11. PROBLEMS of ORE-DEPOSITION in the LEAD and ZINC VEINS of GREAT BRITAIN. By ALEXANDER MONCRIEFF FINLAYSON, M.Sc., F.G.S. (Read January 26th, 1910.)

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I. INTRODUCTION.

THE lead and zinc disfricts of Great Britain afford good opportunities for the study of these ores, owing to the variety of types met with and the advanced state of mining. Unfortunately, however, many interesting districts have been exhausted and abandoned, with the inevitable loss of much valuable information, which was not secured when the mines were in operation. As Franz Posepny has truly remarked,

‘Mining, indeed, constantly furnishes fresh evidences in new openings, but it destroys the old at the same time; and if these are not preserved for science before it is too late, they are lost for ever.’¹

The Geological Survey memoirs, however, have in some cases preserved many data which could not otherwise be obtained. The present work has been carried out on the basis of personal field-work in all the chief districts, coupled with laboratory work at the Imperial College of Science and Technology, where all the analyses tabulated in this paper were made.

The lead and zinc veins of Britain are chiefly of the spathic and barytic types of Freiberg mineralogists. Calcite is the predominant gangue, while fluorspar, barytes, and quartz are also abundant. Zeolites occur locally, as at Strontian in Argyllshire, and at Glendalough (Wicklow). The galena is argentiferous to a varying degree, and rich silver-ores have been mined at Hilderston (Linlithgowshire), at Alva (Stirlingshire), and in parts of Cornwall. These veins, though small and unimportant, are of the Joachimsthal and Annaberg type. The country-rock of the veins embraces nearly all the Palæozoic formations, from pre-Cambrian gneiss to the Carboniferous Limestone.

¹ ‘The Genesis of Ore-Deposits’ Amer. Inst. Min. Eng. 2nd ed. (1902) p. 3 (reprinted from vol. xxiii of the Trans.).

II. SOURCE OF THE ORES.

Since the days when the lateral-secretion theory was first propounded by Sandberger, deposits of lead and zinc ores have afforded much scope for investigation of the source of the metals. In Great Britain there are two general types: namely, veins in the Carboniferous Limestone, and veins in the older slates and granites. Concerning the latter type, there is no clear ground for argument; the ores have obviously been derived from a deep source, probably from deep-seated igneous masses. Attention is, therefore, here confined to the source of the ores in the limestone districts.

Fluorine.—Four samples of limestone were analysed by the method of W. F. Hillebrand,¹ with the following results:—

<i>Locality.</i>	<i>Fluorine percentage.</i>
Halkyn (Flintshire)	0·21
Matlock (Derbyshire)	0·11
Nenthead (Cumberland)	0·04
Rookhope (Durham)	0·13

Duplicate analyses of these specimens yielded sometimes discordant results, due probably to imperfections in the method of assay, as pointed out by Hillebrand; but the results leave no doubt as to the presence of small quantities of fluorine in the limestones. The constituent has probably been derived from seaweeds or other organic matter in the original sediments, or from the fluorine-bearing calcium phosphate of shells.

It is highly improbable, however, that this can be the source of the fluorine in the vein-fluorspar. The quantities present are extremely small, and the occurrence of fluorine in the rocks bears no relation to the occurrence of fluorspar in the veins. The occurrence and mineralogical relations of the fluorspar indicate that fluorine has been one of the original elements in the vein-solutions. The presence of fluorine is believed to indicate, in short, a deep-seated origin, dating probably from processes of magmatic extraction.

Lead and Zinc.—In searching for these constituents, a series of rocks was examined, the material being ground very fine. Quantities of from 30 to 100 grams were taken, and analysed by methods previously used by W. F. Hillebrand² and by James D. Robertson.³ The following table gives the results:—

¹ 'Analysis of Silicate & Carbonate Rocks' Bull. U.S. Geol. Surv. No. 305 (1907) p. 157.

² 'Geology & Mining Industry of Leadville, Colorado' Monogr. xii, U.S. Geol. Surv. 1886, p. 591.

³ Geol. Surv. Missouri, vol. vii (1894) pp. 479, 740.

<i>Rock.</i>	<i>Locality.</i>	<i>Lead.</i>	<i>Zinc.</i>
		Per cent.	Per cent.
Granite	Foxdale.	·004	·005
Granite	Threlkeld.	·003	·011
Granite	Glendalough.	·004	·001
Granite	Dartmoor.	·002	·002
Diabase (Whin Sill)	Rotherhope.	·003	·0005
Diabase (Toadstone)	Darleydale.	·001	·001
Volcanic ash	Conway.	·0025	not found.
Volcanic ash	Greenside.	·006	·002
Slate	Leadhills.	·001	not found.
Limestone	Halkyn.	·0005	·0015
Limestone	Matlock.	·001	·0005
Limestone	Alston.	·0015	·001

The results were verified as far as possible by blank experiments, and by tests of the reagents used; while some duplicate analyses made indicated that the figures were generally correct to within 30 per cent. of the amount stated. The results correspond with those of W. F. Hillebrand on the Leadville porphyries, where the average amount of lead oxide was determined to be 0·002 per cent.¹ Similarly, J. D. Robertson, in the Archæan rocks of Missouri, records 0·004 per cent. of lead and 0·009 per cent. of zinc.² The foregoing analyses, like those of Luther Wagoner for gold and silver in rocks at San Francisco,³ show a higher percentage of metals in the igneous than in the sedimentary rocks, suggesting the conclusion that the metals in the latter rocks have been derived by denudation of the older igneous and crystalline rocks.

A consideration of the areas which were basins of deposition in Britain during the Carboniferous Limestone epoch shows that these basins received the drainage from the older rocks, and gives some ground for the belief that the traces of metals found in the limestones by analysis have been derived from the older rocks and deposited contemporaneously with the limestones. Thence, it is only a step to assume that the ores of the veins have been concentrated by circulating waters from the disseminated metals in the limestones. There are several objections to this view, and these may be tabulated as follows:—

(1) Analyses were made of specimens of limestone from the Vieille Montagne Company's mine at Nenthead. The specimens were taken along a cross-cut, at varying distances from the vein and along one and the same stratum—the Great Limestone. The results were as follows:—

¹ *Loc. supra. cit.*

² *Loc. supra. cit.*

³ *Trans. Amer. Inst. Min. Eng.* vol. xxxi (1901) p. 808.

No.	Position of Sample.	Lead.	Zinc.
		Per cent.	Per cent.
1	Limestone in the vein.	·012	·040
2	Do. on the vein-wall.	·025	·015
3	Do. 10 feet from the vein.	·015	·030
4	Do. 20 " "	·001	·004
5	Do. 40 " "	·002	·001
6	Do. 70 " "	·0005	·001

There is no uniform variation in passing from the vein into the country-rock, but the analyses clearly show a much higher metal-content in the limestone adjoining the vein than in the rock farther away. A similar phenomenon has been recorded by J. S. Curtis at Eureka (Nevada),¹ and the difference is certainly due to impregnation of the adjacent rock by the vein-solutions.

(2) A strong objection to the lateral-secretion theory is the close similarity in all respects between veins in limestone, in granite, and in older slates, especially in adjoining districts. Thus the veins in the limestone districts of Alston Moor and Dufton Fell are exactly similar mineralogically to the veins in the slates and ash-beds of the Lake District. Again, in the Isle of Man there are veins in granite extending into the adjoining slates, numerous veins in the slates themselves, and veins in the Carboniferous Limestone at Castletown. It is not conceivable that the ores of these different veins can have different sources of origin.

(3) In the United States, where this problem has been very fully investigated, there are two general types of lead and zinc-ore deposits: firstly the silver-lead or 'hard-lead' ores, typified at Leadville, Aspen, Rico, Tintic, Cœur d'Alène, and Eureka; and secondly the 'soft-lead' and zinc-ores of the Mississippi and Missouri districts, including Wisconsin, the Ozark district, South-Eastern Missouri, and Northern Arkansas. The general conclusions in regard to these two types are that the silver-lead ores are of deep-seated origin, while the ores of the Missouri type have been concentrated in most cases from a disseminated condition in the same formation or in one adjoining that in which they are now found. The essential features of the deposits of this type, the sedigenetic deposits of H. F. Bain,² are their sporadic occurrence, the absence of defined veins, the non-persistent and shallow character of the deposits, and the generally negligible silver-content of the galena.

Comparing the British occurrences with these conditions, the veins of the limestone areas occur typically in strong fault-fissures, altogether distinct from the shallow non-persistent deposits of Wisconsin.

¹ 'Silver-Lead Deposits of Eureka, Nevada' Monogr. vii, U.S. Geol. Surv. 1884, p. 85.

² 'Economic Geology' vol. i (1906) p. 331.

The silver-content of the galena (4 to 15 ozs. per ton) is much higher than that of sedigenetic ores, and the restriction of the ore in the veins to certain horizons is clearly due to the influence of different strata on ore-deposition, and not to any greater abundance of disseminated metals in these strata. The ore-deposits are totally unrelated to drainage-lines, topographic slopes, synclinal basins, or other features such as are often found to be determining factors in the occurrence of the American deposits.¹ These features were examined during the present investigation in North Derbyshire, with the aid of the geological and topographical maps, but the results were negative or inconclusive. On the other hand, both in that district and in Flintshire, the deposits show a tendency to concentrate beneath anticlinal arches, especially when these are or have been covered by a 'blanket' of impervious shales. Further, the localization of ores in certain tracts, which might suggest a greater original abundance of disseminated metals in these tracts, is not at all marked in the British limestone districts; and, when it does occur, it is seen to be dependent on the localization of fissures or on the presence of strata favourable to ore-deposition.

It is, therefore, concluded that the lead and zinc ores in the limestone districts, like those in the older slates and granites, have been brought into the fissures by solutions ascending from deep-seated sources, at a period subsequent to the deposition of the rocks.

It should here be noted that some limestone areas, particularly North Derbyshire, are characterized by abundant small and scattered deposits of ore occupying solution-cavities and enlarged joint-planes ('flats' and 'pipes'), the galena having generally a very low silver-content. These deposits are comparable in all respects to the sedigenetic type, and are probably the result of later re-arrangement and concentration by circulating waters—the ores found in them being derived chiefly from the ores previously deposited in the adjoining veins, and possibly to some extent from the traces of disseminated metals in the surrounding rocks.

Barium.—The most noteworthy feature in the occurrence of barytes in these veins is its irregular distribution. Thus it is abundant in the Leadhills, the Lake District, Shropshire, and North Derbyshire, while it is rare in the Isle of Man, Flintshire, Cardiganshire, and Devon. The importance of barium as a minor constituent in the rocks of the earth's crust is now widely recognized, and its original source is generally considered to be in the feldspars and micas of the igneous rocks.² It is most probable, therefore, that the barium minerals in the veins were concentrated in the first place by magmatic processes, along with lead, zinc, and fluorine, and that the barium was similarly brought to its present position by solutions ascending from deep-seated igneous rocks.

¹ H. F. Bain, 'Zinc & Lead Deposits of the Upper Mississippi Valley' Bull. U.S. Geol. Surv. No. 294 (1906) pp. 66-70.

² F. W. Clarke, 'The Data of Geochemistry' Bull. U.S. Geol. Surv. No. 330 (1908) p. 14.

III. THE VEIN-SOLUTIONS.

The composition of the vein-solutions on the one hand and their source on the other are cognate subjects, and may therefore be considered under the same head.

Nature of the solutions.—A clue to the chemical composition of the vein-solutions is given in the first place by the hydrothermal alteration of the wall-rocks, an examination of which was made during this investigation. A series of analyses, tabulated below, was made of fresh and altered rocks from five different localities:—

	A ₁ .	A ₂ .	B ₁ .	B ₂ .	C ₁ .	C ₂ .	D ₁ .	D ₂ .	E ₁ .	E ₂ .
H ₂ O	2.05	2.35	1.04	1.21	1.95	1.65	0.89	1.24	2.12	2.48
SiO ₂	64.45	60.42	75.64	80.67	50.46	62.29	75.46	65.68	2.34	15.25
Al ₂ O ₃	13.31	13.45	8.79	6.23	13.89	12.27	12.68	13.49	0.57	0.61
TiO ₂	0.51	0.33	0.68	0.65	2.26	1.13	...	...	...	...
Fe ₂ O ₃	2.32	1.42	3.24	0.19	3.69	1.29	0.85	0.56	0.65	0.42
FeO	3.62	1.23	1.61	0.45	9.02	8.65	0.34	0.28	...	...
CaO	5.73	7.24	1.09	2.48	8.81	3.29	1.21	6.28	51.18	42.83
MgO	3.24	1.15	0.28	0.21	5.03	2.45	1.68	0.31	1.24	5.37
K ₂ O	2.21	3.35	2.31	2.45	1.33	2.66	5.46	5.85	...	...
Na ₂ O	1.55	0.94	3.67	1.38	2.85	0.23	2.48	0.13	...	...
MnO	0.24	0.40	0.46	0.35	0.22	0.27	...	...	...	...
P ₂ O ₅	...	...	...	...	0.37	0.32	...	...	...	...
CO ₂	1.24	8.73	0.31	3.24	0.19	4.34	nil	5.28	42.27	32.66
FeS ₂	...	...	1.05	1.33	...	...	...	...	...	...
Totals	100.47	101.01	100.17	100.84	100.07	100.84	101.05	99.10	100.37	99.62
Specific gravities.	2.564	2.490	2.522	2.318	2.853	2.648	2.621	3.213	...	...

A₁: Leadhills slate, fresh.
A₂: Do. do. altered.
B₁: Conway volcanic ash, fresh.
B₂: Do. do. do. altered.
C₁: Whin Sill diabase, fresh.
C₂: Do. do. altered.

D₁: Foxdale granite, fresh.
D₂: Do. do. altered.
E₁: Halkyn limestone, fresh.
E₂: Do. do. altered.

It will be seen from the foregoing analyses that the different rocks show much variation in the changes of constituents. The Leadhills slate (A₁ & A₂) shows a loss of iron oxides, balanced by an increase in lime, potash, and carbon dioxide. Under the microscope the altered slate shows a great development of dusty sericite, with some secondary calcite and siderite. The alterations in this rock have been sericitization and carbonatization.

The rhyolitic ash from Treacastell, Conway (B₁ & B₂), shows some loss of alumina as well as of iron oxides and soda, with an increase in lime, potash, carbon dioxide, and silica. The fresh rock contains abundant orthoclase and plagioclase phenocrysts, and much secondary quartz-mosaic. The altered rock shows further silicification, while the feldspars are replaced by sericite and calcite aggregates.

The Whin Sill (C₁ & C₂) was examined at Rotherhope, near Alston, where it is intersected by a vein now being worked. The unaltered rock consists largely of andesine-labradorite and ophitic augite, with a good deal of magnetite and ilmenite. Near the vein much secondary quartz and sericite has been produced, with patches of secondary carbonates. The augite is altered to pale-green chlorite, with separation of magnetite. On the vein-walls the rock is white

and granular, and is transformed to an aggregate of siderite, sericite, and quartz. Ilmenite alters first to leucoxene, and this, together with magnetite, changes largely to siderite, which occurs in abundant greyish-brown patches. The rest of the rock is composed of granular secondary quartz and much finely divided sericite, while fresh apatite needles are scattered through it. As seen from the analyses, the principal chemical changes have been a loss of titanium and ferric oxides and a gain in silica, potash, and carbon dioxide. Taking the major constituents, and recalculating the analyses, we obtain the following approximate mineralogical compositions:—

C ₁ (fresh).		C ₂ (altered).	
Augite	34.86	Siderite	14.42
Magnetite and ilmenite .	9.92	Sericite	32.58
Plagioclase (andesine)...	52.69	Quartz	49.29
Apatite	0.74	Apatite	0.74
Totals	<u>98.21</u>		<u>97.03</u>

The intense changes in this rock have been essentially mineralogical, there being no marked percentage loss of bases in the altered rock.

The Foxdale granite also shows very considerable alteration. The fresh rock is a binary granite, containing orthoclase and oligoclase, with some microcline, muscovite, and frequently biotite, and abundant quartz. Adjoining the Foxdale vein the rock is pulverulent and earthy, and of a greenish-yellow colour. It crumbles readily, and swells on the addition of water. Under the microscope the quartz and muscovite are seen to be unchanged, but the feldspars are completely altered to aggregates of sericite. Patches of calcite are frequent, and fine mosaics of secondary quartz sometimes replace feldspar phenocrysts. Biotite is first bleached, and later altered to pale-green chlorite with separation of magnetite. The analyses (D₁ & D₂) show a loss of silica, iron oxides, magnesia, and soda, and a concentration of lime, potash, and carbon dioxide. The changes are in general comparable with those in the other rocks just described, and are in many respects similar to the alteration of the gneiss which carries the silver-lead veins of Freiberg, except for the great loss of constituents in the altered rock at Freiberg.¹

The specific gravities tabulated on p. 304 show that the altered rocks have in general a reduced specific gravity. This, without marked loss of constituents, is in accordance with the alteration to a less dense mineral aggregate. The marked increase in specific gravity of the altered granite of Foxdale (D₂) indicates greater porosity, a property which is revealed by its tendency to swell and disintegrate when exposed in the mine-workings. The accompanying diagrams (fig. 1, p. 306), constructed on W. H. Hobbs's

¹ Th. Scheerer, Zeitschr. Deutsch. Geol. Gesellsch. vol. xiv (1862) p. 87; and A. Stelzner, Neues Jahrb. vol. i (1884) p. 271.

Fig. 1.—Diagrams illustrating the composition of fresh and altered country-rock.

A. Whin Sill diabase (fresh).

C. Foxdale granite (fresh).

B. Whin Sill diabase (altered).

D. Foxdale granite (altered).

[Scale : .01 in molecular ratio = .025 inch.]

modification of Brögger's method,¹ illustrate the changes in composition of two of the types analysed.

The limestones have been affected in a manner altogether different from the silicate-rocks. The analyses (E_1 & E_2) show that the wall-rock alteration has here been silicification and dolomitization. Microscopic examination of the altered limestone reveals the development of abundant quartz grains, either in aggregates or as scattered crystals in the limestone, while small rhombohedra of dolomite are sometimes distinguishable.

The want of uniformity in the changes observed in the different rock-types examined is essentially due to the different mineral and chemical composition of the rocks themselves, which must have greatly affected the results. Thus, a solution low in alkalies would tend to extract potash or soda from a rock rich in these constituents, while the same solution would have a reverse effect on limestone. Such causes, bringing into operation the principle of relative mass of interacting constituents, must make the conditions complex, and prevent uniform changes in a wide district of varied country-rocks.

As a general rule, it appears that in the silicate-rocks the characteristic changes have been a concentration of potash, lime, and carbon dioxide, and a leaching of silica, iron oxides, magnesia, and soda, the mineralogical effects being sericitization and carbonatization. In the carbonate-rocks silica has been generally introduced, and some of the lime has been replaced by magnesia, the changes here being, in other words, silicification and dolomitization. The results are in accordance with the pioneer researches of Waldemar Lindgren.² The processes of alteration indicate that the vein-forming solutions carried carbonates of the alkalies (chiefly potash) and of the alkaline earths (chiefly lime). This conclusion is supported by the great preponderance of calcite as a gangue-mineral in the veins.

The chemical composition of the solutions is indicated in the second place by the minerals which they carried. The lead and zinc may have been transported, either as sulphides dissolved in alkaline sulphides, or as oxidized salts (carbonates or sulphates) dissolved in alkaline bicarbonates. The conclusions just reached suggest the latter hypothesis; but, on this view, it is very difficult to account for the presence of the sulphides in the veins, since organic matter is not generally a prominent constituent of the rocks, and there are no other strong reducing agents present which could have effected the wholesale reduction of oxidized salts of the metals to the sulphides. The great quantity of sulphide-ore in the veins seems to imply that the carriers of the metals must have been alkaline sulphides, the efficiency of which as solvents of the metallic sulphides has been shown by Prof. C. Doelter³ and others.

¹ W. H. Hobbs, 'Suggestions regarding Classification of the Igneous Rocks' Journ. Geol. Chicago, vol. viii (1900) p. 1.

² 'Metasomatic Processes in Fissure-Veins' Trans. Amer. Inst. Min. Eng. vol. xxx (1900-1901) p. 578.

³ Tschermak's Min. Petrogr. Mittheil. n. s. vol. xi (1890) p. 319.

Barium, on the other hand, would be readily carried as the carbonate, dissolved in excess of carbon dioxide, the change to barytes being effected during deposition by reaction with alkaline sulphides, and by oxidation. In this connexion the relations of the sulphate and carbonate of barium in the veins are important. These two minerals are seldom closely associated in the veins, one generally occurring to the exclusion of the other. Further, there is no evidence, except in local cases, of change from the one form into the other. The carbonate (witherite), as at Fallowfield and Settlingstones, generally appears as a direct metasomatic replacement of limestone; while the sulphate (barytes) occurs usually as a compact fissure-filling. Prof. Clowes has suggested that barytes, as a cement in sandstone, has been formed *in situ* by interaction between barium carbonate and soluble sulphates.¹ Herr G. Lattermann has described a deposit of barytes at Lautenthal in the Harz, which has been formed by the interaction of sulphate-bearing mine-waters with spring-water carrying barium chloride.² Mr. C. W. Dickson has shown that it forms by reaction between bicarbonated solutions of barium and oxidizing sulphides.³ This last case is most probable for the barytes in the British districts. The formation of the sulphate seems to be, in every case, brought about during deposition.

Fluorine was doubtless the chief agent in the primary processes of magmatic extraction, forming volatile fluorides or fluosilicates of the metals. As the solutions ascended, and became cooled and diluted, these compounds would be hydrolysed, with the formation of new combinations and release of the fluorine, which was ultimately fixed by combination with calcium.

Summing up, it appears that the vein-solutions carried, in addition to fluorine and volatile fluorides, chiefly alkaline and earthy carbonates, which transported barium in solution and effected the observed alteration of the wall-rock; also alkaline sulphides, which transported the lead and zinc as sulphides.

Source of the solutions.—The conclusion that all the ores are of deep-seated origin, as well as the depth to which the veins extend, indicates that the waters were, in the first place, 'juvenile,' being probably hydrothermal after-effects of deep-seated igneous disturbances and intrusions. This is supported by the occurrence of fluorine; the processes at considerable depth were probably pneumatolytic in nature. Further, it is not likely that meteoric waters played any conspicuous part in the primary ore-deposition in the slate and granite districts.

In limestone areas, however, the conditions are different, and a consideration of the facts strongly suggests that underground atmospheric waters, mingling with the 'juvenile' waters, have played an important part in ore-deposition. The facts are as follows:—

(1) The ores are almost universally distributed throughout the

¹ Proc. Roy. Soc. vol. xlvi (1889-90) p. 368.

² Jahrb. K. Preuss. Geol. Landesanst. 1888-89, p. 259.

³ School of Mines Quarterly, vol. xxiii (1902) p. 366.

British limestone districts, a fact which is difficult of explanation on the assumption of aqueous emanations direct from magmas.

(2) The ore frequently fails at comparatively shallow depths. The vertical range of the ores is, indeed, comparable to the depth of the present underground circulation.

(3) The silver-content of the galena in limestone-districts is frequently much lower than in areas of the older rocks. This, taken in conjunction with the known fact that the silver-value of galena is reduced by prolonged solvent action of water or dilute solutions, indicates that the ores have undergone much more transport in these districts than in the slate and granite areas.

(4) Extensive circulation is further put in evidence by the structure of the deposits. The pipes, flats, and enlarged vein-fissures which are typical of all the limestone-districts are clearly the result of circulation by meteoric waters, and the rich deposits of ore found in them have probably been formed by the same agency, since, in many cases, the deposition of ore has been intimately related to the formation of the cavities. Circulation furnishes the key to ore-deposition in the limestone districts, and it seems improbable that this circulation was effected so uniformly over large areas by juvenile springs.

(5) It is most probable that the main epoch of deposition of all the lead and zinc ores of Britain was Permo-Triassic, a period when the rocks were elevated and fissured, the climate was dry, and erosion was rapid. These conditions were eminently favourable to a deep circulation of atmospheric waters.

(6) The importance of the underground circulation is indicated by the occurrence of underground waters at the present day. The springs in North Derbyshire are a good example: the Buxton spring-water has a temperature of 82° F., indicating an undoubtedly deep circulation. This water carries traces of lead and fluorine.¹ Further evidence comes from Flintshire, where the Halkyn drainage-adit, unwatering the mines on Halkyn Mountain to a depth of 250 feet below the summit of the mountain, delivers a million gallons of water per day, and St. Winifred's Well, at Holywell, is estimated to yield 4400 gallons of water per minute.² A sample of water taken from the Halkyn drainage-adit was analysed for lead in the course of this work, and found to carry from 0·01 to 0·03 grains of lead oxide per gallon. The temperature of the water was 52° F., and the solid contents (chiefly carbonates and chlorides) amounted to 30 grains per gallon.

(7) Lastly, there is the well-known fact that the toadstones of North Derbyshire and the Whin Sill of Northumberland and adjacent counties generally limit the downward extent of the productive parts of veins which cut these rocks. There is in this a further suggestion that the ores were to a large extent deposited by underground waters circulating only above these impervious layers.

¹ 'Geology of North Derbyshire' Mem. Geol. Surv. 2nd ed. (1887) p. 115.

² A. Strahan, 'Geology of Flint, Mold, & Ruthin' Mem. Geol. Surv. 1890, p. 222.

In conclusion, while the vein-solutions were at first and predominantly of truly deep-seated origin, it seems necessary to recognize that underground waters of meteoric origin must have played an important part in the distribution and final deposition of the ores in the upper strata of the limestone-tracts.

IV. METASOMATIC PROCESSES.

The relative part played by replacement on the one hand, and by the filling of fissures on the other hand, is variable, but on the whole the latter process has been dominant in the districts examined. The vein-structures generally show the characters due to filling, except where local silicification and carbonization have occurred. Replacement has played a minor part in the formation of the important deposits which have yielded the bulk of the ores.

Fig. 2.—*Replacement of limestone by quartz and galena: Halkyn Mine (Flintshire).*

[The quartz appears as scattered grains (white), closely followed by granular galena (black), which gradually replaces the rock, enclosing residual plates of recrystallized calcite and quartz-grains. (Transmitted light : $\times 50$.)]

Interesting metasomatic processes are, however, seen under the microscope.

Specimens of limestone from veins at Halkyn show, first, recrystallization with the formation of veinlets and coarse plates of calcite. This has been followed by the introduction of galena, blende, and quartz, all replacing the calcite. The formation of scattered quartz-granules is characteristic, the quartz being most abundant where sulphides are forming. Blende occurs in irregular rounded grains. Galena appears first in small crystals, uniting into strings which penetrate the calcite. These gradually form a network, and finally a solid mass of granular ore, enclosing a few residual patches of

calcite (fig. 2). The silicification appears to be an accompaniment of the formation of the sulphides, and the absence, in the latter, of defined crystal outlines, such as appear when they are deposited in open cavities, is very characteristic.

The rhyolitic breccia at Treacstell, Conway, shows similar processes. It is generally much silicified, cavities and cracks in the rock being filled by coarse quartz crystals, while a fine-grained quartz-mosaic replaces the mass of the rock (fig. 3). Galena and blende occur in the breccia, both replacing quartz, and appearing as irregular rounded grains, which may grow to a considerable size. The galena tends to wrap round the fragments of rhyolite, which act as nuclei (fig. 4, p. 312). The rhyolite is gradually replaced by a quartz-mosaic, and this in turn by galena (fig. 5, p. 312), the replacement of quartz by the ore following closely on the silicification.

The replacement of limestone by fluorspar was observed in

Fig. 3.—*Metasomatic quartz, forming a fine-grained mosaic, accompanied by quartz filling a cavity, with comb-structure: Treacstell Mine, Conway. (Transmitted light: $\times 50$.)*

several specimens from the Mill Close Mine (North Derbyshire). One section showed a dark organic limestone, almost completely replaced by coarse-grained colourless fluorspar. The fluorspar has sharp crystal-faces where it abuts against the limestone, and small crystals of fluorspar in the limestone itself are also generally well formed. The process consists in a general aggregation of small crystals until the whole of the limestone is replaced, the fluorspar individuals frequently growing on one another in crystallographic continuity. The fluorspar is often followed

by galena, with its usual granular structure, replacing both the fluorspar and the residual limestone. In the former it appears first as grains and strings on the edges and along cleavage-planes of the fluorspar, gradually forming larger masses.

Other specimens from the same mine show replacement of fluorspar by quartz. The quartz appears first along cracks and cleavage-planes, and gradually spreads into the fluorspar as a mosaic. One specimen shows a granular fluorspar formed by replacement of an organic limestone, patches of organic matter being

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Fig. 4.—*Rhyolitic breccia, showing replacement by galena.*

[The galena is seen enveloping a residual fragment of the rock :
Trecastell Mine. (Transmitted light : $\times 50$.)]

Fig. 5.—*Rhyolitic breccia, Trecastell Mine.*

[The galena has here replaced spherulitic portions of the breccia, which had
been previously silicified. (Transmitted light : $\times 35$.)]

scattered through the secondary mineral. The fluorspar has been followed by quartz, which occurs as scattered grains or aggregates, and at times the quartz crystals form pseudomorphs after cubic fluorspar.

Specimens from Rotherhope show a mass of crystallized fluorspar, the cracks in which are occupied by infiltrated quartz. Strings of galena have advanced into the fluorspar by replacement of the quartz, and also by further replacement of the fluorspar. The replacement of fluorspar by galena is also seen in specimens from other districts; the reverse change was not observed.

The characteristic metasomatic processes seen under the microscope are, then, as follows:—

1. Replacement of limestone by fluorspar.
2. Do. of limestone by galena.
3. Do. of fluorspar by galena.
4. Do. of limestone and fluorspar by quartz.
5. Do. of limestone by blende.

Galena is much more active than blende in processes of replacement. Quartz and calcite do not replace the sulphides to any extent, but quartz freely replaces both calcite and fluorspar.

The metasomatic formation of fluorspar is a striking feature. While the greater part of this mineral has probably been deposited in open spaces, its practical restriction to limestones or calcareous rocks clearly indicates that the calcium has for the most part been derived from the country-rock, the mineral being deposited at times by direct replacement, and at other times after more or less transport.

It is important to observe that galena always follows fluorspar in replacement, a fact which is of value in determining the order of deposition of the vein-minerals.

V. PARAGENESIS.

The relations and order of deposition of the ores are easily studied in the field, more especially in banded conchy veins and in solution-cavities. The results, however, are frequently conflicting and inconclusive, and the relations may differ in different districts, while anomalous orders of deposition are to be seen in one and the same vein. These anomalies are due to the complex history of the ores in the limestone-districts and to continued re-arrangement and redeposition by circulating waters since the ores were first transported from a deep-seated source. The problems cannot be satisfactorily approached from field-evidence alone, the relations of the ores in cavity-fillings being often notoriously unreliable. Calcite and quartz show no definite order: they have been deposited both before and after the sulphides, and their relations to the other minerals are therefore variable. In this connexion, mention should be made of some brecciated ores found in several mines. At Foxdale the main vein in the lowest levels is frequently brecciated, the ore consisting of

rounded or angular fragments of fine-grained galena, together with decomposed granite, cemented by calcite and quartz. The Brow vein at Leadhills shows a similar breccia in places. The Rampgill vein at Nenthead contains sometimes a filling of crushed limestone with both galena and blende, cemented by strings of calcite. Other interesting specimens are seen at the Treacastell Mine, Conway. Some of these show fragments of volcanic ash with a selvage of galena, constituting typical 'ring-ore.' On the other hand, some fragments of brecciated ash contain strings of galena cut off at the edges of the fragments, the whole being cemented by calcite. There is here evidence of ore-deposition both before and after the brecciation of the vein-stone.

Chalcopyrite generally occurs enclosed in or wrapped round by galena or blende, and has evidently been one of the first sulphides deposited. Pyrite, on the other hand, has generally been later than galena and blende. It is quite a subordinate constituent, and occurs as small crystals in vughs or cavities, deposited on any or all of the other ores. Fluorspar shows variable relations in the field. It commonly occurs as the inner lining of flats and pipes; at times it forms alternating crusts with galena, and it is again often enveloped by calcite and quartz. The relations of barytes are not very definite. It commonly occurs by itself, unaccompanied by much galena or blende—hence the dictum of the miners at the Leadhills and elsewhere that barytes 'poisons' the veins for other ores. This relation, which holds good in many districts, strongly suggests that barytes and galena were closely connected in order of deposition, the physical conditions favourable to the deposition of barytes being prejudicial to the formation of the sulphides.

The examination of thin sections enables the relations of fluorspar to be determined, as has been pointed out in the last section (§ IV) dealing with replacement. As a general rule, fluorspar is observed replacing limestone, and this is succeeded by galena replacing the fluorspar. The priority of the fluorspar is thus clearly indicated. Specimens from the Mill Close Mine show strings of galena penetrating a mass of crystallized fluorspar, while veinlets of fluorspar are crossed by later veinlets of galena. Other specimens show strings of blende penetrating fluorspar. The relations of fluorspar and chalcopyrite were not directly observed, but it is probable that the chalcopyrite is the older, as the fluorspar has been deposited in intimate relation with the galena and blende. That fluorspar should be one of the earlier minerals formed in the primary deposition appears from the fact that the mobile fluorine in the solutions, released at greater depths from combination with the metals, must have been a very potent constituent, and one of the first to form stable combinations whenever temperature became low enough for its combinations to persist. It may be pointed out in objection that fluorspar often forms the inside crust in flats and pipes, but the two cases are not strictly comparable. We have, in the one case, direct formation of fluorspar by replacement of limestone, and, in the other, crystallization in cavities as the last

stage in a series of complex processes, involving much rearrangement of the ores.

The relations of the opaque minerals are most satisfactorily determined by metallographic methods, as recently applied to ores by Dr. W. D. Campbell¹ and Mr. C. W. Knight. In the present investigation the specimens were polished on a series of emery discs, and finally on washed rouge or tripoli. The examinations under low powers were made with a petrographical microscope fitted with a vertical illuminator over the objective, light being supplied by a 220-volt Nernst lamp. For higher powers a Zeiss metallurgical microscope was used, kindly placed at my disposal by Prof. W. A. Carlyle, in the Metallurgical Department of the Imperial College

Fig. 6.—*Etching figures on 'cubical' galena, oriented at right angles to the direction of polishing. (Reflected light: $\times 200$.)*

of Science & Technology. The lenses used were apochromats of 12, 4, and 2-millimetre focal lengths, and the linear magnification ranged from 120 to 700. Of the sulphides examined, the soft galena polishes with a very smooth surface, and gives characteristic etching-pits under the pressure of rubbing. The etching-figures are triangular in outline (fig. 6). Their orientation is unaffected by the direction of rubbing, depending wholly on the

¹ 'The Microscopic Examination of Opaque Minerals' *Economic Geology*, vol. i (1906) p. 751.

Fig. 7.—*Crystal of chalcopyrite (with scratched surface), enveloped by blende (dark) and galena (white): Nenthead Mine, Allendale. (Reflected light: $\times 200$.)*

Fig. 8.—*Crystal of chalcopyrite enveloped by galena: Leadhills Mine, Lanarkshire. (Reflected light: $\times 200$.)*

position of the plane of the specimen with respect to the crystal symmetry. The orientation of different groups of figures on a surface thus indicates the different crystal individuals in the specimen. The figures develop best in cubical galena. Banded or 'steel-grained' ores frequently do not etch without the use of reagents. The blende polishes with a rougher surface, more or less pitted, and grey to brown in colour, while, owing to its greater hardness, it stands up in slight relief above the galena. It does not etch with polishing, and its borders in contact with galena are

Fig. 9.—*Blende, with rough-pitted surface, enclosed in galena : Halkyn Mine, Flintshire. (Reflected light : $\times 200$.)*

frequently rounded or corroded. The chalcopyrite has a rougher surface and a bright yellow colour. It generally shows good crystal outlines, and, like blende, polishes in relief, an effect easily produced by finishing the specimen on parchment or on fairly thick broadcloth.

Examination of a number of specimens showed that chalcopyrite generally occurs well crystallized and wrapped round by galena or blende (figs. 7 & 8, p. 316). The blende is also generally enclosed in galena (fig. 9). These relations are characteristic, not only of typical British ores, but also of ores from some New South Wales and Queensland localities. The general order of deposition of the

Fig. 10.—*Strings of native silver in galena, following the cleavage planes of the galena crystals: Nentsbury Mine, Alston.*
(Reflected light: $\times 200$.)

Fig. 11.—*Strings of native silver in galena: Fordale Mine, Isle of Man.* (Reflected light: $\times 400$.)

sulphides, then, has been: chalcopryite, blende, galena. The distinct crystallization of chalcopryite suggests that some time elapsed between the arrival of this ore and of the other two, which are more intimately related and sometimes intergrown. Venules of galena penetrating blende are commonly seen in ore from Tre-castell, Conway. Specimens from veins on Carrock Fell exhibit crystals of chalcopryite enclosed in and wrapped round by galena. Specimens from the Coniston copper-mine show chalcopryite embedded in quartz, while blende occurs deposited on both chalcopryite and quartz, and finally arsenopryite occurs as groups of crystals deposited on cavities in the blende. The 'bluestone' or granular lead-zinc ore of Parys Mountain (Anglesey) and of Avoca (Wicklow) consists of an intergrowth of galena and blende enclosing earlier crystals of chalcopryite. The general relations of the chief sulphides appear to be fairly well established by these observations. It should be noted that, while galena is generally later than blende in primary ore, the relations may be reversed where the ore has undergone secondary alteration. Thus, some specimens from superficial parts of the Nenthead mine show galena traversed by blende filling irregular cracks and corrosion-cavities.

The silver-content of galena was also investigated by observation of polished ores. Specimens of galena taken from deep levels, unaffected by secondary alteration, showed no silver or silver-compound in any case, even under the highest powers. The galena showed no heterogeneity on etching with various reagents, and the cleavage-planes were not occupied by any extraneous ore. It therefore appears that the silver in these ores exists either in an excessively fine state of dissemination or as a sulphide in intimate isomorphous combination with the galena, a combination which would not be resolved by etching. Specimens of argentiferous galena taken from higher levels, within reach of underground waters, however, showed in several cases strings of greyish-white native silver, running along cleavage-cracks in the galena. The silver occurs generally in straight threads intersecting one another along the cleavage-planes (figs. 10 & 11, p. 318), and stands up in slight relief above the surrounding galena. A similar occurrence, it may be noted, has been recorded by T. L. Phipson in galena from the Phoenix Mine (Cornwall).¹ There is little doubt that this development of native silver is the result of secondary concentration by descending surface-waters, the silver being taken into solution during oxidation of the galena near the surface, and redeposited in the ore at lower levels. These observations appear to have some bearing on ore-dressing problems. Thus, the occurrence of native silver in secondary ore would explain the partial removal of the silver by amalgamation in some experiments of M. Roswag,² and would also account for the notable loss of silver in the dressing of many ores, the fine silver going off in the slimes.³ On the other

¹ C. R. Acad. Sci. Paris, vol. lxxviii (1874) p. 563.

² L. de Launay, 'L'Argent' Paris, 1896, p. 47.

³ W. F. A. Thomae, 'The Zeeban & Dundas Silver-Field, Tasmania' Trans. Inst. Min. & Met. vol. iv (1895-96) p. 60.

hand, where no silver was removed by amalgamation in Roswag's experiments, and where ore-dressing does not affect the silver-value of the ore, it is probable that the silver exists in its primary state of combination with the galena.

In conclusion, the general order of deposition of the vein-minerals, exclusive of calcite and quartz, may be stated as follows:—

1. Chalcopyrite.
2. Fluorspar.
3. Blende. } Barytes.
4. Galena. }
5. Pyrite and arsenopyrite.

It may be mentioned, for comparison, that a common order of deposition in the Upper Mississippi district has been: blende, galena, marcasite.¹

These conclusions are generally supported by the vertical distribution of ore in the veins. Chalcopyrite generally occurs in the deeper parts of the veins, with galena above, as at Ecton in Staffordshire.² Similarly, in the Alston Moor district, chalcopyrite is chiefly found in the 'Copper Hazles' between the Upper Scar and Tynebottom Limestones, which are on a much lower horizon than the lead and zinc ores of the Great Limestone and adjoining strata. Blende replaces galena in the deeper levels of several British mines, as is also the case at Freiberg below 1600 feet.³ A similar vertical succession has been recorded in the Castle Mountain and Elkhorn districts (Montana).⁴ The silver-content of galena becomes distinctly poorer in the deep levels of Foxdale, Leadhills, and other mines. This is in agreement with the observations of A. W. Stelzner and F. Kolbeck at Freiberg,⁵ and of Zirkler in the Upper Harz.⁶ Finally, fluorspar is chiefly confined to the upper horizons of the veins. This has been pointed out by Mr. C. B. Wedd in North Derbyshire,⁷ and the same phenomenon is seen in the Weardale and Alston Moor districts, where it is confined to the upper 300 feet of the metalliferous strata of the Carboniferous Limestone Series. This feature of the occurrence of fluorspar, which is apparently at variance with the fact that fluorspar is one of the earlier minerals deposited, is probably due to the instability of the mineral at high temperatures, since it is decomposed by superheated steam,⁸ and could not therefore exist at greater depths.

¹ C. R. Van Hise, 'A Treatise on Metamorphism' Monogr. xlvii, U.S. Geol. Surv. 1904, p. 1145.

² 'Geology of North Derbyshire' Mem. Geol. Surv. 2nd ed. (1887) p. 158.

³ R. Beck, 'The Nature of Ore-Deposits' (transl. W. H. Weed) New York, 1905, p. 362.

⁴ W. H. Weed & L. V. Pirsson, 'Geology of the Castle Mountain Mining District, Montana' Bull. U.S. Geol. Surv. No. 139, 1896; W. H. Weed, 'Geology & Ore-Deposits of the Elkhorn Mining District, Jefferson Co., Montana' 22nd Ann. Rep. U.S. Geol. Surv. pt. ii (1900-01) p. 503.

⁵ R. Beck, *op. supra cit.* p. 362.

⁶ 'Ueber die Ganguehltnisse der Grube Bergmannstrost bei Clausthal' 'Glckauf' Essen, 1897, p. 84.

⁷ 'The Fluorspar Deposits of Derbyshire' Trans. Inst. Min. Eng. vol. xxxv (1908) pp. 517-21.

⁸ *Ibid.* p. 525; also Henry Watts, 'Dictionary of Chemistry' London. vol. i (1863) p. 718.

In general, then, the vertical succession of ores in the veins is in agreement with their paragenetic relations determined above, relations which are likewise supported by the relative solubilities of the sulphides as determined by Prof. C. Dœlter and G. A. Binder.¹

VI. INFLUENCE OF THE COUNTRY-ROCK ON ORE-DEPOSITION.

The effect of different strata on the distribution of ore in the veins is strikingly shown in many districts. Each area, however, has its own features, determined by local circumstances, and what may be the general rule in one district, sometimes fails in its application to another district. It must be pointed out that enrichments at vein-intersections, accompanied by vertical or pitching shoots of ore, are frequent. These have not been specially investigated in this work, as, owing to the inaccessibility of so many of the old mines and workings, there are not sufficient opportunities to make extended observations. The general facts and principles governing the effect of the country-rock are here summarized, followed by an account of some experiments dealing with the chemical aspect of the problem.

Veins in the older Palæozoic slates and associated rocks show similar features throughout. Where, as is generally the case, strata of different character succeed one another vertically, the relative abundance of ore is dependent on the character of the fissure, and this, in turn, has been determined by the physical properties of the different strata which it intersects. At the Leadhills, the fissures are well defined and the ore good in the grit-beds of the Glenkiln-Hartfell Series, while impoverishment occurs when the fissures pinch or scatter in the associated shale-beds. The same relation holds in the Shelve district of Shropshire, where, by the alternation of slates and shales, there have been formed typical ore-horizons in the slates, separated by unproductive stretches in the shales,² a condition analogous to that described by Mr. C. W. Purington from San Juan (Colorado).³ Similar features occur in the Isle of Man⁴; while in Cardiganshire, the softer shale-beds, the 'metalliferous slates' of Walter Keeping,⁵ are more favourable strata than the hard and resistant grits.⁶ In the Lake district the fissures in the firm Borrowdale ash-beds, as at Greenside and Coniston, are more regular, and the ore more evenly distributed, than in the softer Skiddaw Slates, where, as at Thornthwaite and Threlkeld, the veins are irregular and patchy. In all these and similar cases the essential factor has been the nature of the fissure or circulation-channel, which is best defined in those strata that admit of the cleanest fissuring. The effect is a relative one:

¹ Tschermak's *Min. Petrol. Mitth.* n. s. vol. xi (1890) p. 319, & vol. xii (1891) p. 332.

² D. C. Davies, *'Metalliferous Minerals & Mining'* London, 1901, p. 222.

³ *'Economic Geology'* vol. i (1906) p. 129.

⁴ G. W. Lamplugh, *'Geology of the Isle of Man'* Mem. Geol. Surv. 1903, p. 491.

⁵ *Quart. Journ. Geol. Soc.* vol. xxxvii (1881) p. 141.

⁶ W. W. Smyth, Mem. Geol. Surv. vol. ii. pt. 2 (1848) p. 655.

for, while resistant beds may be most favourable in one district, the fissuring may be concentrated in the softer beds in another area. The influence of the country-rock has been due, in these cases, to its physical character, not to its chemical composition.

In limestone areas the effects are more complex, since they depend on both physical and chemical characters. The influence of the former is well seen in the pinching and dissipation of the fissures in the soft shales of Flintshire and North Derbyshire, and likewise in the hard igneous rocks of Derbyshire and Northumberland. The most favourable beds for fissuring have been the limestones and cherts, beds intermediate in strength between the shales and the igneous rocks. The effect of porosity is also well illustrated, as both the impervious shales and igneous rocks have impeded circulation, the ores being concentrated in the intervening horizons of porous calcareous beds. The chemical influence of the rocks has been important, as seen in the concentration of ore in the calcareous and dolomitic beds. These effects are discussed in connexion with the subjoined experimental results.

Deposition of metals from solution.—In order to obtain information concerning ore-deposition in the presence of different rocks, a series of tests was carried out to compare the quantities of lead and zinc deposited from solutions of their salts by various solid materials. The solutions used were lead nitrate and zinc sulphate of corresponding strength. The solid materials were as follows:—

1. Washed kaolin.
2. Calcareous grit, Leadhills. ($\text{CaO}=10.5$ per cent.)
3. Cherty limestone, Halkyn. ($\text{CaCO}_3=70.45$; $\text{SiO}_2=20.25$ per cent.)
4. Shell limestone, Alston. ($\text{CaCO}_3=90.50$ per cent.; Organic matter= 6.60 .)
5. Magnesian limestone. ($\text{MgCO}_3=36$ per cent.)
6. Crystalline dolomite.
7. Crystalline calcite.
8. 'Curly' shale, Broxburn. (Hydrocarbon= 22.85 ; Fixed carbon= 4.43 ; ash= 71.25 per cent.)
9. Burnt shale, Broxburn. ($\text{C}=5.38$; $\text{SiO}_2=56.00$; $\text{Al}_2\text{O}_3=31.20$; $\text{Fe}_2\text{O}_3=2.84$; $\text{SO}_3=5.06$ per cent.)
10. Coke, Broxburn. ($\text{C}=95$ per cent.)
11. Solid paraffin, Broxburn. (Heavy hydrocarbons.)

The materials were ground to a uniform degree of fineness, and amounts of 10 grams were placed in stoppered jars with 50 cubic centimetres of the solutions. The jars were left for 4 or 5 days at ordinary room-temperatures, with periodical shaking. The solutions, which had been previously standardized, were then filtered off and analysed, to determine the loss of metals in each case. The exact degree of fineness of the powder beyond a certain point makes little difference to the result, provided the solid presents a sufficient surface to the solution to enable it to exert the maximum effect. Again, prolonged contact does not result in corresponding effect, most of the deposition taking place during the first and second days. The percentage results of the tests are recorded in the following table:—

Solution.	Extraction of metal by:—										
	1. Kaolin.	2. Calcareous grit.	3. Cherty limestone.	4. Shell limestone.	5. Magnesian limestone.	6. Dolomite.	7. Calcite.	8. 'Curly' shale.	9. Burnt shale.	10. Coke.	11. Paraffin.
Lead (Nitrate) ...	24.50 ⁰ / ₀	70.85	91.55	92.64	70.21	71.34	90.88	42.50	44.45	40.16	39.38
Zinc (Sulphate) ...	9.25	52.46	85.65	82.57	50.89	54.31	83.29	22.37	21.49	24.53	25.26

It will be seen, first, that lead is deposited more freely, in every case, than zinc. The chemical influence of the rock is evidently more important in the case of lead, a conclusion which is supported by microscopic and field-observations.

With regard to the influence of the different substances, it appears that the silicate, kaolin, is the least active of all, while the carbonates are the most active. In the case of all the carbonates (Nos. 2 to 7), thick deposits of lead and zinc carbonates were formed in the bottom of the jars, binding the powders into a firm cement, while much lime had gone into solution. In these cases the deposition was effected by replacement of the rock-material by the metal. At the same time, it is to be observed that lime is much more effective than magnesia in these laboratory tests, an effect probably due to its greater solubility during replacement. In the veins, on the other hand, dolomitic limestones are the more favourable beds as a rule, especially for the deposition of secondary calamine. This has been ascribed to the greater porosity of the dolomitic rock.¹ The discordance between the experimental results and the facts of observation in the field is probably due to the elimination, in the former case, of the physical element of porosity by fine grinding. Further, the much longer time-factor and the more dilute solutions in nature would greatly modify the results.

Turning to the carbonaceous substances (Nos. 8 to 11), it is seen that the extraction of metals by these is very much lower than by the carbonates. In considering this fact, it must be borne in mind that time, concentration, temperature, and composition of solutions were not comparable with the conditions which existed during ore-deposition. The variation of these factors makes it very difficult to apply the experimental results in explanation of natural phenomena. In particular the solutions in nature were alkaline carbonates and sulphides, whereas those here used were acid sulphates and carbonates. The lower influence of the organic matter as here shown is probably due to its more refractory nature, which rendered it less amenable to replacement. The replacement of calcareous substances, in short, is more effective under the conditions of these experiments than the reducing influence of organic matter on the oxidized salts of the metals. In the case of vein-solutions containing metallic sulphides dissolved in alkaline sulphides, however, the influence of organic matter was probably more important. At the same time, it is probable that organic

¹ H. F. Bain, 'Lead & Zinc Deposits of the Ozark Region' 22nd Ann. Rep. U.S. Geol. Surv. (1901) pt. ii, p. 128.

matter is a less active precipitant of lead and zinc than of the gold and silver, which are extremely sensitive to its influence, as shown by the experiments of Mr. T. A. Rickard,¹ and emphasized in an important paper by Dr. W. P. Jenney.² Further, the influence of different materials must vary greatly according to the metals carried in solution. In this connexion may be mentioned a striking case of selective deposition recorded from Ku Shau Tzu (Mongolia) by J. A. Church.³ Here the veins carry galena in the limestones, and native silver and tetrahedrite in the overlying shales. In general, the influence of organic matter seems to be most marked in the case of those metals the compounds of which are least stable; while it is less active in the presence of those basic metals which form more stable compounds.

The form in which the metals were deposited was not examined in the case of the silicate and the shales. Mr. E. C. Sullivan, in a long series of experiments on the deposition of various metals by natural silicates,⁴ has shown that the principle of adsorption, advocated by Dr. E. Kohler,⁵ does not generally apply, and that, in each instance, an equivalent quantity of base from the silicate passes into solution, in exchange for the metal deposited. Even with the most refractory silicates, this exchange or replacement of bases was found to take place, while it was also observed that the small quantities of metals deposited went into combination as silicates, an exact parallel with the formation of the carbonates in the above-described experiments. Ore-deposition thus resolves itself, in all cases, into a process of osmosis, there being no simple precipitation of metals without an exchange. This has been previously maintained on theoretical grounds by H. P. Gillette.⁶

VII. SECONDARY ALTERATION.

The greatest depths to which mining extends in the British lead and zinc districts are at Foxdale (2010 feet) and at Laxey (1800 feet), in the Isle of Man. At these depths, the ore is becoming poorer, and it is probable that the limit of ore-deposition does not greatly exceed 2500 feet beneath the surface in any of the districts considered. This range is comparable to that of other well-known lead and zinc fields, such as Freiberg (2134 feet), the Upper Harz (2788 feet), Linares (2000 feet), and Eureka, Nevada (3000 feet). Since the formation of the veins, great denudation, amounting to an average of 2000 feet vertical, has taken place. Thus it appears that nearly one-half of the original height of the veins has been shorn off by denudation.

Accompanying this denudation there has been much secondary

¹ 'The Enterprise Mine, Rico, Colorado' Trans. Amer. Inst. Min. Eng. vol. xxvi (1896-97) p. 978.

² 'The Chemistry of Ore-Deposition' *Ibid.* vol. xxxiii (1903) p. 445.

³ *Ibid.* vol. xxxiii (1903) p. 1065.

⁴ 'Interaction between Minerals & Water-Solutions' Bull. U.S. Geol. Surv. No. 312, 1907.

⁵ 'Adsorptionsprozesse als Faktoren der Lagerstättenbildung & Lithogenesis' Zeitschr. f. prakt. Geol. vol. xi (1903) p. 49.

⁶ 'Osmosis as a Factor in Ore-Formation' Trans. Amer. Inst. Min. Eng. vol. xxxiv (1904) p. 710.

alteration and enrichment of the upper parts of the veins, expressed in the formation of a superficial zone of oxidation, succeeded by a zone of cementation, which finally passes down into the zone of unaltered ores. The secondary changes which have taken place indicate that the chemical processes of solution and cementation have proceeded more rapidly than the physical processes of denudation.

In the zone of oxidation, above the permanent ground water-level, secondary oxidized compounds are abundant, and have received considerable notice, especially at the Leadhills and at Caldbeck Fells. In the cementation-zone beneath, Prof. C. R. Van Hise's conception of a second concentration by descending waters, as distinguished from the first concentration by ascending waters,¹ is well illustrated in the limestone districts. The characteristic solution-cavities, that is, 'pipes' and 'flats,' in limestone are clearly the work of descending waters, and they have been more or less filled with ores and gangue-minerals by the same agency. The flats in the Flintshire area frequently contain masses of galena embedded in loose sand derived from the disintegration of calcareous sandstone, while pipes are often similarly filled with more or less detrital matter. In the Halkyn vein, at a depth of 600 feet, a large cavity over 20 feet in width and 60 feet high has been dissolved out along the vein-fissure by underground waters at a point of vein-intersection, with complete removal of both ores and gangue. The depth of effect of the waters is similarly indicated by the remarkable occurrence, in some Flintshire veins, of tree-trunks to a depth of 600 feet.² Sulphides have been abundantly redeposited below the ground water-level, and the many crystallizations of galena and blende in vughs and cavities are largely of secondary origin; while fluorspar has probably also been re-arranged at the same time. The depth to which secondary processes have extended varies between 600 and 1000 feet, according to the permeability and extent of fissuring of the rocks. That much of this work was accomplished before the Glacial Period is evident from the occurrence, in some districts, of pre-Glacial clays containing galena and cerussite, which fill hollows and pipes in the rock. The 'gravel-ore' of Talargoch and other parts of Flintshire,³ containing waterworn fragments of galena and earthy cerussite in a matrix of pre-Glacial clay and sand, is a further remnant of the earlier denudation processes.

One of the most important effects of descending waters has been the enrichment of galena by silver in the upper horizons. The appearance of native silver in the more argentiferous galena, already described, is the result of secondary concentration. At Hilderston, in Linlithgowshire, niccolite in the veins was argentiferous to a depth of 70 feet, below which it quickly became

¹ C. R. Van Hise, 'A Treatise on Metamorphism' Monogr. xlvii, U.S. Geol. Surv. 1904, pp. 1144-58.

² A. Strahan, 'Geology of Flint, Mold, & Ruthin' Mem. Geol. Surv. 1890, pp. 178, 190.

³ A. Strahan, 'Geology of Rhyl, Abergelle, & Colwyn' Mem. Geol. Surv. 1885, p. 47.

impoverished.¹ Another occurrence which is probably of secondary origin, is that of the plumosite and argentiferous tetrahedrite at Foxdale, which were found in vughy and cellular portions of the lode at depths of 600 feet,² and have not been met with in the deeper workings.

An equally important secondary process has been the depletion of blende from the upper parts of the veins by conversion into soluble sulphate, and its subsequent deposition as calamine by the replacement of limestone or dolomite. Calamine has been a common ore in Flintshire veins to a depth of 200 feet, while it has been the chief zinc-ore mined in North Derbyshire. The calamine-deposits of the Mendip Hills in Somerset,³ and of the Silver-mines district in Tipperary,⁴ have been formed by the removal of the blende from the adjacent lead-veins, and the deposition of calamine by replacement of the dolomite beds in which the deposits occur. They are analogous to the calamine deposits of Upper Silesia, South-Western New Mexico, and Virginia.

VIII. SUMMARY.

The natural history of the ores in the districts here discussed may now be summarized.

The fluorine and heavy metals of the ores have been derived from a deep-seated source, probably in the first place by marginal segregation in underlying magmas. They were carried upwards chiefly by 'juvenile' waters emanating from these magmas, fluorine being an important constituent in the deeper zones. In the upper horizons of limestone districts, the underground circulation of meteoric waters has had an important effect on the distribution and deposition of the ores in the veins. The vein-solutions carried alkaline sulphides, which held the metals in solution as sulphides, and also alkaline and earthy carbonates. These latter compounds have effected sericitization and carbonatization in the adjoining country-rock, except in the case of limestones, where silicification and dolomitization took place near the vein-walls. The filling of spaces rather than replacement of rock has been the chief feature in the deposition of the ores, but the process of deposition has itself involved interchange of constituents between rock and solution, as expressed in the chemical alteration of the wall-rocks. The calcium of fluorspar has been very largely derived from the adjoining rocks. Of the vein-minerals, chalcopyrite was first deposited, followed by fluorspar, blende, galena, and pyrite in that order. Ore-deposition has persisted over a maximum vertical range of about 5000 feet, chalcopyrite and blende being characteristic of the lower horizons, galena and fluorspar of the upper. The country-rock has influenced ore-deposition, first by its physical character

¹ M. F. Heddle, 'Mineralogy of Scotland' Edinburgh, vol. i (1901) pp. 10-11.

² W. W. Smyth, Trans. Roy. Geol. Soc. Cornwall, vol. x (1887) p. 82.

³ H. B. Woodward, 'Geology of East Somerset & the Bristol Coalfields,' Mem. Geol. Surv. 1876, pp. 167 *et seqq.*

⁴ Explan. of Sheet 134, Mem. Geol. Surv. Ireland, 1861, p. 31.

and porosity, and secondly by its chemical composition: limestones and dolomites being most favourable for the deposition of lead and zinc ores. Subsequent denudation, to the extent of nearly a half of the original height of the veins, has been accompanied by much secondary alteration, the chief secondary processes being the enrichment of silver and the depletion of blende in the upper parts of the veins, and the formation of metasomatic deposits of calamine. These secondary processes have been effective to depths of over 600 feet.

In connexion with these researches on British ore-deposits, I wish to express my warmest thanks to Prof. R. A. S. Redmayne, Chief Inspector of Mines, to Dr. John Horne, and to the managers of the different mines visited, for opportunities of doing field-work; and to Prof. W. W. Watts for his advice and criticism in the laboratory and in the preparation of the results.

DISCUSSION.

Dr. D. MAWSON remarked that the paper specially interested him, as he had just completed a detailed memoir dealing with the genesis of the Broken Hill Lode. The importance of this latter was witnessed by the fact that within the last twenty-five years, ore to the value of £60,000,000 had been won from it.

In the more important cases mentioned in the paper just read, the speaker was glad to hear that the Author regarded the genesis of the ore as arising from deep-seated sources. His (the speaker's) experience was confirmatory of the fact that the principal sulphidic lead-zinc ores of the world were primary depositions along lines of weakness, and originated from ascending, usually thermal, mineralized waters. The Broken Hill Lode was a case in point, in which he regarded the ore as an ultimate separation-product from a bathylitic igneous intrusion, and in this manner was of the nature of a pegmatite. The genetic connexion between pegmatites and certain ore-deposits had recently been firmly established, and to it special prominence had been given by Mr. Spurr.

Dr. CULLIS congratulated the Author, and was inclined to support the contention that, while the minerals of those British lead-zinc lodes which are enclosed in limestone might possibly have been derived from the country rock, the contents of lodes in killas and other sedimentary rocks were of a more deep-seated origin, and probably originated from some underlying igneous source. The rapid diminution and disappearance of the lode-minerals in the surrounding country with departure from the lode, referred to by the Author, seemed to point to this conclusion; so also did the nature of the veinstones characteristic of lead-zinc veins—calcite, dolomite, quartz, fluorspar, and barytes. The first three of these could hardly be claimed to favour one of the two suggested modes of origin more than the other; but the last two, in view of the frequency of fluorine in the emanations of deep-seated igneous masses, and of barium in the lime-bearing feldspars of igneous rocks, were strongly suggestive of an igneous origin. In claiming a deep-seated origin

for the contents of these lodes, the Author would encounter certain difficulties, such as the fact that lead-zinc lodes are so very much more common in sedimentary than igneous rocks, and the further fact, that the lode-walls in such cases practically never show signs of any characteristic alteration.

Prof. W. W. WATTS congratulated the Author on the outcome of a large amount of work in the field and in the laboratory. So far as his own experience went, he had been unable to establish the presence of barium in feldspars in an area containing many veins of barytes.

The PRESIDENT (Prof. W. J. SOLLAS) expressed his satisfaction at the advocacy of what seemed to him the common-sense view of lode-deposits. He did not think that the theory of lateral secretion had ever taken root in British geology, and the observations of the Author (so far as they went) were opposed to it. The order of deposition of minerals was a difficult subject, and afforded room for much subjective determination. In the Carboniferous Limestone of the North of England it had been supposed that some lodes were filled in by descending solutions. This was not impossible, if lakes supplied by hot springs had extended over the limestone. Barytes was associated with galena in lodes traversing killas, and the probability was that both barium and lead had been supplied by the same magma.

The AUTHOR thanked the speakers, and in reply said that the lead and zinc ores of the Mississippi and Missouri districts were admitted by many workers to have been concentrated from a disseminated condition: it seemed advisable, therefore, to examine carefully any limestone district characterized by lead ores with a low silver-content. In regard to the order of deposition of the sulphides, his experience had always been that the chalcopyrite occurred in well-formed crystals enclosed in and wrapped round by galena or blende. This was the case in ores from Conway, Coniston, and Wicklow, where the 'bluestone' found with the pyritic ores enclosed occasional crystals of chalcopyrite. Ores from other parts of the world showed the same relations, including galena- and blende-bearing specimens from the pyritic masses of Southern Spain. He had not in this paper considered the possible application of the hypothesis of deposition of the ores *per descensum*.

He agreed with Dr. Cullis that fluorine indicated a deep-seated origin, at least in the districts studied; and with another speaker that it was frequently difficult to apply the results of artificial laboratory experiments in explanation of the natural phenomena.

He was much interested in Dr. Mawson's observations on Broken Hill. He had lately examined some Broken Hill ores by metallographic methods, which indicated that the garnet and rhodonite had been more or less granulated and re-cemented by later galena and blende. This agreed with the observations of Prof. R. Beck: and the deposition of the sulphides at Broken Hill appeared to be the last of the complex series of disturbances which had affected that area.