométrique (cristal négatif) contenant un bulle de gaz transparente; remplissage gazeux faible.

II inclusions claires à contour régulier contenant une bulle de gaz transparente ou sombre; remplissage gazeux faible.

III inclusions claires ou sombres à contour irrégulier contenant une bull

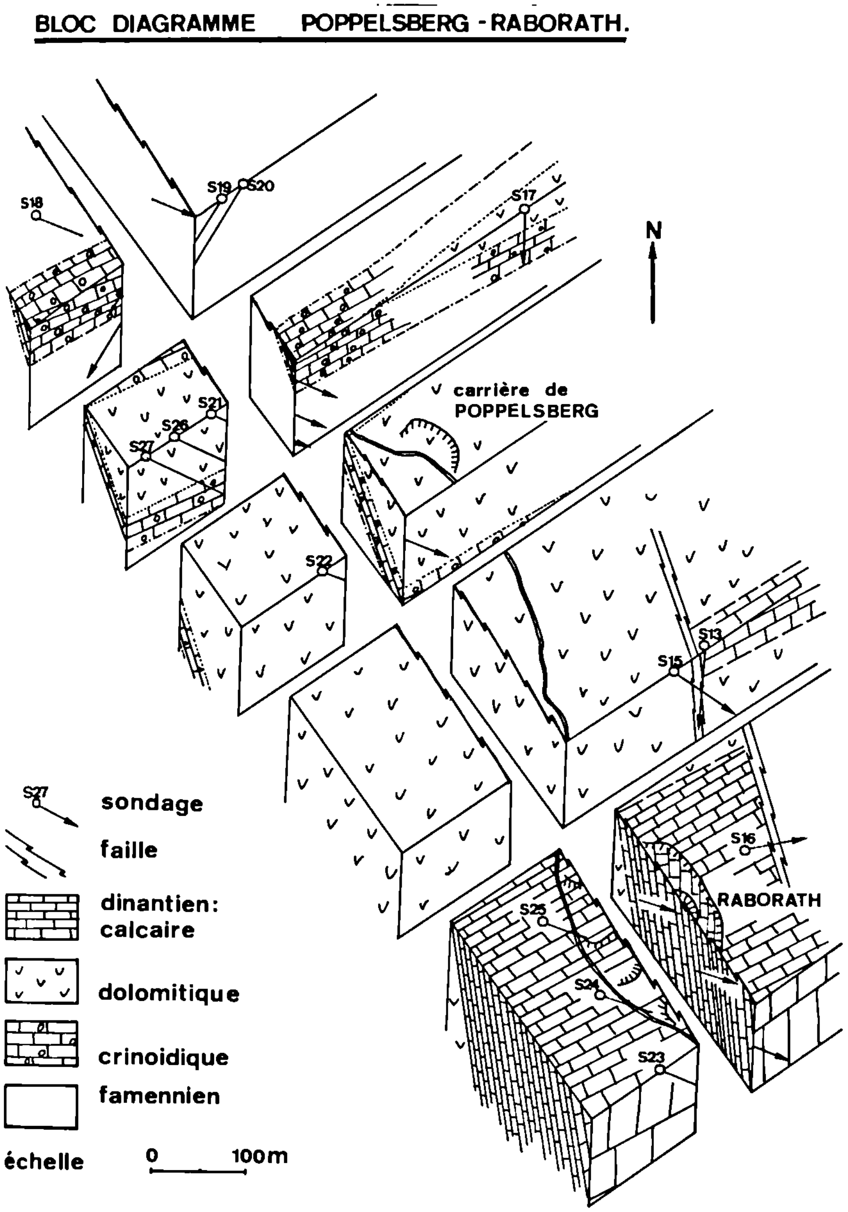

Fig.2. Description géologique du site de Poppelsberg; localisation des carrières et sondages

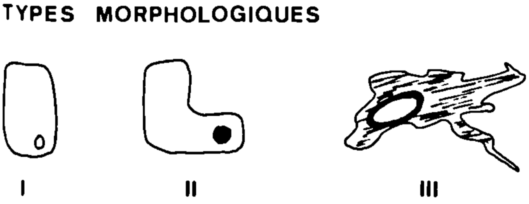

Fig.3. Types morphologiques d'inclusions fluides les plus fréquents.

de gaz à halo noir; remplissage gazeux variable.

La taille des inclusions varie de 5 microns à plusieurs centaines de microns. La taille des bulles de gaz varie de 5 microns à 200 microns. La fréquence des inclusions change d'une calcite à l'autre ou d'une plage à l'autre dans la même calcite.

Le taux de remplissage gazeux varie de 3/100 à 70/100. Les mesures au spectromètre de masse indiquent un taux en

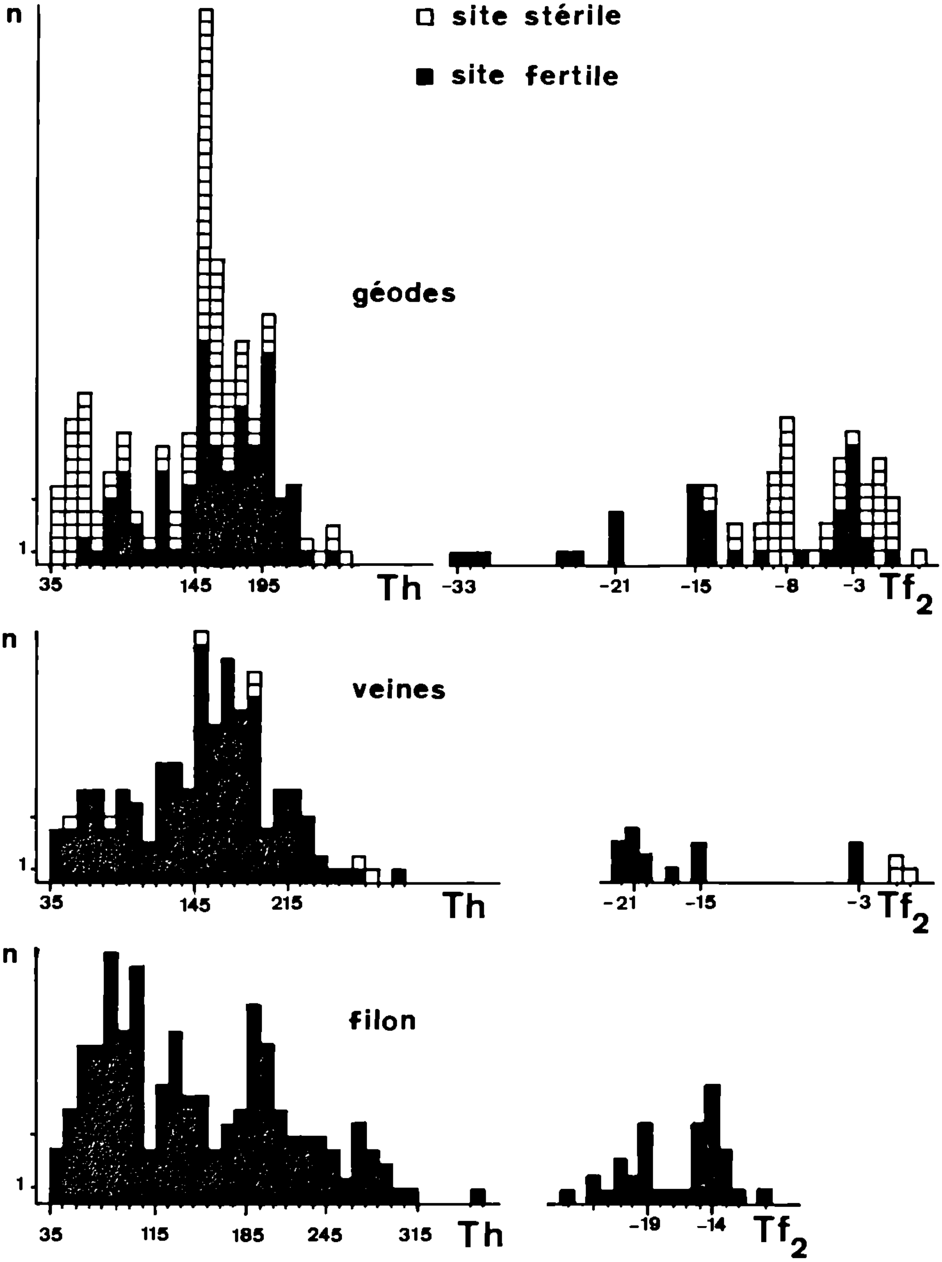

Fig.4. Distribution des températures d'homogénéisation Th et des températures de fin de fusion Tf_2 observées dans les calcites en géodes, veines et filon, provenant du site fertile (Poppelsberg) et du site stérile (Belle Roche)

CO_2 inférieur à 0.25 moles%. Aucune phase liquide CO_2 n'a été observée.

Les inclusions biphasées à caractère nettement secondaire sont alignées le long des plans de clivage. Elles se sont homogénéisées à des températures inférieures à 100°C.

RESULTATS THERMOMETRIQUES

Les températures d'homogénéisation varient de 30°C à plus de 360°C. L'homogénéisation se produit en phase liquide. La calcite éclate vers 370°C. Certaines inclusions ne se sont pas homogénéisées à cette température; parmi celles-ci quelques-unes contiennent une bulle de gaz qui s'expanse pendant la chauffe (après refroidissement à 20°C, la bulle reprend sa taille initiale).

La répartition des températures d'homogénéisation est reproduite à la Figure 4 suivant l'appartenance de la calcite aux groupes filon, veines, géodes pour les sites fertile (Poppelsberg) et sté-

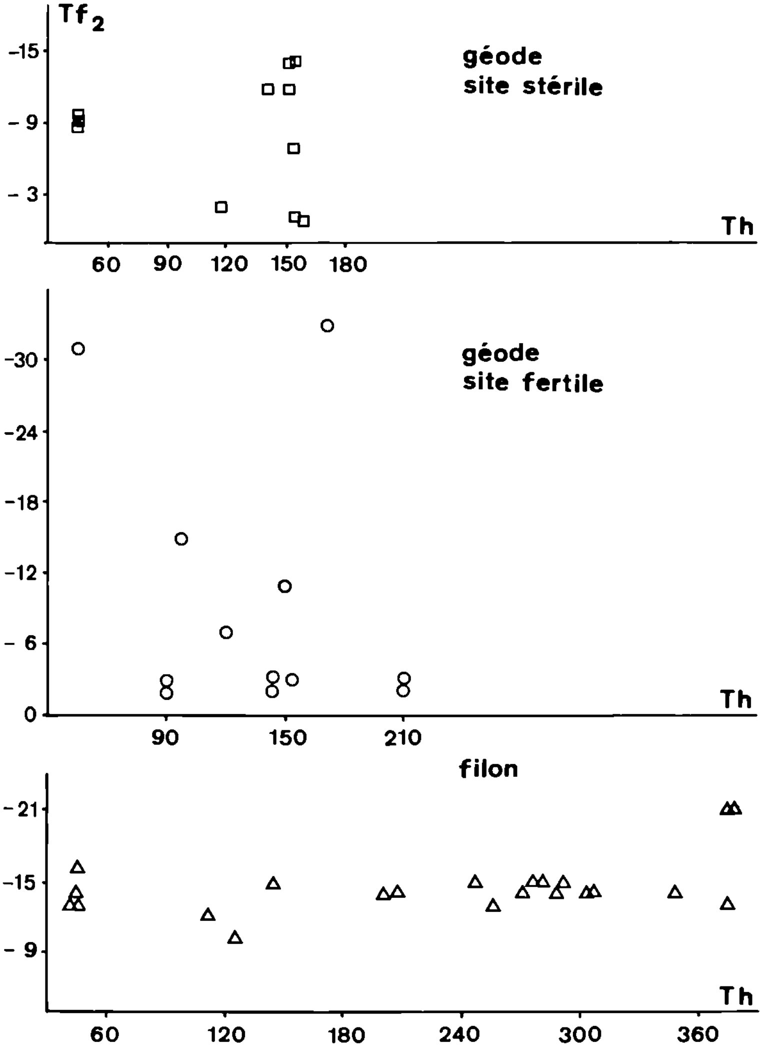

Fig.5. Corrélations entre les températures d'homogénéisation Th et les températures de fin de fusion Tf_2 observées dans trois échantillons: une géode du site stérile, une géode du site fertile et une calcite du filon

rile (Belle Roche). Plusieurs pics se dessinent dans les histogrammes: 60°-90°, 150°, 210°. Les températures les moins fréquentes voisinent 105°C. Il n'existe aucune relation évidente entre les variétés morphologiques et les températures d'homogénéisation.

Lors de la congélation, plusieurs comportements sont observés: certaines inclusions se craquèlent, les cristaux de glace sont nettement visibles; d'autres restent homogènes (un seul cristal?). Lorsqu'il n'y a pas de craquelures, l'évolution de la fusion est perçue à travers la déformation de la bulle de gaz.

Les températures de première fusion (first melting point) généralement inférieures à -50°C, attestent de la présence d'autres sels que NaCl dans la solution, tels que $CaCl_2$, $MgCl_2$....

Les températures de fin de fusion (freezing point) varient de -33°C à +1°C (Fig.4.). Trois pics s'individualisent: -21°, -14°, -3° à Poppelsberg; et un pic à Belle Roche: -8°.

CORRELATIONS TEMPERATURES D'HOMOGENEISATION-TEMPERATURES DE FIN DE FUSION

Les corrélations entre les températures d'homogénéisation Th et les températures de fin de fusion Tf_2 au sein d'un même individu s'expriment de différentes façons (Fig.5):

1- Th variables, Tf_2 constantes
2- Th variables, Tf_2 variables
3- Th constantes, Tf_2 variables.

Le cas 1 s'observe dans les calcites filoniennes de Poppelsberg ($30°C < Th < 360°C$; $Tf_2 = -21°C$ et $Tf_2 = -14°C$), ou en veines ($30°C < Th < 360°C$; $Tf_2 = -21°C, -14°C, -3°C$);

le cas 2 s'observe dans les calcites en géodes de Poppelsberg ($30°C < Th < 360°C$; $-33°C < Tf_2 < 0°C$;

le cas 3 s'observe dans les calcites en géodes du site stérile de Belle Roche ($Th = 150°C$; $-14°C < Tf_2 < 0°C$).

Les corrélations Th-Tf_2 permettent de distinguer les calcites provenant du site stérile des calcites du site fertile:

a- les calcites géodiques du site stérile sont caractérisées par une température d'homogénéisation de 150°C, température minimale de piégeage, correspondant vraissemblablement aux températures régionales lors de l'enfouissement des couches dolomitiques hôtes. Les variations des températures de fin de fusion (à Th constante) font penser à la présence d'un fluide localement dérivé, contrôlé par la minéralogie encaissante. La température de fin de fusion la plus fréquente est voisine de -8°C.

b- les calcites du site fertile sont caractérisées par une grande dispersion des températures d'homogénéisation.

Parmi les calcites de ce site, les calcites associées à la minéralisation plombo-zincifère se distinguent par l'existence d'inclusions fluides dont les températures de fin de fusion se répartissent en deux groupes: -21°C et -14°C. Certaines calcites en veines prélevées autour de la minéralisation sont apparentées aux calcites filoniennes (même Tf_2). Quant aux calcites issues des niveaux dolomitiques encaissants la minéralisation, elles contiennent des inclusions fluides dont les températures de fin de fusion varient de -33°C à 0°C. Cette variation peut résulter d'un mélange de fluides.

INTERPRETATION

La dispersion des températures d'homogénéisation observée dans les inclusions fluides des calcites du site fertile pose un problème. Pour discerner les températures significatives d'un point de vue génétique ou utilisables sous l'angle de la prospection, il est indispensable de connaitre les processus responsables des dispersions enregistrées.

Plusieurs processus peuvent être envisagés:

1- fuites après piégeage (leakage)
2- variations des conditions pression-température pendant la cristallisation
3- mélange de plusieurs fluides
4- division par étranglement des inclusions (necking down)
5- ébullition (boiling).

1- Les inclusions logées dans des zones fissurées peuvent avoir été vidées de leur contenu totalement ou en partie. Toutefois, certaines plages non fissurées d'inclusions isolées montrent des dispersions de températures d'homogénéisation énormes.

2- Les conditions pression-température peuvent varier au cours du dépôt de la calcite. Il n'est cependant pas possible de mettre en évidence un gradient de température lorsqu'on examine des calcites prélevées dans le filon à partir de l'éponte jusqu'au coeur: toutes contiennent une large gamme de températures d'homogénéisation.

3- Le mélange de plusieurs fluides influence autant les salinités, c'est-à-dire les températures de fin de fusion, que les températures d'homogénéisation. Les calcites en géodes contiennent des inclusions fluides dont les températures de fin de fusion montrent une grande dispersion qui pourrait effectivement s'expliquer par le mélange de fluides de salinités différentes.

4- La recristallisation du minéral hôte peut conduire à la division d'inclusions en plusieurs inclusions. Il en résulte une grande dispersion des températures d'homogénéisation. (Darimont et Coipel, 1982).

Sans l'appui de renseignements morphologiques, la signification des différents domaines de températures obtenus est difficile à élucider. De plus, la recristallisation n'affecte pas nécessairement toutes les inclusions; et elle peut se produire à différentes températures.

5- L'ébullition est le processus le plus séduisant: il conduit à la connaissance de la température de piégage sans correction de pression. Malgré la présence de bulles de gaz qui s'expansent pendant la chauffe, non homogénéisées à 360°C, l'ébullition n'a pu être mise en évidence. La non détection d'inclusions à très fort remplissage gazeux nous empêche d'apprécier les températures d'homogénéisation minimales, correspondant aux températures probables de formation.

CONCLUSIONS

Les caractéristiques thermométriques des inclusions fluides des calcites permettent de distinguer les calcites "fertiles" des calcites "stériles":

- A Belle Roche, site stérile, les calcites en géodes dans les niveaux dolomitiques ou bréchiques ont cristallisé à des températures proches ou supérieures à 150°C. La salinité des fluides piégés, exprimée en température de fin de fusion, bien que variable, se situe le plus souvent autour de -8°C.

- A Poppelsberg, site fertile, les inclusions fluides des calcites à contenu CO_2 faible (< 0.25 moles %) se sont formées à des températures certainement supérieures à 110°C. Sans évidence d'ébullition, on peut considérer que les fluides minéralisateurs sont des fluides "chauds". Les homogénéisations en phase liquide se font à des températures pouvant dépasser 360°C.

Au sein du site fertile, les calcites filoniennes se distinguent par deux types de températures de fin de fusion: -21°C et -14°C. Certaines calcites en veines y sont apparentées (même Tf_2). Les températures de fin de fusion rencontrées dans les calcites géodiques sont variables.

En raison du doute qui pèse sur l'interprétation de la dispersion des températures d'homogénéisation des inclusions fluides des calcites de Poppelsberg, il est prématuré de poser des limites quant aux mécanismes de dépôt, ou d'essayer d'envisager une origine quelconque.

Les investigations dans d'autres sites, et sur d'autres minéraux, soutenues par une étude isotopique s'avèrent indispensables pour situer les inclusions dans un contexte génétique.

Remerciements. Cette étude a été subsidiée par la Communauté Economique Européenne et par les Services Belges de la Politique Scientifique. Elle a été menée dans les laboratoires de

Géologie Appliquée et de Géologie, Pétrologie, Géochimie de l'Université de Liège.
L'Union Minière nous a permis d'échantillonner les sondages de la zone minéralisée de Poppelsberg.
Nous remercions J.Coipel, B.Kreulen et T.Shepherd pour leur collaboration, J.Touret pour son acceuil à Amsterdam et ses critiques positives.

BIBLIOGRAPHIE

Darimont, A., Coipel, J.: Dispersion des températures d'homogénéisation: ébullition ou division par étranglement? Chem.Geol. 37, 151-163 (1982)

Giordano, T.H., Barnes, H.L.: Lead transport in Mississippi Valley Type Ore solutions. Econ.Geol. 76, 2200-2211 (1981)

Hollister, L.S.and others: Practical aspects of microthermometry. In: Short Course in fluid inclusions. Hollister, L.S., Crawford, M.L.(ed. 278-304 (1981)

Timmerhans, Ch.: Les gîtes métallifères de la région de Moresnet. Congrès international des mines, de la métallurgie, de la mécanique et de la géologie appliquée, Liège, 1905

Received: July 27, 1982
Accepted: March 24, 1983

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Mineral.Deposita 18, 387-398 (1983)

MINERALIUM
DEPOSITA

Geochemical Proximity Indicators of Massive Sulphide Mineralization in the Iberian Pyrite Belt and the East Pontic Metallotect

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A comparative lithogeochemical study of mainly surface rocks of the Iberian Pyrite Belt (volcanic-sedimentary sequence) and the East Pontic metallotect (volcanic island arc system with few intercalations of marine sediments) has been performed in order to find facies-independent proximity indicators of massive sulphide mineralizations. As, Sb, Tl, and Na seem to be the most promising indicator elements for primary hydrothermal exhalation and/or alteration haloes. The size of the alteration haloes largely depends on the permeability of the country rocks and is best defined by ratios such as As/Na, Sb/Na, and Tl/Na.

INTRODUCTION

During geochemical prospecting for strata-bound volcanogenic massive sulphide deposits increasing emphasis is being placed on lithogeochemical methods (e.g. Govett & Pwa 1981, Large 1981, Pirie & Nichol 1981, Selinus 1981, Sopuck et al. 1980, van den Boom et al., 1980). In contrast to conventional soil geochemistry, litho- or rockgeochemistry (Govett 1983) may supply information about the primary geochemical environment of ore deposition, and is less sensitive to secondary contaminations. Proximity indicators derived from lithogeochemical patterns thus directly reflect the pathways of the mineralizing solutions.

Lithogeochemical exploration concepts for volcanic-sedimentary sulphide deposits stem from models that regard such mineralization as the product of submarine hydrothermal activity. Not only would perculating hydrothermal fluids alter the mineralogy and geochemistry of the rocks (e.g. the well documented footwall alteration pipes or stockwork zones with intensive chloritization, sericitization and silification), but they should also determine the development of geochemical zonations on the sea floor around the sites of discharge.

The purpose of this study was to develop lithogeochemical proximity indicators of general applicability for strata-bound base metal deposits by analyzing mainly the distribution patterns of some highly mobile elements such as Sb, As, Tl, and F in different geological environments.

Analytical Methods

Neutron activation analysis, atomic absorption spectrophotometry, and potentiometry have been applied as analytical methods. The behaviour of 42 elements has been studied, but only results on As, Sb, Na, Tl, F, and Au will be reported here in detail.

GEOLOGICAL SETTING AND MINERALIZATION

Iberian Pyrite Belt

In the Pyrite Belt massive stratiform pyrite orebodies associated with disseminated sulphides of copper, lead and zinc are hosted by a Lower Carboniferous volcanic-sedimentary sequence of marine origin (Fig.1). These sulphide mineralizations are spatially and temporally related to felsic cycles of a bimodal volcanism. The host rocks at proximal locations are mainly quartz-keratophyric pyroclastics and rarely lavas, whereas in more distal locations they are slates, including black slates. The products of mafic volcanism (spilites, spilitic tuffs, dolerites) are quantitatively much important and do not indicate genet relations with the sulphide mineralizations. In general the sulphide-bea ing horizons are topped by jaspery o dic Mn-Fe rich sediments which, toge with the sulphides, mark the waning stage of the felsic volcanic activity Using the assumption that the manganese-iron mineralization should have been fed from nearly the same hydrothermal volcanic sources as the underlying sulphide bodies we interpret them as genetically associated exhalative Mn-Fe aureoles. Our lithogeochem cal investigation concentrated on thi marker horizon. The whole volcanic-sedimentary pile is overlain by non-mineralized slates and graywackes of the Culm group.

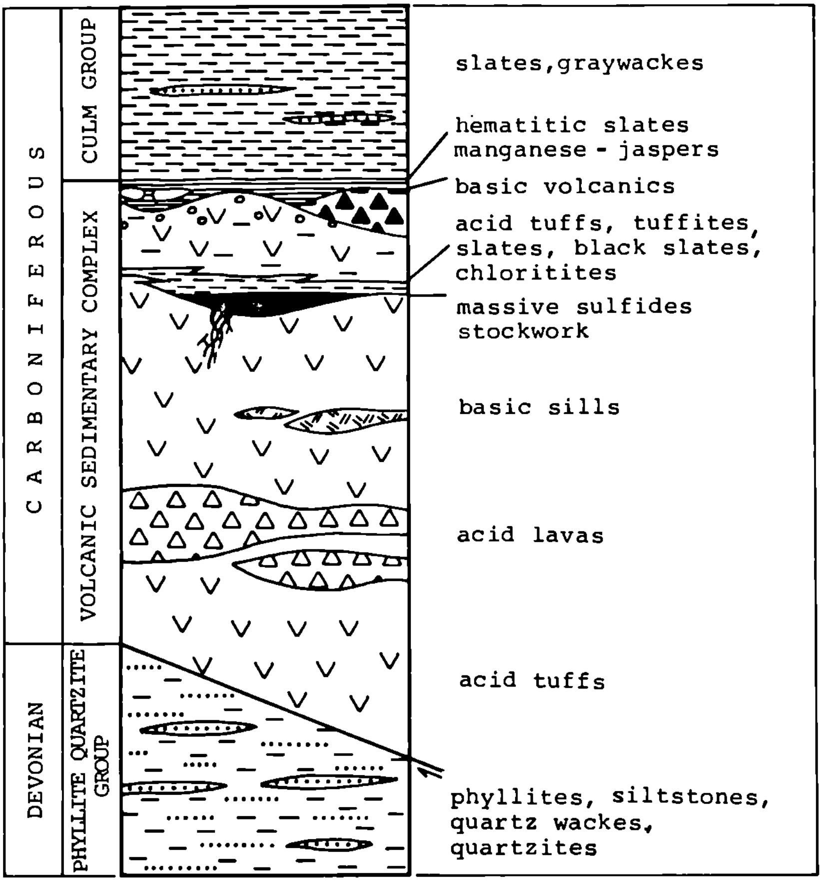


Fig.1. Schematic lithostratigraphic column for the ore-bearing sequence at the northern flank of the Rio-Tinto Syncline

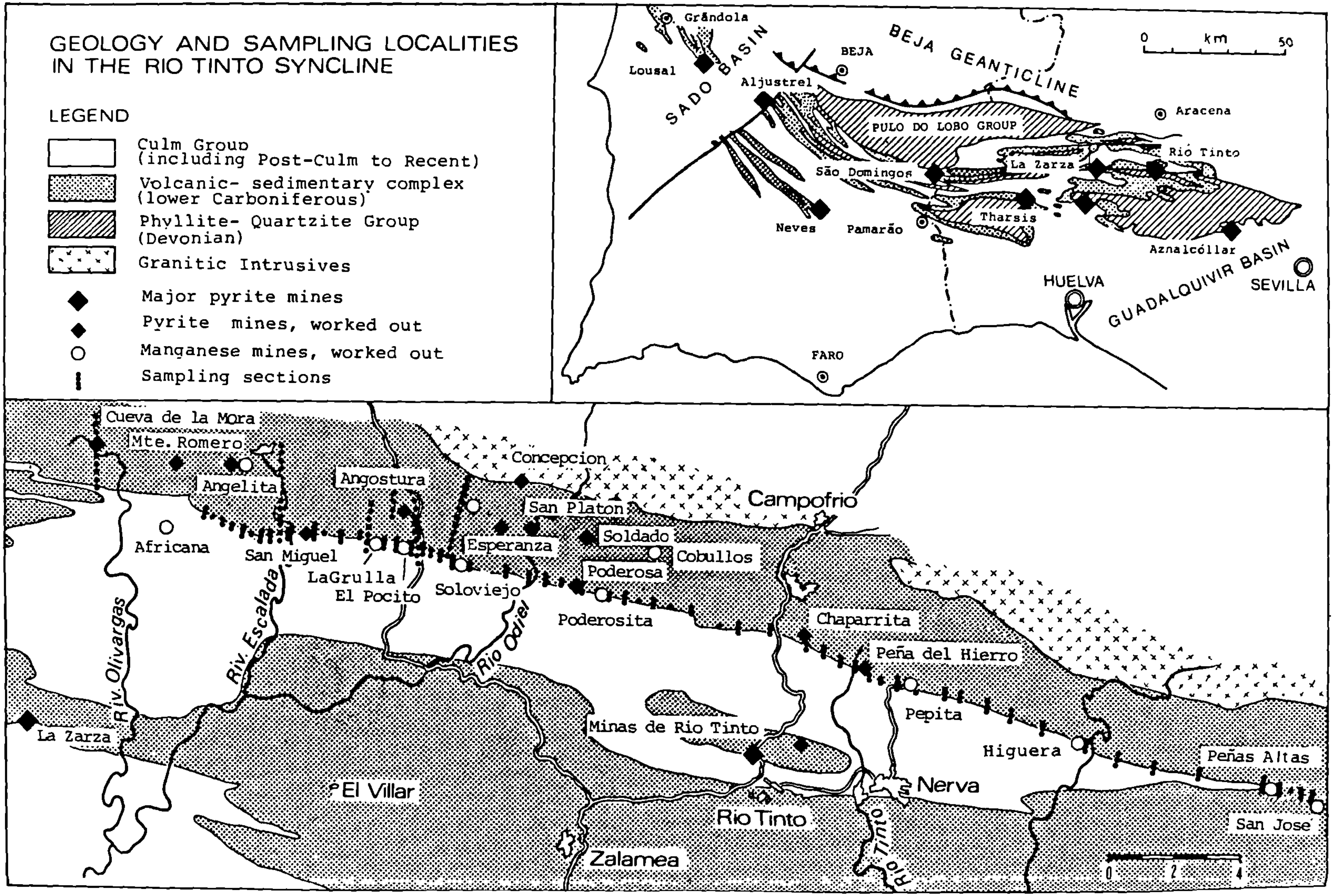
Geological and metallogenetical oblems of the SW-Iberian Pyrite lt (the type area of Iberian type volcanogenic polymetallic pyritic posits according to Schermerhorn 81) recently have been dealt with in epth by Bernard and Soler (1980) and outhier et al. (1978). Previous stuies of lithogeochemical haloes in the all rocks around orebodies (Kersabiec nd Roger 1976, Strauss et al.1981) sing trace element distributions (mainy Cu, Pb, Zn, Co, Ni) stressed the lack f any relationship between the ore and ts volcano-sedimentary environment. here are, however, indications of ydrothermal alterations located mainy in footwall zones which resulted in g and K enrichment and Na impoverishent (e.g. Garcia Palomero 1980, Berard and Soler 1980, Straus et al. 981). In general previous exploraion for sulphide deposits in the Pyite Belt has mainly been based on conentional geological and geophysical ethods (Strauss et al. 1977). Cu-Pb-Zn oil geochemistry did not prove to be f much practical use, because suitble soils were either lacking or were eavily contaminated by the extensive ining and smelting activities. Howver, mercury surveys of soils and soil ases have yielded more promising reults (Robbins, 1975).

The northern flank of the Rio Tinto yncline (Rambaud 1969), where both sulhide and associated manganese mineraliations occur, has been chosen as the ain study area (Fig.2). About 1000 amples were taken along strike from a 6 km long section of the most promient manganese-bearing horizon overying the uppermost sulphide level.Also ampled were sections across the sulhide-bearing volcanic-sedimentary seuence in the vicinity of some known oreodies.

ast Pontic Metallotect

ccording to plate tectonic concepts, he East Pontic metallotect represents volcanic island arc system of Cretaeous to Tertiary age which hosts a reat number of base metal deposits Akin 1979, Akinci 1980, Aslaner 1977, Leitch 1981, and Sawa et al. 1970). The entire metallotect extends over more than 350 km in an east-west direction and constitutes the mobile belt between the Pontic and the Anatolian plate (Fig.3). The ratio of economically interesting base metals is changing in the general striking of the metallotect from east (Cu >>Pb+Zn) to west (Pb+Zn >Cu).

Volcanic activity in the East Pontic Belt began in the Upper Jurassic-Lower Cretaceous with the extrusion of a 4000 m thick sequence of various basic volcanics onto crystalline basement (Fig.4) (Akin 1979, Aslaner 1977, Buser et al. 1973, Maucher et al. 1962). A locally exposed disconformity separates this sequence from Upper Cretaceous dacitic volcanics of approximately 1000 m thickness which consist mainly of lava flows and intercalated pyroclatics. Mineable mineralization is confined to a distinct phase of dacitic-rhyolitic eruptives within the Upper Cretaceous (Maucher 1969, Tugal 1969). Volcanic products are extremely variable from place to place and the presence of interfingering lava flows and pyroclastic layers as well as agglomerate pipes suggests the existence of a number of eruptive centers. It may be possible to correlate these variable sequences using a distinctive series of tuffs and small lenses of sandstone at the top of the sequence which can be identified everywhere by their intensive alteration (e.g. silification and kaolinitization). It is noteworthy that according to our observations the mineralization nowhere traverses this "marker bed", and that in addition to being barren the transgressive rocks do not exhibit any geochemical dispersion haloes (e.g. "flysch limestones" at Akarsen, dacite at Murgul, andesites and basalts at Madenköy etc.). Therefore, the volcanic hydrothermal mineralization must have been limited to a relatively short time interval during the Upper Cretaceous. It was regionally confined to isolated spots. This feature is also substantiated by the geochemical results. A lesser mineralizing event seems to be linked to dacitic and andesitic volcanics of Paleocene to Eo-



GEOLOGY AND SAMPLING LOCALITIES IN THE RIO TINTO SYNCLINE

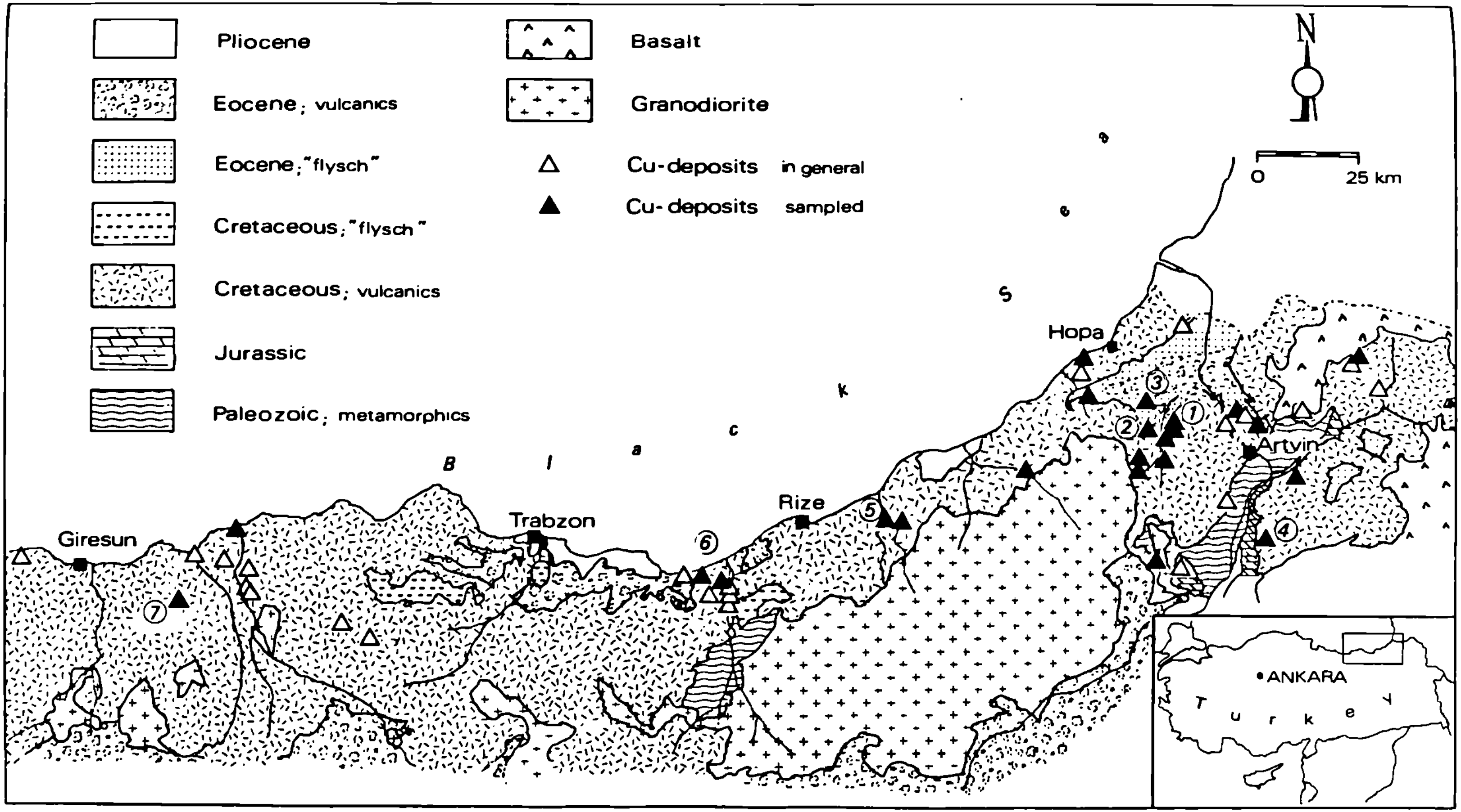


Fig.3. Geological setting of the East Pontic metallotect generalized after various authors; Main deposits: 1 - Murgul, 2 - Akarsen, 3 - Basköy, 4 - Hotmaden, 5 - Madenköy, 6 - Kutlular, 7 - Lahanos

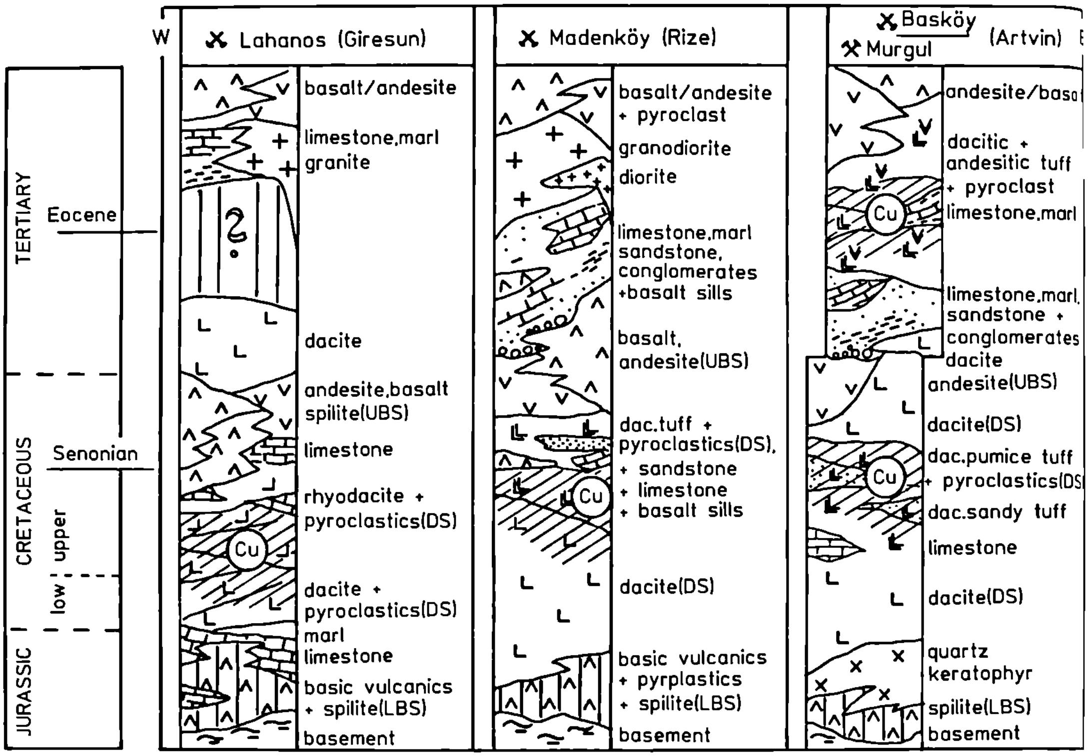


Fig.4. Simplified lithostratigraphic columns for the East Pontic metallotect; Cu-base metal mineralization in general, cross hatching - alteration zone, mainly kaolinization and silicification; UBS - Upper Basic Series; DS - Dacitic Series; LBS - Lower Basic Series

cene age (e.g. Basköy, Fig. 3 and 4), but the results reported here are restricted to the Upper Cretaceous group.

Comprehensive geologic investigations of the entire belt are still lacking and the "stratigraphic" correlation of the mineralized members is somewhat uncertain since most of the isolated mining areas have only been surveyed locally (Aslaner 1977, Buser et al. 1973, Cagatay et al. 1980, Leitch 1981, Tugal 1969, Sawa et al. 1970). Nevertheless, a semi-strata-bound nature of the mineralization seems to be acceptable and leads us to propose a common mode of genesis. Some additional observations support this hypothesis. Maucher (1969) and Maucher et al. (1962) have pointed out the stratiform and syngenetic nature of the Upper Cretaceous base metal deposits in the western part of the metallotect and an increasing number of authors have confirmed this concept (e.g. Akin 1979, Akinci 1980, Aslaner 1977, Cagatay et al. 1980, Leitc 1981, Tugal 1969). We would suggest that the semistrata-bound character of these mineralizations could be used as a tool for further prospecting activities.

The sampling programme has been confined to the vicinity of the numerous known mineralizations (abandoned mines) and the area of the working Murgul mine in order to obtain a regional comparison. Commonly surface rocks have been sampled, in 100 to 600 m profiles cutting the whole rock sequence from the unmineralized base to the barren overlying members (Fig.6) As a whole about 1400 host rock and ore samples were taken from 25 profiles. The results discussed here refer to only about 50% of the analytical work.

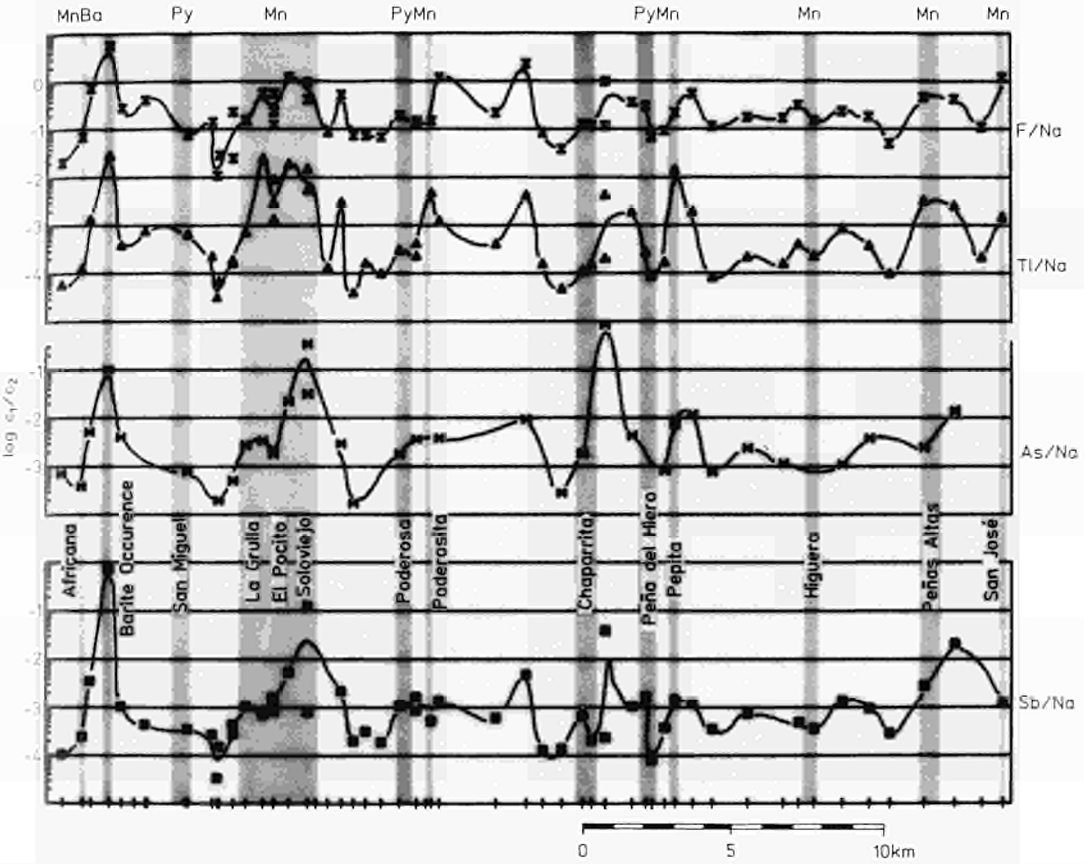


Fig.5. Distribution of F/Na, Tl/Na, As/Na and Sb/Na ratios in hematitic slates along a 36 km striking profile at the northern flank of the Rio-Tinto Syncline. X-axis: Sampling locations as indicated in Fig.2

For improvement of the hard rock geochemistry at some places additionally soil and stream sediment samples have been analyzed indicating unknown base metal anomalies (e.g. south of the Murgul deposit and south of Sirtköy).

DISCUSSION

Iberian Pyrite Belt

By combining petrographic and geochemical analysis a detailed petrologic classification has been established for the most important rock types of the volcanic-sedimentary complex. Altogether 16 rock types can be distinguished which exhibit exclusively unimodal frequency distributions of their most characteristic major, minor, and trace elements. Based on these lithologies, geochemical profiles for different indicator elements have been worked out of which one selected example is discussed below.

In the hematitic slates of the manganese-iron formation the proximity of jasper/manganese ore bodies (e.g. La Grulla, El Pocito, Soloviejo, Pepita) and a barite ore body W of San Miguel is indicated by anomalously high concentrations (compared to the regional background) of the mobile elements As, Sb, Tl, and F, and by lowered concentrations of Na. Using elemental ratios, the anomalies of As/Na, Sb/Na, Tl/Na, and F/Na (Fig.5) are most prominent near manganese ore bodies, but some of the stratigraphically lower sulphide

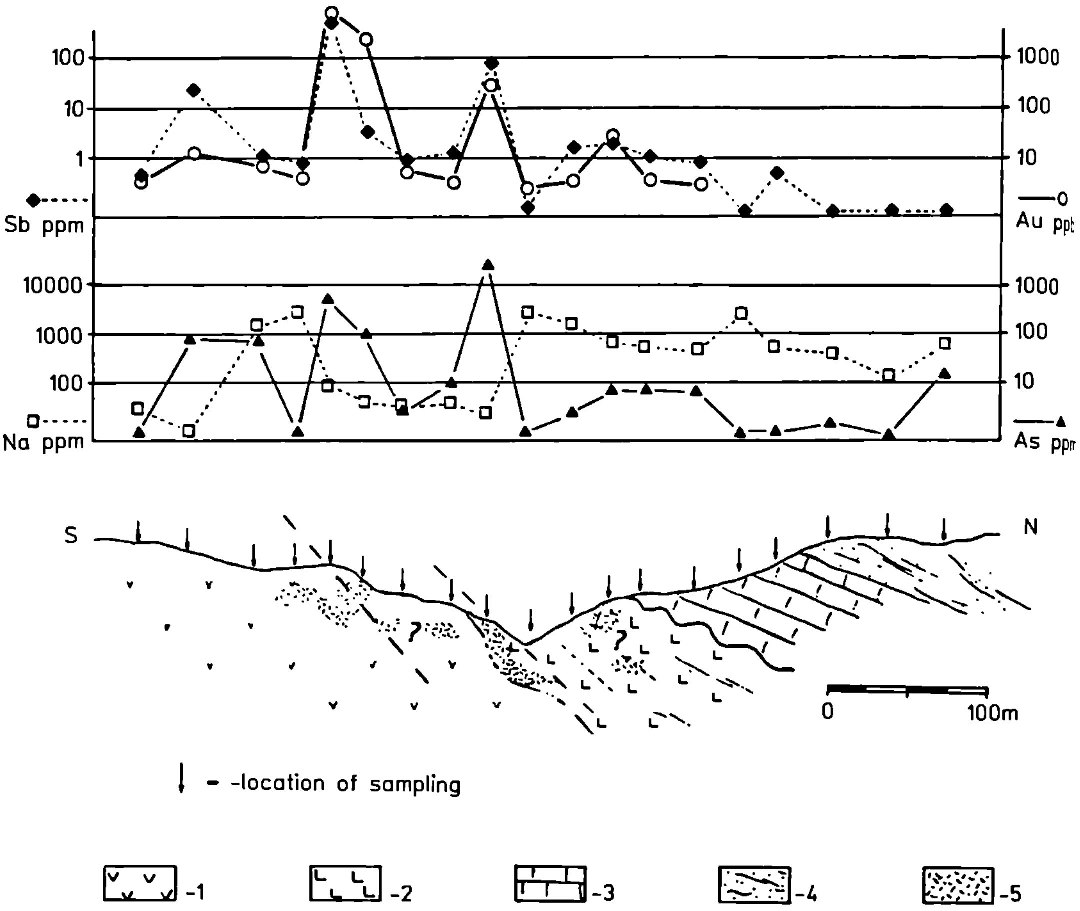


Fig.6. Akarsen deposit, Murgul area. Combination of two N-S sampling profiles crossing the deposits. Observe the positive Sb-Au-As anomalies and the negative Na anomaly in the mineralized areas in contrast to the barren transgressive se ments in the northern part 1 - dacite, 2 - dacite tuff, 3 - marine sediments (limestone), 4 - "flysch", 5 - mineralization

ore bodies (Poderosa, Chaparrita) are clearly detectable, too. Additional anomalies occur away from known deposits e.g. W of Chaparrita; they possibly indicate blind ore bodies.

In similar geochemical sections in the stratigraphically lower acid volcanics, which are the immediate host rocks of the sulphide ore bodies, the elemental ratios clearly indicate zones of hydrothermal fluid-rock interactions in the vicinity of sulphide ore bodies (e.h. San Miguel, Peña del Hierro).

In the slates of the overlying Culm group underlying ore bodies can be traced by the same geochemical indicators, although with less contrast. These anomalies can be considered as secondary dispersion haloes from the underlying accumulations which resulted from diagenetic or metamorphic solution transport. In all cases Zn does not show significant anomalies.

Anomalous Cu and Pb contents seem to be restricted mainly to host rocks in the immediate vicinity of sulphide bodies or sulphide-bearing horizons.

Hence Cu anomalies observed in the footwall of Mn-Fe formations could indicate blind sulphide bodies.

The geochemical contrast of the anomalies of major and trace elements as evaluated from regional background ratios taken from partitioned probability frequency distributions decreases in the order: Cu - As - Tl - Na - Sb - Pb - Ba. Enrichment factors for As and Tl are about 10, for Sb ~5, and the depletion factor for Na is ~8.

The spatial dimensions of the anomalies have been studied by geostatistical methods. One-dimensional variograms exhibit mean horizontal diameters of haloes between around 700 m for Sb and 1500 m for Na. The spatial dimensions of the anomalies increase in the order: Cu - Sb, As, Tl - Pb - Na - Ba - Mn.

In addition to Mn-enrichment the geochemical facies of the Mn-Fe formation is characterized by regionally elevated contents of Ba which locally culminate in stratiform low-Sr barite bodies. These are accompanied by F anomalies.

Footwall zones of autochthonous sulphide bodies (e.g. San Miguel) and locally hanging-wall or lateral peripheral positions of host rocks may be characterized by intensive chloritic alterations resulting in Mg and Fe anomalies. Also, silicification and sericitization (Rio Tinto, La Zarza) may accompany pyrite ore bodies. In summary, the geochemical pattern of the ore-bearing volcanic-sedimentary sequence of the Pyrite Belt is characterized by broad anomalies which may attain regional size as in case of manganese.

East Pontic metallotect

The data on trace elements in bedrock samples from the overlying and underlying volcanic formations do not indicate extensive geochemical dispersion haloes and anomalies except within the near vicinity of the ore bodies. Here, conspicuous increases in mobile elements as Tl, As, Sb, Au, and F, and a decrease in Na are observed.

Within the mineralized area of the well exposed Murgul deposit, the highest F values delineate lineaments which may be considered as the feeder veins for the ascending hydrotherms. Outside of this area, as well as in the overlying barren dacite member, the F values decrease rapidly. Since the F contents vary over nearly one order of magnitude, the F data could be applied as a local geochemical indicator for covered mineralizations.

Within the silicified dacitic-andesitic tuffaceous sequence As, Sb, Tl, Na have been found to behave like F in Murgul and change their concentration levels only in the near vicinity of mineralizations (Fig.6). This indicates that geochemical contamination caused by the ascending metal-bearing solutions did not permeate the host rocks to any large extent, whereas the silicification and propylitization affected the whole rock body. The primary alteration haloes are in the order of 10-50m wide. A second stage of spatially restricted silicification is strictly bound to the sulphide mineralization.

The occurrence of anomalous Au values in the altered country rock seems to be linked to zones of positive Sb and As and negative Na anomalies (Fig. 6). The Au concentrations range up to 8 ppm with typical values of about 30 ppb. Enhanced concentration of either Au or Mo is of general genetic interest. Since Mo in all samples analyzed has been found to be below the detection limit of about 100 ppb, the elevated Au values probably indicate a genetic relationship of the E-Pontic copper deposits with the copper porphyries of the island-arc type.

In the studied area the anomalies of the elements As, Sb, Tl, F, Au, and Na are rather narrow and restricted to the vicinity of the ore bodies probably due to a spot-like exhalative mineralization in a prevailing nonmarine environment.

CONCLUSIONS

In both areas very similar geochemical wall rock alterations have been observed which involve loss of Na and gain of As, Sb, Tl, and F. However, the spatial extent of these phenomena differs considerably in the two areas.

Loss of Na during hydrothermal alteration is a well known phenomenon (Spitz and Darling 1978, Ramsden and Ryall 1979). Grigorjan (1976) reports that the largest dispersions in wall rocks of hydrothermal deposits are those of Sb and As.Furthermore, he points out that these elements are some of the most important indicators of polymetallic deposits. Tl is enriched in hydrothermal alteration zones where it is preferentially hosted by micas (De Albuquerque and Shaw 1969). F species are common constituents of volcanic gases and are easily adsorbed and incorporated by various clay minerals and micas. In this way anomalous F in clay minerals may be used to define marker horizons of ancient hydrothermal or fumarolic activity (Schneider et al.1975).

The elements As, Sb, Tl, and F characterize hydrothermal solutions by their enhanced concentrations. During cooling As, Sb, and Tl will be coprecipitated with or adsorbed by the minerals near the discharge area.

Following Large's (1977) hypothetical solution recycling convective model most of the metals could have been leached from the volcanic host rocks at depth. The heating of the fluids could have resulted from the volcanic activity.

In principle such a model would explain the different geochemical features of both areas. The difference is that in the Iberian Pyrite Belt the fluids discharged into highly permeable sediments in a marine environment with a chance of extensive lateral dispersion. In contrast, in the Pontides local hydrothermal conduits may prevailingly have discharched subaerialy. After some erosion this area was covered by barren volcanites and sediments. Alteration and exhalation haloes therefore differ in size and range from tens of metres in massive volcanic rocks of the Pontides to km in volcanic-sedimentary sequences of the Pyrite Belt. The main controlling factors thus seem to be the paleo-permeability of the medium and the environment of deposition.

In conjunction with geologic mapping and petrographic analysis, lithogeochemistry of mobile elements such as As, Sb, and Tl can therefore be used as an effective technique in the exploration for strata-bound sulphide deposits particularly in mixed volcani sedimentary environments.

Acknowledgements. The authors are indebted to the Commission of the European Communities for their financial support under contract No. 117-80 MPP D. The help of the following companie and organizations is gratefully ackno ledged: Comisión Nacional de Geologia, Madrid, M.T.A. and Etibank, Ankara. We are also indebted to Prof.G.K.Mueck (Halifax) and Prof.G.Friedrich (Aachen for their criticism and improvement of the text.

REFERENCES

Akin, H.: Geologie, Magmatismus und Lagerstättenbildung im ostpontisch Gebirge/Türkei aus der Sicht der Plattentektonik. Geol.Rdsch. 68, 253-283 (1979)

Akinci, O.T.: Major copper metallogeni unites and genetic igneous complexes of Turkey. In: European Copper Deposits, S. Jankovic, R.H.Silitoe, Eds., 199-208, Proc. Internat. Sy Belgrad, Dpment. Econ. Geol. 1980

Aslaner, M.: Studies of Cu-Pb-Zn Deposits and Comparison between thei Geological Setting and Plate Tectonics in Turkey (Turkish). 70 pp., Trabzon: Karadeniz Teknik Universitesi 1977.

Bernard, A.J., Soler, E.: Problèmes géologiques et métallogéniques en province de Huelva (Espagne). Publ. 26^{e} Congrès Géol. Inter., 26 CGI D 5, 1-54, Paris (1980)

Buser, S., Cvetic, S.: Geologie der Umgebung der Kupfererzlagerstätte Murgul in der Türkei. MTA Bull.81, 22-44 (1973)

Cagatay, M.N., Boyle, D.R.: Geology, geochemistry and hydrothermal alteration of the Madenköy massive sulphide deposit eastern Black Sea ragion, Turkey. In: IAGOD Symposiu

J.D.Ridge, Ed., 5th Proc. 653-678. Stuttgart: E.Schweizerbart 1980

De Albuquerque, C.A.R., Shaw, D.M.: Thallium. In: Handbook of Geochemistry, K.H. Wedepohl, Ed., Vol.II/5, 81-F-1 to 81-F-8. Berlin, Heidelberg, New York: Springer 1969

Garcia Palomero, F.: Caracteres Geologicos y Relaciones Morfologicas y Geneticas de los Yacimientos del "Anticlinal de Riotinto". 264 pp., Huelva: Insti. de Estudios Onubenses "Padre Marchena" 1980

Govett, G.J.S.: Rock Geochemistry in Mineral Exploration. In: Handbook of Exploration Geochemistry, G.J.H. Govett, Ed., Vol. 3, 461 pp., Amsterdam: Elsevier 1983

Govett, G.F.S., Pwa, A.: Regional reconnaissance exploration rock geochemistry for massive sulphides, New Brunswick, Canada. J. Geochem. Explor. 15, 139-158 (1981)

Grigorjan, S.W.: Primäre geochemische Aureolen bei der Suche und Erkundung von hydrothermalen Lagerstätten. Z. angew. Geol. 22, 398-405 (1976)

Large, D.: The geochemistry of sedimentary rocks in the vicinity of the Tom Pb-Zn-Ba deposit, Yukon Territory, Canada. J. Geochem. Explor. 15, 203-217 (1981)

Large, R.R.: Chemical evolution and zonation of massive sulphide deposits in volcanic terranes. Econ. Geol. 72, 549-572 (1977)

Kersabiec, A.M.de, Roger G.: Sur la distribution de quelques éléments en traces dans l'encaissant des amas pyriteux de la partie centrale de la province de Huelva (Espagne). B.R.G.M.Bull. sect. II, no. 5, 439-488 (1976)

Leitch, C.H.B.: Mineralogy and textures of the Lahanos and Kizilkaya massive sulphide deposits, NE Turkey, and their similarity to Kuroko ores. Mineral.Deposita 16, 241-257 (1981)

Maucher, A.: Die Kieserze von Keltas, ein Beispiel submariner Gleitfalten in exhalativ-sedimentären Erzlagerstätten. N.Jb.Miner.A. 94, 495-505 (1960)

Maucher, A., Schultze-Westrum, H., Zankl. H.: Geologisch-Lagerstättenkundliche Untersuchungen im ostpontischen Gebirge. Bayer. Akad. Wiss., math.-nat. Kl., Abh. NF 109, 1-97, München (1962)

Pirie, I.D., Nichol,I.: Geochemical dispersion in wallrocks associated with the Norbec deposit, Noranda, Quebec. J. Geochem. Explor. 15, 159-180 (1981)

Rambaud Perez, F.: El sinclinal carbonifero de Rio Tinto (Huelva y sus mineralizasiones asociadas. Mem.Inst.Geol.Min.Espana 71, 1-229 (1969)

Ramsden, A.R., Ryall, W.R.: The Lachlan Fold Belt: Contributions to Mineral Exploration. Investigation Rep. 128 of the Institute of Earth Resources, CSIRO, 112 pp. 1979

Robbins, J.: Mercury as a Geochemical Trace Element. Scintrex Rep., 31 pp., Concorde: Scintrex 1975

Routhier,P., Aye,F., Boyer,C., Lecolle,M., Molière,P., Picot,P., Roger,G.: La ceinture sud-ibérique à amas sulfurés dans sa partie espagnole médiane. Tableau géologique et métallogénique. Synthèse sur la type amas sulfurés volcano-sédimentaires. Mém. B.R.G.M. 94, 1-265 (1978)

Sawa, T., Sawamura, K., Tesrekli, M.: Report on the Copper Deposits of the Murgul Mine and the Adjacent Area. (Turkish). Unpubl. Report, 70 pp., Ankara: M.T.A. 1970)

Schermerhorn, L.J.G.: Framework and evolution of Hercynian mineralization in the Iberian Meseta. Leidse Geol. Mededelingen 52, 23-56 (1981)

Schneider, H.-J., Möller, P., Parekh, P.O.: Rare earth elements distribution in fluorites and carbonate sediments of the East-Alpine Mid-Triassic sequences in the Nördliche Kalkalpen. Mineral.Deposita 10, 330-344 (1975)

Selinus,O.: Lithogeochemical exploration data in sulphide prospecting in Northern Sweden. J.Geochem.Explor. 15, 181-201 (1981)

Spitz,G., Darling,R.: Major and minor element lithogeochemical anomalies surrounding the Louvem copper deposit Val d'or, Quebec. Can.J.Earth Sci. 15, 1161-1169 (1978)

Sopuk,V.J., Lavin,O.P., Nichol,I.: Lithogeochemistry as a guide to identifying favourable areas for the discovery of volcanogenic massive sulphide deposits. Can.Inst. Min.Metall.Bull. 73, 152-166 (1980)

Strauss,G.K., Madel, J., Fernandez Alonso,F.: Exploration practice for strata-bound volcanogenic sulphide deposits in the Spanish-Portuguese Pyrite Belt: Geology, geophysices and geochemistry. In: Time- and Strata-Bound Ore Deposits, D.D.Klemm, H.-J.Schneider, Eds., 55-93. Berlin, Heidelberg, New York: Springer 1977

Strauss, G.K., Roger,G., Lecolle,M., Lopera,E.: Geochemical and geologic study of the volcano-sedimentary sulphide orebody of La Zarza, Huelva Province, Spain. Econ.Geol. 76, 1975-2000 (1981)

Tugal,H.T.: The Pyritic Sulphide Deposits of the Lahanos Mine Area, Black Sea Region, Turkey, Doct. Thesis, 182 pp., Univ. Durham 1969

Van den Boom,G., Rehder,S., Kottrup, G.: Geochemical patterns in the rocks surrounding the Woodlawn volcanogenic ore deposit, New South Wales, Australia. Geol.Jb.D 40, 169-200 (1980)

Received: March 15, 1983
Accepted: April 21, 1983

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Mineral.Deposita 18, 399-410 (1983)

MINERALIUM
DEPOSITA

Stable Isotope Studies of Sulphide Mineralisation on the Leinster Granite Margin and some Observations on its Relationship to Coticule and Tourmalinite Rocks in the Aureole

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Galena and sphalerite occur in brecciated veins along the eastern margin of the Caledonian Leinster Granite in south-east Ireland. This mineralisation is spatially related to the occurrance of spessartine quartzites (coticules) in the aureole rocks. Tourmalinites are closely associated with these coticules. A decrease in the temperature of mineralisation from about 500°C in the northern Unit I to 250°C in the central Unit III to possibly less than 200°C in the southern Unit V of the intrusion is suggested by decreasing sulphide $\delta^{34}S$ values, increasing sulphate $\delta^{34}S$ values and sulphide-sulphate fractionation values. Sulphur, carbon and oxygen isotope data suggest the involvement in the vein mineralisation of sulphur, carbon and mineralising fluids at least partially derived from the coticule and tourmaline bearing aureole schists.

INTRODUCTION

The late-Caledonian Leinster Granite in SE Ireland (Fig. 1) intrudes a sequence of slates, greywackes, quartzites and calc-alkaline volcanic rocks ranging from Cambrian to Silurian in age. Pb-Zn sulphide mineral deposits occur at intervals along the eastern margin of the intrusion. Though there has been no doubt for many years concerning the age of the granite itself, that of the mineralisation has been a matter of some debate. Finlayson (1910), for instance, favoured a Hercynian age. Tremlett (1959) related the mineralisation to the granite emplacement. Lead isotope data (Moorbath, 1962) appear to favour the former opinion; the interpretation of the data is, however, open to doubt regarding the model used. Kennan (1978) recognised a relationship between the siting of sulphide deposition and the occurrence in the aureole of garnet quartzites and suggested that the source of the metals might lie in the aureole. The mechanism of metal transport envisaged aureole-derived hydrothermal waters set in motion as a result of the emplacement nearby of hot granite. Brück and O'Connor (1980, 1982) arrived at a similar conclusion and proposed, in addition, that a suite of major transverse fractures-faults acted as selective channelways for circulating ground waters and governed the siting of the base-metal deposits. Elsdon and Kennan (1982) presented additional evidence supporting a Caledonian age for the mineralisation.

Stable isotope and ore textural studies were undertaken (by F.W.) in order to further refine models explaining the

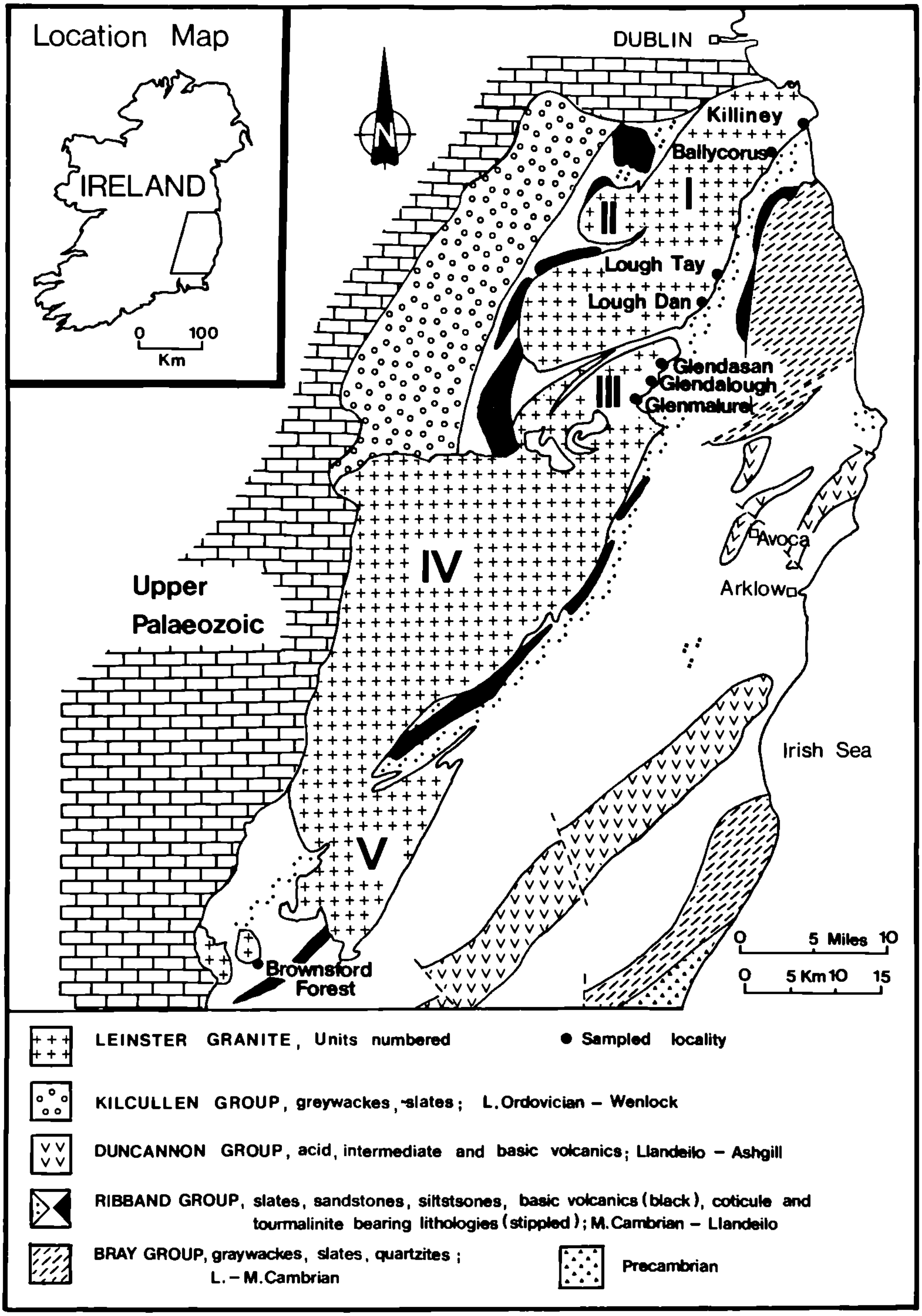

Fig. 1. Location and general geology (Based on Fig. 1 of Brück et al., 1979)

origin of the sulphide deposits on the granite margin. In this paper the results of this work are related to continuing studies on certain aureole lithologies (by P.S.K.). The aim is the creation of a model enabling the prediction of sites of significant mineralisation.

MINERALISATION

Sulphide mineralisation in the granite occurs along the eastern contacts of Units I, III and V (Fig. 1.). The sulphides occur in veins that often trend perpendicular to the granite contact. Some continue into the aureole schists for several metres. They are most abundant in Unit III. Some individual veins continue along strike for up to 3 km. They rarely exceed a width of 6 m.

In typical veins coarse grained galena and sphalerite with minor chalcopyrite and pyrite occur in a quartz and baryte gangue. Calcite is a common gangue mineral in Unit III only. Baryte is absent in Unit V. A generalised paragenetic scheme is shown in Figure 2.

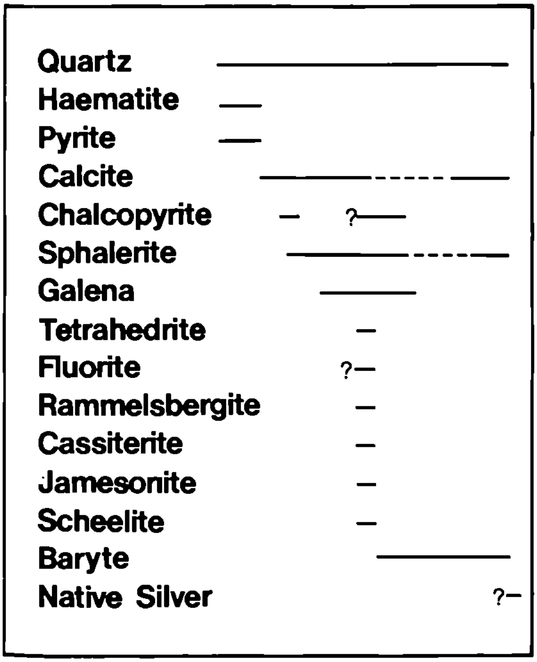

Fig. 2. Generalised paragenesis of the vein mineralisation

The veins are often associated with the occurrence of red feldspar bearing pegmatites (Kennan, 1978). These pegmatites occur as narrow veins and ill-defined aggregates of coarse crystals (Kennan, 1974). The red feldspar is characteristic as is the absence of the tourmaline, spodumene, beryl and garnet, common in other Leinster pegmatites.

Many of the veins show clear evidence of brecciation before and after sulphide deposition. This brecciation is likely to have been a factor contributing to both the migration of the ore bearing fluids and the provision of large surface areas on which the sulphides and their gangue minerals crystallised.

STABLE ISOTOPE STUDIES

Analytical Methods

Sulphur, carbon and oxygen isotope determinations were carried out on sulphide and sulphate minerals and whole rock samples. Sample localities are shown on Figure 1. Results are presented in Tables 1 and 2 and Figure 3. A Table giving the values of the 82 sulphur isotope analyses will be provided on request.

Extraction of sulphur dioxide from sulphides followed the method of Robinson and Kusakabe (1975), from baryte that of Coleman and Moore (1978) and from whole rock samples that of Thode and Monster (1965). Samples were run on a VG Micromass 602C double collector mass spectrometer at The Institute of Geological Sciences, London. Results have been corrected for instrumental crosstalk and isobaric interference (Coleman, 1980) and are expressed as ^{o}/oo differences from the troilite phase of the Canyon Diablo meteorite standard.

Carbon dioxide was extracted from calcite and whole rock samples by reacting them with 100% phosphoric acid at 25°C (McCrea, 1950). Samples were run on a VG Micromass 903 triple collector mass spectrometer. Results have been corrected for instrumental crosstalk and isobaric interference (Craig,

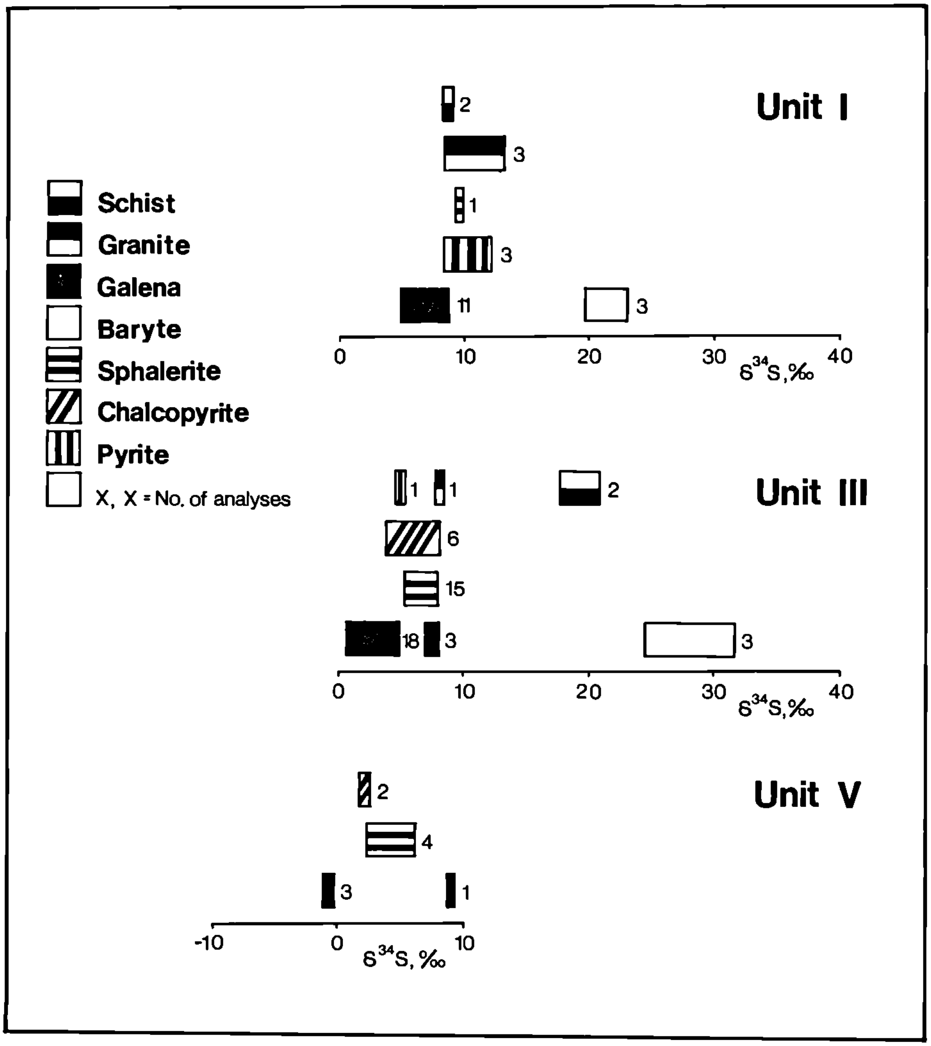

Fig. 3. Sulphur isotope results. All $\delta^{34}S$ values determined are included

1957) and are expresses as $^{0}/oo$ differences from the Chicago PDB standard for carbon and Standard Mean Ocean Water for oxygen.

Sulphur Isotope Determinations

A systematic difference in the $\delta^{34}S$ values can be seen in galenas from the three mineralised granite units (Fig. 3). $\delta^{34}S$ values of the galena from Unit I fall within the range +5.0 to +8.9$^{0}/oo$, those values from Unit III fall within the range 0.8 to 5.0$^{0}/oo$, with the exception of three values, and those from Unit V fall between -1.0 and -0.2$^{0}/oo$ with one exception. Baryte from Unit I has values in the range 19.7 to 23.0$^{0}/oo$, while those from Unit III range between 24.6 and 31.9$^{0}/oo$. No baryte was found in Unit V.

A control on the variation in the $\delta^{34}S$ values of tip heap samples was established using additional samples collected at varying spacings along several outcroping veins. The maximum variation between different sulphide samples from the same sulphide vein is 2.6$^{0}/oo$. The analytical error was

Table 1. Sulphur isotope values used to calculate sulphur isotope equilibration temperatures

Location	Sample No.	Gang.	Min.	δ^{34}S ^{o}/oo	Δ^{34}S ^{o}/oo	T. Err. T^{o}C ±( )
Unit 1						
Ballycorus	810662.2	None	Ga	+ 6.2	+ 5.7	166(4)
Ballycorus	810662.1		Py	+11.9		
Ballycorus	810654.81	Qtz	Ga	+ 5.0	+14.8	490(30)
Ballycorus	810654.83		Ba	+19.8		
Ballycorus	810654.84	Qtz	Ga	+ 6.3	+13.4	529(35)
Ballycorus	810654.82		Ba	+19.7		
Killiney	810704.2	Ba	Ga	+ 8.0	+15.0	485(29)
Killiney	810704.1		Ba	+23.0		
Killiney	810704.3	Ba	Ga	+ 8.9	+14.1	509(32)
Killiney	810704.1		Ba	+23.0		
Killiney	810703.2	Qtz	Ga	+ 6.3	+ 2.1	450(18)
Killiney	810703.1		Py	+ 8.4		
Unit 3						
Glendalough	810678.2	Ba	Ga	+ 2.7	+21.9	335(12)
Glendalough	810678.1		Ba	+24.6		
Glenmalure	802668.33	Ba	Ga	+ 7.0	- 0.5	Ds. --
Glenmalure	802668.31		Sph	+ 6.5		
Glendasan	810687.4	Qtz	Ga	+ 0.8	+ 5.2	157(4)
Glendasan	810687.5		Sph	+ 6.0		
Glendasan	810682.3	Qtz	Ga	+ 3.0	+ 4.9	170(5)
Glendasan	810682.4		Sph	+ 7.9		
Glendasan	810689.2	Qtz	Ga	+ 3.5	+ 4.1	211(6)
Glendasan	810689.3		Sph	+ 7.6		
Glendasan	810689.6	Qtz	Ga	+ 4.3	+ 2.3	278(13)
Glendasan	810689.5		Sph	+ 6.6		
Glendasan	810689.8	Qtz	Ga	+ 4.0	+ 3.4	259(8)
Glendasan	810689.9		Sph	+ 7.4		
Glendasan	810693.5	Qtz	Ga	+ 4.1	+ 2.6	335(12)
Glendasan	810693.4		Sph	+ 6.7		
Glendasan	810672.2	Qtz	Ga	+ 3.3	+ 2.9	303(10)
Glendasan	810672.1		Sph	+ 6.2		
Glendasan	810684.6	Qtz	Ga	+ 3.9	+ 2.0	297(14)
Glendasan	810684.2		Cpy	+ 5.9		
Glenmalure	802668.313	Cal	Sph	+ 7.8	+ 0.3	434(159)
Glenmalure	802668.314		Cpy	+ 7.5		
Glendasan	810687.12	Cal	Ga	+ 8.2	- 2.3	Ds. —
Glendasan	810687.13		Sph	+ 5.9		

Table 1 (continued)

Location	Sample No.	Gang.	Min.	$\delta^{34}S$ $^{o}/oo$	$\Delta^{34}S$ $^{o}/oo$	T. Err. $T^{o}C$ ±( )
Glendasan	810693.3	Cal	Ga	+ 2.3	+ 1.5	385(23)
Glendasan	810693.2		Cpy	+ 3.8		
Glendasan	810695.4	Cal	Cpy	+ 5.3	+ 2.4	Ds. --
Glendasan	810695.3		Sph	+ 7.7		
Glendasan	810694.2	Cal	Ga	+ 4.9	+ 4.6	102(5)
Glendasan	810694.4		Cpy	+ 9.5		
Glendasan	810670.5	Cal	Ga	+ 8.6	- 0.7	Ds. --
Glendasan	810670.4		Sph	+ 7.9		
Unit 5						
Brownsford	810699.1	Qtz	Ga	- 0.9	+ 7.2	92(3)
Brownsford	810699.2		Sph	+ 6.3		
Brownsford	810699.3	Qtz	Cpy	+ 1.9	+ 4.4	Ds. --
Brownsford	810699.2		Sph	+ 6.3		
Brownsford	810699.1	Qtz	Ga	- 0.9	+ 2.8	208(9)
Brownsford	810699.3		Cpy	+ 1.9		
Brownsford	810699.5	None	Ga	+ 9.0	- 6.4	Ds. --
Brownsford	810699.4		Sph	+ 2.4		

The quoted error reflects analytical errors, not published fractionation factor uncertainties. Temperatures were calculated using fractionation factors determined for the sphalerite-galena pair experimentally by Chamanske and Rye (1974) and theoretically by Sakai (1968). The chalcopyrite-sphalerite, pyrite-galena and chalcopyrite-galena fractionation factors used were those determined by Kajiwara and Krouse (1971). The baryte-galena fractionation factor used was that of Ohmoto and Rye (1979).
Ds. = Inferred disequilibrium

0.1^{o}/oo. The whole rock granite $\delta^{34}S$ values obtained from Units I and III are similar (+9^{o}/oo), as are the values of two schist samples from widely separated localities on the margin of Unit I. They differ markedly from the $\delta^{34}S$ values of +18.3 and +20.9^{o}/oo obtained from two schist samples collected from the margins of Unit III.

Sulphur Isotope Fractionation Values

The fractionation of sulphur isotopes between sulphide pairs depends on their temperature of crystallisation provided that they formed contemporaneously and in equilibrium with each other. Mineral pairs provide reasonable temperatures as long as both formed in equilibrium with solutions of uniform temperature and chemical states (Ohmoto and Rye, 1979).

In Unit I, the fractionation values obtained from galena-baryte pairs are considered the most reliable (see Rye and Ohmoto, 1974). They give an average temperature of mineralisation of 500°C (Table 1). The $\delta^{34}S$ values of the galena in the galena-pyrite pairs is within the same range as that of the galena-baryte pairs. This suggests that the

$\delta^{34}S$ values of the pyrite are heavy; galena and pyrite are not in equilibrium. Ore textural evidence suggests that the pyrite formed earlier in the paragenetic sequence.

In Unit III, the galena-sphalerite pairs in a quartz gangue give scattered positive fractionations; these are, however, adequate to indicate depositional temperatures of 200-350°C. The disequilibrium shown by sulphides in a calcite gangue suggests that the fluid was at too low a temperature to allow isotopic equilibration. This suggests a depositional temperature of less than 200°C for the calcite (see Rye, 1974). In the galena-sphalerite pairs which show disequilibrium the galena $\delta^{34}S$ values lie outside the normal 0.8 to +5°/oo range for Unit III and all are heavy.

The Unit V fractionation values imply disequilibrium and may reflect a temperature of deposition which was probably less than 200°C. Thus the depositional temperature appears to drop from about 500°C in Unit I to about 250°C in Unit III and to possibly less than 200°C in Unit V.

Source of Sulphur

The data for Units I and III show a systematic decrease in the $\delta^{34}S$ values of galena with a corresponding increase in those of baryte with falling temperature. This strongly suggests that the change in $\delta^{34}S$ values is due to equilibrium fractionation between sulphide and sulphate species at decreasing temperatures while the $\delta^{34}S$ value of the sulphur source remained constant (Fig.3; see Coleman, 1977).

The $\delta^{34}S$ values obtained from sulphides in Unit V could be due to low temperature sulphide-sulphate fractionation from a source with a $\delta^{34}S_{\Sigma s}$ value of +9°/oo. No sulphate minerals are known to be associated with the sulphide minerals implying that if a sulphate phase was present it was deposited elsewhere. The observed values could also be due to the influence of a magmatic sulphur source with a $\delta^{34}S_{\Sigma s}$ of 0°/oo or to a combination of both a 0°/oo and a +9°/oo source.

In Unit I, the essentially equal $\delta^{34}S$ values of trace sulphur in the granite, the aureole schist and the postulated vein sulphur source suggest a common sulphur source with a $\delta^{34}S_{\Sigma s}$ value of about +9°/oo. In Unit III, the essentially equal $\delta^{34}S$ values of the trace sulphur in the granite and the postulated vein sulphur source suggest that they also shared a common sulphur source with a $\delta^{34}S_{\Sigma s}$ value of about +9°/oo. However, the $\delta^{34}S$ values of the schist are very high (+18.3 and +20.9°/oo) and are not consistent with a $\delta^{34}S_{\Sigma s}$ value of +9°/oo. These values suggest bacterial reduction of sulphate in a closed basin and may reflect conditions that were restricted. In Unit V the vein sulphur could have been derived from a source with a $\delta^{34}S_{\Sigma s}$ value of +9°/oo by low temperature sulphide-sulphate fractionation. The higher than normal $\delta^{34}S$ values of one galena sample from Unit V and of three galena samples in disequilibrium with sphalerite in Unit III may also reflect partial re-equilibration from a +9°/oo source. Although the data do not establish a source with a $\delta^{34}S_{\Sigma s}$ value of +9°/oo for all three Units, such is plausible.

Thus it may be that the granite, the sulphide veins, and the aureole schists of Unit I shared the same sulphur source. The aureole rocks are suggested as the source of sulphur for the granite and the veins. The same source is plausible for Units III and V. The $\delta^{34}S_{\Sigma s}$ value of +9°/oo in the aureole rocks could have originated by bacterial reduction of seawater sulphate in an earlier open system. Assuming an average fractionation between bacteriogenically reduced sulphide and sea water sulphate of 15°/oo (Sangster, 1976) the $\delta^{34}S$ value of the corresponding sea water sulphate would be expected to be about +24°/oo. This lies in the lower end of the range of values for Lower Palaeozoic sea water given by Nielsen (1979).

Oxygen Isotope Determinations

The $\delta^{18}O$ values of calcite gangue in the sulphide in Unit III have a narrow range of 4.4°/oo, from +14.2 to 18.6°/oo (Table 2). Secondary trace

Table 2. Carbon and oxygen isotope results

Location	Sample No.	Description	$\delta^{13}C^{o}/oo$	$\delta^{18}O^{o}/oo$
Unit 1				
Killiney	810709	Granite	-11.3	+15.2
Lough Tay	810659C	Schist	-18.5	-
Unit 3				
Glendasan	810687.11	Calcite	- 6.8	+17.5
Glendasan	810670.3	Calcite	- 6.9	+17.6
Glenmalure	802668.317	Calcite	- 7.1	+16.0
Glendasan	810694.3	Calcite	- 7.8	+15.6
Glendalough	810678.3	Calcite	- 8.3	+14.2
Glendasan	810693.1	Calcite	- 8.9	+15.3
Glendasan	810689.7	Calcite	-12.8	+15.4
Glendasan	810689.1	Calcite	-13.0	+17.8
Glendasan	810695.2	Calcite	-14.6	+18.6

carbonate from a bulk granite sample from Unit I has a $\delta^{18}O$ value of +15.2°/oo. The analytical error was 0.05°/oo.

Source of Oxygen

The narrow range of $\delta^{18}O$ values (4.4°/oo) suggests that both the temperature of the fluid and the source of its oxygen remained constant. Any temperature variation would have produced large variation in the $\delta^{18}O$ values. A change of oxygen source would also produce a large range of values. The $\delta^{18}O$ value of trace oxygen in calcite in a bulk granite sample from Unit I also lay within the narrow range shown by the gangue calcite suggesting that they shared the same oxygen source. No carbonate is present in association with mineralisation in Units I and V.

Sulphur isotope values suggest that the calcite was deposited at temperatures less than 200°C (see above). Given this conclusion, the $\delta^{18}O$ values of the carbonate (Table 2) may constrain the nature of any waters involved. Magmatic $\delta^{18}O$ water values fall in the range +5.5 to +10°/oo (Taylor, 1974). At temperatures below about 180°C, the equilibrium fractionation between calcite and water assumed to have retained its magmatic signature is such that the measured range of carbonate $\delta^{18}O$ values would not be attained (see O'Neil et al., 1969). The implication is that non-magmatic water (e.g., hydrothermal-meteoric or formation waters), was likely to have been present during calcite deposition in the sulphide veins and in the granite.

Carbon Isotope Determinations

The $\delta^{13}C$ values of calcite samples from sulphide veins in Unit III have a large range (from -14.5 to -6.8°/oo). There is no systematic correlation between $\delta^{13}C$ and $\delta^{18}O$ values of the same calcite samples. A bulk aureole schist sample and a bulk granite sample from Unit I analysed for trace carbonate have $\delta^{13}C$ values of -18.5 and -11.3°/oo, respectively. Analytical error was 0.05°/oo. Due to lack of suitable exposure the samples could not be placed in paragenetic sequence.

Source of Carbon

Oxygen isotope data indicate that the temperature of deposition of calcite remained constant. Sulphide disequilibrium assemblages suggest a temperature of less than 200°C. If carbon was present in the system not only as dissolved carbonate species but also as methane, graphite or CO_2, then the $\delta^{13}C$ values for the carbonate minerals will represent maxima for the $\delta^{13}\Sigma_C$ of the system (Fritz, 1976). Thus the $\delta^{13}C_{\Sigma C}$ value for the system may have been considerably less than the -14.6 to -6.8°/oo values observed but it could not have been higher.

Organic matter has typical $\delta^{13}C$ values between -15 and -30°/oo (Fritz, 1976). A $\delta^{13}C_{\Sigma C}$ value equal to or less than the observed $\delta^{13}C$ values of the lighter carbon (-14.6 to -12.8°/oo) strongly suggests a biogenic source for this carbon. Small changes in the pH or fO_2 of the system could produce the total range of observed $\delta^{13}C$ values from a biogenic source with a $\delta^{13}C_{\Sigma C}$ of -15°/oo or less (see Ohmoto, 1972). The total range of values could also have been produced by the mixing of biogenically derived carbon ($\delta^{13}C_{\Sigma C} \approx -18$°/oo) with magmatically derived carbon ($\delta^{13}C_{\Sigma C} \approx -5$°/oo, Ohmoto, 1972). A biogenic source for some of the carbon present in the granite and the veins is implied. The source of this biogenic carbon is very likely to have been the aureole schists, which have a $\delta^{13}C$ value of -18.5°/oo.

THE AUREOLE ROCKS: COTICULES AND TOURMALINITES

The isotope data do not, by themselves, allow an unambiguous conclusion regarding the origin of the mineralisation. They do, however, serve to refocus attention on the aureole rocks. A spatial association between the sulphide deposits on the granite margin and the presence of spessartine quartzites in the adjacent aureole has been noted (Kennan, 1978). These quartzites are coticules as defined by Renard (1878). They are themselves closely associated with other quartzites and more pelitic rocks all of which are unusually rich in tourmaline. The use of tourmaline as a guide to mineralisation has been recently documented by Slack (1980, 1982). Both of these rather unusual rock types are a distinctive feature of some otherwise largely pelitic sequences of the Cambro-Ordovician Ribband Group of SE Ireland as defined by Brück et al. (1974).

In SE Ireland, tourmaline has often been noted in the Leinster Granite and in the aureole rocks. In the granite it is a constituent of some pegmatite, aplite and quartz veins (Brindley, 1954) and of hydrothermally altered granite (Brück and O'Connor, 1977). In the aureole the mineral is especially obvious as fringes to some cross-cutting aplite veins and as an apparently late addition to the metamorphic assemblages (Brindley, 1957). To date, the conclusion drawn from these facts has been the common one that the aureole tourmaline reflects post-intrusion pneumatolysis; the implication has been that the necessary boron derived, as a late magmatic concentrate, from the nearby granite. No evidence has been presented in support of an external source although Brück and O'Connor (1980, p. 361, 1982, p. 156) include tourmalinisation in a list of alterations related to thermally induced circulation of ground waters in the envelope.

Recent observations show that the amount of tourmaline in the aureole far outweighs that present in the granite or its veins; some aureole rocks contain in excess of 75% tourmaline. Rocks composed of tourmaline and quartz only are prominent. A soda rich feldspar occurs as an additional constituent. These tourmalinites sometimes show layering on a fine scale. Some small folds defined by tourmaline rich layers are typical pre-intrusion structures.

Tourmalinites occur in those particular parts of the aureole where the coticules are a distinctive feature. The coticules and tourmalinites may be partial lateral equivalents; the coticules are especially common adjacent to Units I and III whereas the tourmalinites are more often encountered close to Units IV and V.

These tourmalinites are in every way comparable with such rocks in volcanic sequences elsewhere. Of special interest to this study is the fact that they are associated with massive exhalative Pb-Zn ores at Broken Hill, New South Wales (Plimer, 1980) - ores sited in ironstones that have, as further lateral equivalents, manganese-garnet quartzites that compare closely with those of Leinster (see Stanton, 1976). The recently discovered metal and manganese bearing sediments in the south-west Pacific island arc may be modern analogues (Cronan et al., 1982).

In the Aldridge Formation, British Columbia, rip-up clasts of laminated quartz-tourmaline rock in an intraformational conglomerate serve to establish the early, probably syngenetic, introduction of boron (Ethier and Campbell, 1977). In SE Ireland, it is not yet possible to prove a synsedimentary origin; however, the quantity and the distribution of the tourmaline make it very difficult to envisage the necessary boron as other than a constituent of the original sediments.

Tourmaline rich rocks have not been recognised in and around the volcanogenic Cu-Fe-Pb-Zn sulphide ores at Avoca (Platt, 1977 and Fig. 1.) nor at the nearby Ballard magnetite deposit (Downes and Platt, 1978). However, to both NE and SW along strike, coticules occur in Ribband Group sediments. Although the stratigraphic-structural relationship between the coticule bearing sequences and Avoca-Ballard ores remains to be established, it is a fact that these distinctive quartzites are confined to narrow elongate tracts of ground in SE Ireland where significant ore deposits occur. This regional pattern and the lithologies present identify the coticule and tourmalinite bearing rocks in the granite aureole as a potential source for the metals now deposited on the granite margin. Analyses of stream sediments support this conclusion (Brück, 1977). It is interesting to speculate that the ultimate source of the metals at Avoca may also be coticule bearing Ribband Group strata.

CONCLUSIONS

1. The sulphides in Unit I of the Leinster Granite were deposited at a temperature of about 500°C, those of Unit III at about 250°C and those of Unit V at possibly less than 200°C. The aureole rocks are suggested as the source of sulphur for the granite and veins, particularly for Unit I. The data suggest the involvement in the vein mineralisation of sulphur, carbon and mineralising fluids at least partially derived from the aureole rocks.

2. It is likely that the emplacement of the granite resulted in the mobilisation of base metals previously resident in the aureole rocks to form sulphide mineral deposits near to and on the granite margin.

3. The rocks of the pelitic Cambro-Ordovician Ribband Group containing coticules, tourmalinites or related sediments are prospecting targets for base metals in SE Ireland. This is especially so where later intrusions are present.

Acknowledgements. The substance of this paper derives from studies undertaken as part of EEC Research Contract MPP-126-EIR(G). We wish to thank Dr. M. Coleman (IGS, London) for his help with the mass spectrometry and for stimulating discussion, Dr. C. Halls (Imperial College, London) for his help in the study of ore textures and their interpretation, Mr. P. McArdle and Dr. C. Williams (Geological Survey of Ireland) for their continuing support and our colleagues at University College Dublin, notably T. Culligan and G. Doyle.

REFERENCES

Brindley, J.C.: The Geology of the northern end of the Leinster Granite: Part I - internal structural features. Proc. R. Ir. Acad. 56B, 159-190 (1954)

Brindley, J.C.: The Aureole Rocks of the Leinster Granite in South Dublin, Ireland. Proc. R. Ir. Acad. 59B, 1-18 (1957)

Brück, P.M.: Stream sediment base metal geochemistry on one-inch sheets 120 and 121. Geol. Surv. Ireland Rept. Ser. RS 77/1, 15-23 (1977)

Brück, P.M., O'Connor, P.J.: The Leinster Batholith: geology and geochemistry of the northern units. Geol. Surv. Ireland Bull. 2, 107-141 (1977)

Brück, P.M., O'Connor, P.J.: Major transverse and other linears in the Leinster Granite. Geol. Surv. Ireland Bull. 2, 349-370 (1980)

Brück, P.M., O'Connor, P.J.: Relationship of hydrothermal phenomena within the Leinster Granite to crustal fractures delineated from Landsat Imagery. Photogrammetria 37, 151-159 (1982)

Brück, P.M., Potter, T.L., Downie, C.: The Lower Palaeozoic stratigraphy of the northern part of the Leinster Massif. Proc. R. Ir. Acad. 74B, 75-84 (1974)

Brück, P.M., Colthurst, J.R.J., Feely, M., Gardiner, P.R.R., Penney, S.R., Reeves, T.J., Shannon, P.M., Smith, D.G., Vanguestaine, M.: South-east Ireland: Lower Palaeozoic stratigraphy and depositional history. In: The Caledonides of the British Isles - Reviewed. A.L. Harris, C.H. Holland, B.E. Leake, (eds), pp 533-544. Edinburgh: Scottish Academic Press, Ltd., 1979

Coleman, M.L.: Sulphur isotopes in petrology. J. Geol. Soc. Lon. 133, 593-608 (1977)

Coleman, M.L.: Corrections for mass-spectrometer analysis of sulphur dioxide. Stable Isotope Report No. 45, Pub. by Institute of Geological Sciences, London (1980)

Coleman, M.L., Moore, M.P.: A method for the direct reduction of sulphates to sulphur dioxide for isotopic analysis. Analyt. Chem. 50, 1594-1595 (1978)

Craig, H.: Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. Geochem. Cosmochem. Acta 12, 133-149 (1957)

Cronan, D.S., Glasby, G.P., Moorby, S.A., Thomson, J., Knedler, K.E., McDougall, J.C.: A submarine hydrothermal manganese deposit from the south-west Pacific island arc. Nature 298, 456-458 (1982)

Czamanske, G.K., Rye, R.O.: Experimentally determined sulfur isotope fractionation between sphalerite and galena in the temperature range 600° to 275°C. Econ. Geol. 69, 17-25 (1974)

Downes, K.M.J., Platt, J.W.: The Avoca-Ballard mineralised belt, County Wicklow. J. Earth Sci. R. Dübl. Soc. 1, 121-133 (1978)

Ethier, V.G., Campbell, F.A.: Tourmaline concentrations in Proterozoic sediments of the southern Cordillera of Canada and their economic significance. Can. J. Earth Sci. 14, 2348-2363 (1977)

Elsdon, P., Kennan, P.S.: Age of Sulphide Deposits on the Margin of the Leinster Granite, Ireland. In: Metallization Associated with Acid Magmatism, A.M. Evans (ed) John Wiley, 1982

Finlayson, A.M.: The Metallogeny of the British Isles. Q. Jl. geol. Soc. London 66, 281-296 (1910)

Fritz, P.: Oxygen and carbon isotopes in ore deposits in sedimentary rocks. In: Handbook of Strata-bound and Stratiform ore deposits. K.H. Wolf, (ed), Vol. 2, pp 191-215. Amsterdam-Oxford-New York, Elsevier 1976

Kajiwara, Y., Krouse, H.R.: Sulfur isotope partitioning in metallic sulfide systems. Can. J. Earth Sci. 8, 1397-1408 (1971)

Kennan, P.S.: The petrography of some red-feldspar pegmatites and their association with late hydrothermal changes in the Leinster Granite. Sic. Proc. R. Dubl. Soc. 5A, 77-84 (1974)

Kennan, P.S.: The origin of the sulphide deposits in the Leinster Granite. J. Earth Sci. R. Dubl. Soc. 1, 41-47 (1978)

McCrea, J.M.: On the isotope chemistry of carbonates and a palaeotemperature scale. Jour. Chem. Phys. 18, 849-857 (1950)

Moorbath, S.: Lead isotope abundance studies on mineral occurrences in the British Isles and their geological significance. Phil. Trans. R. Soc. (London) 254A, 295-360 (1962)

Nielsen, H.: Sulfur isotopes. In: Lectures in Isotope Geology, E. Jäger, J.C. Hunziker, (ed), pp 283-312, Berlin-Heidelberg-New York, Springer, 1979

Ohmoto, H.: Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. Econ. Geol. 67, 551-578 (1972)

Ohmoto, H., Rye, R.O.: Isotopes of sulphur and carbon. In: Geochemistry of Hydrothermal Ore Deposits. H.L. Barnes (ed) pp 509-561, 2nd ed., New York-Chichester-Brisbane- Toronto, Wiley-Interscience 1979

O'Neil, J.R., Clayton, R.N., Mayeda, T.K.: Oxygen isotope fractionation in divalent metal carbonates. J. Chem. Phys. 51, 5547-5558 (1969)

Platt, J.W.: Volcanogenic mineralisation at Avoca, Co. Wicklow, Ireland and its regional implications. In: Volcanic Processes in Ore Genesis, pp 163-170, London, Inst. Min. Metall. and Geol. Soc. 1977

Plimer, I.R.: Exhalative Sn and W Deposits Associated with Mafic Volcanism as Precursors to Sn and W Deposits Associated with Granites. Mineral. Deposita 15, 275-289 (1980)

Renard, A.: Sur la structure et la composition mineralogique du coticule. Mém. Cour. et Mém. des Sav. Acad. Roy.de Belg. 16 (1878)

Robinson, B.W., Kusakabe, M.: Quantitative preparation of sulphur dioxide for $\delta^{34}S$ analyses from sulphides by combustion with cuprous oxide. Analyt. Chem. 47, 1179-1181 (1975)

Rye, R.O.: A comparison of sphalerite-galena sulphur isotope temperatures with filling temperatures of fluid inclusions. Econ. Geol. 69, 26-32 (1974)

Rye, R.O. Ohmoto, H.: Sulphur and carbon isotopes and ore genesis: A review. Econ. Geol. 69, 826-842 (1974)

Sakai, H.: Isotopic properties of sulphur compounds in hydrothermal processes. Geochem. J. 2, 29-49 (1968)

Sangster, D.F.: Sulphur and lead isotopes in strata-bound deposits. In: Handbook of Strata-bound and Stratiform ore deposits. K.H. Wolf (ed), Vol. 1, pp 219-266. Amsterdam-Oxford-New York, Elsevier 1976

Slack, J.: Tourmaline - A prospecting guide for massive base-metal sulphide deposits in the Penobscot Bay Area, Maine. Maine Geol. Surv. Special Economic Studies Series No. 8, 1-25 (1980)

Slack, J.: Tourmaline in Appalachian-Caledonian massive sulphide deposits and its exploration significance. Trans. Inst. Min. Metall. B91, 81-89 (1982)

Stanton, R.L.: Petrochemical studies of the ore environment at Broken Hill, New South Wales: 3-banded iron formations and sulphide ore bodies: constitutional and genetic ties. Trans. Inst. Min. Metall. B85, 132-141 (1976)

Taylor, H.P.: The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. Econ. Geol. 69, 843-883 (1974)

Thode, H.G., Monster, J.: Sulphur isotope geochemistry of petroleum evaporites and ancient seas. Am. Assoc. Petrol. Geol. Mem. 4, 367-377 (1965)

Tremlett, W.E.: The Pre-Cambrian Rocks of Southern Co. Wicklow (Ireland). Geol. Mag. 96, 58-68 (1959)

Received: September 14, 1982
Accepted: May 5, 1983

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Mineral.Deposita 18, 411-421 (1983)

MINERALIUM
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Geochemical Investigations of Paleozoic Shales and Carbonates in the Aachen Region

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In the western part of the Rheinisches Schiefergebirge geochemical investigations were carried out on Paleozoic black shales and carbonates in the Aachen region. Primary and secondary metal distributions were determined in selected units of sedimentary rocks by XRF-analysis and in stream sediments by AAS-analysis. The primary geochemical pattern and the results of geological studies reveal that Frasnian (Upper Devonian) black shales and nodular limestones were deposited in a restricted environment under euxinic conditions of a swell and basin facies. Black shales and nodular limestones are enriched in Zn and Cu resp., possibly indicating stratiform sulphide mineralization. Geochemical anomalies in stream sediments with increased values of Pb, Zn, Cd, Cu, Co, and Ni were found in areas of Lower Paleozoic sedimentary rocks and associated acid intrusives which are known to contain low grade sulphide mineralization of the "porphyry copper-type".

INTRODUCTION

During the last years detailed geochemical studies were carried out in the eastern part of the Rheinisches Schiefergebirge, especially near the stratiform sulphide-baryte deposit of Meggen (e.g. Hilmer, 1972; Friedrich et al., 1977, 1979; Gwosdz and Krebs, 1977; Brinkmann et al., 1978). Facies and stratigraphy of the Paleozoic area south of Aachen in the western part of the Rheinisches Schiefergebirge were also studied in detail by different research groups (e.g. Kasig et al., 1978), but there was still a lack of lithogeochemical data, especially concerning the primary trace element distribution.

Investigations of the secondary dispersion of trace elements in surface waters, stream sediments and soils in selected areas were started in an earlier phase of our research projects: Kulms and Friedrich (1970), Hermann (1979) and by other groups e.g. Emmermann et al. (1981).

Subject of the present study is the investigation of primary and secondary metal distributions in two areas of different geological setting, the Venn Massif and the Inde Syncline (Scheps, 1982). Rock geochemistry was carried out in selected lithological units:

in the Venn Massif
Revinian 4 and 5 (Cambrian),

in the Inde Syncline
Frasnian (Upper Devonian),
Visean (Lower Carboniferous).

Due to contamination by former mining industries in the Inde Syncline area (vein-type Pb-Zn-deposits near Aachen, Stolberg and Moresnet) the investigation of stream sediments was restricted to the Venn Massif.

GEOLOGICAL SETTING

The area south of Aachen is characterized by a thick series of Paleozoic rocks including black shales and marginal reef facies which are known to be favourable environments for the formation of stratiform sulphide mineralization. Geology and stratigraphy of the two investigated areas (Venn Massif and Inde Syncline) are shown in Fig. 1 and 2.

Venn Massif

The anticlinal core of the Venn Massif consists of a series of Cambrian (Revinian) and Ordovician (Salmian) black shales, sandy shales, quartzitic sandstones and quartzites with a thickness of about 2000 m. This sequence was deformed by the Caledonian orogeny and discordantly overlain by Lower Devonian sediments (Gedinnian). The Revinian and Salmian sedimentary rocks are locally intruded by tonalites and tonalite porphyrites, e.g. in the area near Lammersdorf (Fig. 1).

Lithogeochemical studies were carried out on samples from the Lower Paleozoic strata: Revinian 4 and 5 (Cambrian). The Revinian 4 (Fig. 1, profile 9) is characterized by alternating quartzites, quartzitic sandstones and black phyllitic shales of 300 to 400 m thickness (Knapp, 1978). The Revinian 5 (Fig. 1, profile 11) mainly consists of black phyllitic shales with minor quartzites of 300 to 500 m thickness.

Inde Syncline

The Inde Syncline consists of Lower Devonian to Upper Carboniferous sedimentary rocks of a thickness of about 4000 to 5000 m. The sedimentation was highly influenced by the Old Red Continent in the north and was interrupted by two main periods of transgression (Hollerbach and Kasig, 1980):

1. A large carbonate platform was formed in the Givetian and the early Frasnian, followed by a sequence of nodular limestones and black shales up to the end of the Frasnian.

2. A second carbonate platform was formed during the Lower Carboniferous.

The whole sequence was folded and thrust-faulted during the Asturian orogeny (Upper Carboniferous).

Detailed lithogeochemical investigations were carried out in the following units: Frasnian (Upper Devonian) reef limestones, nodular limestones and black shales.

Generally the Devonain carbonate platform has a total thickness of about 250 m. The cyclic growth of the biostromal reefs started in the Givetian. During the Frasnian the reefs were overlain by nodular limestones and black shales (Kasig, 1967, 1980a). South of Aachen the reef limestones represent a part of the southeastern flank of the Inde Syncline.

Within this sequence several profiles were sampled (Figs. 2, 3 and 4): profile 8 which comprises a shaly intercalation at the basis of the Frasnian reefs of about 4 m thickness (the so-called "Grenzschiefer"), a tuffaceous bed of 1 m thickness (profile 5) within the Frasnian reefs, and a sequence of 120 m thickness (profiles 1 and 2) comprising the upper part of the reefs and the transition zone from the reef facies to nodular limestones and black shales. Due to the lack of outcrops, the upper part of the Frasnian black shales and nodular limestones could not be sampled continously (profile 3 and 6).

Visean Limestones (Lower Carboniferous)

The Visean limestones were deposited in a shallow lagoonal environment (Boonen and Kasig, 1979; Kasig, 1980b, 1981). In contrast to the Devonian reefs, the

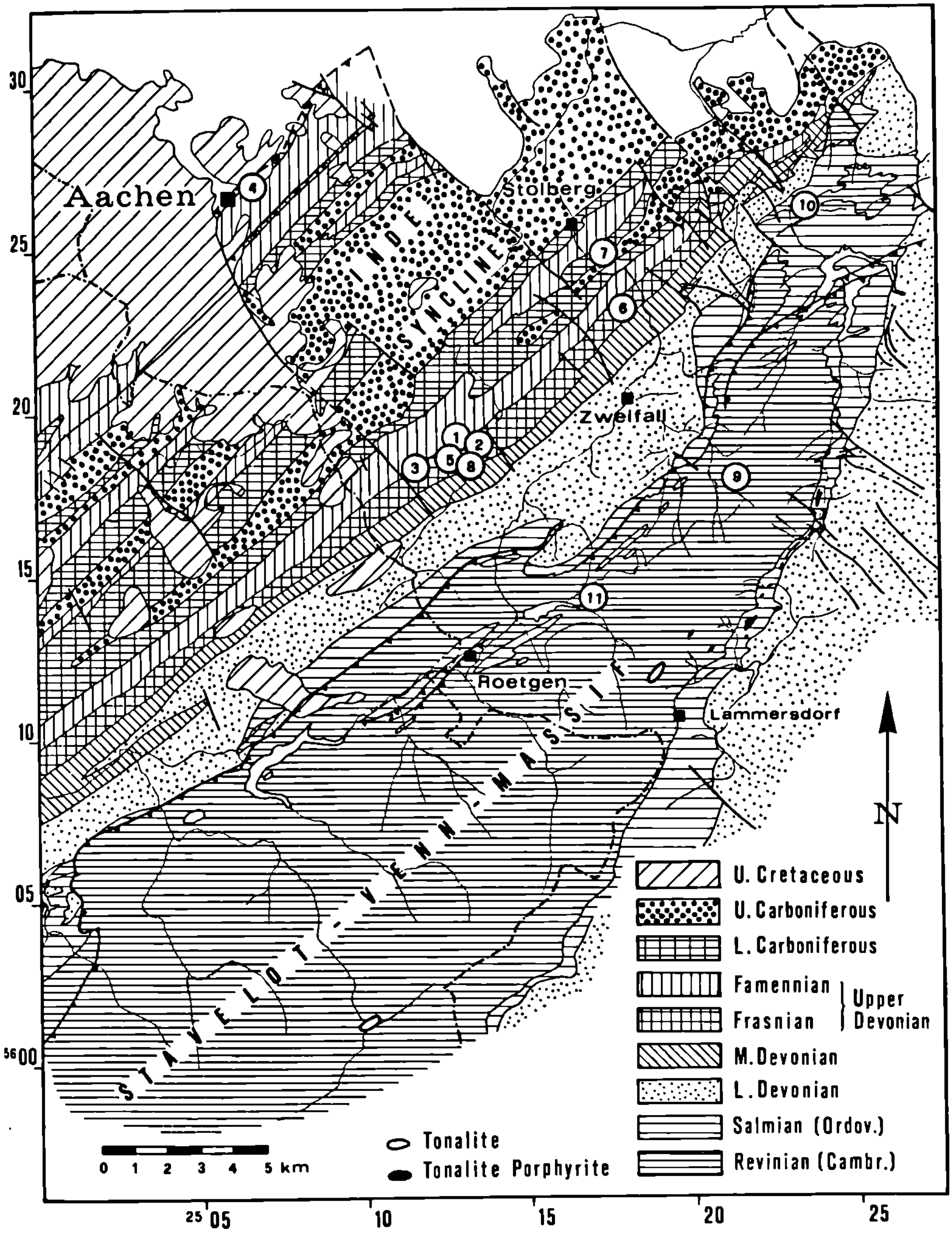

Fig. 1. Geological map (after Knapp, 1978) showing the Inde Syncline, the Venn Massif and the rock sampling locations 1 to 11

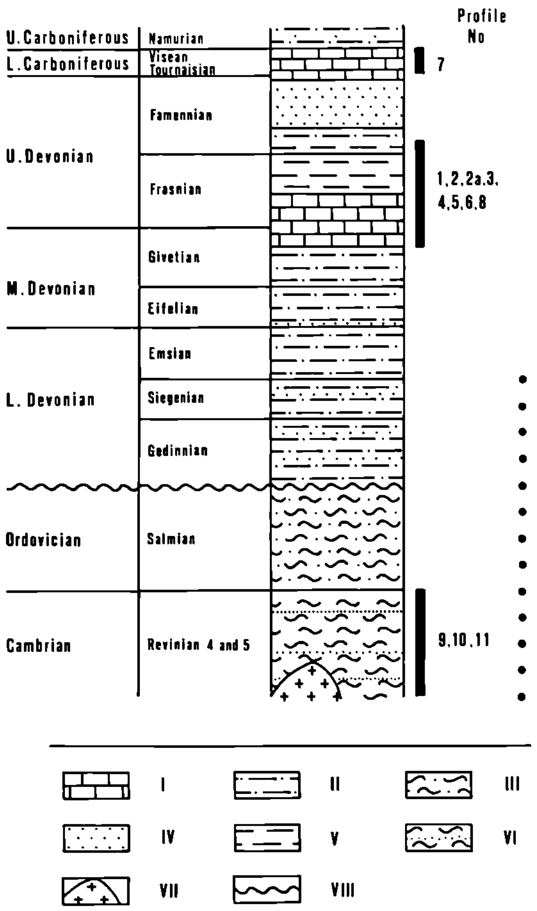

Fig. 2. Stratigraphy of the Inde Syncline and the Venn Massif (simplified after Knapp, 1978). The black lines show the stratigraphic position of the investigated sedimentary rock profiles (nos. 1 to 11), the dotted line indicates the area of the stream sediment survey. I = Carbonates, II = Sandy shales, III = Sandy shales and black shales, partly metamorphosed, IV = Sandstones, V = Shales, VI = Black shales and quartzites, partly metamorphosed, VII = Acid intrusives (Tonalite of Lammersdorf), VIII = Unconformity

Lower Carboniferous sediments mainly consist of chemical precipitates and clastic carbonates. The investigated profile (Figs. 3 and 4; profile 7) comprises a section from the upper part of the "Vaughanites Oolith" (V1a) to the "Coated Grain Succession" (V3a?) with a thickness of 110 m[1].

Pb/Zn Deposits

The vein-type Pb/Zn deposits in the Stolberg-Aachen-Moresnet area are structurally controlled and connected to Devonian and Lower Carboniferous carbonate rocks (Gussone, 1964). The genetic interpretation of these epigenetic, hydrothermal mineralizations is still being discussed. They may be of magmatic-hydrothermal origin related to deep seated structures or were mobilized from older sedimentary rocks by hydrothermal activity.

GEOCHEMISTRY OF SELECTED SEDIMENTARY ROCKS

A total of 698 rock samples was analyzed for 20 elements by XRF. Pure carbonate rocks, which contain trace element concentrations below the detection limit of the XRF measurement method (e.g. Na) were decomposed with HF, HNO_3 and HCl and analyzed by AAS. The geochemical data were evaluated by statistical methods. In addition to the statistical interpretation of geochemical data the geological setting of every profile was studied in detail. According to their relative stratigraphic position, the average metal concentrations ($\bar{x}$) and the standard deviations (s) of the profiles are given in Figs. 3 and 4.

Generally two types of sedimentary rocks were investigated in the course of this study: shales and limestones. The evaluation of geochemical data of these rock types has indicated clearly that most of the analyzed elements are dominantly related to clay minerals and organic matter due to the adsorption capacity of these compounds. In addition elements as Ba and Pb, Zn and Cu

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[1] The profile was studied in detail by Kasig (1981). The sample material was kindly placed at the authors' disposal for further geochemical studies

may be bound in specific minerals as baryte and as sulphides, respectively.

From the analyzed 20 elements, Co is always below the detection limit of the XRF measurement method (< 20 ppm) and was not analyzed by AAS. According to our own results and data from literature (e.g. Gwosdz and Krebs, 1977; Large, 1980; Swennen et al., 1982) the following elements are especially suitable as indicators for certain sedimentary environments: increased Na and Sr concentrations may indicate hypersaline conditions during the formation of carbonate sediments, increased V contents indicate an euxinic environment, high K concentrations and increased K/Rb ratios point to volcanic activities during the deposition. Pb, Zn, Cu, Co, Ni, Ba and Mn are used as pathfinder elements for stratiform sulphide mineralization, and in comparison with the distribution patterns of the other elements it can be distinguished, if the enrichments are of syngenetic or of epigenetic origin. A "manganese halo" is a well known proximity indicator for stratiform sulphide mineralization.

Results and Discussion

Revinian 4 and 5 (Cambrian) black phyllitic shales

Compared with other shales the Lower Paleozoic black phyllitic shales of the Revinian 4 and 5 are characterized by a significant lack of Ca, Na, Mn and Ni (Figs. 3 and 4; $<0.5\%$ CaO, $<0.1\%$ Na_2O, $<0.04\%$ MnO, <25 ppm Ni). This probably indicates extreme depositional conditions with low pH and Eh values. Cu is slightly increased in the Revinian 4 and 5 (up to 150 ppm) and Pb in the Revinian 4 (up to 130 ppm). High concentrations of V within the same samples (up to 200 ppm) indicate that these Cu and Pb contents are related to an euxinic black shale environment.

Anomalous metal enrichments could not be detected within the Revinian black phyllitic shales, but considering the extension of these wide spread rocks and the great depth of burial (at least 3000-4000 m below the Inde Syncline), they form a remarkable potential for hydrothermal metal mobilization. This potential could be increased by the duplication of beds in the Paleozoic area south of Aachen. According to recent geophysical studies this area (s. Fig. 1) was overthrusted to the NW along the "Aachener Überschiebung", a thrust fault at the northwestern rim of the Inde Syncline (Meissner et al., 1981, Bless et al., 1980).

Frasnian Reef Limestones, Nodular Limestones and Black Shales

The sequence of the Upper Devonian reef limestones locally contains small, epigenetic sphalerite mineralizations bound to veinlets and bedding planes. Significant stratiform mineralization could not be detected within the reefs. The cyclic growth of the biostromal reefs is generally not reflected by geochemistry, in a few cases only the clay content increases slightly towards the top of the cycles. The uppermost 15 m of the reef sequence are characterized by an increase of Mg, Na and Sr, indicating a hypersalinar environment that probably caused the end of the reef growth. In general the investigated Upper Devonian reefs were not suitable for stratiform sulphide formation. The biostromes were deposited in a relatively shallow water (Kasig, 1980a). Rather uniform extending over large distances, they did not form any structures suitable as "sulphide traps".

Profile 8 (Figs. 3 and 4) which represents a transgressive phase of shale sedimentation within the reefs ("Grenzschiefer"), is slightly increased in Zn and Cu (300 ppm Zn, 180 ppm Cu) bound to tuffaceous layers of some millimeters thickness.

Another tuffaceous horizon of nodular limestones of about 1 m thickness occurs in the middle of the reef sequence (Figs. 3 and 4; profile 5). In contrast to other Upper Devonian rocks the clay fraction is characterized by anomalous K contents ($> 7\%$ K_2O) and increased K/Rb ratios (> 200), possibly pointing to volcanic activities during the deposition of this horizon.

At the end of the reef growth the sedimentary environment changed to the

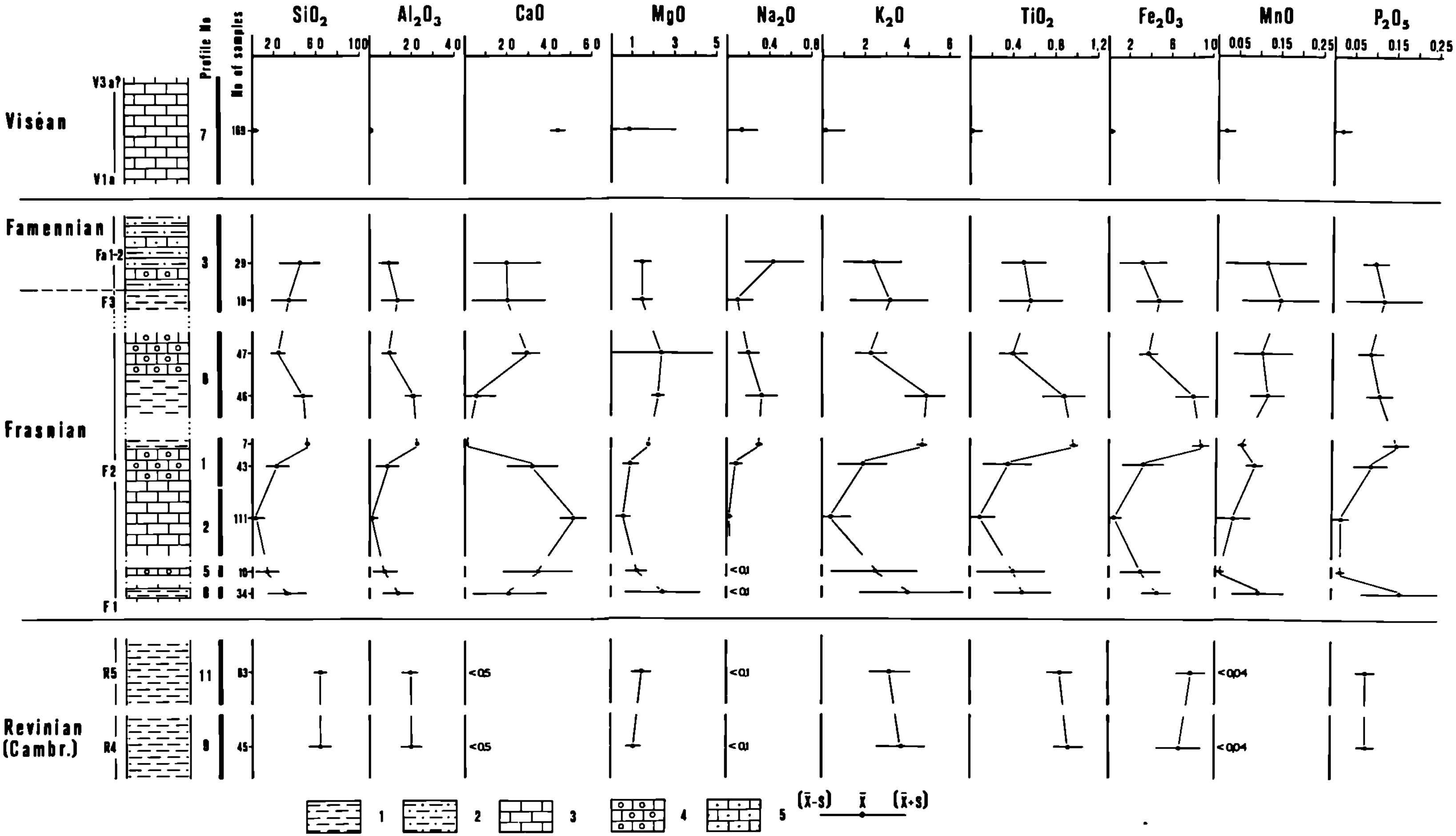

Fig. 3. Distribution of major and minor elements in selected Paleozoic sedimentary rocks of the Aachen region (concentrations in percent); arithmetic mean ($\bar{x}$) ± standard deviation (s). 1 = Shales, 2 = Sandy shales, 3 = Limestones, 4 = Nodular limestones, 5 = Sandy limestones

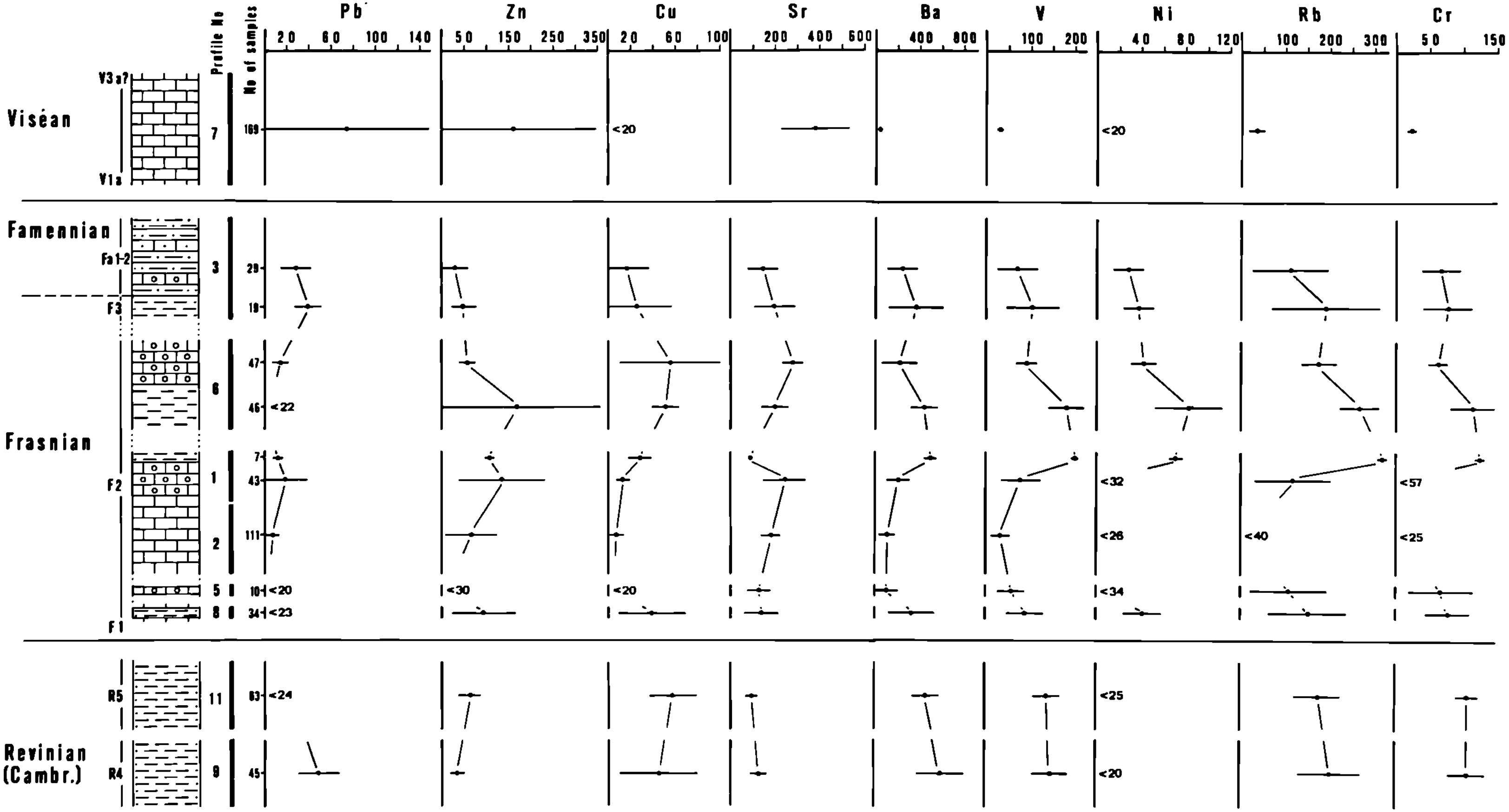

Fig. 4. Distribution of trace elements in selected Paleozoic sedimentary rocks of the Aachen region (concentrations in ppm, explanation see Fig. 3)

deposition of nodular limestones and black shales in a swell and basin facies which is in particular favourable for the formation of sulphides (Figs. 3 and 4; profile 6): syngenetic chalcopyrite in markasite nodules was found within nodular limestones which are generally enriched in Cu (profile 6; $\bar{x}$ = 55 ppm Cu). A stratiform Zn anomaly up to 1000 ppm of 4 m thickness was found within the underlying black shales (profile 6). The Mn content of the nodular limestones and black shales (on the average 0.11% to 0.15% MnO), is generally increased, but due to the vertical profiles a stratabound "manganese halo" could not be detected. Evidence for the swell and basin facies is given by field observations and literature (e.g. Knapp 1978) showing extreme variations of the thickness within the Frasnian black shales and nodular limestones at the south-eastern rim of the Inde Syncline.

Further evidence for stratiform mineralization on the stratigraphic level of Frasnian black shales is given by the Ba (Fe, Zn, Pb) mineralization near Chaudfontaine in Belgium (Dejonghe, 1979). The F2/F3 transition zone, where the Chaudfontaine mineralization occurs, could not be investigated in this study as this section is not exposed at the surface.

Visean Limestones

The Visean limestones studied in this program contain the highest Pb-Zn-values of all profiles (Fig. 4; profile 7). Positive correlations of Pb and Zn with V and Sr show that the enrichments of Pb (up to 630 ppm) and Zn (up to 1300 ppm) are bound to euxinic conditions and increased salinity of an evaporitic environment. According to Kasig (1980b) the stratigraphic position of these enrichments is the "Upper Cyclic Succession" of V2b. In a lower section of Visean limestones similar metal enrichments were found by Swennen et al. (1982) in the adjoining Vesder Basin/ Belgium.

Sedimentary enrichments as proved in Visean limestones may be the potential source for vein-type Pb-Zn-deposits of the Inde Syncline. Mobilization by lateral secretion of stratiform low grade sulphides probably leads to the formation of epigenetic mineralization in veins. A similar genetical model, based on mobilization of sulphides from Frasnian sediments, could recently be proved in Belgium by Dejonghe et al. (1982).

GEOCHEMISTRY OF STREAM SEDIMENTS

The hot extractable contents of Pb, Zn, Cd, Cu, Co, Ni, Mn, and Fe from the -80 mesh fraction of 347 stream sediment samples were analyzed by AAS. As shown in Table 1, the average concentrations of Pb and Zn are about two times higher than those in other parts of the Rheinisches Schiefergebirge. The first evaluation of data has shown that this increase is caused by the Pb-Zn-Cd-contamination derived from the ancient mining industries near Aachen and Stolberg, which is obviously not only restricted to the area of the Inde Syncline where the epigenetical ore deposits were exploited. Waste materials containing traces of sphalerite and galena were frequently used for road constructions. In this way contamination was also spread over the Venn Massif. This made it very difficult to separate anomalies of mineralized bedrock from false anomalies due to anthropogenetic contaminations. Therefore the numerous anomalies found in the Venn Massif had to be studied in detail by additional methods:

- determination of metals and pH-values in stream waters by AAS,
- determination of major, minor and trace elements in selected stream sediment samples by XRF.

As a result of these studies it can be shown that "true" anomalies are due to the following reasons.

Variation of pH-Values

Large areas of the Venn Massif are covered by swamps which causes low pH-

Table 1. Pb, Zn, Cd, Cu, Co, Ni, Mn, and Fe in stream sediments of the Venn Anticline (hot extractable contents from the -80 mesh fraction, n=347, AAS)

max = maximum $\bar{x}$ = arithmetic mean
min = minimum s = standard deviation

	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Mn (ppm)	Fe (%)
max	2820	7400	60.0	326	813	251	16750	35.30
min	20	18	0.1	9	3	3	5	0.63
$\bar{x}$	188	574	6.6	33	59	43	1848	4.02
s	239	836	9.7	24	88	45	2632	3.05
A	73	132	-	25	18	55	-	-
B	105	207	-	34	-	-	-	-
C	80	270	-	40	-	-	-	-

A) Average metal content of stream sediments (about 660 samples from the vicinity of the Meggen ore deposit (Hilmer 1972)
B) Average metal content of stream sediments (about 4000 samples) of the eastern part of the Rheinisches Schiefergebirge (Friedrich et al. 1977)
C) Anomalous metal contents of 5200 stream sediments in the Eifel/Hunsrück area (Emmermann et al. 1981)

values (pH 2-4) especially in the central regions of the Venn Massif. Towards marginal areas the pH-values increase (pH 4-7) caused by dilution with water of higher pH-values and carbonate supply by carbonate rocks. This increase of pH-values effects the precipitation of metals which were in solution before and leads to the formation of anomalies in marginal areas of the Venn Massif.

Mn-Rich Sedimentary Rocks

The sedimentary rocks of the Ordovician (s. Fig. 2) are enriched in Mn (up to 25% MnO, Kramm, 1980). This is in sharp contrast to the Cambrian shales forming the anticlinal core which are relatively poor in Mn (< 400 ppm Mn, see above). This increased Mn-content of Ordovician rocks may lead to increased Mn-concentrations in stream sediments (> 7000 ppm Mn) depending on pH-values. Several metal enrichments, especially of Co, Ni and Cd, are due to their adsorption by Mn-hydrolysates. Contrary to Mn the frequently occurring precipitates of Fe-hydroxides do not play any role concerning metal enrichment.

Vein-type Baryte-Sulphide Mineralization

Baryte mineralization is known on NW-SE striking faults at the northern rim of the Venn Massif northeast of Zweifall (Holzapfel 1910, Fig. 1). The occurrences are characterized by distinct Ba-anomalies in stream sediments (> 700 ppm Ba). Pb and Zn anomalies corresponding to the Ba-enrichments show, that the faults may contain Pb-Zn-sulphides besides baryte.

Mineralization of Acid Intrusives

The most important anomaly (Pb > 700 ppm, Zn > 2000 ppm, Cd > 25 ppm, Cu > 80 ppm, Co > 250 ppm, Ni > 140 ppm) was found at the southeastern rim of the Venn Massif in the drainage system of the "Weißer Wehbach" NE of Lammersdorf (Fig. 1). The anomaly corresponds to outcrops of acid intrusive rocks of uncertain Paleozoic age, the "Tonalite of Lammersdorf" and the tonalite-porphyrites NE of Lammersdorf in the valley of the "Weißer Wehbach". Another igneous rock complex in the adjoining Belgium, the tonalite of "La Helle" (Fig. 1), which is similar to the Tonalite of Lammersdorf, contains mineral associations similar to those of the porphyry copper deposits (Weis et al. 1980). Further investigation of this anomaly is limited due to the widespread thick weathering crust covering the Venn Massif and requires shallow core drilling. The "Tonalite of Lammersdorf" for example was discovered during the construction of a railway track. The exposure is deeply weathered and fresh material cannot be sampled at the surface.

CONCLUSIONS

As result of this research work two geological structures in the Aachen region are recommended for further exploration.

1. The Upper Devonian Black Shale Facies of the Inde Syncline

The black shales and nodular limestones were deposited under euxinic conditions in a restricted environment of a swell and basin facies on top of an irregular subsiding shelf platform. This sedimentary environment is favourable for sulphide mineralization. Further evidence for the existence of sulphides on this stratigraphic level is given by the mineralization of Frasnian beds near Chaudfontaine (Belgium).

2. Lower Paleozoic Sediments of the Venn Massif associated with Acid Intrusives

The southeastern rim of the Venn Massif is characterized by a distinct geochemical anomaly in stream sediments related to Lower Paleozoic (Revinian and Salmian) sedimentary rocks which are associated to acid intrusives ("Tonalite of Lammersdorf" and tonalite porphyrites). These intrusives may contain a "porphyry copper-type" mineralization similar to the igneous rock complex of "La Helle" in Belgium.

Acknowledgements. The authors are indebted to Drs. U. Hack and P. Möller who critically reviewed the manuscript. Funding of the research work was provided by the "Commission of the European Communities" and the "Deutsche Forschungsgemeinschaft".

REFERENCES

Bless, M.J.M., Bouckaert, J., Papproth, E.: Environmental aspects of some Pre-Permian deposits in NW Europe. Meded. Rijks Geol. Dienst 32 (1), 3-13 (1980)

Boonen, P., Kasig, W.: Das Dinantium zwischen Aachen und Lüttich. Z. dt. Geol. Ges. 130, 123-143 (1979)

Brinkmann, J. (ed): Projekt Rhenoherzynikum; Untersuchung der Metallverteilung in geosynklinalen Sedimenten des Rhenoherzynikums in stratiformen Konzentrationen. Bundesanst. f. Geow. u. Rohstoffe, pp 133, 1978

Dejonghe, L.: Discovery of a Sedimentary Ba (Fe, Zn, Pb) Ore Body of Frasnian Age at Chaudfontaine, Province of Liège, Belgium. Mineral. Deposita 14, 15-20 (1979)

Dejonghe, L., Rye, R.O.. Cauet, S.: Sulfur isotopes of barite and lead isotopes of galena from the stratiform deposit in frasnian carbonate and shale host-rocks of Chaudfontaine (Province of Liège, Belgium). Ann. Soc. Géol. Belgique 105, 97-103 (1982)

Emmermann, K.-H., Fauth, H., Hindel, R., Ree, C.: Geochemische Übersichtsprospektion im linksrheinischen Schiefergebirge. Erzmetall 34, 152-159 (1981)

Friedrich, G., Katsch, A., Plüger, W.L., Horion, B., Keller, C.: Untersuchung der Metallverteilung in geosynklinalen Sedimenten des Rhenoherzynikums in stratiformen Konzentrationen. Teilprojekt Aachen. Abt. angew. Lagerst. Lehre RWTH Aachen (unpubl.) 1977

Friedrich, G., Katsch, A., Keller, C.: Geochemische und explorationsgeochemische Untersuchungen im Rhenoherzynikum, Nachfolgeuntersuchungen. Inst. f. Mineralogie u. Lagerst. Lehre RWTH Aachen (unpubl.) 1979

Gussone, R.: Untersuchungen und Betrachtungen zur Paragenesis und Genesis der Blei-Zink-Erzlagerstätten im Raume Aachen-Stolberg. Diss. RWTH Aachen, pp 130, 1964

Gwosdz, W., Krebs, W.: Manganese halo surrounding Meggen ore deposit, Germany. - Appl. earth sc., Trans. Inst. Min. Met. 86, B73-B78 (1977)

Hermann, R.: Untersuchungen zur Bestimmung von Pb, Cu, Zn, As, Se and Sb in Böden und deren Ausgangsgesteinen mit ausgewählten Beispielen aus der nördlichen Eifel. Diss. RWTH Aachen, pp 124, 1979

Hilmer, E.: Geochemische Untersuchungen im Bereich der Lagerstätte Meggen, Rheinisches Schiefergebirge. Diss. RWTH Aachen, pp 162, 1972

Hollerbach, A., Kasig, W.: Organic matter in Paleozoic sediments of the Aachen Region, east of the Brabant Massif. Meded. Rijks Geol. Dienst 32, 106-110 (1980)

Holzapfel, E.: Die Geologie des Nordabfalles der Eifel mit besonderer Berücksichtigung der Gegend von Aachen. Abh. Kgl. Preuß. Geol. Landesanst., n.F., 66, pp 218, Berlin, 1910

Kasig, W.: Biofazielle und feinstratigraphische Untersuchungen im Givetium und Frasnium am Nordrand des Stavelot-Venn-Massivs. Diss. RWTH Aachen, pp 177, 1967

Kasig, W.: Cyclic sedimentation in a Middle-Upper Devonian shelf environment in the Aachen Region, F.R.G. Meded. Rijks Geol. Dienst 32, 26-29 (1980a)

Kasig, W.: Dinantian carbonates in the Aachen Region, F.R.G. Meded. Rijks Geol. Dienst 32, 44-52 (1980b)

Kasig, W.: Zur Geologie des Aachener Unterkarbons. Habilitationsschrift RWTH Aachen, pp. 253, 1981

Kasig, W., Spaeth, G., Stoltidis, J. Walter, R.: Stratigraphie, Paläogeographie und Tektonik des nördlichen linksrheinischen Schiefergebirges. Exkursionsführer 130. Hauptversammlung DGG Aachen, pp 1-26, 1978

Knapp, G.: Erläuterungen zur geologischen Karte der nördlichen Eifel 1:100.000. 2. Aufl., pp 152, 1978

Kramm, U.: Herkunft und Ablagerungsmilieu der manganreichen ordovizischen Gesteine des Stavelot-Venn-Massivs, Ardennen. Z. dt. Geol. Ges. 131, 867-888 (1980)

Kulms, M., Friedrich, G.: Geochemische Untersuchungen der Böden im Lagerstättengebiet Bleialf/Eifel. Geol. Mitt. 10, 305-332 (1970)

Large, D.E.: Geological parameters associated with sediment-hosted, submarine exhalative Pb-Zn-deposits: an empirical model for mineral exploration. Geol. Jb. D40, 59-129 (1980)

Meissner, R., Bartelsen, H., Murawski, H.: Thin-skinned tectonics in the northern Rhenish Massif, Germany. Nature 290, 399-401 (1981)

Scheps, V.: Geochemische Untersuchungen in der nördlichen Eifel - Ein Beitrag zur Geochemie der Flußsedimente und der paläozoischen Schwarzschiefer und Karbonatgesteine des Venn-Massivs und der Inde-Mulde. Diss. RWTH Aachen, pp 104, 1982

Swennen, R., Boonen, P., Viaene, W.: Stratigraphy and lithogeochemistry of the Walhorn section (Lower Visean; Vesder Basin, E.-Belgium) and its implications. Bull. Soc. Belg. Geol. 91, 239-258 (1982)

Weis, D., Dejonghe, L., Herbosch, A.: Les associations des mineraux opaques et semi-opaques de la roche ignée de la Helle. Ann. Soc. Géol. Belgique 103, 15-23 (1980)

Received: May 5, 1983
Accepted: May 26, 1982

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Mineral.Deposita 18, 423-434 (1983)

MINERALIUM
DEPOSITA

Exploration for Antimony Deposits in Southern Tuscany, Italy

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The idealized prototype of a southern Tuscan antimony deposit can be described as follows: The irregular mineralization is situated in the upper part of the highly porous Calcare Cavernoso, overlain by an impermeable unit, normally a flysch-type rock. The deposits are bound to the edge of horst positions and also to areas of elevated geothermal gradient and resulting hydrothermal activity. These observations were used as variables for statistical probability calculations for antimony-deposit formation. Within the areas determined to be of high probability, 47 target areas were selected for geochemical soil sampling. Positive correlation of antimony with barium, strontium and lead, corresponding to gangue and accessory ore minerals in the deposit was found. Local distribution of Sb of 3 representative areas are discussed in detail. Although no high anomalies so far unknown were identified, known mineralizations were extended or neighbouring anomalies found. Regional correlation with horst structures and especially their fault margins (e.g. eastern margin of the ridge of Monticiano) was confirmed. The high density of mineralizations in the Tafone area is also reflected in the geochemical results of the soil sample prospection. A possible explanation for this accumulation may be seen in the large outcrops of pre-Carboniferous rocks, which generally are expected to be the primary source of antimony. From these pre-Variscan units antimony was remobilized and transported hydrothermally to its present position.

1. GEOLOGICAL SETTING AND MINERALIZATION

Southern Tuscany was already famous for it's variety of ore deposits during Etruscan times. Besides the antimony deposits, the province homes massive pyrite deposits, hematite and magnetite deposits, mixed sulfide vein deposits and disseminated Hg-mineralizations.

Aim of this study was to shed more light on the genesis of the antimony deposits and to define areas of economic interest by means of geochemical prospection in addition to those already knwon.

1.1 *Stratigraphy*

The stratigraphic units present in Southern Tuscany can be grouped as follows (Fig. 1).

A) Tuscan Basement

This group includes all pre-Sudetian rocks known in the area. Whereas in

Northern Tuscany a variety of old Paleozoic units is exposed in the Pisan Mountains and even more so in the Apuan Alps, Southern Tuscany contains only a small number of pre-Sudetian rocks in mostly limited and separated outcrops. The oldest fossil-dated rock is of Devonian age (Bagnoli & Tongiorgi, 1979). It is however generally accepted that older rocks are also involved. According to Rau et al. (1974), Bagnoli et al. (1978) and (1979), the basement comprises a variety of rock types, mainly phyllites with occasional evaporite lenses, black schists, metasandstones and scarce metabasites and porphyroids. Carbonates are very rare, only few lenses or thin layers occur.

B) Tuscan Series

The sediments of the Tuscan series range from the Upper Carboniferous to the lowermost Miocene. Since Carnian the sequence is complete but, because of the complex tectonic situation, can hardly ever be found in one profile. A synopsis is given in Giannini et al. (1971). The Permotriassic clastic Verrucano is followed by carbonate deposition during the Triassic and Jurassic. Important for Sb deposit formation is the evaporite-rich dolomitic Calcare Cavernoso (Carnian to Norian). Cretaceous and Tertiary sediments are clays and marls with occasional carbonates. The miogeosynclinal cycle ends in the Miocene with clastic deposition (Macigno sandstone).

C) Ligurian Nappe

The eugeosynclinal deposition started in the upper Jurassic with well developed ophiolites, followed by some carbonates and thick flyschtype sediments. Occasionally clastic deposits (e.g. Pietraforte Sandstone) can be found. For a more detailed description see Abbate et al. (1970) and Giannini et al. (1971).

D) Neoautochthonous and Quarternary

The Miocene, Pliocene and Quarternary sediments reflect repeated re- and transgressions resulting in quick changes between high and low energy clastic sediments. More details see Sestini (1970) and Giannini et al. (1971).

The Plio- to Pleistocene period is also characterized by widespread magmatic activity represented by granodioritic intrusions in the west (e.g. Elba) and rhyolitic to intermediate volcanites in the east (e.g. Mte. Amiata). Locally large covers of travertine are associated with hydrothermal activity. See also Pichler (1970) and Marinelli (1975).

1.2 *Structural Geology*

Two orogenic cycles are known in Southern Tuscany: the Variscan and the Alpine cycle.

A) Variscan Orogenesis

Due to the few outcrops of old Paleozoic rocks, the knowledge of the Variscan orogeny in Southern Tuscany is limited. The Sudetian phase is generally taken as the culmination. Nappe-type structures were identified and the autochthony of the basement is therefore a point of debate.

B) Alpine Orogenesis

The compressional phase leads to the gliding of the Ligurian nappe onto the Tuscan series, which in turn is being compressed and, particularly in the portion above the Calcare Cavernoso shows also nappe-type movements and the intensive development of small scale wedges. Where still present, the Ligurian nappe forms a rather impermeable cover over the generally more permeable Tuscan series. The tensional phase, starting in the Miocene and probably still continuing results in a well developed horst-graben system which generally runs WNW-ESE. The Miocene to recent magmatism is strongly correlated with this structural pattern

1.3 *Geothermal Activities*

The magmatic phase leads to a variety of geothermal phenomena which may still be observed in the area. The geothermal gradient in Southern Tuscany is regionally about 5°C/100m. In some particularly "hot" areas it rises to over 30°C/100m and is economically used for the production of electricity (e.g. Lardarello, Travale-Radicondoli, Mte. Amiata). The Triassic and Jurassic carbonates, in particular the Calcare Cavernoso with their highly permeable rocks form the main aquifer in Southern Tuscany. A large number of thermal wells, steam and gas emanations are spread all over the area. See also Benvenuti et al. (1971).

2. THE ANTIMONY DEPOSITS

Today, the antimony deposits are generally accepted to be epigenetic. The ore mineral content of the deposits consists of

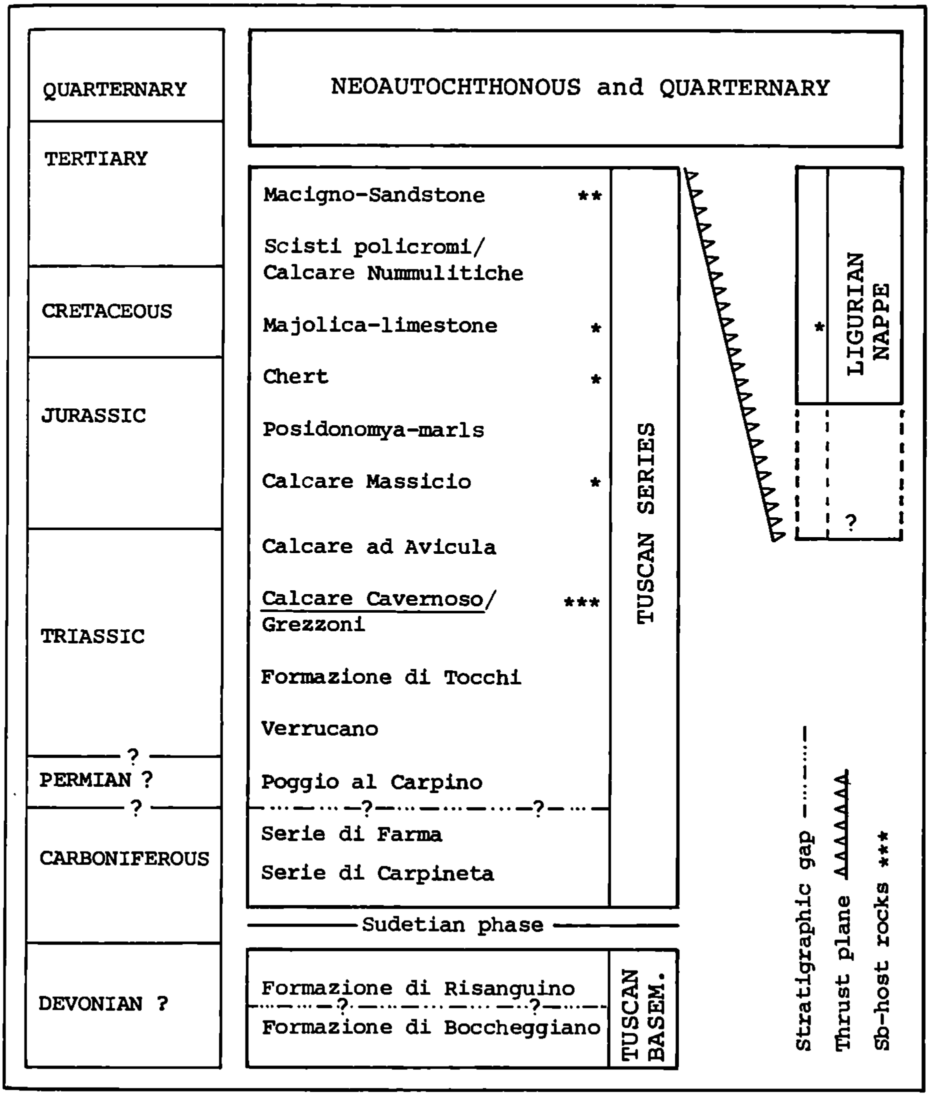

Fig. 1. Schematic stratigraphy of rocks relevant for ore formation and outcropping in Southern Tuscany, which are dated with a certain reliability. Uncertainties are indicated by questionmarks

- main components: antimonite (up to 10% in the ore), pyrite and marcasite (absent to about 10%)
- accessories: metastibnite, cinnabar, orpiment, realgar, sphalerite, galena, arsenopyrite, tetrahedrite, chalcopyrite
- some secondary alteration products.

The gangue is formed by quartz, calcite, gypsum; subordinate are barite and fluorite. Most deposits show intense silification of the host rocks. The genesis of the near-surface formed mineralizations is controlled by the following parameters.

A) Stratigraphic-Petrographic Control

Sb-minralizations are limited to highly permeable units within the Tuscan series, except for some minor mineralizations in Ligurian rocks (s. Fig. 1). The Calcare Cavernoso is the most frequent and the only economically important host rock. The high permeability results from the dissolution of the anhydrite component of the evaporitic sediment. The typical position for the mineralization is just below the contact to the impermeable cover, which is mostly formed by Ligurian flysch. Occasionally clay-rich members of the Tuscan series may take the same function (e.g. Schisti Policromi).

B) Structural Control

The Miocene nappe phase often transported impermeable Ligurian onto permeable Tuscan rocks. The following block tectonics generated the faults necessary for hydrothermal convection between different stratigraphic levels. The Sb-mineralizations are concentrated in highly faulted areas at the margins of horst structures. Occasional mineralizations along the faults emphasizes their function as transport media.

C) Ore Genesis and Magmatism

There is no obvious correlation between Plio-Pleistocene magmatism and ore deposition, neither is there a simple dependence on the geothermal gradient. Generally however, Sb-mineralizations are found in areas of elevated thermal activity or their former equivalents.

Concerning these factors the views of different authors are unanimous. The point of discussion however is the source of the deposit-antimony. In contrast to a number of articles by Dessau (e.g. 1974 and 1977) and his colleagues (e.g. Dessau et al. 1969 and 1972) the authors of this article do not consider the deposit-antimony to be derived from the young magmatism or from in situ remobilization within today's host rock.

The authors' studies lead to the following genetic model: Mobilization of Sb-Concentrations from deeper seated series; transport in hydrothermal convection cells and near-surface precipitation in permeable rocks. The magmatism and the correlated rise of the geothermal gradient deliver the necessary energy. Primary Sb-concentrations are expected in pre-Carboniferous rocks In Southern Tuscany however undoubtedly primary concentrations could not yet be identified with certainty.

3. SAMPLING AND ANALYTICS

Neumann (1979) carried out a multivariate statistical analysis to identify areas of high probability for Sb-deposit-formation in Southern Tuscany. Additional geological studies lead to the selection of 47 target areas (Fig. 2).

A total of 5840 soil samples were taken between autumn 1979 and spring 1982. The samples were taken with a drilling rod, max. depth 100 cm, from the B-horizon. During the sampling several field variables, dealing with the sample itself and the geological underground were documented in a data sheet. For local scale exploration sampling was usually carried out in a rectangular grid with point distances of 50 × 100 m or 100 × 200 m. In special cases denser grids for mine scale exploration or on the other hand reconnaissance profiles for regional scale exploration were taken.

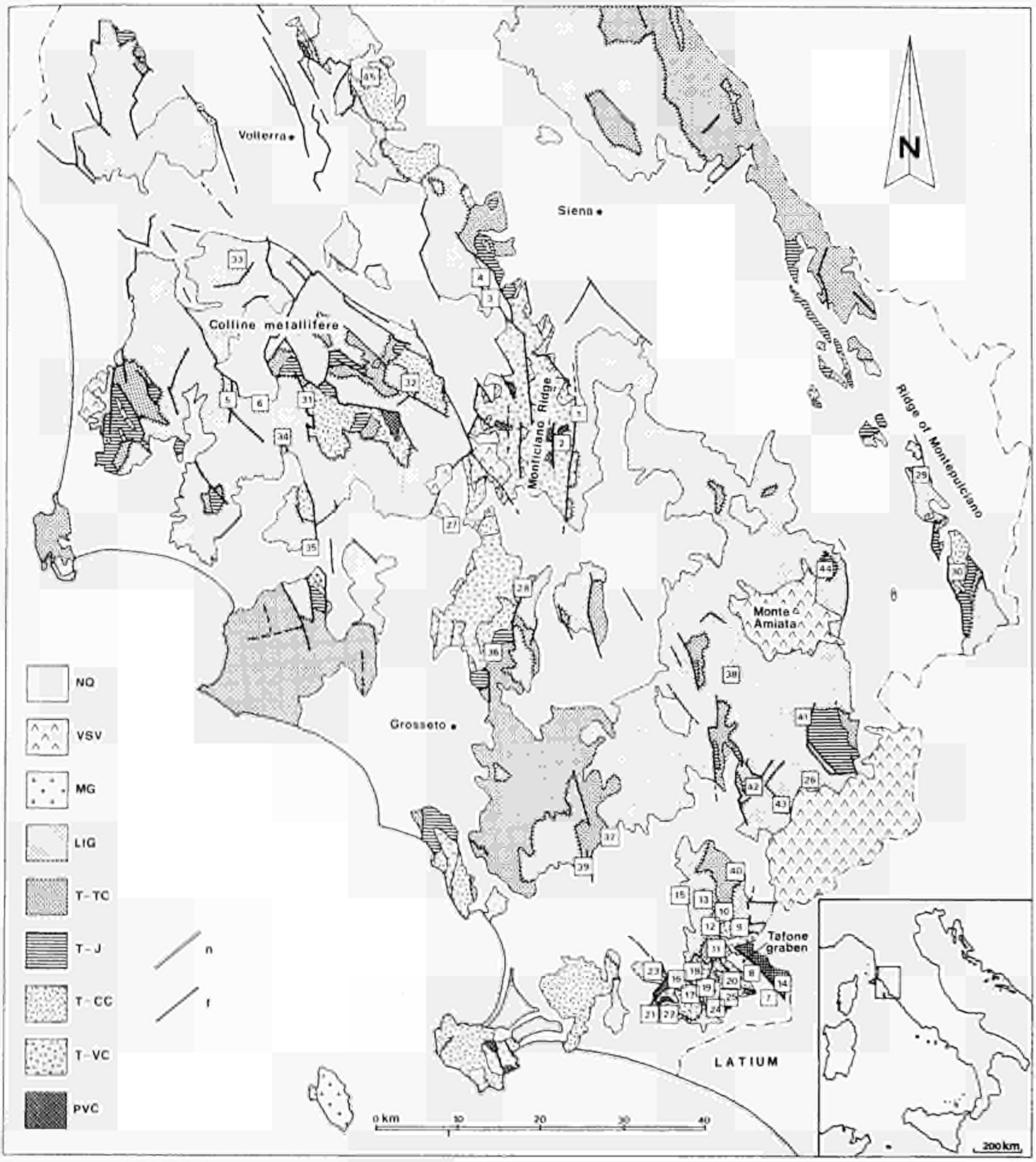

Fig. 2. Simplified geological map of Southern Tuscany with sampling areas. (NQ: Quarternary and Neoautochthonous; VSV: Plio- and Pleistocene volcanic and subvolcanic rocks; MG: Pliocene intrusive rocks; LIG: Ligurian nappe; T-TC: Tertiary and Cretaceous of Tuscan series; T-J: Jurassic of Tuscan series; T-CC: Calcare Cavernoso of Tuscan series; T-VC: Verrucano of Tuscan series; PVC: All units older than Verrucano; n: Nappe contact; f: Fault

Table 1. Average antimony contents (ppm) of total data and separated sampling areas (N = number of samples)

No	Sampling grid	N	Sb
	Total data	5841	209
1	Bagni di Petriolo	137	48
2	Fonderia di S.Martino	79	614
3	Cetine South	370	498
4	Cetine North	54	6
5	Frassine I	303	295
5A	Frassine Special	693	14
6	Frassine II	85	91
7	Montauto	146	203
8	Tafone	213	42
9	Pelagone	156	215
10	Poderi del Bufalo	58	1299
11	La Campigliola	157	488
12	S. Gerolamo	106	1951
13	Bottro del Inferno	40	231
14	Poggio Costone	71	349
15	La Pianaccia	25	2
16	Lagaccioli	275	189
17	Poggio Vaccaro	112	337
18	Poggio Capraio	129	181
19	Poggio Castellaccia	78	735
20	Capanelle I	21	1380
21	Capalbio SW	95	274
22	Capalbio SE	33	194
23	Marrucherone	145	70
24	Scaroncia W	50	87
25	Scaroncia E	42	62
26	Montebuono	136	3
27	Venturi	65	8
28	Paganico	393	145
29	Cappuccini	93	4
30	Mte. Cetona	51	3
31	Mte. Rotondo	157	45
32	Montieri	140	17
33	Micciano	27	9
34	Massa Marittima	164	55
35	Casa Bianca	68	140
36	Prunicce	45	9
37	Pomonte	93	47
38	Mte. Labbro	45	1
39	Magliano	107	28
40	Manciano	132	200
41	Selvena	80	22
42	Poggio Capanne	34	111
43	S. Martino sul Fiora	100	329
44	Campiglia d'Orcia	108	1
45	Casa Vogli	120	4

The samples were transported to Munich in plastic bags, dried in the oven at max. 70°C for three days. They were then ground in a powder mill with widia or silit inserts to less than 100 microns. For XRF-analysis, the powder was mixed homogeneously with a polymerisation chemical in the ratio7:3 and was pressed in aluminum caps to powder pellets.

The 13 trace elements, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Sb, Ba, Pb were analyzed by energy dispersive X-ray analysis (EDXRF). Control-measurements by atomic absorption analysis were carried out especially for Sb. Major and minor elements in selected samples were analyzed with EDXRF.

Field and chemical data were computerized, using the data base management system SIR (Robinson et al. 1979). For statistical analyses the program packages SPSS (Nie et al., 1975) and BMDP (Dixon et al., 1981) were used. In addition programmes for special requirements and computer plots were developed

4. RESULTS

4.1 Regional Distribution Patterns

The regional distribution pattern (Fig. 2) indicates that the Sb-deposits or anomalies are connected to the elongated horst structures, which also cause the outcropping of paleozoic rocks.

The remarkable accumulation around the Tafone Graben extends to the SW to Capalbio and possibly into N. Latium. Although the geology of the Tafone area is expected to continue into N. Latium, detailed knowledge is not available because of the thick Pleistocene volcanic cover. All deposits presently being exploited are situated in the Tafone area The majority of all grids in this area have anomaleously high Sb-contents (see Table 1).

The Sb-anomalies of other areas are also associated with tectonic structures:

- Elevated values are found along the Monticiano ridge and in its southern and northern prolongation (grids No. 1, 2, 3, 28, 36) in particular at its eastern margin. Further to the west, in the pyrite and mixed sulfide containing "Colline Metallifere", a number of smaller horsts contain locally elevated Sb-values. Except for one single grid (Frassine I, grid No. 5) the values are, although clearly anomaleous, not comparable with some of the really high anomalies.

- Sb-mineralizations are not known in the area north of Siena. The sampling grid Casa Vagli (No. 45) although structurally and petrographically favourably situated, contains no Sb values above the background. This may be explained by the general absence of geothermal anomalies.

The area Cappuccini (No. 29) and Monte Cetona (No. 30) situated on the ridge of Montepulciano, do not contain values above the background, although their position is theoretically very favourable. Numerous fault systems, permeable aquifers and thermal wells as indicators of geothermal activity are present. There are two possible reasons for the absence of Sb mineralizations:
a) primary Sb-enrichments are not available in the underlying rocks.
b) According to Wagner (1980) the formation of ore deposits depends on the development of hydrothermal convection cells in connection with the from W to E prograding igneous activity. Although there is evidence of a hydrothermal system in the ridge of Montepulciano the geothermal gradient established may not be high enough to allow near-surface precipitation of antimony.

- In the Mte. Amiata area a large number of Hg-mineralizations occur, some also containing antimonite as accessory mineral. There are also some smaller Sb mineralizations. Grids sampled in this area generally show elevated Sb values. With the exception of S. Martino sul Fiora (grid No. 43) however, the anomalies are rather low.

The following target areas are recommended as economically attractive: Cetine South (3), Frassine (5), La Campigliola (11), S. Gerolamo (12), Poderi del Bufalo (10), Pelagone (9), Le Capanelle (20) and Paganico (28). In some of these areas detailed work such as: dense grid sampling, geophysical studies for better transparency of the local structure and finding of antimonite-accompagnying pyrite ore have begun.

Another group of high anomalies need further investigation: Lagaccioli (16), Poggio Vaccaro (17), Poggio Capraio (18), Poggio Castellaccia (19) and Manciano (4).

4.2 *Local Distribution Patterns*

Cetine (Fig. 3): This locality is known for the abandoned Sb-mine of the same name. According to the knowledge of the local geology gained by superficial and mining works, the mineralization is bound to a NW-SE running fault which brings the Calcare Cavernoso in contact with a widespread flysch-type rock, the Galestri e Palombini. The ore deposit was mined in the Calcare Cavernoso.

According to the results of the geochemical sampling (Fig. 3) there is a clear separation between areas of high and low Sb contents. The Sb-anomalies however do not coincide with the fault. Two possible explanations may be given:
a) The fault mapped is not the main controlling factor for ore formation,
b) the fault mapped is part of a series of faults oblitterated by the flysch,

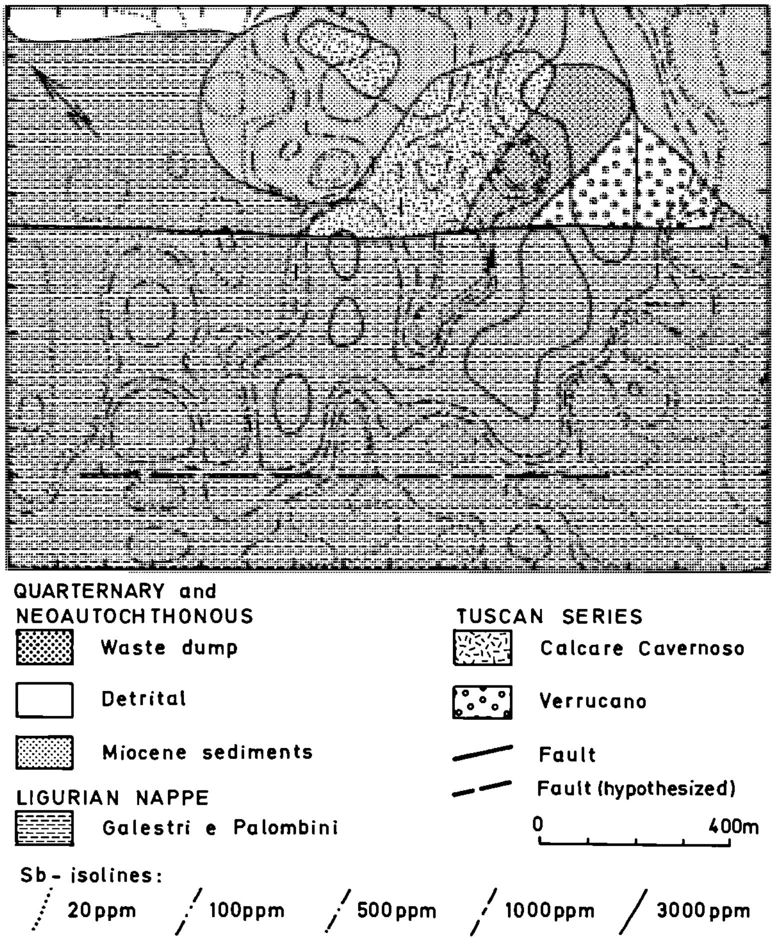

Fig. 3. Geological map and isoline plot of Sb contents in soil samples of the Cetine South area (grid No. 3). Geology: Enlargement of survey maß 1:100.000; No. 120. Grid indicated at map margin. The hypothesized fault is based on the pattern of geochemical Sb-distribution

which may all have acted as transport media for ore solution. Under these circumstances it may be hypothesized that to the SW of the fault mapped there is only a thin layer of flysch covering a mineralized zone of the Calcare cavernoso.

La Campigliola (Fig. 4): This locality is situated within a large area of numerous known and partly exploited Sb-mineralizations, just S of the abandoned mine Macchia Casella.

The Tafone graben extends to the SE to the Tafone mine, presently together with the nearby Montauto, the only Sb-productive localities. Tectonic and hydrothermal activities are evident.

Soil samples were taken in a 100 by 350 m grid. The isoline plot shows large areas with more than 1000 ppm and four centers with values higher than 3000 ppm. Two of these are in alluvial terrain. The two others are in a contact area of Calcare Cavernoso/Santa Fiora flysch and in Macigno sandstone respectively, both in a strongly faulted zone and should be sampled in a denser grid. Additional geophysical methods should be carried out.

Cappuccini (Fig. 5): No Sb anomalies were found. This may be due to a) hydrothermal convection cells causing ore formation have not yet been established

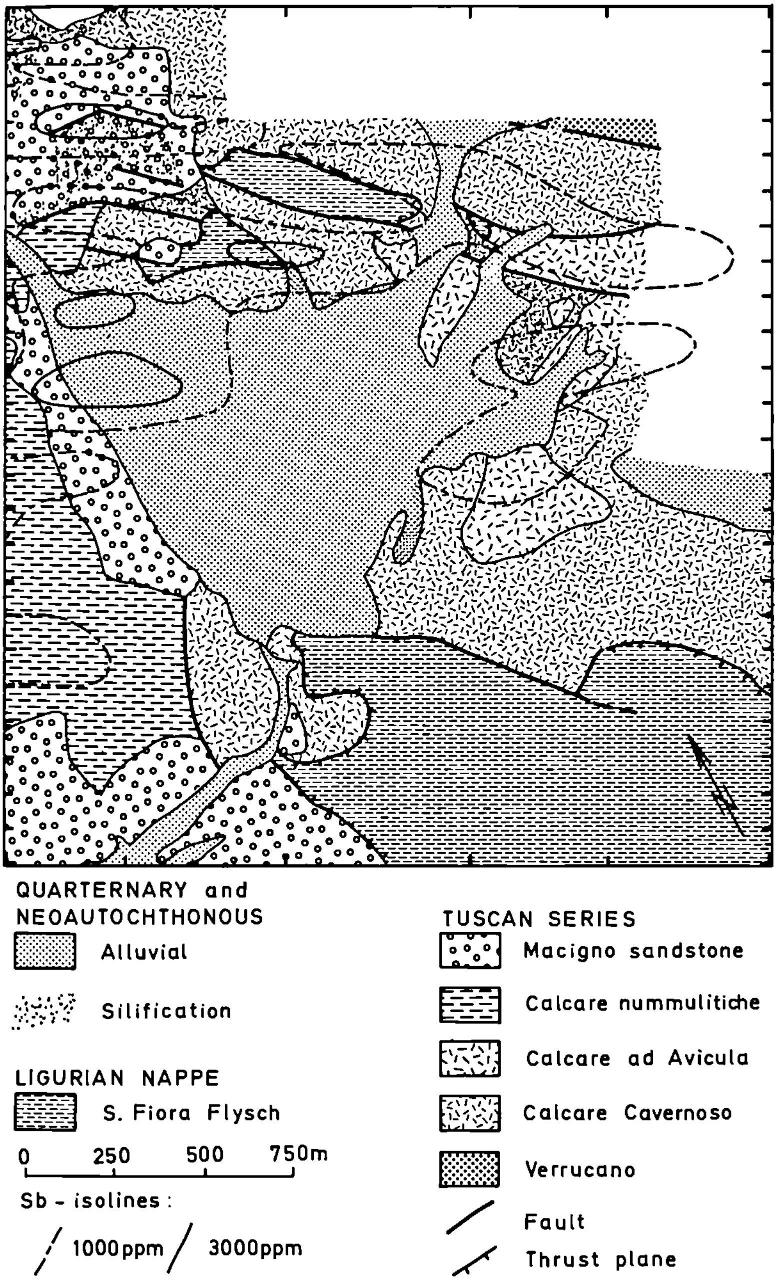

Fig. 4. Geological map and isoline plot of Sb contents in soil samples of the Campigliola area (grid No. 11). Geology: R. Siegert 1982. Grid indicated at map margin

or b) the ridge of Montepulciano is not underlayn by Sb-containing Paleozoic series.

Taking into consideration the W to E prograding Plio- to Pleistocene magmatism of Southern Tuscany, it may be expected that the ridge of Montepulciano will be the area affected next by igneous and thermal activity. Thermal wells as first indicators of rising temperatures in the lower levels support this extrapolation. Two areas

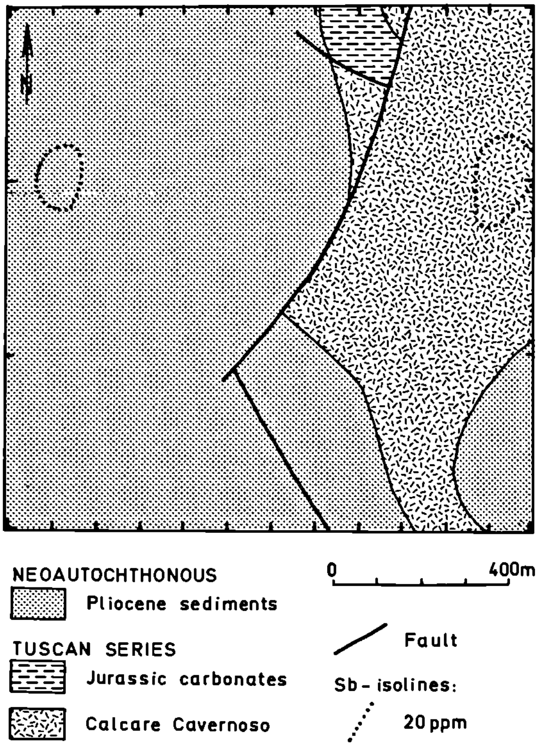

Fig. 5. Geological map and isoline plot of the Cappuccini area (grid No. 29) near Montepulciano; geology: Enlargement of Survey map 1:100.000; No. 121. Grid indicated at map margin

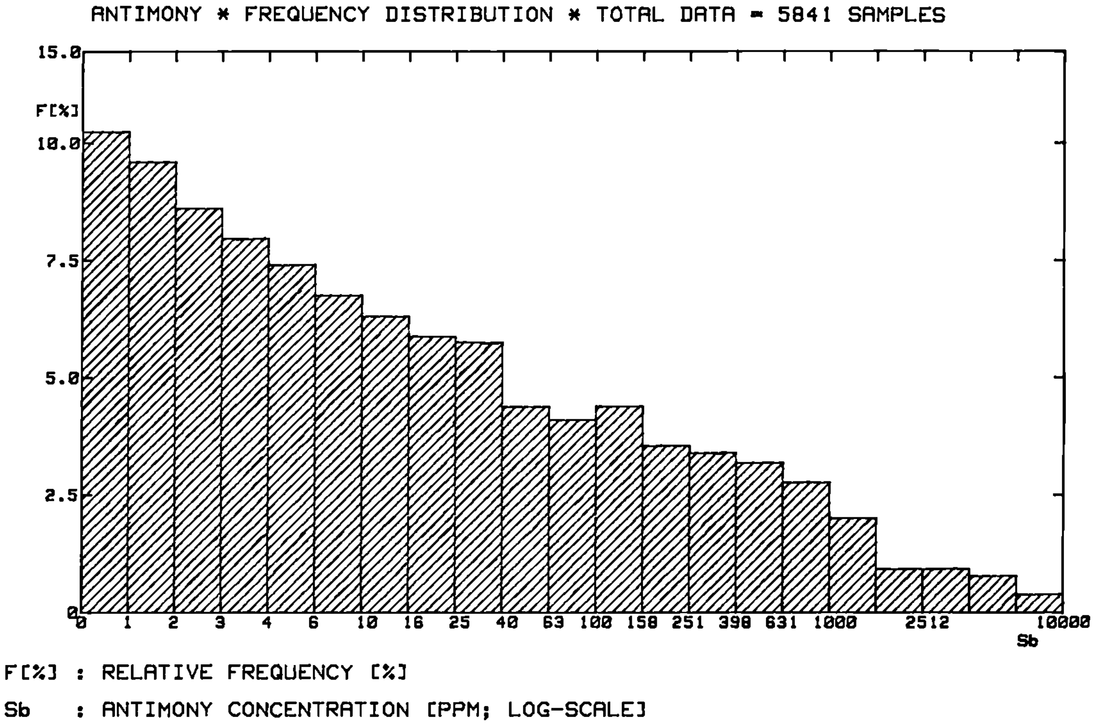

Fig. 6. Frequency distribution of antimony contents (ppm) in 5840 soil samples. Semi-quantitative range below 20 ppm Sb

(Cappuccini and Monte Cetona) were therefore sampled in favourable position to identify Sb-anomalies which might be interpreted as signs of present ore deposit formation.

4.3 Data Analysis

Data collected and processed as described in 3.5 were treated with uni-, bi- and multivariate statistical methods. Aim of this study was to reveal the geochemical behaviour of the analyzed elements, especially the trace elements and their dependence of the different geological situations. Fig. 6 shows frequency distribution for Sb of all 5840 samples. Whilst the overall diagram in Figure 6 shows a chi-square distribution, areas with elevated Sb-values produce a binominal distribution, which is characteristic for mineralized and hydrothermally altered areas. This observation also applies to the elements Sr, Ba and Pb, which generally can be correlated with Sb. The observation that these elements were transported and precipitated together with Sb is supported by the variety of accessory minerals (galena, sphalerite, Pb-Sb sulfosalts) and the gangue minerals (baryte, calcite) within the known ore deposits. A detailed analysis of the geochemical aspects will be published in a geochemically orientated paper.

5. CONCLUSIONS

The results of the geochemical soil survey show that the statistical probability determinations were satisfactory and that the statistical treatment of geological data can be used as a powerful tool in exploration. It should be mentioned however that southern Tuscany offers very favourable conditions for statistical analysis since the density of data available in the area exceeds that of an average prospection area remarkably.

Besides the areas indicated with high probability for Sb-ore formation by the statistics, some more areas were selected for geochemical sampling because of their suitability, judged on the basis of conventional geological observation. None of the grids sampled in these areas however showed Sb-values above the average. On the other hand, some areas, indicated with a high probability by the statistics, appeared unsuitable by conventional geological standards. These areas, too, contained only low Sb-values. No highly anomalous areas so far unknown were found. However, quite a few extensions of known mineralizations were detected. The geochemical methods applied can be regarded as appropriate. Geared for the aim of the study, the point distances of the grids can be adjusted according to the subsequent steps: finding and delineation of the mineralizations.

The mobility of Sb and the near-surface formation typical for these deposits also favour the method applied. Transferred to other metals, the system has to be adjusted accordingly. Still problematic is the detection of anomalies through impermeable cap rocks, in this case the clay-rich flysch-type rocks.

The extensive study produced a detailed picture of the Sb-distribution of southern Tuscany. The potentially mineralized zone was narrowed down to the area south of Siena and west of the ridge of Montepulciano. To the South, the area is bordered by the thick cover of Pleistocene tuff in Northern Latium.

Within this zone mineralization is petrographically bound to permeable rocks of the Tuscan series and overlying impermeable covers. The ore deposits are structurally controlled by fault zones of Pliocene to subrecent block tectonics.

The accumulation of Sb-deposits and mineralizations in the Tafone area was also veryfied by geochemical prospecting. A possible explanation for this may be an underlying particularly Sb-rich formation as primary source. Pre-Carboniferous rocks with primary Sb enrichments are considered to be the source of the deposit antimony. Unusually large outcrops of paleozoic rocks in the area do contain antimony in small amounts (up to 20 ppm), which are however not yet proven to be of primary origin.

Acknowledgements. The authors wish to thank RI.MIN. S.p.A., Follonica, for cordial cooperation and the Commission of the European Communities for financial support.

REFERENCES

Abbate, E., Sagri, M.: The eugeosynclinal sequences. Sed. Geol. 4, 251-340 (1970)

Bagnoli, G., Gianelli, G., Puxeddu, M., Rau, A., Squarci, P., Tongiorgi, M.: The Tuscan Paleozoic: A critical review. In: Tongiorgi M. (ed) (1978): Report on the Tuscan Paleozoic basement. CNR: Rapporto interno del Sottoprogetto Energia Geotermica, Progetto Finalizzato Energetica. Pisa, 9-26,1978

Bagnoli, G., Tongiorgi, M.: New fossiliferous Silurian (Mt. Corchia) and Devonian (Monticiano) layers in the Tuscan Paleozoic. Mem. Soc. Geol. It. 20, 301-313 (1979)

Bagnoli, G., Gianelli, G., Puxeddu, M., Rau, A., Squarci, P., Tongiorgi, M.: A tentative stratigraphic reconstruction of the Tuscan Paleozoic basement. Mem. Soc. Geol. It. 20, 99-116 (1979)

Benvenuti, G., Brondi, M., Aglio, M. dall, Roit, R.da, Cassan, P.de, Ghiara, E., Gigli, C., Marinelli, G., Martini, M., Gragnani, R., Orlandi, C., Paganin, G.: L'idrologia. In: Autori Vari: La Toscana. Meridionale. Rend. Soc. Mineral. Petrol. 27, 211-316 (1971)

Dessau, G.: Die Lagerstätten Toskanas im Lichte der Geologischen Entwicklung des Landes. Archiv für Lagerstättenforschung in den Ostalpen, Sonderband 2, 51-77 (1974)

Dessau, G.: Die Quecksilber- und Antimonlagerstätten der Toskana. Freiberger Forschungshefte, Reihe C, Nr. 328, 47-71 (1977)

Dessau, G., Stefanis, A.,de: Studio geologico-minerario della zona mercurifera di Cerreto Piano (Scansano, Provincia di Grosseto). Mem. Soc. Geol. It. 8, 289-323 (1969)

Dessau, G., Duchi, G., Stea, B.: Geologia e depositi minerari della zona Monti Romani - Monteti (Communi di Manciano e Capalbio (Grosseto) e Ischia di Castro (Viterto)), Mem. Soc. Geol. It. 11, 217-260 (1972)

Dixon, W.J., Brown, M.B., Engelmann, L., Frane, J.W., Hill, M.A., Jennrich R.I., Toporek, D.D.: BMDP statistical software. Berkeley, 736 pp, 1981

Giannini, E., Lazzarotto, A., Signorini R.: Lineamenti di stratigrafia e di tetonica. In: Autori Vari: La Toscana Meridionale. Rend. Soc. Ital. Mineral Petrol. 27, 33-168 (1971)

Marinelli, G.: Magma evolution in Italy In: Squyres, C.H. (ed) Geology of Italy. Tripolis, 165-219, 1975

Neumann, N.: Geologische und geochemische Bildungsparameter der Hg-/Sb-Lagerstätten der Südtoskana, Italien. Unpublished Ph.D. thesis, University of Munich, 132 pp, 1979

Nie, N.H., Hull, C.H., Jenkins, J.S., Steinbrenner, K., Bent, D.H.: SPSS. Statistical Package for the social sciences. New York, 675 pp, 1975

Pichler, H.: Italienische Vulkangebiete I. Stuttgart, 248 pp, 1970

Rau, A., Tongiori, M.: Geologia dei Monti Pisani a sud-est della Valle del Guappero. Mem. Soc. Geol. It. 13, 227-408 (1974)

Robinson, B.N., Anderson, G.D., Cohen, E., Gazdzik, W.F.: SIR - Scientific information Retrieval. Evanston, 488 pp, 1979

Sestini, G.: Postgeosynclinal deposition. Sed. Geol. 4, 481-520 (1970)

Siegert, R.: Bericht über die Kartierung, sowie petrografische, lagerstättenkundliche und bodengeochemische Bearbeitung eines Gebietes bei La Campigliola (Südtoskana, Italien). Unpublished Diploma thesis, Universit of Munich, 150 pp, 1982

Wagner, J.: Die Eisen- und Kupfersulfid lagerstätten der Toskana in ihrem geologischen Rahmen. Unpublished Ph. D. thesis, University of Munich, 9 p,

Received: March 24, 1983
Accepted: May 26, 1983

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Price (excluding VAT) in Luxembourg
ECU 8.71 BFR 400 IRL 6.40 UKL 5 USD 7.50

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ISBN 92-825-4086-3

9 789282 540862