THE GEOCHEMISTRY OF GANGUE MINERALS FROM CARDIGANSHIRE, MIDWALES*

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ABSTRACT

Quartz and calcite are the commonest vein minerals associated with sulphide mineralization in Cardiganshire

Fifty samples of quartz were analysed for Al, Ti, Fe^{+3}, P, Mn, Li, Na, K, Ca, Mg, Sr, Pb, Zn, Cu, Ag, Cd, Co and Ni. Chromium, F^{-1} and Cl^{-1}, were determined in only a few samples. All these elements show different ranges of variation. Cobalt, however, is characteristically constant, and occurs in unusually high amounts. The absolute Cation ratio of alkalis, Ca, andn Mg in quartz approaches that of Red Sea brines. Quartz also seems to be very rich in Fluorine and Chlorine. The ratio of Zn/Pb/Cu in quartz can be used for geochemical prospecting, but does not reflect the true contents of the proportions of these elements as sulphides.

Sixteen samples of Calcite were analysed for, Fe^{+3}, Mn, Mg, Sr, Na, K, Zn, Pb, Cu, Ag, Co, Ni, Cr, F^{-1} and Cl^{-1}. All these elements vary a lot except manganese which is practically constant. The ratio of Zn/Pb/Cu can be used as a geochemical tracer, but as in the case of quartz, it does not reflect the true proportion of these elements as sulphides.

The partition coefficients of the different trace metals in quartz and calcite reflect the paragenetic sequence and temperature of deposition of these minerals. The ratio of Na, K, both in quartz and calcite, seems to be temperature controlled.

The mineralization in Cardiganshire seems to have been caused by Na-K-Cl type brines highly enriched in fluorine and lithium, suggesting a probable contribution from juvenile waters.

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Contents:

Calcite is the next most abundant gangue mineral in Cardiganshire. It occurs as thin veins usually parallel to the mineral-fractures, but at places a cross-cutting relationship with respect to the quartz veins is also displayed.

The general pattern of the deposition of Calcite veins is rather ambiguous, but as a general rule it follows quartz, sphalerite, and galena in paragenctic sequence. Calcite veins tend to be more abundant, where chalcopyrite is one of the sulphide mineral phases. Sixteen calcite samples were collected for analysis.

No information is available as to the original depth of formation of the sampled quartz and calcite veines. The location of the samples is shown in fig 1.

METHODS AND TECHNIQUES

Two hundred grams of Quartz sample was crushed to about 300 mesh. Quartz, crushed in tungston carbide Tema machine, is contaminated with tungston carbide which is highly resistent to all acids, and hence, can be collected as a residue after the evaporation of quartz powder with HF. Many such replicate measurements showed that the contamination amounts to about 20 µg/gm of quartz powder. This result was reproducible to within 10-15 % error. Contamination of quartz powder by tungston carbide was previously noted by Fuge (1970, personal communication).

In order to study the best optimum analytical conditions, quartz samples were treated with different acids. Data collected on different elements shows a wide variation of content and precision of analysis.

Five grams of quartz powder was dissolved in HF and evaporated. This procedure was repeated several times until all the silica had been volatilized. The water bath temperature was maintained at 60°C.

Several of these replicate solutions were dissolved separately in HCL, HNO_3, (HNO_3—$HCLO_4$), $HCLO_4$. A separate batch of samples was treated with (HNO_3—$HCLO_4$) without recourse to HF and the data collected were compared with other analyses.

The results in HCL were consistently lower, possibly because of the high volatility of the chlorides of most elements. Morever, the precision of the analyses was not good and the results fluctuated between wide limits.

The HNO_3—solution has been recommended by Price and Ragland (1966). In this case, while, the results were found to be fairly consistent with a high degree of precision, they were lower as compared to (HNO_3 – $HCLO_4$) treatment. The results for aluminium showed a great amount of fluctuation. Yamaguchi, *et al.*, (1962) have suggested that this is due to the relative insolubility of the fluoride in HNO_3, which, therefore, gets volatilized at high temperatures.

The best optimium conditions were obtained with HF—$HCLO_4$ treatment. Consequently in all the data collected, quartz was treated with HF-$HCLO_4$.

The partial leaching of quartz powder with (HNO_3—$HCLO_4$) gives almost identical results as compared with the total solution method. The precision is also as that obtained in the latter method. Aqua regia treatment yields variable results, which can not be reproduced easily.

Five grams of quartz was dissolved in HF—$HCLO_4$, and after several evaporations, the residue was twice treated with 4 ml $HCLO_4$ and 10 ml H_2O, and heated on a water bath for two hours. The solution was then transferred to a 50 ml flask containing one ml. 0.5 N HNO_3 and made upto volume with distilled water. A reagent blank was made in the same way.

One gram calcite powder was dissolved in 1:1 HNO_3. After the effervescence was over, the solution was evaporated to get rid of the excess HNO_3. Ten ml 0.1 N HNO_3 was added to the residue and filtered. There was usually no residue left over after the filtrate

FIG.-1 LOCATION OF QUARTZ AND CALCITE SAMPLES except in the case of two samples. The final volume was made upto 50 ml ready for use.

Residue was left over on the filter paper in the case of two calcite samples. This residue along with the filter paper was washed and transfered to a platinum crucible. Five ml HF were added to the crucible and the contents evaporated. After this the evaporate was treated with 1:1 HNO_3 twice, and evaporated each time. The final residue was dissolved in O.1 HNO_3 and transferred to the original solution and the total made upto 50 ml. Two reagent blanks, one with a filter paper and another without were made in a similar way.

Standards were prepared for quartz in the usual way, but for calcite solutions the standards were made in $CaCO_3$ solutions and neutralized with HNO_3, so that the final solution contained one gm $CaCO_3$/50 ml. equivalent to the amount of calcite powder used, in order to minimize the difference of the effect due to calcium ions on other metals. Standards prepared in distilled water were also used to check the varying effects of Ca-ions on various elements. No attempt was made to precipitate calcium from the calcite solutions because of the fear of occlusions of other ions on the precipitate.

Aluminium and Titanium were determined by a slight modification of Davids' (1965) method adjusted to the autoanalyser purposes. Phosphorus was determined by Scholes and Thulbornes' (1963) method slightly modified to adjust to the autoanalyser purposes. Chlorine, fluorine and chromium were determined in solutions by alkaline fusion, Fuge (1969, 1970).

All the other elements in quartz and calcite were determined by atomic absorption spectrometry using a unicam Sp. 90 spectrometer. Lanthanum oxide buffer was used in the case of Ca^{+2}, Mg^{+2}, and Sr^{+2} in order to suppress the ionization effects due to aluminium. Walsh and Howie (1967); Rama Krishna *et al.* (1967). Cobalt, nickel, silver, lead, zinc and copper were also determined by AA method, Chakarbarti *et al.* (1966), Rawling *et al.* (1961) and Rama Krishna (1967).

Sodium and potassium were determined by flame photometary using Ammonium sulphate buffers. Lithuim was also determined in the same way using KCL buffer, Gaddy, (1965).

ACCURACY AND PRECISION

In order to check the accuracy and precision of the results sixty replicate analyses of a quartz sample were obtained. Besides, the Canadian Sulphide Standard (CAAS) was also analysed. Data from other sources quoted by Sine *et al.*, (1969) and Weber (1965) as averages for CAAS is presented for comparision in Table 1.

The analytical error in all determinations was found to very linearly with the concentration of each element present, in an inverse manner.

In quartz the relative deviation for cobalt, sodium and lithium lies within 5%. The results for alunimium and manganese vary between 5-10%, for calcium, magnesium, and iron, 10-15%, potassium and nickel have a relative deviation of 15-20%, phosphorus, titanium and zinc have a relative deviation of 20-30%, copper and silver vary from 30-40%, and lead varies between 40-50%. The highest relative deviations recorded for strontium and cadmium, being 62.81% and 113.3% respectively, are due to their extremely low concentrations in all the samples.

Fifteen replicate samples were analysed for calcite. In order to check the effect of calcium ions on other elements, standards were made in $CaCO_3$ solution and water respectively. A comparison of the respective standards indicated that cobalt and nickel are strongly affected by calcium ion concentration in the solution. The results for all the other elements in $CaCO_3$ solution and in water agreed well within the experimental error. The effect on nickel and cobalt is probably due to Camouflaging by Ca-ions.

In calcite the relative deviation of Fe^{+3} and Mn^{+2} is within 5%, cobalt and magnesium vary 5–10%, copper and potassium 10–15%, lead, zinc, strontium and sodium have a relative deviation between 15-20%, nickel varies 27.5%, and silver 33.5%.

All the analytical results are quoted to within 95% confidence level.

Table-1

Three samples of Canadian sulphide standard were analysed along with other replicate solutions for all the elements. Data from other sources quoted by Sine *et al*, (1969) and Weber (1955) as averages for CAAS is qouted below for comparison.

Present Work		*Data from* *Weber* (1965)	*Data from* *Sin eet al.* (1969)
LEAD : ppm			
range (R)	200-255	200-310	184-315
mean (X)	255	248	249
St. Dev. (S)	22.73		
Rel. Dev. (C)	10.10%		
ZINC : ppm.			
range	350-500	160-550	228-360
mean	425	298	294
St. Dev.	61.24		
Rel. Dev.	14.40%		
COPPER : ppm.			
range	8,000-10,000	1,000-12,000	7,200-9,500
mean	8,766	8,291	8,215
St. Dev.	69.55		
Rel. Dev.	0,79%		
IRON: %			
range		20.0-25.18	
mean	25.0	22,.87	
St. Dev.	0.0		
Rel. Dev.	0.0%		

Present Work		*Data from Weber* (1965)	*Data from Sine et al.* (1969)
CADMIUM: ppm.			
range	13-18	1-50	0.3-10
mean	15	?	
St. Dev.	1.15		
Rel. Dev.	7.86%		
SILVER: ppm.			
range	3.5	2-6.0	2.6-4.0
mean	3.5	3.9	4
St. Dev.	0.0		
Rel. Dev.	0.0%		
COBALT: ppm.			
range	..	300-730	410-540
mean	675	546	540
St. Dev.	0.0		
Rel. Dev.	0.0%		
NICKEL: ppm.			
range	13,000	1,000-20,000	13,000-15,000
mean	13,000	13,103	12,835
St. Dev.	..		
Rel. Dev.	..		
MANGANESE: ppm			
range	1275-1350	1352-1584	774-1117
mean	1342	1144	990
St. Dev.	51.53		
Rel. Dev.	3.83%		
CALCIUM: %			
range	3.23-3.85	3.2-4.49	4.2
mean	3.43	3.96	4.1
St. Dev.	0.36		4.0
Rel. Dev.	10.55%		
MAGNESIUM: %			
range	3.0-3.50	2.5-5	..
mean	3.21	3.93	..
St. Dev.	0.189		
Rel. Dev.	5.89%		

Table-2

TRACE ELEMENTS IN QUARTZ VEINS UG/G

(N. D. Not detected)

Sample No.	Pb	Zn	Cu	Fe^{+3}	Mn	Ca	Mg	Sr	Na
1	38	25	8	173	10	42	23	1	288
2	50	70	55	312	5	44	149	N.D.	305
3	25	65	40	124	9	32	28	N.D.	399
4	11	18	30	241	7	46	69	N.D.	595
5	50	43	10	305	12	610	205	6	314
6	25	43	30	102	12	96	11	4	288
7	38	53	5	69	7	22	6	1	185
8	50	23	5	138	12	32	39	3	222
9	25	35	5	345	44	110	73	2	444
10	25	65	5	103	14	181	69	N.D.	185
11	75	65	5	379	54	646	139	5	296
12	25	700	4900	466	16	7	81	N.D.	370
13	75	25	15	241	10	433	32	9	296
14	63	40	10	897	16	32	232	1	296
15	50	58	5	69	4	68	7	2	222
16	100	75	20	103	7	22	15	2	296
17	25	53	5	69	6	68	7	2	185
18	30	5	2	36	2	36	2	4	119
19	5	54	2	41	5	145	8	5	96
20	50	15	2	48	6	12	7	N.D.	45
21	2	150	4	28	3	11	0.1	2	126
22	45	29	6	97	252	852	134	6	111
23	5	15	1	28	3	20	1	2	126
24	5	16	4	269	5	92	7	N.D.	222
25	5	11	5	59	6	30	9	2	237
26	10	7	1	35	2	7	0.1	N.D.	45
27	110	53	2	69	2	25	10	2	148
28	5	8	4	35	4	39	5	3	126
29	220	33	2	179	9	25	13	1	400
30	15	12	5	331	5	4	17	2	324
31	2	20	4	97	4	71	4	ND	148
32	5	31	2	59	2	9	2	2	134
33	5	45	4	114	16	22	11	3	222
34	45	6	2	114	4	12	8	N.D.	200
35	5	5	3	390	2	3	4	1.	229

Continued Table-2

K	Co	Ni	Al	Li	Ti	P	Cd	Ag	Sample No.
107	440	15	365	289	9	7	1	0.6	1
158	420	13	374	622	19	45	1	2	2
124	650	10	367	237	18	1	0.1	0.6	3
332	560	23	390	1000	21	5	N.D.	0.3	4
166	440	8	229	28	23	3	0.2	0.3	5
83	460	5	86	28	12	0.4	N.D.	0.3	6
166	125	10	398	892	16	11	1	..	7
124	150	5	411	475	25	5	1	..	8
83	350	13	325	160	17	1	0.2	..	9
124	190	75	390	400	23	7	N.D.	..	10
83	270	13	351	95	24	9	8	..	11
415	175	25	406	2100	58	15	6	..	12
83	380	5	97	30	27	180	3	..	13
83	275	13	406	330	30	18	1	..	14
41	305	13	86	25	18	2	1	..	15
83	235	13	406	415	19	12	3	..	16
41	280	13	74	25	25	11	2	..	17
66	370	5	56	N.D.	18	8	1	0.6	18
42	200	5	52	5	21	4	N.D.	..	19
83	180	3	94	245	21	6	N.D.	..	20
108	160	5	406	1200	19	15	1	..	21
100	100	14	127	30	23	13	1	..	22
75	350	5	44	10	19	0.4	0.2	..	23
75	390	9	416	1300	44	0.4	1	..	24
91	420	5	189	120	65	20	0.2	..	25
75	140	5	255	235	22	9	1	..	26
83	140	N.D.	367	105	27	6	1	..	27
100	250	N.D.	91	170	23	14	1	..	28
158	320	6	411	970	32	7	t	..	29
216	230	7	390	955	30	34	1	..	30
91	490	5	73	5	24	9	t	..	31
66	390	7	104	75	25	4	7	..	32
91	460	10	88	20	24	5	1	..	33
83	390	5	94	10	24	4	6	..	34
166	490	5	294	210	41	26	t	..	35

Continued Table-2

Sample No.	Pb	Zn	Cu	Fe^{+3}	Mn	Ca	Mg	Sr	Na
36	30	48	5	1715	16	5	12	N.D.	178
37	50	6	4	1300	13	2	54	1	296
38	135	8	4	1094	5	2	24	N.D.	185
39	20	23	5	133	8	58	21	2	236
40	4400	1200	9	680	11	3	16	2	355
41	5	9	1	121	2	7	6	2	126
42	5	11	2	38	2	2	3	1	370
43	10	5	2	121	2	3	9	1	74
44	2	810	6	1232	3	2	1	N.D.	59
45	9400	19	20	956	5	3	12	N.D.	444
46	90	45	1070	1888	302	64	149	2	1998
47	100	1250	470	1888	6	2	115	2	170
48	2	10	2	100	2	9	21	2	96
49	2	5	2	204	3	8	42	N.D.	67
50	t	5	2	45	3	4	6	N.D.	141

Continued Table-2

K	Co	Ni	Al	Li	Ti	P	Cd	Ag	Sample No.
191	560	5	359	65	56	15	N.D.	0.6	36
374	270	5	406	850	70	60	t	2	37
191	420	6	307	160	46	30	t	0.6	38
62	412	9	99	25	32	60	1	0.6	39
432	420	25	406	905	50	12	12	1.4	40
33	480	3	81	10	32	5	N.D.	0.6	41
42	170	1	86	30	32	10	1	0.3	42
75	190	2	198	200	35	15	1	1.3	43
42	300	18	130	190	38	18	1	1.3	44
299	370	140	416	95	65	34	3	7.3	45
2490	200	32	325	1300	177	129	1	8	46
282	300	1	307	850	89	34	44	3	47
91	370	5	198	N.D.	46	18	N.D.	0.6	48
33	440	5	127	N.D.	40	11	t	0.05	49
42	440	5	138	25	43	15	t	0.1	50

Table-3

GENERAL STATISTICAL ANALYSIS OF TRACE ELEMENTS DETERMINED IN QUARTZ IN PPM.

Element	Range	Mean	Mode	Median	St. Dev.	Rel. Dev.	Skewness	Kurtosis
Li	t - 2100	350	25	120	465	132.55	2.79	5.49
Na	45 - 1998	161	150	175	277	106.31	25.04	31.57
K	33 - 2490	175	150	165	348	198.9	36.16	40.0
Mg	71 - 232	38	25	20	55	144.61	3.72	5.89
Ca	2 - 852	82	25	20	175	214.08	9.87	12.06
Sr	Nil - 9	1.8	..	..	..	..	..	..
Al	44 - 416	246	75 & 350	215	140	56.70	0.0	1.26
Ti	9 - 177	35	25	34	26	75,70	11.91	18.11
P	0.5 - 180	20	5	6	31	158.70	12.81	16.72
Pb	2 - 9400	311	5	20	1450	465.62	29.99	32.79
Zn	5 - 1250	108	5	20	273	253.80	11.14	12.87
Cu	1 - 4900	136	5	2	706	518.55	39.70	42.26
Ag	t - 8	1.5	0.6	0.6	..	..	..	..
Cd	Nil - 44	2	1	..	..	..	..	..
Fe	28 - 1888	354	50	106	491	138.98	3.88	5.82
Co	100 - 650	330	150 & 450	280	131	39.5	0.0	2.22
Ni	1 - 140	13	3	5	22	170.0	21.26	25.75
Cr	3 - 4	3	..	3	..	..	..	..
Mn	2 - 302	19	5	3	54	282.42	20.26	22.04
F	310 - 460	390	..	400	..	19.35	..	..
Cl	366 - 602	437	..	521	..	17.10	..	..

Table-4

MATRIX OF CORRELATION COEFFICIENTS FOR TRACE ELEMENTS IN QUARTZ SIGNIFICANT AT 95% LEVEL — D.F.—48, t—2.02

Element	Li	Na	K	Mg	Ca	Al	Ti	P	Pb	Zn	Cu	Fe	Cu	Ni	Mn
Li	0.0														
Na	.41	0.0													
K	.46	.93	0.0												
Mg	..	.38	.33	0.0											
Ca	..	..	..	.52	0.0										
Al	.66	.41	.46	..	..	0.0									
Ti	.39	.72	.84	..	..	..	0.0								
P	..	.50	.50	..	..	..	.51	0.0							
Pb	..	..	..	..	..	..	..	..	0.0						
Zn	.40	..	..	..	..	..	..	..	..	0.0					
Cu	.61	.6	.31	..	..	..	.32	.51	..	.36	0.0				
Fe	.30	.45	.56	.36	..	.36	.75	.39	..	.46	..	0.0			
Co	..	..	..	..	..	..	..	..	..	..	..	..	0.0		
Ni	..	..	..	..	..	..	..	..	.81	..	..	..	..	0.0	
Mn	..	.67	.72	.45	.47	..	.55	.36	..	..	..	.32	..	..	0.0

Table-5

T-TEST FOR SIGNIFICANCE OF SIMPLE CORRELATION OF TRACE LEMENTS IN QUARTZ D.F.—48

Level of Significance	.8	.7	.6	.5	.4	.3	.2	.1	.05	.02	.01	.001
T-Value	.26	.39	.53	.68	.85	1.05	1.30	1.68	2.02	2.42	2.70	3.55

Element	Li	Na	K	Mg	Ca	Al	Ti
Li	0.0						
Na	3.15	0.0					
K	**3.59**	**17.74**	0.0				
Mg	1.39	2.84	2.44	0.0			
Ca	1.39	0.05	0.31	**4.20**	0.0		
Al	**6.02**	2.11	1.75	2.28	0.69	0.0	
Ti	2.97	7.13	**10.89**	1.80	1.04	1.54	0.0
P	1.07	3.97	4.15	1.38	1.0	0.18	..
Pb	0.05	0.81	0.69	0.55	0.58	1.72	..
Zn	2.98	0.07	0.78	0.77	0.80	1.30	..
Cu	**5.35**	1.76	2.23	1.36	0.48	1.34	..
Fe	2.17	3.53	**4.72**	2.71	0.76	2.65	7.78
Co	1.88	0.01	0.83	0.61	0.97	0.75	0.39
Ni	0.65	1.84	1.54	0.67	0.11	2.33	1.58
Mn	1.19	**6.29**	7.20	3.53	3.68	0.24	**4.54**

Continued Table-5

P	Pb	Zn	Cu	Fe	Co	Ni	Mn	Element
								Li
								Na
								K
								Mg
								Ca
								Al
								Ti
0.0								P
..	0.0							Pb
..	..	0.0						Zn
..	..	..	0.0					Cu
2.94	1.50	**3.57**	1.20	0.0				Fe
0.30	0.54	0.34	1.39	0.51	0.0			Co
0.60	9.54	0.36	0.72	1.51	0.18	0.0		Ni
2.66	0.27	0.32	1.04	2.36	1.96	0.82	0.0	Mn

THE GEOCHEMISTRY OF QUARTZ

Trace Elements in Quartz.

The distribution of trace elements in quartz is shown in fig. 2.

The analyses are reproduced in tables 3. Tables 4, and 5 show the general statistical results.

1. Lithium

Lithium varies from trace amounts to 2100 ppm with an average of 350 ppm. The values of mode and median are 25 ppm and 120 ppm respectively. The relative deviation is 132.6%

2. Sodium

Sodium has a range of 45 ppm to 1998 ppm with an average of 261 ppm. The mode is 175 ppm and median is 275 ppm. The relative deviation is 106.3%. Sodium and lithium show a correlation with each other (r = 0.41).

3. Potassium

Potassium ranges from 33 ppm to 2490 ppm with a mean of 175 ppm. The mode and median are 150 ppm and 165 ppm respectively. The relative deviation is 198.9%. There is a positive correlation between potassium and sodium (r =0.93) and potassium and lithium (r= 0.46). All the alkali metals show quite a large variation in content.

4. Magnesium

Magnesium has a range of less than 1 ppm to 332 ppm with an average of 38 ppm The mode and median are 25 ppm and 20 ppm respectively. The relative deviation is 144.6%. Magnesium is positively correlated with sodium (r = 0.38) and potassium (r=0.33)

5. Calcium

Calcium ranges from 2 ppm to 252 ppm with an average of 82 ppm. The mode and median are 25 ppm and 20 ppm respectively. The relative deviation is 214.08 %. Calcium is positively correlated with magnesium (r =0.52).

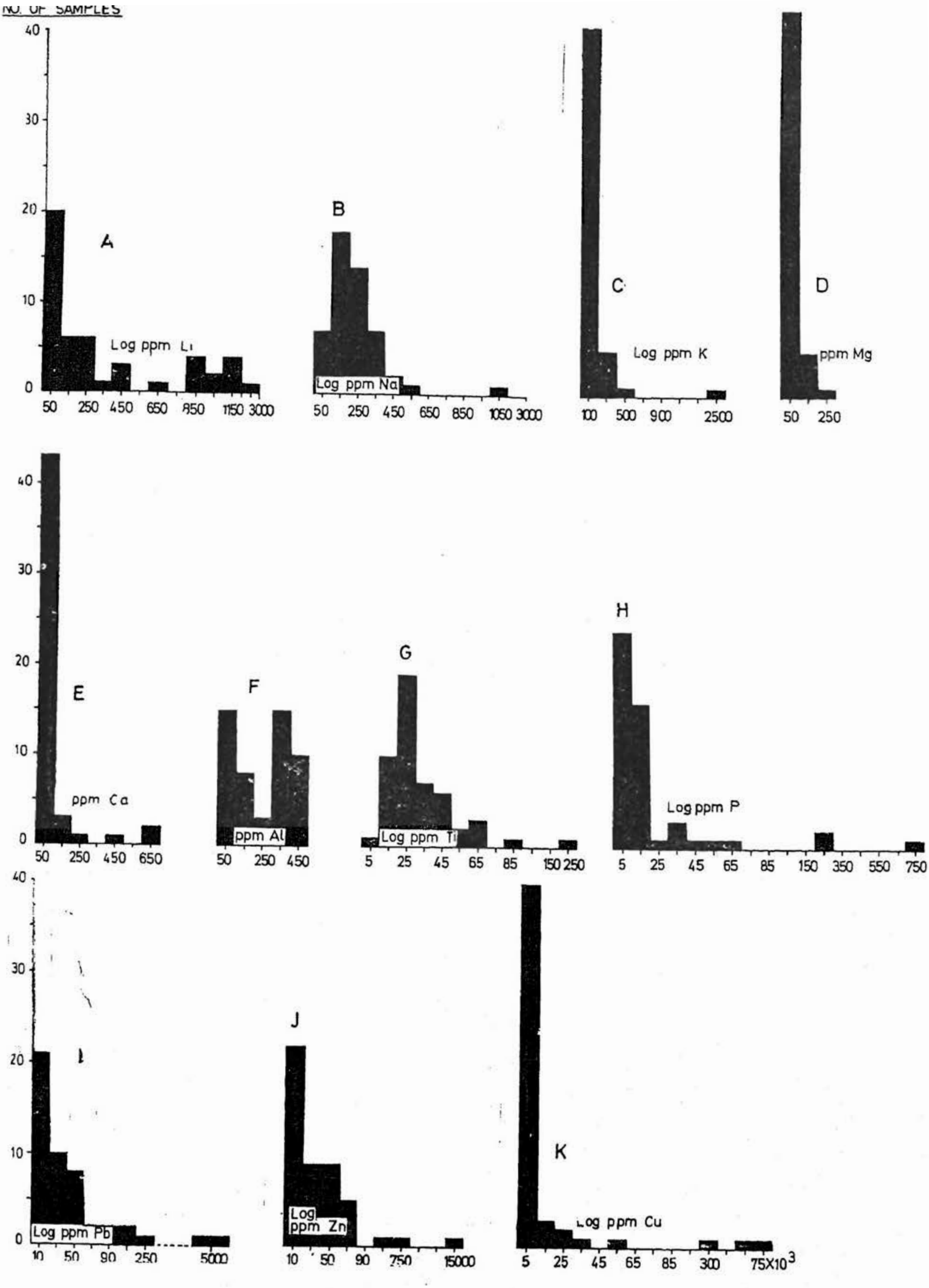

Fig. 2A. Distribution of trace elements in quartz veins.

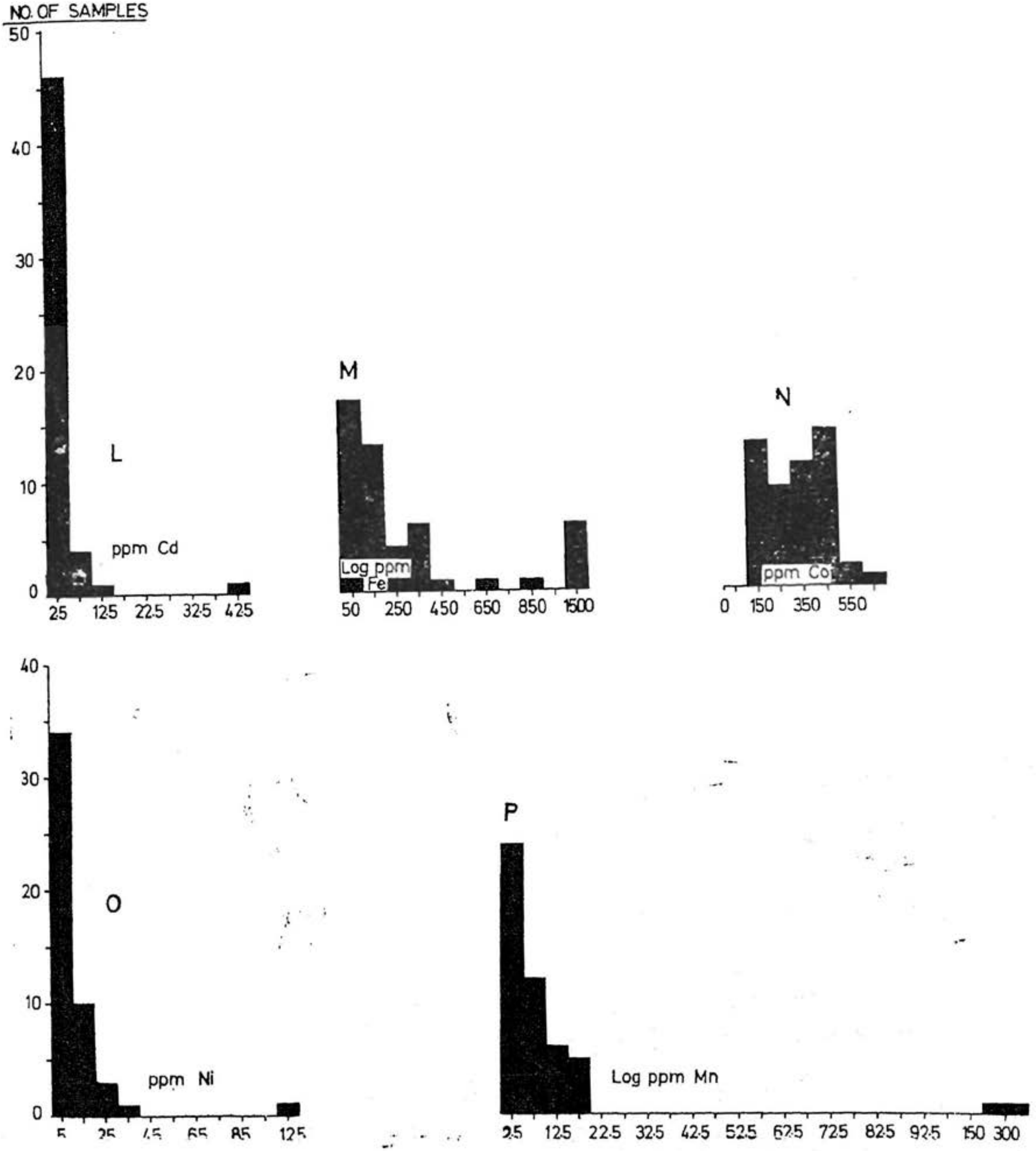

Fig. 2B. Distribution of trace elements in quartz veins.

6. Strontium

Strontium is detectable in only a few samples and occurs in amounts up to 9 ppm with an average of 1.8 ppm. The mode is 1.0 ppm. The distribution of strontium is entirely controlled by calcium and magnesium in quartz.

7. Aluminium

Aluminium varies within a range of 44 ppm averaging 246 ppm. The distribution of aluminium is bimodal, the two modal concentrations occurring at 50 ppm and 350 ppm respectively. The median is at 215 ppm. The relative deviation is 56.7% Aluminium is correlated with lithium (r =0.66), sodium (r=0.29) and magnesium (r=0.31).

8. Titanium

Titanium ranges from 9 ppm to 177 ppm with a mean of 35 ppm. The mode and median are 25 ppm and 34 ppm respectively. The relative deviation is 75.7%. Titanium is correlated with lithium (r=0.39), sodium (r=0.72) and potassium (r=0.84). There is no correlation between aluminium and titanium in quartz.

9. Phosphorus

Phosphorus has a range of 0.5 to 180 ppm with a mean of 20 ppm. The mode is 5 ppm and the median is 6 ppm. The relative deviation is 158.7%. Phosphorus is correlated with titanium (r =0.51), sodium (r = 0.50), and potassium (r=0.51).

10. Lead

Lead ranges from 2 ppm to 9400 ppm, averaging 311 ppm. However, the harmonic mean which is a better measure of central tendency in this case is 9 ppm. The mode and median are 5 and 20 ppm, respectively. The relative deviation is 465.6%. Lead probably occurs as disseminated crystals of galena in quartz.

11. Zinc

Zinc has a range of 5 ppm to 1250 ppm with an arithmetic mean of 108 ppm and harmonic mean of 15 ppm. The mode and median are 5 ppm and 20 ppm, respectively. The relative deviation is 253.8%. The distribution is positively skewed and is similar to lead, though the two elements are not correlated to each other. Zinc is correlated with lithium (r =0.41). Samples of quartz from Pumpsaint gold mines show enrichment in zinc similar to those of Cardiganshire, while samples from Cader Idris only show lesser amounts.

12. Copper

Copper varies from 1 ppm to 9400 ppm. with an arithmetic mean of 136 ppm and harmonic mean of 4 ppm. The mode and median are 5 ppm and 2 ppm, respectively. The relative deviation is 518.5%. Copper is correlated with lithium (r= 0.61), potassium (r=0.31), titanium (r=0.32), and zinc (r = 0.36). There is no correlation between lead and copper. Copper probably occurs as chalcopyrite in quartz, but its close correlation with alkalis suggests that some of the copper may be present in some other form, probably in fluid inclusions.

13. Silver

Silver varies from trace amounts to 9 ppm with an average of 1.5 ppm. The mode and median are 0.6 ppm and 0.7 ppm, respectively.

14. Cadmium

Cadmium varies from undetactable amounts to 44 ppm with an average of 2 ppm. The mode and median are 1 ppm each. The concentration of cadmium varies directly with zinc, suggesting that most of the cadmium is contributed by sphalcrite.

15. Chromium

Chromium was determined in only four samples and varies from 3-4 ppm, with an average of 3 ppm.

16. Iron

Iron ranges from 28 ppm to 1888 ppm with a mean of 354 ppm. The mode and median are 50 ppm and 106 ppm, respectively.

Iron, like most other elements, shows a very wide range of variation with a relative deviation of 138.98%. Iron is correlated with lithium (r=0.31), sodium (r=0.45), potassium (r=0.56), magnesium (r=0.36), titanium (r=0.75), and zinc (r=0.46).

17. Cobalt

Cobalt ranges from 100 ppm to 650 ppm. The distribution of cobalt tends to be bimodal in character. The median is 280 ppm. The relative deviation is 39.5%. Cobalt is not correlated to any other element in quartz. Compared to other elements, the content of cobalt does not show great variation. The ratio of cobalt content to the sum of the zinc, lead and copper contents varies between 2 and 65.5 with a mean value of 9.4. This points to the siderophile nature of cobalt, which, when given a choice between chalcophile and oxyphile association would go with the latter.

18. Nickel

Nickel varies from 1 ppm to 140 ppm, averaging about 13 ppm. The mode is 2.5 ppm and the median value is 5 ppm. The relative deviation is 170.0%. The distribution is positively skewed and closely resembles lead, zinc and copper in aspect. Nickel is strongly correlated with lead (r=0.81). There is no correlation with any other elements. The ratio Co: Ni has a range of 2.5 to 170 with an average of 61.7.

19. Manganese

Manganese has a range of 2 ppm with an average of 19 ppm. The mode is 5 ppm and the median is 3 ppm. The relative deviation is 228.42%. Manganese is correlated with sodium (r= 0.47), titanium (r=0.51), phosphorous (r = 0.38), and iron (r = 0.32).

20. Fluorine

Fluorine was determined in only three samples and has a range of 310 ppm to 460 ppm with an average of 390 ppm. As the compound SiF_4 is highly volatile, it is probable that fluorine exists as a CaF_2 or as an alkali fluoride salt in the fluid inclusions in quartz. It may also be forming some complex metallic fluorides.

21. Chlorine

Chlorine was determined in only four samples and varies from 366 ppm to 602 ppm, with an average of 502 ppm, Chlorine like fluorine, is possibly restricted to alkalis and alkaline earths as chlorides in the fluid inclusions in quartz.

A GENARAL DISCUSSION OF GEOCHEMISTRY OF QUARTZ

Introduction.

Extensive literature exists concerning the various physicochemical aspects of quartz. The vast amount of literature, however, is confined to only a few aspects of quartz, like thermoluminescence, absorption spectra and the development of colour centres in quartz, etc. These studies have contributed a lot to the knowledge of the mode of occurrence of trace elements in quartz. However, little detailed geochemical work has been done on the occurrence of trace elements in quartz. Most of the studies of this kind are confined to only a very few elements, viz., Li, Na, Al, Ti. Fe and Mn, Dennen, (1966). On the other hand, the study of fluid inclusions in quartz has contributed valuable information, Yermakov *et al.* (1965).

Theories of the mode of occurrence of trace elements in quartz.

The crystallo-chemical laws which govern the mode of occurrence of foreign elements in minerals in general have been discussed in many works, Burns (1970); Nickel (1970); Shaw (1961), and Ahrens (1953-1965). Substitution of foreign elements in quartz lattice is known to be a common phenomenon. Stanely and Theokritoff (1956) have shown that Al^{+3}, Ti^{+4}, Ge^{+4}, Zr^{+4}, Sn^{+4}, Pb^{+2}, Ag^{+1}, As^{+3} and B^{+3} can replace Si^{4} atoms in the quartz lattice. The defficiency of an electronic charge is usually compensated for by the substitution of monovalent atoms such as Na^{+1}, Li^{+1} and H^{+1}. Bambauer (1961) has shown that the predominant monovalent element is lithium, that forms the pair (Li^{+1}, Al^{+3}), while the pairs (Na^{+1}, Al^{+3}) and (H^{+1}, Al^{+3}) are thought to be of a subsidiary nature. He has also suggested that some aluminium in quartz may be replaced by magnesium. There are usually two magnesium atoms for each aluminium atom replaced, and the charge balance is compensated for by the replacement of an oxygen atom by a halide ion.

The replacement of Si^{+4} atoms by the pair (Li^{+1} Ti^{+4}) has been long known, Dear *et al.* (1968). Dennen (1965) believes that all foreign elements in quartz can be explained in terms of charge balance. Amongst the other elements that could possibly go into the tetrahedral Si^{+4} sites are nickel (Cohen, 1956); and cobalt Wood and Ballman (1966). Goni and Guillmin (1968) have shown that in sedimentary minerals, from the Jurassic rocks in France, cobalt tends to be concentrated in quartz as compared to any other mineral, a fact which suggests that the capture of cobalt by the SiO_2 lattice is a rather common phenomenon not yet fully recognized. The high content of cobalt in quartz veins from Cardiganshire further corroborates this. Canney and Wing (1966) have suggested this feature of cobalt in quartz as a good geochemical prospecting tool.

Many authors have suggested various other possibilities for the capture of foreign ions in minerals. These include previously unoccupied oxygen sites and interstitial site spaces in the quartz lattice, Milne and Gibbs, (1964); interruption of growth processes at certain loci of crystallization, Zerfoss and Slawson (1956), weakness planes and misalignments, Frederickson (1955), polarized zones that would give rise to unstable bonds and disequilibrium energy centres that could capture other elements, Fyfe (1964), Burns (1962), Azaroff (1960). The polarized character of quartz surfaces, Devor (1956), coupled with many other lattice defects, Chepizhny (1969), Lyaskov (1969), and Kamentsew (1965), etc, facilitate and aid the capture of foreign ions in quartz.

The study of fluid inclusions in quartz has revealed a wide range of trace elements present in the inclusions, which has also been widely used as reliable geothermometers, Roeder (1967), Groves *et al.* (1970). Pinckney and Haffty (1970) recorded up to 1C40 ppm Zn, 350 ppm Cu, and from 2500 ppm to 152 x 10^3 ppm Cl^{-1} in fluid inclusions in crystals of fluorite, quartz and barites. Alkali metal halides and sulphates have long been noted as the commonest constituents of fluid inclusions, Groves and Soloman (1970), Ganeyev (1970), Roedder (1967). The direct relationships existing between chlorine, cadmium and silver, as well as, other metals in fluid inclusions, indicate the presence of a controlling chemical factor in the distribution of different cations in minerals and their fluid inclusions, Taylor and Radtke (1969), Vlasov (1964), and Mookerjee (1962).

Occurrence of Trace Elements in Quartz.

Twenty one elements were determined in various samples of quartz. There is a wide range of variation in the total content of trace elements in individual quartz samples. The individual elements in quartz also show a wide range of variation from sample to sample. Cobalt is a relative exception in that it tends to vary slightly as compared to other elements. The content of trace elements in quartz is usually supposed to be subject to the availability of the various elements at the time of the deposition of quartz, Dennen (1968). The unusual enrichment of these quartz veins in most of trace elements can, therefore, be explained on the basis of the ready availability of these elements in the hyhrothermal solutions which deposited quartz.

The ore-forming elements, viz zinc, cadmium, lead, and copper possibly occur in part as sulphides in the form of sphalerite, galena and chalcopyrite crystals disseminated in quartz. However, the close correlation between zinc and lithium on the one hand, and between copper, potassium and lithium on the other, suggest that in part at least, the ore-forming elements might be occurring in fluid inclusions in the form of oxy-halide complexes. Some of these elements could also be occurring in lattice sites. There is a close correlation between iron, manganese and alkalis. This possibly suggests isomorphous substitutions whereby iron can occur in the form Fe^{+3}, the charge may be compensated for by Li^{+1} or Na^{+1}.

It could also occur in the form Fe^{+3} where it probably replaces Al^{+3} in the silica lattice. The charge may by compensated for by the replacement of oxygen by an hydroxyl or a halide ion, Bambauer (1961); Dennen (1968). Manganese, on the other hand, has been suggested to occur in interstitial sites in 6-fold co-ordination Linwood and Weyle, quoted in Ginther (1959).

Titanium is correlated on the one hand with copper, iron, manganese and phosphorus, and on the other with alkalis. The diodochic substitution of Ti^{+4} for Si^{+4} in tetrahedral sites is well known. However, it is also possible that some Ti^{+4} might exist in in interstitial sites. The close correlation between titanium and phosphorus is possibly suggestive of diadochy. Phosphorus is known to exist in silicate tetrahedra replacing Si^{+4} as a camouflaged ion (Landergren, in Goldschmidt, 1954). The isomorphous substitutions of phosphorus for silicon in silicate tetrahedra is now a recognized fact Koritnig (1965), Mason and Bergren (1941). The charge imbalance caused by the replacement of tetravalent silicon by pentavalent phosphorus is supposed to be compensated for by Al^{+3}, or the replacement of trivalent by bivalent, and bivalent by monovalent ions in the lattice, Koritnigh (1965).

Calcium, magnesium and strontium occurring in varying amounts in quartz may possibly be in the form of carbonates. They could also occur in fluid inclusions. Calcium and strontium may also be occupying vacant sites in the silicon lattice, but in view of their large sizes it seems improbable.

Relationship Between the Ionic Parameters and the Correlation. Coefficient of Elements with eaeh other.

Most of the trace elements in quartz show various degrees of correlation with others. The alkali metals, lithium, sodium and potassium are correlated individually with eight elements. The correlation coefficients of one element with all the rest, when plotted against their respective ionic radii, electronegativities and ionic potentials, etc., suggest direct relationships of these ionic parameters and the corresponding degrees of correlations of these elements. Lithium is correlated with Al^{+3}, Cu^{+2}, K^{+1}, Na^{+1}, Zn^{+2}, Ti^{+4} and Fe^{+3} in order of decreasing correlation coefficients, respectively. These correlation coefficients have been plotted against the ionic radii of the elements in fig. (3). It seems from the diagrams that the coefficient of correlation increases with decreasing ionic radii.

Sodium is correlated with K^{+1}, Ti^{+4}, Mn^{+2}, P^{+5}, Fe^{+3} and Mg^{+2}. But in this case the correlations between these relations and the respective ionic parameters of other elements are not very good, possibly suggesting that sodium is not strongly bound in the lattice and possibly occurs in interstitial spaces or probably in fluid inclussions. If the last suggestion is correct it would be safe to conclude that all these elements with which sodium is related in part exist in fluid inclusions as well.

Potassium is correlated with Li^{+1}, Na^{+1}, Cu^{+2}, Fe^{+3}, Mn^{+2}, Mg^{+2}, Ti^{+4} and P^{+5}. The ionic radii of these elements are plotted against their correlation coefficients with potassium in fig. (4). The results are highly significant, suggesting that potassium is bound in the lattice with these elements.

Iron is correlated with Li^{+1}, Na^{+1}, K^{+1}, Al^{+3}, Ti^{+4}, P^{+5}, Mg^{+2} and Mn^{+2}. The correlation coefficients of these elements with iron have been plotted against their ionic radii and electronegativities in fig. (5) and fig. (6), respectively. From the figures, it is apparent that in both the cases the relations are not strongly significant. However, in this case again the electronegativity seems to exert a maximum influence. This possibly suggests that while some iron may be bound in the lattice in quartz, most of it is probably unbound. It is also probable that iron is mostly in ionic form.

Manganese is correlated with Na^{+1}, K^{+1}, Fe^{+3}, P^{+3}, Ti^{+4}, Mg^{+2} and Ca^{+2} and its relations are shown in fig. (7) and fig. (8) respectively. The behaviour of manganese is similar to that of iron with the exception that in the case of manganese the ionic radius is the stronger influence as compared to the electronegativity in the case of iron.

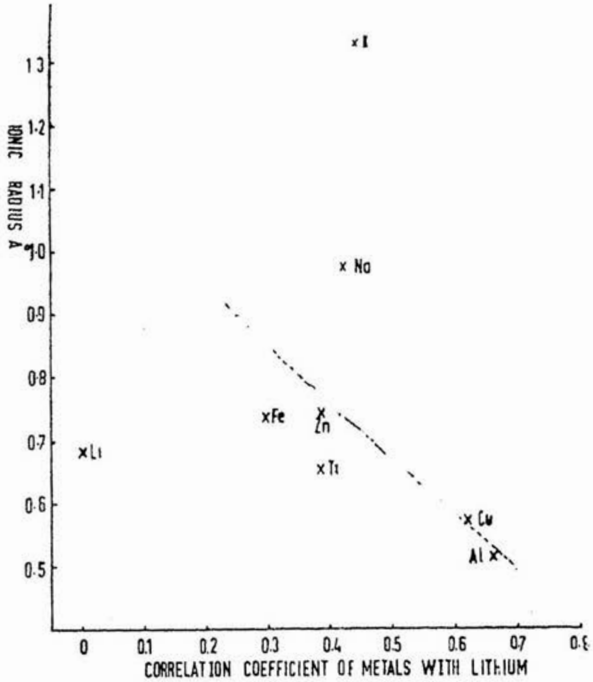

FIG. 3. Relationship of the Coefficient of Correlation of other Elements with Lithium in Quartz with their Ionic Radii.

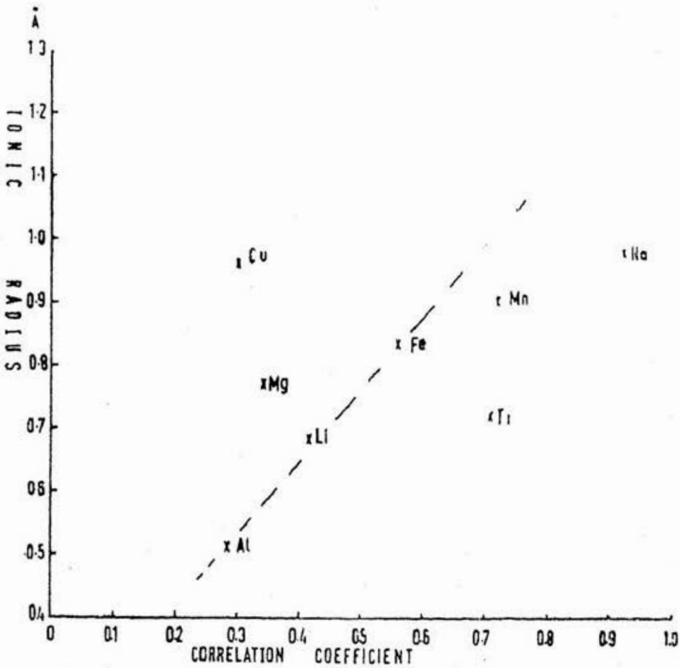

FIG. 4. RELATION BETWEEN THE CORRELATION COEFFICIENTS OF OTHER ELEMENTS WITH POTASSIUM IN QUARTZ AND THEIR IONIC RADII

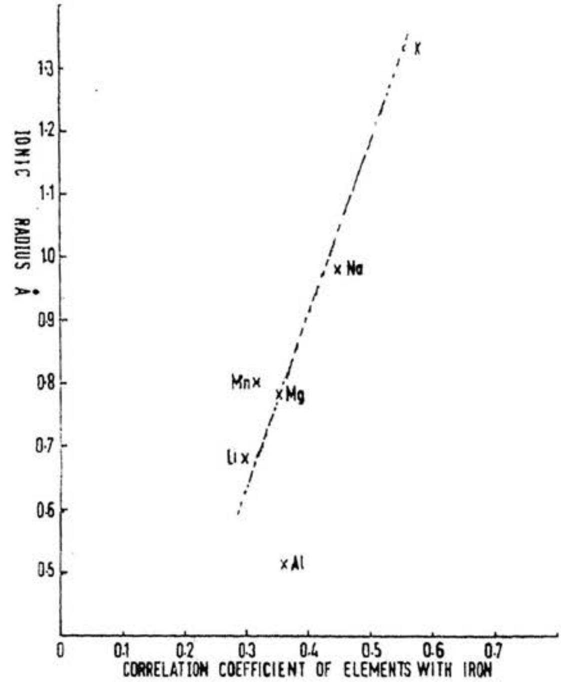

FIG. 5. Relation between the Correlation Coefficients of other Elements with Iron in Quartz and their Ionic Radii

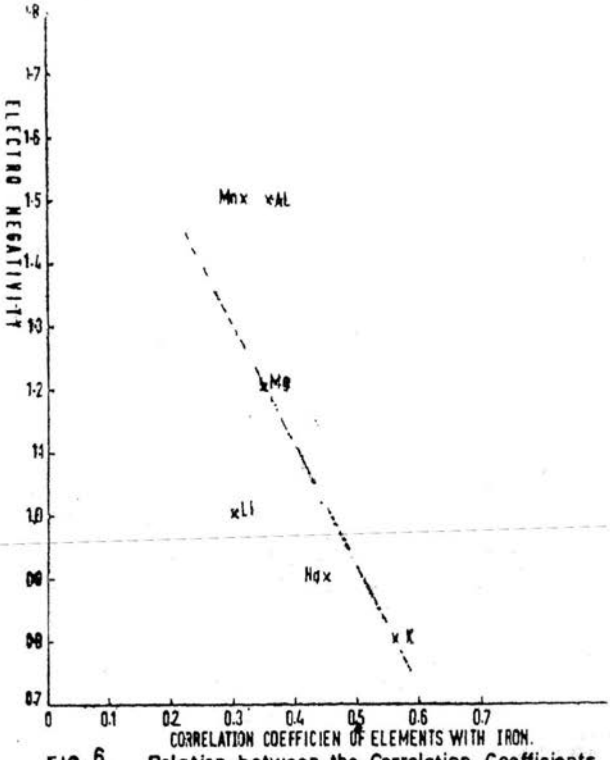

FIG. 6. Relation between the Correlation Coefficients of other Elements with Iron in Quartz and their Electronegativities.

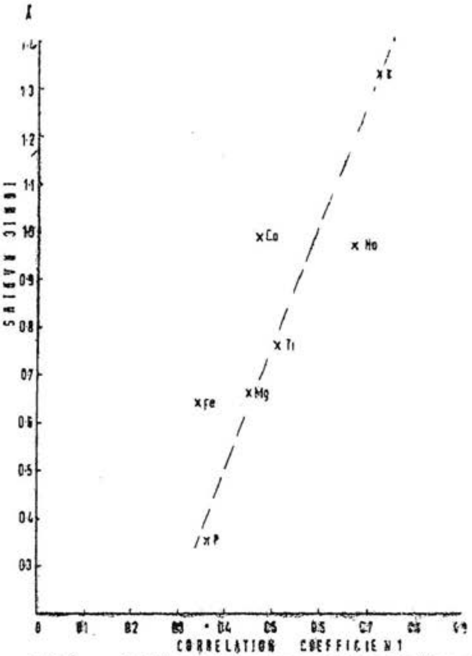

FIG 7. Relation between the Correlation Coefficients of other Elements with Manganese in Quartz and their Ionic Radii.

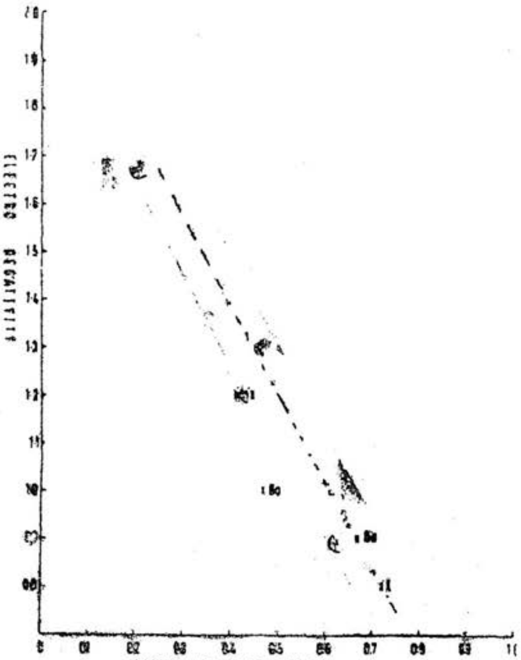

FIG. 8. Relation between the Correlation Coefficients of other Elements with Manganese in Quartz and their Electronegativities

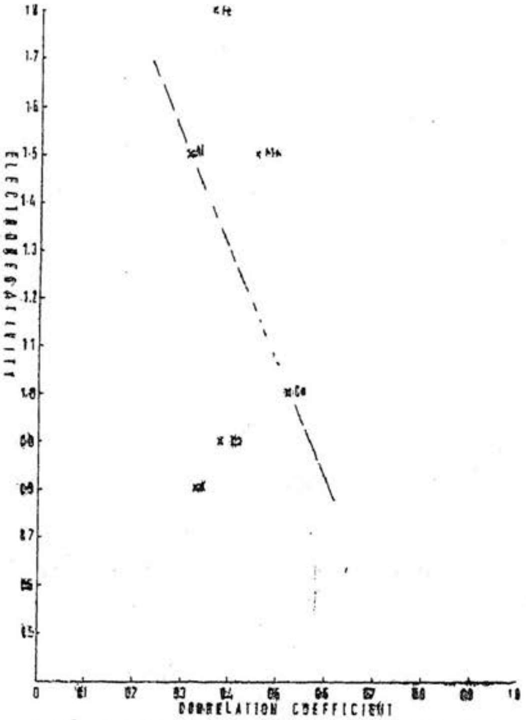

FIG 9. Relation between the Correlation Coefficients of other Elements with Magnesium in Quartz and their Electronegativities.

Magnesium is correlated with Al^{+3}, Ca^{+2}, Fe^{+3}, Mn^{+2}, Na^{+1} and K^{+1}. The correlation coefficients of these elements are plotted against their respective electronegativities in fig. (9). From a statistical analysis of this data it seems that both the ionic radius and electronegativities have equivalent influence, though opposite in sign.

The relationship of aluminium with other elements is directly proportional to their ionic radii, showing that probably all aluminium is bound in quartz. Phosphorus has a similar behaviour to aluminium, while titanium exhibits a correlation between electronegativity and the correlation coefficients with other elements much more significantly than with their ionic radii.

All these relations are very important as they throw some light on the mode of occurrence and inter-relations of elements in quartz. The most commonly held view, that all the elements can be accounted for in quartz on the basis of balance of charges, Dennen (1968), cannot explain the unusually high amounts of all these trace elements in quartz veins from Cardiganshire. It is, therefore, suggested that much of the trace element content is not bound and probably these elements occur in interetitial cavities and occupy sites of crystal defects which are quite common. A lot of these elements can also be accounted for on the basis of their existence in fluid inclusions which are commonly seen in quartz veins.

The cation ratios of (Na + K) Ca : Mg are plotted in fig. (10). The relationship between alkalis, calcium and magnesium in this figure indicates that quartz is very rich in alkalis as compared to calcium and magnesium. If to the amount of alkalis, the lithium content of quartz veins is also added, it would appear that the ratio between the alkalis and alkaline earth elements is more than 90 : 10. Comparing this figure with Dunham's (1970), and also with Derbyshire brines, shows that the composition of quartz in terms of alkalis and alkaline earth elements is very near to sea water and almost identical with Red Sea brines, a fact which has strong implications.

The ratio of Pb: Zn: Cu is plotted on a triangular diagram in fig. (11). Most of the points in this figure tend to lie on the Pb-Cu join, indicating that quartz is relatively enriched in these metals as compared to zinc. However, the most important significance of this figure lies in its possible use as geochemical prospecting tool. The extreme enrichment of these elements in quartz clearly shows that the Pb: Zn: Cu contents of quartz can be used as indicators of mineralization. This figure, however, does not yield a quantitative estimate of the true contents and ratios of these elements in the form of ore-minerals as they occur in the field.

Regional Variation in the Composition of Quartz.

A cluster analysis of fifty quartz samples for eleven variables was made in order to see if there is any correspondence between the resultant cluster groups and their regional distribution. Two major clusters were obtained which roughly correspond to the Gwestyn shales facies and another arenaceous facies in which these quartz veins were formed.

The group of quartz samples distributed in the shaly facies is higher in Zn, Fe and Co, and lower in Pb, Cu, Mn, Na and K. The second cluster group restricted to the sandy facies is poorer in Zn, Fe and cobalt. The contents of Ca and Mg between these two groups do not vary significantly. This suggests a lithological control on the chemical composition of quartz. The alternating pattern of the two clusters closely corresponds with the alternation of shaly and sandy facies controlled by the regional structure.

Temperature of Formation of Quartz Veins.

Probably the best and most reliable methods of geothermometry are those based on the study of fluid inclusions and decripitation techniques, Roedder (1967). However, in the absence of any such data, the alternative left is the use of trace elements in the determination temperatures of formation of quartz.

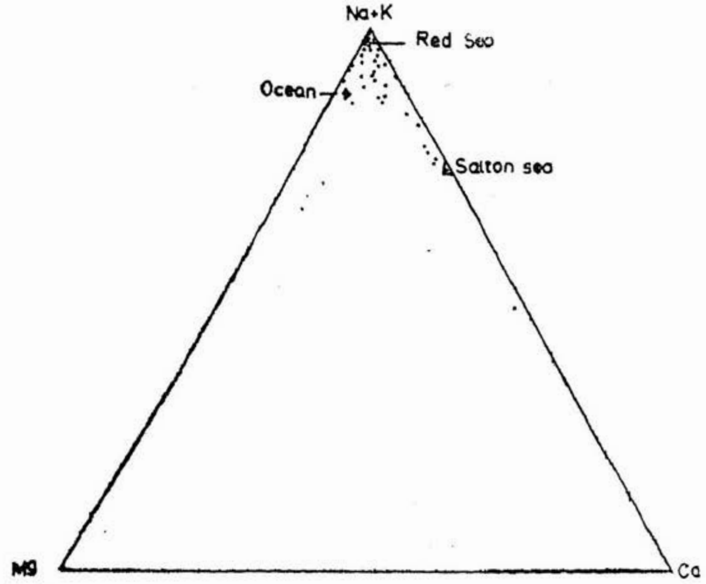

FIG. 10. CATION RATIOS IN QUARTZ FROM CARDIGANSHIRE

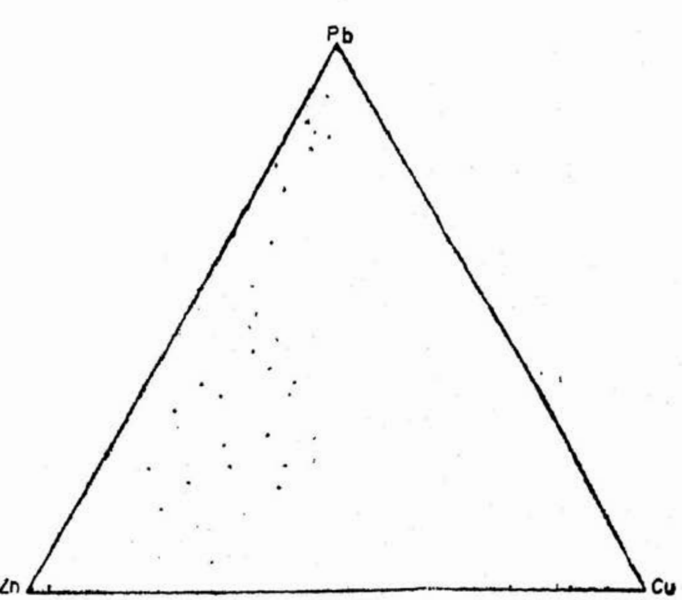

FIG. 11 RATIO OF Pb:Zn:Cu IN QUARTZ.

Isomorphous substitution of silica by aluminium in quartz is said to increase with an increase in temperature. Dennen (1970) attempted to use aluminium content of quartz as a geothermometer on the same principle. He used the relation existing in ideal solutions, i.e. where,

$u_i = u_i^\circ = RT/nX_i$

u_i =chemical potential of the component in the mixture

R =gas constant.

T =absolute temperature.

X_i =molar fraction of the component (i) in the mixture.

u_i° =chemical potential of (i) in the standard stage.

The fundamental assumption made to justify this relation is based on the idea that most of the mineralizing solutions are usually very dilute and hence can be considered to approach ideality.

Using Dennen's method, a temperature range of 400°C to over 1000°C was obtained for the quartz veins in Cardiganshire, and this clearly shows that the method is unsuitable. The mineralization in Cardiganshire is known to be of a very low-temperature kind.

As was pointed out earlier, it is probable that most of the elements in quartz may not be bound in the lattice and could exist in any form in many other sites. This would explain the failure of Dennen's method which is based on the use of the content of aluminium directly bound in the SiO_2 lattice.

Ellis (1965) attempted to use the ratio Na_2O/K_2O of thermal spring waters of New Zealand as a function of temperature. He suggests that as the temperature rises, this ratio tends to approach unity. The author made use of the same princple and obtained a temperature range 250°C to 384°C, which is nearer the probable range of the temperatures of formation of quartz veins of 350-150°C, Sharp (1965).

In order to use the alkali ratio of quartz as a function of temperature, however, certain assumptions had to be made. It was assumed that the hydrothermal solutions which deposited quartz had the same alkali ratio as is found in quartz or equivalent thereof (Verhoogen, 1938, in Smith, 1963), and that the alkali ratio in them was also temperature controlled. However, no proper work has been done on this method and nothing can be said as to its reliability.

The partition coefficients of quartz and calcite for certain elements were also used. Temperatures in the range 100°C—500°C were obtained for quartz while for calcite the temperatures obtained varied between 50°C and 100°C.

These various approximate estimates show that the probable temperatures of deposition of quartz might have been within a range of 200°C to 400°C.

Conclusions.

Finally it is concluded that quartz contains many trace elements in varying amounts and that it is a very good geochemical prospecting tool. There is a distinct regional variation pattern in the chemical composition of quartz which suggests a lithological control. Quartz was probably deposited within a temperature range of 200°C to 400°C.

THE GEOCHEMISTRY OF CALCITE

Trace Elements

The distribution of trace elements in calcite is shown in fig. 12. The analytical results are shown in tables 6, 7, 8 and 9.

A. *Sodium.*

Sodium has a range of 481 ppm to 962 ppm with a mean of 656 ppm. The mode and median are 575 ppm each. Sodium varies within a narrow range with a relative deviation of 22.3 %. It does not show any correlation with any other element.

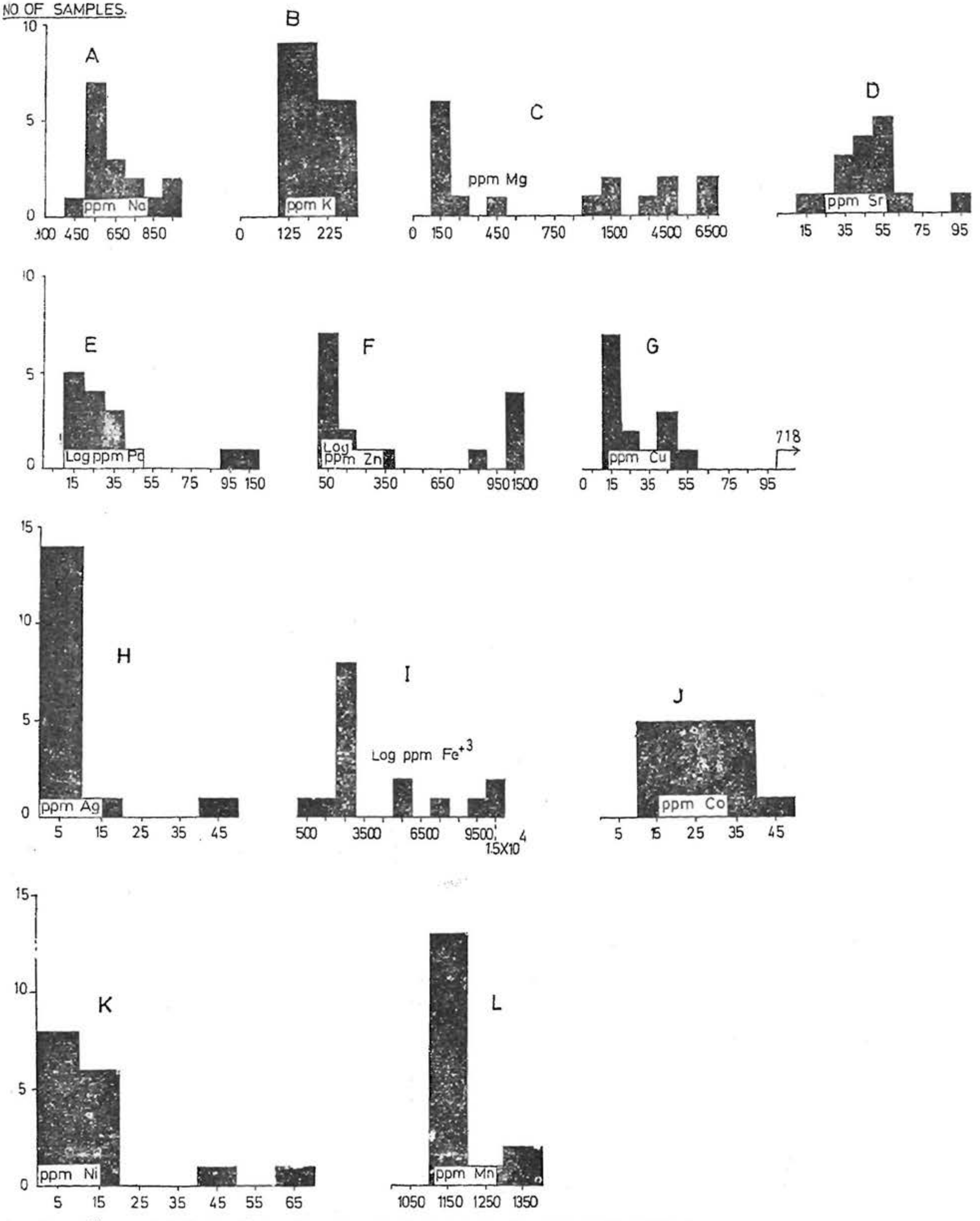

FIG. 12 DISTRIBUTION OF TRACE ELEMENTS IN CALCITE VEINS

B. *Potassium.*

Potassium has a range of 126 ppm to 334 ppm with a mean of 185 ppm. The mode and median are 150 ppm and 160 ppm respectively. The overall distribution tends towards normality and varies within a relatively narrow range, with a relative deviation of 33.23%.

Sodium and potassium both probably occur as halides in fluid inclusions in calcite.

C. *Magnesium.*

Magnesium has a range of 114 ppm to 6000 ppm with an average of 1860 ppm. The mode and median are 125 ppm and 225 ppm, respectively. The distribution of magnesium in calcite shows a great variation with a relative deviation of 120.83%.

D. *Strontium.*

Strontium ranges from 17 ppm to 91 ppm with an average of 49 ppm. The mode and median are 55 ppm and 42 ppm, respectively. The distribution tends to approach normal and does not show a very great variation. The relative deviation is only 36.99%.

Strontium is selightly correlated with magnesium ($r=0.416$), significant at the 90% level. Strontium probably occurs as a carbonate or may also be replacing Ca^{+2} in isomorphous substitution in the calcite lattice, though the great differences in their ionic parameters presents it as a limited possibility.

E. *Lead.*

Lead has a range of 15 ppm to 290 ppm with an average of 55 ppm. The mode and median are 15 ppm and 22 ppm, respectively. It shows a great range of variation with a relative deviation of 128.97%. Lead probably occurs as inclusions of galena in calcite but its occurrence as carbonate is not improbable.

F. *Zinc.*

Zinc has a range of 50 ppm to 1400 ppm with an average of 460 ppm. The mode and median are 75 ppm and 100 ppm, respectively.

Table-6

TRACE ELEMENTS IN CALCITE (IN PPM)

No.	Locality	Na	K	Mg	Sr	Pb	Zn
1	Esgairlle	938	238	141	45	37	213
2	Esgairfraith ..	851	209	4500	58	20	325
3	N. Van	962	209	1050	58	25	55
4	Plynlimon ..	555	126	120	50	25	1150
5	Bodcolli ..	592	168	138	58	20	65
6	Penbont rhydybeddau	629	126	165	58	30	50
7	Cwmerfin ..	555	250	435	91	35	1300
8	Nantyricket ..	481	209	930	42	31	1350
9	Tyllwydd ..	592	168	6000	17	25	85
10	Ceylan ty Isaf ..	555	126	1590	50	20	78
11	Nantybeddau ..	555	126	114	34	140	85
12	Bwadrain ..	740	126	3750	70	20	900
13	Grugwynion ..	703	334	210	34	48	115
14	Trerddol ..	639	126	4500	34	15	110
15	Dolwen	518	168	150	58	100	78
16	Bryngwyn ..	629	250	6000	26	290	1400

Continued Table-6

Cu	Ag	Fe	Co	Ni	Mn	Locality	No.
14	4.6	2836	33	14	1143	Esgairlle	1
18	2	11320	25	6	1355	Esgairfraith ..	2
13	9	5796	30	10	1166	N. Van	3
38	4	1587	30	16	1134	Plynlimon ..	4
43	4	2795	18	8	1134	Bodcolli ..	5
10	15	2898	23	10	1146	Penbont rhydybeddau	6
40	3	2536	35	16	1134	Cwmerfin ..	7
13	42	2536	18	6	1146	Nantyricket ..	8
58	2	10300	23	5	1134	Tyllwydd ..	9
15	2	5296	18	10	1146	Ceylan ty Isaf ..	10
25	4	2018	23	6	1118	Nantybeddau ..	11
20	2	2967	30	5	1134	Bwadrain ..	12
12	4	259	26	41	1146	Grugwynion ..	13
43	2	9953	18	5	1229	Trerddol ..	14
275	2	2691	14	6	1103	Dolwen	15
718	7	7625	45	67	1355	Bryngwyn ..	16

Table-7

STATISTICAL ANALYSIS OF TRACE ELEMENTS IN CALCITE VEINS

	Range	Mean	Mode	Median	R. Dev.	Skewness	Kurtosis
Pb	15-290	55	15	22	128.97	6.14	8.16
Zn	50-1400	460	75	100	118.20	0.71	1.81
Cu	12-718	85	13	15	213.17	8.52	10.19
Co	14-45	26	22	25	31.36	0.51	3.00
Ni	5-67	14	7	8	114.87	5.37	7.31
Ag	2-42	7	2	3	147.33	8.38	10.21
Fe	259-11316	4590	2750	2450	74.66	0.70	2.22
Mn	1118-1355	1170	1125	1100	6.81	1.69	3.39
Mg	114-6000	1860	125	225	120.83	0.73	1.98
Sr	17-91	49	55	42	36.99	0.14	3.00
Na	481-962	656	575	575	22.30	0.99	2.68
K	126-334	185	150	160	33.32	0.64	2.83

Table-8

MATRIX OF CORRELATION COEFFICIENT OF TRACE ELEMENTS IN CLACITE SIGNIFICANT AT 95 PERCENT LEVEL

Element	Na	K	Mg	Sr	Pb	Zn	Cu	Ag	Fe	Co	Ni	Mn
Na	0.0											
K	0.0	0.0										
Mg	0.0	0.0	0.0									
Sr	0.0	0.0	0.0	0.0								
Pb	0.0	0.0	0.0	0.0	0.0							
Zn	0.0	0.0	0.0	0.0	0.0	0.0						
Cu	0.0	0.0	0.0	0.0	0.90	0.0	0.0					
Ag	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				
Fe	0.0	0.0	0.85	0.0	0.0	0.0	0.0	0.0	0.0			
Co	0.0	0.0	0.0	0.0	0.50	0.56	0.0	0.0	0.0	0.0		
Ni	0.0	0.61	0.0	0.0	0.74	0.0	0.75	0.0	0.0	0.69	0.0	
Mn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table-9

T—TEST FOR SIGNIFICANCE OF SIMPLE CORRELATION COEFFICIENTS OF TRACE ELEMENTS IN CALCITE, D.F.—14.

Level of significance: ..	.9	.8	.7	.6	.5	.4	.3	.2
Value of 'T' ..	0.13	0.26	0.39	0.54	0.69	0.87	1.08	1.35
	.1	.05	.02	.01	.001			
	1.76	2.13	2.62	2.98	4.14			

Element	Na	K	Mg	Sr	Pb	Zn	Cu	Ag	Fe	Co	Ni
Na	0.0										
K	1.21	0.0									
Mg	0.39	0.17	0,0								
Sr	0.33	0.19	1.71	0.0							
Pb	0.66	0.87	1.04	1.49	0.0						
Zn	1.11	0.87	0.57	0.79	1.25	0.0					
Cu	0.62	0.87	1.77	1.13	7.73	1.55	0.0				
Ag	0.90	0.37	0.72	0.30	0.13	1.57	0.26	0.0			
Fe	0.92	0.48	5.94	1.31	0.13	0.56	0.77	0.82	0.0		
Co	1.51	1.85	0.99	0.22	2.15	2.54	2.06	0.60	0.07	0.0	
Ni	0.09	2.90	0.86	1.23	4.14	1.60	4.27	0.21	0.19	3.52	0.0

The distribution of zinc in calcite shows a great variation and is similar to that of lead. The relative deviation is 118.20%. There is no correlation between lead and zinc. Zinc probably occurs as sphalerite but some of it may be in the form of carbonate in solid solution with calcite.

G. *Copper.*

Copper has a range of 12 ppm to 718 ppm with a mean of 85 ppm. The mode and median are 13 ppm and 15 ppm, respectively. It has a relative deviation of 213.17%. There is a strong correlation between lead and copper (r = 0.90) and none between copper and zinc. Copper probably occurs as inclusions in the form of chalcopyrite. Some may probably occur in the form of a carbonate or hydroxycarbonate.

H. *Silver.*

Silver ranges from 2 ppm to 74 ppm with an average of 7 ppm. The mode and median are 2 ppm respectively. The distribution of silver in calcite is logarithmic. The relative deviation is 147.3%. Silver does not show any correlation with any other element. It may be replacing copper or iron in the calcite, Rankama and Sahama (1949), or it probably exists in the form of some halide or sulphate.

I. *Iron.*

Iron has a range of 259 ppm to 1136 ppm with an average of 4590 ppm. The mode and median are 4590 ppm and 2750 ppm respectively. The relative deviation is 74.66%. Iron also shows a strong correlation with magnesium (r=846).

J. *Cobalt.*

Cobalt ranges from 14 ppm to 45 ppm with an average of 26 ppm. The mode and median are 22 ppm and 25 ppm respectively. The overall distribution seems to approach normality, and the variation is not as great compared with the other elements. It has a relative deviation of 31.36%. Cobalt is closely correlated with lead (r=0.498) and zinc (r=0.561), and at a lower level of significance with copper and potassium. It probably occurs as a carbonate in solid solution with calcite.

K. *Nickel.*

Nickel has a range of 5 ppm to 67 ppm with an average of 14 ppm. The mode and median are 7 ppm and 8 ppm respectively. The relative deviation is 114.87%. Nickel is closely correlated with lead (r =0.742), copper (r=0.752), cobalt (r=0.686) and potassium (r = 0.613). Nickel like cobalt seems to be existing as a carbonate in solid solution with calcite.

L. *Manganese.*

Manganese ranges form 1118 ppm to 1355 ppm with a mean of 1170 ppm. The mode and median are 1170 ppm and 1100 ppm respectively. The distribution of manganese varies within a very narrow range with a relative deviation of only 6.81%. Manganese is not correlated with any element and probably exists as a carbonate in solid solution with calcite.

General discussion of the Geochemistry of Calcite.

A great deal is known about the solid solution of other metal carbonates with calcite. Diadochic substitution of many cations for calcium in calcite is also a common feature. The mode of occurrence of various trace elements in calcite can, therefore, be explained away by solid solution of their respective carbonates with $CaCo_3$ or by isomorphous substitution in the calcite lattice itself. On the other hand, the study of fluid inclusions in calcite indicates that it usually contains great concentrations of calcium and sodium chloride. Khitarov *et al.* (1958) found that the liquid inclusions in Siberian calcites contained 320 gms/Lt. of $CaCl_2$ and NaCl. Cobalt and zinc also appear to be soluble in calcite. Hacquaert (1925, in Deer, Howie and Zussman) reports 1.96% cobalt in some Katangan calcites. Iron can replace calcium in calcite, Shaw (1959), Rosenberg and Harker (1956), Goldsmith (1959). In the system calcite-rhodochrostie, there is perfect miscibility at higher temperatures, Goldsmith and Graf (1957). A limited amount of miscibility exists between $CoCO_3$ and $CaCO_3$, Goldsmith *et al.* (1965). The capacity of $CaCO_3$ to take $MgCO_3$ is well known in connection with dolomitization. Strontium can also replace calcium in calcite to a limited extent.

In the light of all this research, it seems reasonable to presume that most, if not all, of the trace elements exist as carbonate phases in solid solution with calcite, or in the form of isomorphous substitutions. Some cations occur in solution in fluid inclusions. This is suggested by the rather high content of fluorine in one sample. It is also possible that all the calcite veins may be rich in halides on the whole. These halides, which usually occur in the form of fluid inclusions, carry many cations in solution. For example, the close relationship between potassium and nickel may be suggestive of the fact that some nickel possibly occurs in solution in the halides in fluid inclusions in calcite.

The solubility of cations in $CaCO_3$ precipitating solutions seems to have played an important part. This is suggested from fig. (13), where the correlation coefficients of nickel, zinc and lead with respect to cobalt are plotted against the solubility products of the respective sulphides and carbonates of these metals at 25°C. It is evident from the figure that there is a straight line relationship between the two parameters, suggesting that with an increase in the solubility of these cations, their intake in the mineralizing solutions increased. On the other hand, the ionic radii of these cations seem to have exerted some influence. In fig. (14), the coefficients of correlation of nickle, zinc and lead with respect to cobalt are plotted against their respective ionic radii. From the figure, it seems that there is some correlation between the magnitude of the ionic radii and the degree of correlation of these elements with respect to cobalt. With increasing ionic radii of the cations of Ni, Zn and Pb, the coefficient of correlation decreases with respect to cobalt. Thus nickel is seen to have the highest correlation with cobalt and lead has the least, a fact which suggests an interplay of various ionic parameters and possibly solubility product is a pointer towards an isomorphous relationship of cobalt and nickel carbonates in calcite.

The ratio of Co/Ni varies from 0.6 to 4.6 with an average of 2.7 and has a normal distribution. No data is available as to the behaviour of cobalt and nickel in hydrothermal solutions precipitating calcium carbonate. However, it seems that in a whole paragenetic sequence of sulphide mineralization, from beginning to end, cobalt tends to show a stronger oxyphile character as compared to nickel.

The ratio of Cu: Pb: Zn averages 1:2:31, suggesting a greater mobility of zinc in solutions precipitating calcium carbonate. This ratio, however, does not depict a true quantitative estimate of the three cations in mineralizing solutions.

The ratio of Na/K in calcite varies from 2.08 to 5.87 with an average of 3.9, which is four times higher than that of quartz. Following Ellis (1965) assumption that the Na/K ratio tends to approach unity as the temperature rises, a deposition temperature of 40°C – 175°C was obtained for calcite by this method. The true temperature of deposition of calcite was probably within a range of 100°C. But since this method has not been corroborated by further research, its reliability is very doubtful.

The very high content of ore-forming cations like lead, zinc and copper in calcite, makes it a very good prospecting tool.

A Comparison of the Geochemistry of Quartz and Calcite.

The geochemistry of quartz and calcite was discussed in the preceding pages, individually. It seems appropirate at this stage to compare the two gangue minerals. Table 10, presents the average composition of quartz and calcite.

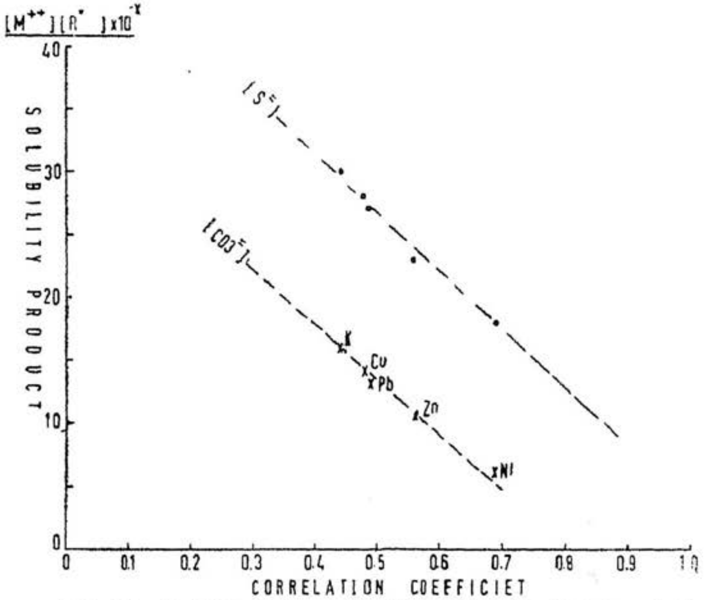

FIG. 13. Relation between the Correlation Coefficients of other Elements with Cobalt in Calcite and their Solubility Products as Carbonates and Sulphides

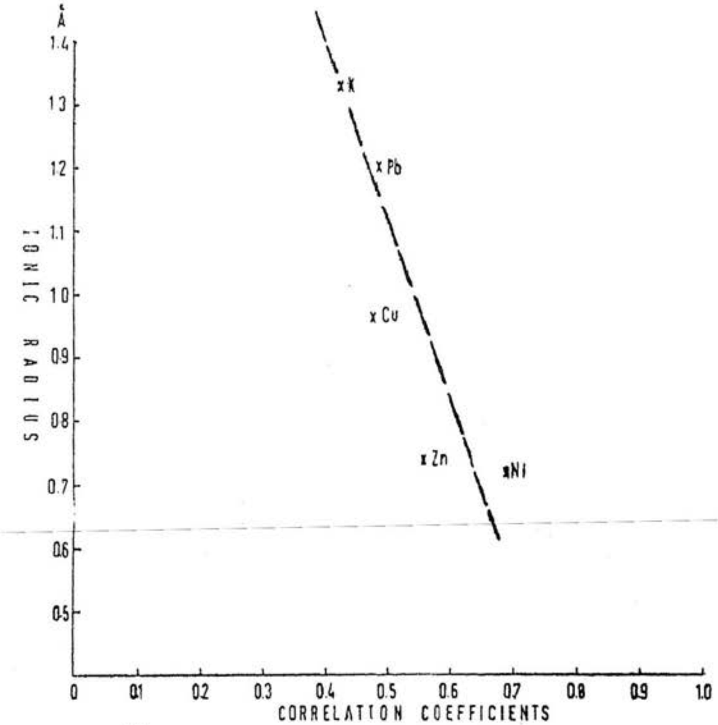

FIG 14. Relation between the Correlation Coefficients of other Elements with Cobalt in Calcite and their Ionic Radii.

Table-X. Average Trace Element Content of Quartz and Calcite in Cardigan-Shire.

Element	Pb	Zn	Cu	Cd	Ag	Fe	Mn	Co	Ni	Mg	Sr	Na	K	Cr	F
Quartz	311	108	136	0.2	0.1	354	19	330	13	38	1	261	175	3	390
Calcite	55	460	85	0.2	7	3590	1170	26	14	1800	48	656	185	3	310

	Zn:Pb	Zn:Cd	Co:Ni	Na:K
Quartz	0.3	540	54.4	1.1
Calcite	8.3	2300	2	3.9

A look at the table suggests that quartz is enriched in lead, copper cobalt and potassium, while calcite is enriched in zinc, silver, iron, manganese magnesium, strontium and sodium. The average contents of cadmium, nickel, chromium, potassium and fluorine, both in quartz and calcite are roughly the same. The ratios of Zn: Pb, Zn: Cd, and Na: K are higher in calcite as compared to quartz, while the ratio of Co: Ni is higher in quartz. The higher ratio of Co: Ni and lower ratio of Na: K in quartz suggests its higher temperature of formation. The higher Co: Ni ratio in quartz also points to the stronger oxyphile character of cobalt as compared to nickel in hydrothermal solutions. The higher Zn: Pb ratio in calcite probably indicates a higher solutbility and mobility of zinc as compared to lead in hydrothermal solutions. The ratio of Zn :Cd in quartz (540) is nearer to the corresponding ratio (900) in igneous rocks, Rankama and Shama (1949), while in calcite it is very high.

GENERAL DISCUSSION

The geological situation in Cardiganshire.

The rocks in Cardignashire consist of a thick succession of geosynclinal sediments, probably with some volcanic rocks in the Lower Ordovician which are not exposed in this area. The total thickness of these rocks amounts to about 30,000 feet.

The continuous deposition of sediments in Ordovician and Silurian times resulted in the sinking of these rocks which ultimately resulted in folding and some igneous activity. The first phase of the folding was a compressive one and resulted in the formation of periclines and domes. This was followed by a tensile phase which resulted in the formation of normal faults. On the basis of a dynamic model, Philips (1970) has suggested that these normal faults probably extend in depth up to about 5 km. The pore-water pressure calculated is suggested about 0.6 of the load.

These tectonic epochs and ensuing volcanic activity probably generated hydrothermal solutions. These were probably initially connate waters which were heated and remobilized due to a rise in the geothermobaric gradients. These hot solutions ascended upwards and travelled through the faults reacting with the country rocks.

According to Phillips (1970), the water pressure of these mineralizing solutions was greater than the pore-water pressure and, therefore, they permeated the country rocks adjacent to the fault zones.

The excess pressure of these solutions also caused extension of the faults and brecciation of the permeated rocks. During their upward ascent these solutions slowly cooled and their pressure also dropped. When these solutions passed through the thick mudstone horizons of the M. Llandovery, they probably reacted with these highly pyritous mudstones (about 600 feet thick), and it is likely that this brought about the precipitation of sulphides above.

Lovering (1961) has suggested that within a "hydrothermal conduit there is usually a relatively small gradient, which implies that temperature under such conditions is a minor factor in the precipitation of minerals form the solutions while a pressure drop and reaction with the wall-rock or material precipitated form earlier emanations is of major importance. The sulphur rich earlier emanations will react with the indigenous iron of the rocks, or the iron carried in the carbon dioxide rich solutions, to form pyrite.The latter sulphur defficient solutions subsequently react with this pyrite, thus depositing metal sulphides and releasing iron in solutions".

This suggestion is corroborated by the relatively low temperatures of formation and the predominent structural control in this district. The localization of ores above pyritous mudstones indicates the possibility that there might have been a reaction between these solutions and pyrite, resulting in the release of iron, which was deposited around breccias as hematite in near surface conditions. Hematization, is a very common feature along with mineralized fault zones in this area.

Geochemical Set-up in Cardiganshire.

It has been suggested that the mineralizing solutions were probably interestitial waters which were mobilized due to a change in the geothermobaric environment of the region during Caledonian times, round about 430-40 m. years, Moorbath (1962).

Considering the average amounts of copper (22 ppm), zinc (250 ppm) and lead (109 ppm) in one cubic kilometer of rock (approximate density = 2.5 gm/cm^3) in Cardiganshire would yield 55,000 metric tons of copper, 425,000 tons of zinc and 273,000 tons of lead. It would, therefore, seem reasonable to suggest that the source of the base metals was in these very rocks at depth. However, some contribution from deep seated juvenile fluids, related to Caledonian magmatism, is not precluded.

An idea as to the nature of the mineralizing solutions can be formed by the existing geochemical relations between mineralized rocks, gangue and ore-minerals, Kakar (1971-unpublished results).

In the rocks zinc is negatively correlated with Fe_2O_3, Ba^{+2} and Ce^{+3}. The more mineralized a sample is, the richer it is in zinc and consequently poorer in Fe_2O_3, and Ba^{+2}. Assuming that this is a true reflection of the chemical relations existing during mineralization this feature is suggestive of leaching under reducing conditions. The highly volatile rich solutions could leach these elements, especially Ba^{+2} and Ce^{+3} (and probably other rare earths as well as soluble salts), and thus deplete the rocks in these elements. Iron is known to be easily leachable in wall rock alteration processes.

The mineralizing solutions deposited mainly sphalerite, galena, quartz and calcite along with some minor chalcopyrite. Virtually no barite and fluorite is recorded in this area. The absence of barite would again suggest very strong reducing conditions. Barton (1958), has shown that at low temperatures the deposition of calcite and barite, etc., is a function of the ratio of aCO_3/aSO_4, where (a) is the activity of the two anions. He states that this ratio must be greater than (10^{-3}.7), or anhydrite would be formed instead of calcite, and less than (10^{-3}.5), or witherite would be formed instead of barite. If these figures are tentatively accepted within the temperature ranges, an approximate partial oxygen pressure can be suggested which may be interpreted as indicative of the degree of mixing of the oxygenated meteoric waters and hydrothermal solutions.

Lead is positively correlated with soda and negatively correlated with K_2O, TiO_2, Y^{+3} and Co^{+2} in sedimentary rocks. On the one hand this can be interpreted as suggestive of an isomorphous relationship between potassium and lead in feldspars, clay minerals and other dark minerals containing alkalis and titania, etc. This would explain only up to about 100 ppm lead. As to the added lead in mineralized rocks again this could mean a reaction of the mineralizing solutions with the country rocks, whereby, when more and more lead was added, more K_2O, TiO_2, Co^{+2} and Y^{3+} (and possibly other rare earths) were removed while soda was added during the process. This suggestion is further corroborated by the study of epigenetic patterns, Kakar, (1970).

During the period of wall-rock alteration many minerals are known to form as secondary products of alteration while many more are broken down. Feldspars break down and form kaolinite and sericite etc., while the breakdown of micas and other ferromagnesian minerals results in the formation of kaolinite, sericite, montmorillonite and epidote etc. It is also known that soda is usually added to the rocks by mineralizing solutions while K_2O, TiO_2 etc. are usually carried away, Tooker (1963), Hawkes and Webb (1958). The tendency of titanium and yttrium and many other elements towards complex formation are well known. The study of epigenetic patterns in Cardiganshire shows that changes were brought about in the country rock. The formation of new minerals due to wall rock alteration is not evident in this area. Some X-ray diffraction patterns exhibited the existence of sericite, which could very well be a primary authigenic mineral. This is probably because the temperatures of mineralization were rather low and the mineralization was rather rapid both of which factors could have contributed to the lack of characteristic minerals associated usually with wall rock alteration.

Silver in mineralized mudstones shows a positive correlation with flourine, a fact which probably suggests that the relationship between these two elements is of secondary nature due to mineralization. Silver content directly rises near fault zones where flourine content is also highest. This probably suggests that most of the silver was carried as a flouride complex in the original solution, Krauskopf (1964).

The abnormal concentrations of fluorine along fault zones suggests that flourine was probably one of the most active elements during mineralization. High flourine contents were noted also in a few samples of quartz and calcite. The extreme enrichment of hydrothermal solutions might probably have been of juvenile origin or at least some of the volatiles probably in gaseous form were added to these solutions from some deep seated magmatic chamber. Magmatic activity in Caledonian times was widespread. It is therefore, possible that the very solutions, in whatever form they were, are broken down. Feldspars break down and form kaolinite and sericite etc., while the breakdown of micas and other ferromagnesian minerals results in the formation of kaolinite, sericite, montmorillonite and epidote etc. It is also known that soda is usually added to the rocks by mineralizing solutions while K_2O, TiO_2 etc. are usually carried away, Tooker (1963), Hawkes and Webb (1958). The tendency of titanium and yttrium and many other elements towards complex formation are well known. The study of epigenetic patterns in Cardiganshire shows that changes were brought about in the country rock. The formation of new minerals due to wall rock alteration is not evident in this area. Some X-ray diffraction patterns exhibited the existence of sericite, which could very well be a primary authigenic mineral. This is probably because the temperatures of mineralization were rather low and the mineralization was rather rapid both of which factors could have contributed to the lack of characteristic minerals associated usually with wall rock alteration.

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Chlorine is relatively constant in rocks but is also found in quartz and calcite. Chlorine might also have been a very active volatile mineralizing agent in these solutions. The fact that chlorine is not as reactive as fluorine possibly explains why it is not so abundant near mineralized zones.

The Probable Nature of Hydrothermal Solutions in Cardignashire and Neighbouring Areas.

In Cardiganshire quartz is an ubiquitous vein mineral accuring along side other minerals. In paragenetic sequence it is usually the first mineral followed by sphalerite or galena. A few samples of quartz and a calcite sample were analysed for chlorine and fluorine. They showed large amounts of these two elements. The study of epigenetic patterns in Cardiganshire show very high fluorine peaks near mineralized areas. This strongly suggests that halides played a very active role in mineralization in Cardiganshire.

Dunham (1970) in a recent review on the composition of deep formation water, connate waters, inclusion fluids, mineralizing fluids, the ocean water, and deep subsurface waters from Derbyshire (Downing and Howitte, 1967), has shown that they are usually very rich in alkalis (Na-K), but also contain large amounts of calcium and sometimes magnesium. A characteristic of these deep subsurface waters is their tendency towards enrichment in calcium and magnesium with aging. A comparison of the various anions, chloride, carbonate, sulphate, etc., shows that with age all these waters tend to get enriched in sulphate.

A comparison of this feature of mineral waters with age and their occurrence in different stratigraphic horizons, as was shown for British mineral and thermal waters, Edmonds *et al.*, (1968), indicates that most of these mineral waters in older formations are alkali chloride types while in younger formations they are Na-Ca sulphate type. It, therefore, seems that the relationship of the chemistry of the mineral waters with respect to aging and their stratigraphic horizon is inverse. It may be pointed out here that mineral waters occurring in older formations may not be older than the ones occurring in younger formations though the probability of the correspondence between the true ages of these waters and their stratigraphic horizon is not precluded.

Dunham (1970) has plotted the cation ratios of (Na + K) Ca: Mg of all these mineral waters from various parts of the wrold. It can be seen that these fluids extend in range form chloride-soda to chloride-clacium waters. The concentration of most of the points is along the (Na + K) – Ca join.

The ratios of (Na – K) Ca: Mg in quartz from Cardiganishire have been plotted in fig. 10. These ratios are based on the absolute concentrations of these elements in quartz, because no data is available on the composition of fluid inclusions in quartz veins. It was assumed that the cation ratio in the solid phase is a true reflection of the same ratios in the hydrothermal solutions (Verhoogen, 1938 in Smith).

It is apparent from the figure, that in Cardiganshire, these cation ratior approach nearest in composition to Red Sea brines. Allowing for the high enrichment of fluroine in Cardiganshire minera-izing solutions, it would be reasonable to suggest that these solutions might have been more reactive than the ones in Red Sea brines. The enrichment in fluorine of some subsurface waters as compared to sea water has been previously recorded for some waters in the Lovozero massif, Kraynov (1970).

The relatively high alkali to calcium ratio in quartz veins in Cardiganshire and veins from Pumpsaint Gold mines, suggests that apart from enrichment in fluorine, the composition of the mineralizing solutions in these areas was very near to the average composition of the sea water. This suggests the probability that mineralization did not start long after the deposition of sediments in Plaeozoic times in this area.

Fluorine in these waters can be ascribed to a possible contribution from deep seated magmatic chambers in Caledonian times. This might have been in the form of volatile gases or alternatively this might have been due to a mixing of juvenile hot waters form the magmatic chambers, with the meteoric or connate waters in the then recently deposited sediments.

The prevalence of Caledonian orogeny and magmatism in those times would have set up geothermobaric gradients probably of a moderate kind which would mobilize the solutions and thus start the ascent, during which time they would leach the country rock and possibly remobilize some older existing veins in the basement which would be redeposited afterwards.

The relation of ore-deposition to doming has been long recognized, Wisser (1960). Dunham (1967) suggested that all the mineral belts, on both sides of the Atlantic, are situated at basement structural highs and that most of the mineralizing brines are connected with domes. The mineral belt of Cardiganishire and Montogomeryshire does occur around cader Idris and Plynlimon Domes. Cadar Idris Dome is known to be a structural high, and probably that is where the original mineralizing solutions were originated. Llewellyn and Stabbin (1968) observed that the Pennine mineral belt in Derbyshire is surrounded on the one side by a structural domes and on the other by the North Sea. The same is true of the mineral deposits in Wales, which suggests that there is a closer correspondence between the two mineral belts than has been hitherto recognized.

Conclusion.

Finally it is concluded that the mineral deposits in Cardignashire and neighbouring districts were probably formed by brines, which were originally meteoric and connate waters activated by the addition of halides by mixing with juvenile waters, and probably also some gases. As a result of the Caledonian orogeny the thermobaric gradient of the area was modified which resulted in the remobilization and heating of these waters. On their way, during their ascent, they probably leached the surrounding rock and thus were enriched in metal ions. These waters might also have redissolved already existing mineral veins in the basement complex and thus were further enriched.

As these solutions travelled upwards the pressure and temperature slowly dropped. The drop in temperature could have been effected by mixing with cooler waters and to a certain extent by conduction and probably reaction with the country rock. The changes in pressure and temperature thus might have resulted in the deposition of ore-minerals, possibly at a depth of 2 to 5 kilometers.

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