

*Reconstitution processes in shales, slates, and phyllites.**(With Plate VI.)*

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*1. Introduction.*

IT is the author's good fortune to collaborate with Dr. J. W. Evans in describing the rock specimens which he collected on the expedition to Caupolican in Bolivia during 1901-2.<sup>1</sup> These specimens contain a very large proportion of shales, slates, and phyllites, and in their investigation certain petrographic methods devised for a detailed study of the slates of North Wales, Devon, and Skiddaw were followed. The present paper is intended primarily to describe these methods as applied particularly to the Bolivian rocks and to a Skiddaw slate facies which, for purposes of comparison and contrast, is of special interest. It is not suggested that between groups of rocks from places so widely separated as Bolivia and Skiddaw close correlation is possible; the products of the reconstitution processes which the two groups record differ considerably in detail; but as providing data for the study of the mechanism of these processes the two groups can be conveniently examined together.

*2. Petrological description.*

The Bolivian specimens represent shales, slates, and phyllites found *in situ* on the track from Sorata to Mapiri. They are characterized by mineral assemblages and structural features which are remarkably constant throughout a zone some twenty miles in width (measured across the strike, which is roughly NW.-SE.) on the eastern flank of

<sup>1</sup> J. W. Evans, Expedition to Caupolican, Bolivia. *Geographical Journal*, 1908, vol. 22, pp. 601-642, map.

the Cordillera Real. The beds are much disturbed and often strongly folded, and Dr. Evans considers it probable that specimens collected from localities many miles apart may represent one and the same stratum; he believes the beds to be of Devonian age, though they have yielded no identifiable fossils. To the south and south-east they appear to be represented among the 'contact' rocks about an extensive mass of granodiorite lying to the south of the Rio Tipuanhi.

The rocks as a whole have the following in common:

(a) A fine-textured groundmass consisting of secondary white mica, chlorite (with optical properties closely concordant with those of either penninite or clinocllore), and obscure chloritic matter. The definitely crystalline chlorite is intergrown with extremely thin lamellæ of white mica.

(b) Porphyroblasts of ilmenite, which may be partly or completely altered to limonite and rutile or to a granular, transparent, yellowish aggregate having little resemblance to the usual leucoxene and consisting mainly of titanite with a little rutile and, much more rarely, anatase (pl. VI, fig. 1).

(c) Clastic tourmaline, as anhedral, brown or blue-brown grains; and authigenic tourmaline, as extremely minute, euhedral, pale-green, or greenish-brown crystals (fig. 2).

(d) Rutile, as needles and stouter prisms, frequently twinned.

(e) Grains of zircon (common) and garnet (rare); clastic quartz is variable in amount; mineral grains suggesting much decomposed felspar are recognizable only in the more sandy and shaly types.

(f) Carbonaceous matter is present, usually in some abundance.

The various facies constitute a series recording different grades of reconstitution, and ranging from rocks which are little more than shales to highly indurated and cleaved slates and phyllites.

In the shale facies:

(a) The indefinitely crystalline chloritic matter is abundant.

(b) The definitely crystallized chlorite is scanty, and occurs as minute flakes and radial aggregates. Its optical properties correspond closely with those of penninite (negative) rather than clinocllore. Lamellæ of white mica in parallel intergrowth with the chlorite are common, but excessively thin.

(c) The white mica is of extremely fine grade; its flakes have a distinct greenish tinge, show absorption and pleochroism, and polarize in first-order greys and whites; yellow ( $270 \mu\mu$ ) is very rarely attained.

(d) The mica flakes occur mainly as suspensions in colourless trans-

parent blebs or 'flocks' which recall quartz grains but are distinguished from the latter by a lower birefringence, sectoring of interference-colours, and welding of grains: a sharp line of demarcation between 'flocks' in contact is rare. These 'flocks' are often somewhat clouded by suspensions of the fineness of flour: other inclusions are rutile needles and carbonaceous matter.

(e) Porphyroblasts of ilmenite are fairly common, but the alteration products of this mineral are characteristically limonite with associated rutile, rather than titanite.

(f) The carbonaceous matter is, in the main, amorphous.

The shale facies differs little, either in hand-specimens or in thin section, from the non-chiastolite-bearing black slate of Skiddaw except that in the latter ilmenite is wanting and rutile needles are scanty.

As the shale facies progresses towards slate and phyllite (fig. 5), the following features are to be noticed:

(a) The obscure chloritic matter decreases in amount or vanishes completely; while the definitely crystallized chlorite increases in amount, becomes of coarser grade, forming well-individualized lath-like crystals which have clinocllore rather than penninite affinities and show pleochroic haloes around inclusions of zircon. Intercalates of white mica become more conspicuous: strip sections of the mica lamellae, coextensive with the (001) traces of the chlorite flakes, may be ten to fifteen times longer than the average for the mica flakes in the groundmass.

(b) The white mica becomes of coarser grade, loses its greenish body-colour and pleochroism, and its interference-colours may attain the second order: that is, the mica which, in the shale type, resembles chlorite in some few respects, becomes more definitely muscovitic in the slates and phyllites.

(c) The transparent 'flocks' of the groundmass become more definitely individualized and tend to lose their dust-like suspensions though retaining their inclusions of rutile and carbon; in immediate contact with ilmenite crystals they are definitely quartz.

(d) The ilmenite porphyroblasts are abundant and show partial or complete alteration, typically to a honey-yellow, granular aggregate of titanite, with a little rutile and (rare) anatase. This mode of alteration is shown in fig. 1. The ilmenite is frequently bordered by a selvage composed of wedges of limpid-clear quartz and flakes of high-grade white mica, with occasional well-formed laths of chlorite and occasional granules of titanite and rutile; but carbon is almost completely absent from this selvage, however abundant it may be in the rest of the ground-

mass (fig. 3). It is a noteworthy fact that white mica in contact with altering ilmenite or its selvage is more definitely muscovitic and of coarser grade than the average for the groundmass proper.

(e) The carbonaceous matter is mainly graphitic.

### 3. *Chemical Investigation.*

This was directed to determining the approximate composition of the mica, the colourless transparent 'flocks', the chloritic matter, and the more definitely crystallized chlorite, in a typical shale and in a typical slate or phyllite, with the view of ascertaining whether analyses would yield data bearing upon the trend of the chemical changes involved in the reconstitution processes.

The Bolivian rocks selected for the purpose were a phyllite from the neighbourhood of Calvario and a shale type from near Ingenio. The Skiddaw slate, from Glenderaterra, shows, however, so close a general correspondence with the Ingenio rock, yet so sharp and significant a contrast as regards lime and titanium-dioxide content, that the Skiddaw slate, in preference to the Ingenio rock, has been selected for the purpose of the present paper.

(a) *Preparation of fractional extracts of the groundmass.*—Fractional extracts of the groundmass and samples of the mica with its associated silica 'flocks' were prepared for analysis:

In the case of the Calvario phyllite, a sample of the unweathered rock was fragmented; fragments showing any limonite staining were rejected; the remainder were finely powdered, and a partial separation of ilmenite was effected with the electromagnet. The ore fraction thus separated was found to contain also some titanite mainly adherent to the ilmenite, and a little rutile. Separation was made more complete by repeated decantation of the rock powder with water, but neither ilmenite nor its alteration products could be completely eliminated from the slime.

Two fluid extracts of the dried slime were prepared by heating equal weights in a Jena flask on a water-bath (1) with 20 per cent. hydrochloric acid for one hour; by this means an extract was obtained representing the more easily soluble chloritic substance; (2) with 50 per cent. acid for three hours; this extract represented the less soluble, more definitely crystallized chlorite. The stronger acid doubtless attacked ilmenite and titanite still present in very small amount, but minute grains of these minerals were found to be present in the residual slime. The difficulty of completely extracting gelatinized silica from the residue was a further disadvantage. On the other hand, the alumina,

iron oxides, magnesia, lime, and manganous oxide present in the chlorite substances were concentrated in the extracts, and a consideration of the molecular proportions of these oxides, irrespective of silica, yields some data as to the trend of the reconstitution processes.

(b) *Composite flakes*.—The almost black residual slime from operation (2) above was thoroughly washed and dried, and samples were mounted; they were found to consist of 'flocks' with abundant inclusions of mica (fig. 4), detached mica flakes, carbon, and heavy residues in very small quantity. Repeated decantation with water separated much but not all of the latter. Treatment with dilute hydrofluoric acid, in the cold, dissolved much of the silica from the 'flocks' and thus increased the amount of free mica. The slime, after neutralization with sodium carbonate solution, was collected by repeated passage through a separating funnel, freed from gelatinized silica by hot caustic soda solution, thoroughly washed with hot dilute hydrochloric acid, and finally with water. The slime was deemed to be free from gelatinized silica when samples failed to fix a stain of malachite-green. At this stage the dried slime was silvery dark grey.

(c) *Removal of free carbon*.—The carbon particles were removed by transferring the slime to a broad-bodied flask half full of water to which a few drops of amyl alcohol, paraffin, and sodium silicate had been added. Vigorous shaking of the flask produces a copious froth which floats off the carbon and is removed by rapid passage through the separating funnel. The slime freed from particles of carbon was air-dried, washed with benzole, then with hot dilute hydrochloric acid, hot dilute caustic soda solution, and finally with distilled water. At this stage the dried slime was silvery grey—nearly white.

(d) *Elutriation*.—Elutriation of the slime yielded a fine-grade fraction rich in free mica, and a coarse grade relatively richer in the composite 'flocks'; neither fraction proved to be wholly free from minute grains of titanite, rutile, and tourmaline. Both fractions contained comparatively large flakes of mica (suitable for optical examination) which could be abstracted from a microscope field by the aid of a moistened camel-hair brush.

The procedure adopted in the case of the Skiddaw slate was generally similar to the above, though the process was simplified by reason of the absence of ilmenite. The *composite flakes* have the appearance shown in fig. 4. Each flake consists of mica embedded in a transparent anisotropic substance, which polarizes sectorally in first-order greys and whites. 'Flocks' wholly composed of this substance are found to be made

up of optically distinct textural units which give undulose extinction. The substance is readily soluble in hydrofluoric acid, less easily soluble in caustic alkali. It is unattacked by hydrochloric acid, &c. When a molten bead of sodium carbonate supported on a platinum loop is dipped into a small pile of these 'flocks' effervescence is brisk and instantaneous. The substance appears to be silica with the optical properties of opaline or chalcedonic quartz.

The suspensions in the Calvario phyllite 'flocks' are: mica, graphite, and rutile, tourmaline being extremely rare; those in the Skiddaw slate 'flocks' are: mica, amorphous carbon, and rutile.

The mica is muscovitic in habit, though cleavage traces are only faintly discernible. It may be colourless or very pale green and faintly pleochroic in either rock. The interference-colours shown by the flakes from the Skiddaw slate are on the whole distinctly lower than those shown by the flakes from the Calvario phyllite. The value of  $2E$  is remarkably inconstant, even for flakes from the same rock and of the same grade size: it is below  $60^\circ$ , and often as low as  $50^\circ$ .

*Heavy residues* are not obtainable from the dried slimes by the use of heavy liquids. Those separated otherwise from the Calvario phyllite were: ilmenite, rutile, titanite, anatase (very rare), tourmaline (clastic and authigenic), zircon, pyrites, and garnet (rare); from the Skiddaw slate: pyrites, rutile, and authigenic tourmaline—all very scanty.

#### 4. Chemical Analyses: their interpretation.

##### (a) The chemical composition of the mica.

Analyses of the composite flakes gave the following results:

	I. Phyllite (Calvario).		II. Black slate (Skiddaw).		Computed comp. of Mica.		Theoretical Muscovite.
	Per cent.	Mol. Prop'ns.	Per cent.	Mol. Prop'ns.	I a.	II a.	
SiO <sub>2</sub>	65.81	1091.8	59.48	986.4	45.74	45.84	45.2
Al <sub>2</sub> O <sub>3</sub>	22.71	222.2	25.21	246.6	37.99	37.00	38.5
Fe <sub>2</sub> O <sub>3</sub>	0.82	2.0	0.37	2.31	0.54	0.54	—
FeO	0.18	2.5	0.15	2.08	0.30	0.23	—
MgO	0.31	7.68	0.18	4.46	0.51	0.26	—
CaO	0.25	4.45	1.80	33.89	—	2.64	—
Na <sub>2</sub> O	0.95	15.3	1.89	22.41	1.53	2.04	—
K <sub>2</sub> O	5.19	55.0	4.60	48.83	3.68	6.75	11.8
H <sub>2</sub> O(<110°)	0.05	—	0.29	—	—	—	—
H <sub>2</sub> O(>110°)	3.07	170.3	*6.60	—	4.63	4.69	4.5
TiO <sub>2</sub>	0.44	5.49	0.62	7.78	—	—	—
C	0.64	53.3	—	—	—	—	—
Total	99.92		100.69		99.97	99.99	100.0

\* Inclusive of carbon (amorphous).

Thus the titanite-rich phyllite yields flakes with a very low lime content, whereas the titanite-free slate yields flakes with a relatively high lime content.

In computing the mineral composition of the flakes :

(i) *For the phyllite (Calvario)*: Carbon is allotted to graphite; lime is allotted to titanite, and the balance of titanium dioxide to rutile; ferrous oxide and magnesia are combined in Tschermak's *M*-molecule ( $Mg_6Si_3O_{12}$ ) as a constituent of white mica; alumina, together with the small amount of ferric oxide, is combined with the alkalis and water, in proportions to satisfy Tschermak's *K*-molecule ( $H_2KAl_3Si_3O_{12}$ ); and the balance of silica is allotted to quartz.

(ii) *For the black slate (Skiddaw)*: Lime, together with ferrous oxide and magnesia, is allotted to the *M*-molecule; the titanium dioxide is allotted to rutile; the *K*-molecule is constituted as in the preceding case; and the balance of silica is allotted to quartz.

The percentage composition of the mica so computed is given under Ia and IIa of the foregoing table and shows that the Skiddaw mica is richer in *M*-molecule constituents (notably lime) than the Calvario mica, the ratio *K*-molecule : *M*-molecule being 16.6 : 1 and 88 : 1 respectively.

As a check upon the composition of the Calvario mica (computed from an analysis of flakes in the preparation of which hydrofluoric acid was used), a sample of flakes was prepared, avoiding the use of this acid, prolonged treatment with hot caustic soda solution being substituted; the composition of the mica was computed from the following analyses of this sample :

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	H <sub>2</sub> O
Per cent.	63.63	25.11	0.21	0.31	0.30	0.26	0.94	5.80	0.36	3.41
Mol. Prop'ns.	1055.2	245.6	1.31	4.31	7.44	4.63	15.16	61.57	4.49	189.2

This analysis is significant: the molecular concentration of lime is in excess of that of titanium dioxide; therefore the lime cannot be allotted wholly to traces of titanite. Moreover, some titanium dioxide must be allotted to rutile, hence a lime content, though extremely low, must be assumed for the mica. The percentage composition of the mica, as computed from this analysis, is as follows :

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O
45.75	38.13	0.32	0.47	0.45	trace	1.43	8.81	4.65

which agrees very closely with that previously obtained, and further shows that prolonged boiling with caustic soda does not enrich the mica molecule with soda.

*(b) Coarse-grade and fine-grade mica ; Chemical composition compared.*

To determine whether there is any appreciable difference in chemical composition between the coarser and the finer flakes of mica in one and the same rock, fractions relatively rich in coarser-grade flakes were prepared from both rocks. Traces of titanite could not, however, be wholly eliminated from the Calvario sample; and as the criteria rested mainly in the diad-oxide content (notably lime) the presence of titanite in this sample introduced at the outset a source of error, the magnitude of which might be great as compared with any small differences in composition demonstrable by analyses. But the Skiddaw sample contained no titanite, and this sample was analysed. The analysis is set down in column I below; the composition of the mica was then computed (column II); and in order that it may be compared with that of the average (column III), this composition is readjusted to a constant for alumina (column IV):

	I.	II.	III.	IV.
SiO <sub>2</sub> ...	59.71	46.21	45.84	44.73
Al <sub>2</sub> O <sub>3</sub> ...	27.00	38.20	37.00	37.00
Fe <sub>2</sub> O <sub>3</sub> ...	0.49	0.69	0.54	0.66
FeO ...	0.07	0.10	0.23	0.096
MgO ...	0.09	0.12	0.26	0.11
CaO ...	0.63	0.89	2.64	0.86
Na <sub>2</sub> O ...	1.38	1.95	2.04	1.88
K <sub>2</sub> O ...	4.89	6.92	6.75	6.69
H <sub>2</sub> O(<110°)	0.44	—	—	—
H <sub>2</sub> O(>110°)	4.96	4.91	4.69	4.75
Total ...	99.66	99.99	99.99	—

Comparing the figures given in columns III and IV, the molecular ratio of losses to gains is found to be as follows:

Losses.	:	Gains.
31.73(CaO) + 3.72(MgO) + 1.8(FeO)		0.75(Fe <sub>2</sub> O <sub>3</sub> )
2.57(Na <sub>2</sub> O) + 0.63(K <sub>2</sub> O)		3.32(H <sub>2</sub> O)
18.40(SiO <sub>2</sub> )		

The total loss of alkalis is due mainly to the loss of soda, and is almost exactly balanced by gain of water—adjustments which may be regarded as affecting the *K*-molecule. The main constituents lost are lime and silica; and if the diad-oxides be regarded as located in the *M*-molecule, their loss, totalling 37.25 molecules, should involve the break-down of this molecule with the consequent elimination of silica (*theoretically* 18.6 molecules). The actual loss revealed by analysis is

18.4 molecules. So close a concordance suggests that the evolution of coarse-grade mica from the fine-grade mica involves the purification of the latter by the elimination of *M*-molecule constituents.

(c) *The fractional extracts of the groundmass.*

The analyses, expressed directly in molecular proportions, are set out below :

	Calvario Phyllite.			Skiddaw Slate.		
	50% HCl extract.	20% HCl extract.	Diff.	50% HCl extract.	20% HCl extract.	Diff.
SiO <sub>2</sub> ...	4.08	8.54	{ Note 1 below	0.38	95.88	{ Note 1 below
Al <sub>2</sub> O <sub>3</sub> ...	98.38	10.05	88.30	167.18	100.47	66.71
Fe <sub>2</sub> O <sub>3</sub> ...	74.41	12.86	61.55	163.07	99.31	63.76
MgO ...	113.09	2.97	110.12	117.83	72.17	45.66
CaO ...	6.214	0.58	5.634	4.385	4.38	0.005
MnO ...	1.64	trace	1.64	2.28	2.28	0.27
Na <sub>2</sub> O ...	n. d.	1.11	—	n. d.	2.01	—
K <sub>2</sub> O ...	n. d.	0.74	—	n. d.	2.22	—
TiO <sub>2</sub> ...	0.66	nil	—	nil	nil	—

The following considerations bear on the interpretation of these analyses :

1. The low figure for silica in every case is accounted for by the early coagulation of colloidal silica and the retention of the greater portion of the silica gel by the undissolved residue. For this reason the percentage weight of rock extracted by each of the two acid solutions was not determined.

2. Though rutile needles are present in the Skiddaw rock, not a trace of titanium was detected in either of its extracts; rutile must therefore be regarded as virtually insoluble under the conditions of the experiment. Hence the titanium present in the more acid extract of the Calvario rock must be attributed to partial solution of ilmenite and titanite particles.

3. The relatively high figure for lime in the more acid extract of the Calvario rock, considered in relation to the almost complete absence of lime from the Calvario mica, must be due partly at least to the solution of titanite. On the other hand, the *concentration* of lime in the more acid extract of the Skiddaw rock is much lower than in the weaker extract—so much lower, in fact, that any appreciable ‘leaching’ of lime from sericite by the stronger acid must be ruled out. It follows, therefore, that the lime is concentrated specially in the more soluble chlorite matter rather than in the less soluble chlorite.

4. In the Skiddaw rock the molecular concentration of manganous oxide is 1 in 88 for the stronger extract, 1 in 200 for the weaker extract, and 1 in 653 in the 'difference'; and as the 'difference' figures must approximate more closely to the actual composition of the less soluble chlorite than do those for either of the extracts, it is inferred that manganese is concentrated mainly in the more obscure chloritic matter. In the Calvario phyllite it is apparently located mainly in the more definitely crystalline chlorite.

5. The less acid extracts reveal the presence of alkalis in the obscure chloritic matter.

6. The iron content was necessarily estimated as ferric oxide, though Dr. Harwood observed that much of it was still in the ferrous condition in solution. The actual proportion of ferrous to ferric oxide in each of the mineral fractions extracted would be extremely difficult to determine, even approximately, under the conditions. In such rocks, however, reconstitution processes involve the extensive reduction of ferric to ferrous oxide, especially in the presence of free carbon. For the 'average shale', the ratio  $\text{FeO} : \text{Fe}_2\text{O}_3$  is estimated by Leith and Mead<sup>1</sup> to be 2.48 : 4.07 (by weight); but both of the rocks under consideration are of somewhat higher grade than a shale, and it is safe to assume for them a considerably higher figure for ferrous iron. This figure should rise with degree of reconstitution, and should vary therefore for each of the extracts analysed. For the moment, however, Leith and Mead's estimate will be adopted; and omitting silica, titanium, and alkalis, the analyses of the extracts approximate to the following:

	Calvario Phyllite.			Skiddaw Slate.		
	50% HCl extract.	20% HCl extract.	Diff.	50% HCl extract.	20% HCl extract.	Diff.
$\text{Al}_2\text{O}_3$ ...	98.4	10.1	88.3	... 167.2	100.5	66.7
$\text{Fe}_2\text{O}_3$ ...	43.8	7.6	36.2	... 95.9	58.4	37.5
$\text{FeO}$ ...	61.3	10.6	50.7	... 134.3	81.8	52.5
$\text{MgO}$ ...	113.1	3.0	110.1	... 117.8	72.2	45.6
$\text{CaO}$ ...	6.21	0.58	5.63	... 4.385	4.38	0.005
$\text{MnO}$ ...	1.64	trace	1.64	... 2.28	2.01	0.27
Total Mols.	324.5	31.9	292.6	521.9	319.3	202.6

In the following table the letter *A* refers to the 20 per cent. HCl extract representing the more soluble chloritic matter; *B* refers to the 50 per cent. HCl extract representing a less soluble, more definitely

<sup>1</sup> C. K. Leith and W. J. Mead, *Metamorphic Geology*, 1915, p. 63.

crystalline fraction, and *C* refers to the 'difference', which approximates rather more closely than either of the extracts to the composition of the crystallized product actually present in the respective rocks.

Calvario Phyllite.			Skiddaw Slate.				
$\frac{\text{Mols. Al}_2\text{O}_3}{\text{Total Mols.}}$	$\frac{\text{Mols. R}_2\text{O}_3}{\text{Mols. RO}}$	$\frac{\text{Mols. MgO}}{\text{Total Mols.}}$	$\frac{\text{Mols. Al}_2\text{O}_3}{\text{Total Mols.}}$	$\frac{\text{Mols. R}_2\text{O}_3}{\text{Mols. RO}}$	$\frac{\text{Mols. MgO}}{\text{Total Mols.}}$		
(Calculated on the basis of the ratio $\text{Fe}_2\text{O}_3 : \text{FeO}$ initially assumed):							
<i>A</i> ...	1 : 3.15	1 : 0.80	1 : 10.63	...	1 : 3.17	1 : 1.01	1 : 4.42
<i>B</i> ...	1 : 3.29	1 : 1.28	1 : 2.87	...	1 : 3.12	1 : 0.98	1 : 4.43
<i>C</i> ...	1 : 3.31	1 : 1.35	1 : 2.66	...	1 : 3.03	1 : 0.94	1 : 4.44
(Assuming complete reduction of ferric oxide):							
<i>A</i> ...	1 : 2.91	—	1 : 13.16	...	1 : 2.76	—	1 : 5.23
<i>B</i> ...	1 : 2.74	—	1 : 3.25	...	1 : 2.69	—	1 : 5.24
<i>C</i> ...	1 : 2.72	—	1 : 2.98	...	1 : 2.60	—	1 : 5.26

Comparing the data for *A*, *B*, and *C* in order:

As reduction of ferric oxide becomes more complete, both the concentration of alumina and the proportion of  $\text{R}_2\text{O}_3$ -mols. to RO-mols. increase. The alkalis present in the indefinite chloritic matter ultimately combine with alumina to augment the mica content of the rock, and the alumina-concentration in the chloritic matter (*A*) tends to fall. The reduction of ferric oxide yields increment of ferrous oxide to the diad-oxide content of *A* and the  $\text{R}_2\text{O}_3$ -concentration tends to be still further reduced. Nevertheless, if more complete reduction of ferric oxide is assumed the concentration of both alumina and  $\text{R}_2\text{O}_3$ -molecules increases from *A* to *C*. The concentration of magnesia shows a marked increase in the case of the Calvario phyllite, but actually decreases in the case of the Skiddaw slate.

Thus the data for the Calvario phyllite indicate that, as reconstitution of the chloritic matter progresses, the crystallized product assimilates alumina in greater proportion than ferric oxide, and magnesia in greater proportion than ferrous oxide; the residual chloritic matter is progressively impoverished in magnesia and enriched in ferrous oxide. The trend of chemical change is thus consistent with the evolution of an orthochlorite (rather than chloritoid) along the line Serpentine → Amesite, and the porphyroblasts of ilmenite receive a probable explanation as a consequent product: the residual chloritic matter becomes a hydrous system promoting chemical reaction between ferrous oxide and finely divided titanium dioxide (i.e. rutile needles, present in abun-

dance), preliminary solution of the latter and diffusion towards ilmenite crystallization-foci being probable<sup>1</sup> (See fig. 6).

In the case of the Skiddaw slate: as reconstitution of the chloritic matter progresses, the crystallized product assimilates more alumina than ferric oxide and more ferrous oxide than magnesia. For this rock (as also for the Calvario phyllite) the variation in the ratio  $R_2O_3 : RO$  is consistent with evolution of an orthochlorite along the line Serpentine→Amesite, but the decreasing concentration of magnesia is a feature suggesting a chloritoid rather than chlorite. In this connexion it is of interest to note that a mineral present in some abundance in this slate is tentatively referred by Rastall<sup>2</sup> to otterelite.

The presence of authigenic tourmaline in both rocks may record the activity of volatile mineralizers derived from the acid intrusives and permeating strata beyond the outer limit of the observed aureole in each

<sup>1</sup> The data thus brought to bear upon the problem of the genesis of these ilmenite porphyroblasts, correlated with corresponding data obtained in an investigation of pyritous slates, particularly those from Penrhyn slate quarry, Carnarvonshire, suggest a somewhat similar mechanism for the genesis of porphyroblastic pyrites and epidote: when reconstitution-trend is in the direction of chlorite, the residual chloritic matter tends to become enriched in ferrous oxide; and if sulphates are also undergoing reduction to sulphides, porphyroblasts of pyrites may develop. Magnesia thus liberated would become an increment available for evolving chlorite. But lime is not markedly assimilable to chlorite, and like ferrous oxide it tends to be relegated to the residual chloritic matter; in the latter, a hydrous system, it may react with ferrous oxide and triad-oxides to form epidote.

In the case of the Calvario phyllite, titanite may conceivably develop in preference to ilmenite at some foci, and ilmenite constituted at a stage when the lime-concentration in the chloritic matter was low may become liable to alteration to titanite as the lime-concentration increases.

The wedges and prisms of quartz within the selvage of the ilmenite crystals described, and similar quartz structures about porphyroblasts of pyrites (e. g. in the Penrhyn slate), are in the main disposed normal to the crystal wall or matrix wall of the selvage: they recall the structures assumed by quartz crystals sessile on a cavity wall. A reduction of volume is achieved by the chemical combinations yielding porphyroblastic ores; tendencies towards a similar reduction of volume are operative around foci of re-crystallization in the groundmass and may continue to be operative after ores have separated. It is suggested that tension within the groundmass may partly detach the latter from the ores and tend to produce around them a cavity which is ultimately infilled with quartz. It is proposed to discuss this phenomenon more generally in a later paper.

<sup>2</sup> R. H. Rastall, The Skiddaw granite and its metamorphism. Quart. Journ. Geol. Soc., 1910, vol. 66, p. 126.

case. It has been identified in several Cornish and Devon slates, but not in the slates of Penrhyn, Carnarvonshire.

### *Summary.*

The microscopical study of shales, slates, and phyllites is assisted by comminuting the rock specimen and examining the particles after they have been cleansed of chloritic matter and freed from attached carbon. The study of the trend of reconstitution processes is also assisted by analyses of fractional extracts of the groundmass.

Hutchings<sup>1</sup> has shown that (a) re-crystallization begins at a very early stage in the consolidation of clay material: secondary mica may be present in abundance in a shale which is soft enough to be cut with a knife; (b) this primitive mica is essentially sericitic but impure—in the sense that it contains magnesia, lime, and ferrous and ferric oxides, which are alien to pure muscovite as represented by Tschermak's *K*-molecule, and that as reconstitution proceeds, the sericite sheds its impurities; (c) the development of sericite is accompanied by that of a chlorite-like substance, which is at first obscure and indefinitely crystallized; but in slates and phyllites chlorite is sharply separated from the mica, and the latter is definitely muscovitic.

The further observations which this paper records indicate that the trend of reconstitution in shales, slates, and phyllites is towards the establishment of a metastable ternary system of white mica, chlorite (or chloritoid), and quartz: it is essentially a process of molecular differentiation—into (a) monad-oxides, type  $R_2O$ , combined with alumina, silica, and water; (b) diad-oxides, type  $RO$ , combined with alumina, ferric oxide, silica, and water; and (c) free silica; accessory minerals such as rutile, ores, epidote, &c., being products which, in large measure, are consequent upon this essential differentiation. In the early stages, differentiation is imperfect; for example, appreciable quantities of magnesia, lime, &c., are temporarily accommodated in the micaceous mineral, and alkalis are to some extent absorbed by the obscure chloritic matter; but as reconstitution proceeds the mica tends to lose its magnesia, lime, &c., which thus supply increment to the chloritic substance; similarly, the latter loses its alkalis and some alumina, which thus supply increment to the mica. The alkali-content of the rock-mass exercises an early and a preferential claim upon the available

<sup>1</sup> W. M. Hutchings, *Geol. Mag.*, 1890, pp. 264, 316; 1891, p. 164; 1892, pp. 154, 218; 1894, pp. 36, 64; 1896, p. 309.

alumina; the identity of the mineral-species towards which reconstitution of the chloritic substance trends during any phase depends largely upon the ratios  $R_2O_3:RO$  and  $MgO:FeO$ . Both  $R_2O_3$  and  $RO$  are in part dependent upon the reduction of ferric to ferrous oxide.

In the particular rocks discussed in this paper the lime content is of special interest. In the Skiddaw slate the finer-grade mica is relatively rich in lime; but as the mica is re-crystallized, it sheds an appreciable proportion of this lime. In the Calvario phyllite the mica has a negligible lime content, though abundant titanite is present as an alteration product of ilmenite and the mica is especially coarse and muscovitic about the margins of altered ilmenite crystals; it is suggested that in this case also primitive mica on re-crystallization sheds its lime content and that this lime is fixed mainly in the titanite encrusting or partly replacing ilmenite.

#### EXPLANATION OF PLATE VI.

Photomicrographs of thin sections and drawings of isolated preparations from the phyllite of Calvario, Bolivia.

Fig. 1.—Porphyroblasts of ilmenite altering to titanite and rutile.  $\times 35-40$ . (p. 212.)

Fig. 2.—Authigenic tourmaline.  $\times 45$ . (p. 212.)

Fig. 3.—Ilmenite with selvage composed of prisms and wedges of quartz, with laths of white mica and chlorite.  $\times 84$  (an enlargement of the uppermost crystal in fig. 5). (p. 214.)

Fig. 4.—Composite flake, isolated from groundmass, composed of quartz and white mica with suspensions of rutile and graphite.  $\times 30$ . (p. 215.)

Fig. 5.—Ilmenite in a groundmass of quartz, white mica, chlorite, graphite, and a little pyrites.  $\times 10$ . (p. 213.)

Fig. 6.—Crystal of ilmenite in process of growth by diffusion of material along schistosity planes.  $\times 19$ . (p. 222.)

