Electrodialysis of mineral silicates: an experimental study of rock-weathering.

(With Plate XIII.)

By THA HLA, B.Sc. (Rangoon), B.Sc. (London), A.R.I.C., F.G.S.

Assistant Lecturer, Geology Department, University College, London.

[Read March 22, 1945.]

Introduction.

PALMER'S investigation of the chemical and mineralogical aspects of soil-forming processes was restricted to comparative chemical analyses of the weathered shells and the essentially unaltered cores of certain spheroidal basic boulders from Wahiawa in the Hawaiian Islands.[1]

The present writer describes an experimental approach to the general problem of rock-weathering on lines suggested by Dr. A. Brammall:[2]

(a) Electrodialysis of eight typical rock-forming mineral silicates, each of which was dialysed separately after having been ground to an impalpable powder and analysed in detail.

(b) Assessment of the effect of dialysis by comparing the composition of the unaltered mineral with that of the slime left in the mineral-chamber when dialysis was virtually at an end.

(c) X-ray and kathode-ray tests on three of these minerals and the corresponding slimes,[3] to ascertain whether colloidal end-products associated with, or coating, particles of unaltered mineral had integrated to form one or other of the specific 'crystalline colloids' identifiable in soils and clays.[4]

The eight minerals electrodialysed are named, and their chemical composition is given, in table I. As one of the main purposes of this experimental work is to direct attention to the character of the mineral change induced by electrodialysis, constitutional formulae corresponding to the analyses given in table I are set out in table II, and supplemented by partial analyses of the slimes collected (table III). The analytical data (tables I and III) were kindly placed at the writer's disposal by Dr. Brammall, who also selected the minerals to be treated and directed the course of the experiments.

[1] H. S. Palmer, Soil Sci., 1931, vol. 31, pp. 253–265.

[2] A. Brammall and J. G. C. Leech, Sci. Journ. Roy. Coll. Sci. London, 1943, vol. 13, pp. 46–58.

[3] For reasons directly due to war-time conditions, the number of minerals and slimes submitted for these tests had to be reduced to the bare minimum. X-ray test-work was carried out on only two minerals (orthoclase and hornblende) and the corresponding slimes. Kathode-ray tests could be done only on pargasite and the corresponding slime.

[4] S. B. Hendricks and W. H. Fry, Soil Sci., 1930, vol. 29, p. 457; W. P. Kelley, W. H. Dore, and S. M. Brown, ibid., 1931, vol. 31, p. 25; G. Nagelschmidt, A. D. Desai, and A. Muir, Journ. Agric. Sci., 1940, vol. 30, p. 663.

X-ray test-work was done by Mr. F. A. Bannister and Dr. Brian Mason, in the Mineral Department of the British Museum; electron-diffraction tests by Mr. W. G. H. Robins and his colleagues of the Chemical Technology Department, Imperial College, London.

Description of experimental work.

Each mineral, or carefully separated mineral aggregate, was ground in an agate mortar. A visual estimate made by aid of the microscope showed that 70–80% of the particles had a maximum diameter of 3 μ.
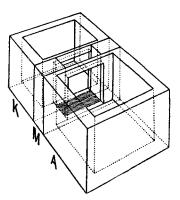

FIG. 1. The electrodialyser.

The electrodialyser used was designed and constructed by Dr. Henn Collins (of the Imperial College), who found 'perspex' preferable to frame-work materials used in earlier patterns devised by Mr. J. G. C. Leech. It consists of three cells or chambers, each built up of shaped 'perspex' slabs, which are held in position between two sheets of wood (not shown in fig. 1), clamped by bolts. The mineral-chamber (M) is separated from the anode-chamber (A) and the kathode-chamber (K) by cellophane. The shaded area represents the floor of the mineral-chamber (M). The cellophane sheet used is the grade '300 PT, un-coated'—obtainable directly from the manufacturers (British Cellophane Co., Bridgwater). It must be sluiced with distilled water for at least twenty minutes before use, in order to eliminate possible traces of sodium silicate.

The apparatus was set up in a dust-proof, reasonably air-tight chamber with a glass wall. The inside temperature of this chamber was kept constant at 28° C. by an appropriate thermostat. The dialyser was filled with distilled water, 50 c.c. in the mineral-chamber, and, in the two others, sufficient to maintain the same water-level in all three chambers. An accurately weighed amount of mineral-powder (about 1 gr.) was transferred to the mineral-chamber, into which CO_2-gas was continuously bubbled. This gas-current was brisk enough to keep the mineral-powder in a state of constant motion. Splash was prevented by a lid of 'perspex' fixed above the mineral-chamber. With the exception of a thermometer suspended in the anode-chamber, glass-ware formed no part of the apparatus. Coiled platinum wires formed the electrodes.

During electrolysis, certain kations, notably K^+, Na^+, Ca^{++}, Fe^{++}, and Mg^{++}, migrate from the mineral-chamber to the kathode; whereas the silicon-ion does not pass through the cellophane partition. A blank experiment established the fact that essentially the whole of the anodic products, comprising hydrated silica, alumina, and ferric oxide, remained with the residual material in the mineral-chamber.[1]

---

[1] Analysis of kathode-chamber products showed that a relatively small amount of aluminium did pass through the cellophane partition into the kathode-chamber.

TABLE I. Chemical analyses of fresh minerals.

	A. Olivine.	B. Augite.	C. Hornblende.	D. Pargasite.	E. Biotite.	F. Clinochlore.	G. Muscovite.	H. Orthoclase.
SiO_2	40·85	49·23	42·70	42·09	38·04	30·03	44·68	64·40
TiO_2	0·03	1·57	1·40	0·68	0·39	trace	0·70	0·01
Al_2O_3	0·74	5·68	10·25	13·60	15·77	18·07	31·80	19·41
Fe_2O_3	1·47	2·45	5·61	2·06	2·62	1·87	4·49	0·02
FeO	5·74	2·91	13·78	5·45	11·13	1·62	0·84	—
MnO	0·09	0·15	0·55	0·07	0·10	0·02	0·04	—
MgO	50·31	15·22	9·18	16·16	18·35	33·51	1·30	—
CaO	0·16	22·19	11·88	13·40	0·91	0·03	0·52	0·14
Na_2O	—	0·26	1·22	2·16	0·27	nil	0·79	2·30
K_2O	—	0·18	1·19	1·43	9·23	nil	10·48	13·26
P_2O_5	—	—	0·10	trace	0·33	trace	0·01	—
CO_2	—	—	0·06	0·30	nil	0·07	nil	—
S	—	—	0·05	—	—	—	—	—
BaO	—	—	0·01	0·01	0·15	nil	0·23	—
SrO	—	—	nil	nil	0·01	nil	0·04	—
Li_2O	—	—	—	—	trace	—	nil	—
Cr_2O_3	—	—	—	—	0·02	0·98	—	—
V_2O_3	—	—	nil	0·02	0·01	0·004	—	—
NiO	—	—	—	—	0·03	0·24	—	—
CoO	—	—	—	—	—	—	—	—
CuO	—	—	0·002	—	0·09	—	—	—
Cl	—	—	—	trace	—	—	—	—
F	—	—	—	2·65	0·26	0·02	0·11	—
H_2O+	0·41	0·26	2·33	0·82	2·24	13·30	3·50	0·20
H_2O-	0·06	0·18	nil	0·04	0·20	0·48	0·28	0·06
Total	99·86	100·28	100·312	100·94	100·15	100·244	99·81	99·80
Less O	—	—	0·03	1·12	0·11	0·01	0·04	—
	99·86	100·28	100·282	99·82	100·04	100·234	99·77	99·80

A, Olivine, separated from dunite, North Carolina, U.S.A. B, Augite, Puy-de-Dôme, France. C, Hastingsitic hornblende, County quarry, Malvern, Worcestershire. D, Pargasite, Finland. E, Green-brown biotite, separated from granite pegmatite, Tollgate quarry, Malvern. F, Clinochlore, West Chester, Pennsylvania, U.S.A. G, Muscovite, separated from granite pegmatite, Tollgate quarry, Malvern. H, Clear, transparent orthoclase, locality unknown.

Analysts: A, B, C, and H, Geochemical Laboratories, London; D and F, Mr. W. J. Dunstall; E and G, Dr. A. W. Groves.

It will be observed that the selected mineral suite ranges from the (SiO_4)-class to the (Si_4O_{10})- and (SiO_2)-classes of crystal-structure and is therefore fairly representative of minerals present in rock families ranging from basic to acid.

Time-current $(T\text{-}C)$ and time-temperature $(T\text{-}t)$ curves.

Readings of current-strength and cell-temperature were recorded and $T\text{-}C$ and $T\text{-}t$ curves were plotted, in order to determine when dialysis was virtually at an end. $T\text{-}t$ curves are omitted in this paper, as they are not entirely relevant in the practical determination of the virtual end-point of dialysis.

Normally, when a solute is electrolyzed under uniform conditions (of temperature, voltage, &c.) the current should rise continuously until a maximum is reached; thereafter, the current should decrease and eventually reach a constant minimum. Theoretically, this minimum should correspond with that of distilled

TABLE II. Constitutional formulae of minerals listed in table I, calculated, from the analyses, to the basis, (O,OH,F) = (x), which is given at the foot of this table.

	Olivine.	Augite.	Horn-blende.	Par-gasite.	Biotite.	Clino-chlore.	Musco-vite.	Felspar
Group A:								
Si	0·98	2·09	6·41	6·16	5·74	5·66	6·15	K(Si$_3$Al)O$_8$
Al	0·02	—	1·59	1·84	2·26	2·34	1·85	78·6%
Al	—	0·28	0·23	0·50	0·55	1·67	3·31	Na(Si$_3$Al)O$_8$ 20·7%
Fe'''	0·03	0·08	0·63	0·23	0·30	0·26	0·46	Ca(Si$_2$Al$_2$)O$_8$
Fe''	0·12	0·10	1·72	0·67	1·41	0·26	0·10	0·7%
Mn	negl.	negl.	0·07	negl.	0·01	negl.	negl.	Total 100·0%
Mg	1·80	1·01	2·05	3·52	4·13	9·39	0·27	
Ca	negl.	0·01	1·88	2·04	0·08	negl.	0·07	
Ti	negl.	0·05	0·16	0·08	0·04	—	0·07	
Na	—	0·02	0·36	0·61	0·08	—	0·21	
K	—	negl.	0·23	0·27	1·78	—	1·84	
Ba	—	—	—	negl.	negl.	—	0·01	
Sr	—	—	—	—	negl.	—	negl.	
V	—	—	—	negl.	negl.	—	—	
Cr	—	—	—	—	negl.	0·15	—	
Ni	—	—	—	—	negl.	0·04	—	
Cu	—	—	—	—	negl.	—	—	
Group B:								
O	3·93	5·93	21·67	21·98	21·62	19·28	20·74	essentially
OH	0·07	0·07	2·33	1·22	2·25	16·71	3·21	unaltered;
F	—	—	—	0·80	0·12	0·01	0·05	anhydrous.
x	4	6	24	24	24	36	24	8
+charges	791	1190	4566	4601	4557	5528	4469	—
−charges	793	1193	4567	4598	4561	5528	4474	—

On a valency basis, the total 'positive' charge, assessed on the values given for constituents acknowledged in Group A, should exactly balance the total 'negative' charge assessed from constituents in Group B. But as the present purpose is to call attention to the disturbance of this balanced condition by the leaching of the more important units in Group A, all values below 0·01 are omitted as being 'negligible'. These omissions have a negligible effect, as shown at the foot of the table.

water electrolyzed under the same conditions. Silicates, however, are unlikely to behave as simple 'solutes' in the same sense as common salt for example; but in general, the graphs (figs. 2 and 3) show the characteristics theoretically expected for such solutes. Electrodialysis was stopped, and the products were collected, when the T-C curve remained essentially horizontal at minimum current-strength (fig. 3).

The period for one continuous dialysis was 24 hours. Current-strength and cell-temperature were recorded at intervals of ten minutes from the start of the operation until maxima were passed. It was found that, in general, both the current and the temperature first rose, then fell to almost constant minima after 7–8 hours from the start of the operation. Thereafter, further recording was considered to be unnecessary; but dialysis was continued for the full period of 24 hours. The circuit was then temporarily broken, while products were collected from the kathode-chamber and anode-chamber. The T-C graphs obtained in this first operation will be termed the 'primary graphs' (fig. 2).

FIG. 2. Primary time-current graphs.

A fresh supply of distilled water was then put into each of the three cells—to the amount required to attain the original level, and dialysis was repeated for another 24 hours. As before, current and temperature were recorded for the first few hours, in order to determine whether 'maxima' were attained as in the case of the primary graphs. The graphs for the second operation will be termed the 'secondary graphs' (fig. 3). The form of the secondary T-C graphs agrees very closely with that for distilled water, except that the latter has slightly lower values. Thus, at the end of the second full-period operation, the anode and kathode products could warrantably be collected, as 'end' products. The 'primaries' and 'secondaries' for augite, hastingsitic hornblende, and clinochlore are shown—as being typical of the whole.

FIG. 3. Secondary time-current graphs.

Treatment of the kathode-chamber slime.

The slime collected from the mineral-chamber was stored in wax-lined bottles. The kathode-chamber slime was evaporated to dryness on a dust-proof water-bath, and the solid residue was partially analysed (table III). As the total kathode-chamber liquid collected ranged between 500 and 700 c.c., evaporation of so large a bulk was a long process, and special precautions were necessary to

TABLE III. Analyses of suspensoid slimes. Analyst: Dr. A. J. C. Welch.

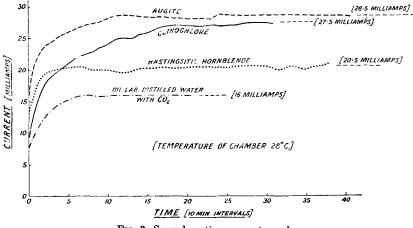|		Olivine.	Augite.	Horn-blende.	Par-gasite.	Biotite.	Chlorite.	Musco-vite.	Felspar.
SiO_2	...	43·26	47·58	38·80	40·70	35·34	29·98	39·85	65·03
R_2O_3	...	9·50	12·18	30·20	21·80	26·47	21·04	32·85	16·66
H_2O+	...	2·28	3·63	9·58	5·69	19·02	17·78	>12·20 <15·19	2·38

prevent contamination of the solid residue by air-borne dust: a convex watch-glass was hung from a support in such a manner that, while it covered the evaporating-dish without touching either the dish or the bath, the rim of the watch-glass was below that of the dish. Hence, water condensed on the inside of the watch-glass trickled down to the rim and fell outside the basin. The whole apparatus was installed in a fume-cupboard from which air, together with dust-suspensions, was continuously exhausted during the whole period of evaporation.

Discussion of the data. Evidence for hydration.

Comparison of tables I and III shows that emphatic hydration of all the minerals occurs during the process of electrodialysis. The degree of hydration induced under the experimental conditions described is assessed in table IV, which shows a maximum for augite and felspar (notoriously unstable under natural weathering conditions), and a minimum for chlorite (one of the more stable rock-forming

TABLE IV. Per cent. water-content above 105–110° C., in (a) the initial mineral and (b) the suspensoid slime.

		Olivine.	Augite.	Horn-blende.	Par-gasite.	Biotite.	Chlorite.	Musco-vite.	Felspar.
(a)	...	0·41	0·26	2·33	0·84	2·24	13·30	3·50	0·20
(b)	...	2·28	3·63	9·58	5·69	19·02	17·78	> 12·20 < 15·19	2·38
Per cent. in-crease of H_2O		456·1	1296·1	331·1	577·3	749·1	33·7	>248·6 <334·0	1090·0

minerals). As already mentioned (p. 138), this hydration is accompanied by the production of colloidal silica, alumina, and ferric oxide, and the extraction of bases, particularly those which yield soluble carbonates or bicarbonates. It is warrantable to suggest that, taken together, these 'alterations' imply some drastic change in the crystal-structure of the original minerals: their initial geometry—maintained by the orderly packing of 'positively' and 'negatively' charged elements, in consistently regular co-ordination—must be partially, or completely, destroyed.

Under natural weathering conditions, the collapse of the initial lattice-structure may be less abrupt than the experimental data suggest: it may proceed by stages

—as in the micas, two species of which were included in the list of minerals treated. Hydromuscovite, for example,[1] is characterized by (a) deficiency of alkalis and (b) excess of $(OH)^-$—as opposed to O^{--}. The suggestion here is that the extraction of K^+ and Na^+ may be accompanied by a corresponding reduction of O^{--} to $(OH)^-$ while the initial structure persists—within limits which may be vaguely defined as 'the range of tolerance'. Hydrobiotites may lend themselves to a similar explanation. One object of these experiments was to determine, if possible, whether analogues of these 'hydromicas', e.g. layer-lattice minerals included in the 'clay' species, could be detected by X-ray or kathode-ray technique among the dialysed products of mineral silicates presumed to yield such species under natural weathering conditions.

Investigation by X-ray technique.

The principles of sedimentation under the influence of gravity and in accordance with Stoke's law were applied to obtain from the slimes collected two fractions, 'fine' and 'coarse'. The 'fine' fraction contained mineral particles below 3 μ diameter; the 'coarse' fraction represented the average grade for the slime as a whole.

Plate XIII, figs. 1–3, shows X-ray diffraction-patterns of the fine and coarse fractions of dialysed orthoclase and of the untreated mineral. The three patterns are apparently identical: they show the same number of lines, the same relative intensities, and the same spacing between any two corresponding lines. This concordance would appear, at first sight, somewhat discouraging: it suggests either (a) that products allied to the 'clay' species were absent from the slimes, or (b) that the quantity of such products was too minute to be effectively concentrated by the method adopted, and too small for detection by X-ray technique, in the presence of preponderant particles of unaltered mineral. It should be stated, however, that the fractionation of the suspensoid slime was based on the assumption that any particulate 'crystalline colloids' produced would be unlikely to coalesce in liquid being continuously freed from positively charged ions and kept in constant agitation. In the writer's opinion, the presence of such crystalline colloids, as independent particles, is at least doubtful. Possibly the conditions of the experiment hardly warrant the expectation, as will be pointed out in the concluding section of this paper. Similarly, negative results were obtained from X-ray work on hastingsitic hornblende and its two 'slime' fractions (pl. XIII, figs. 4–6).

Were the results of X-ray test-work decisive on this matter, they would rule out the further possibility that product-minerals may form a thin superficial layer protectively covering the particles of unaltered mineral. Here, however, the results are not decisive. It is probable that structural changes may be restricted to exceedingly thin superficial layers of the affected mineral particles. X-rays are too highly penetrative to serve as a decisive weapon for the probing of this problem: experiment has shown that X-rays must pass through millions of lattice-planes before they are appreciably absorbed.[2] Even under the most favourable conditions, X-rays would give a pattern corresponding to the predominant

---

[1] A. Brammall, J. G. C. Leech, and F. A. Bannister, Min. Mag., 1937, vol. 24, pp. 507–510.

[2] W. H. Bragg and W. L. Bragg, X-rays and crystal structure, 1915, p. 14.

constituent for a depth of at least 10^5 Å. ($= 0.01$ mm.).[1] Films of such product-minerals (if they really arise under the experimental conditions described) are unlikely to be 0.01 mm. thick, because the mineral particles dialysed have an average diameter of only 0.003 mm., i.e. 3 μ.

Investigation by electron-diffraction.

X-ray technique, applied to only two of the eight pairs of solids, having proved indecisive, facilities were obtained for test-work by kathode-ray technique on one
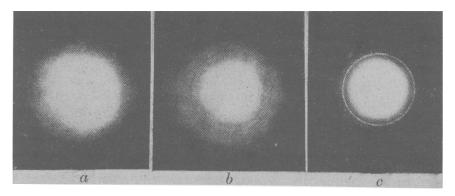

FIG. 4. Kathode-ray transmission photographs (by W. G. H. Robins). (a) Pargasite, fresh mineral. (b) Pargasite, dialysed slime. (c) Kaolinite.

selected pair. For this test the pargasite pair was submitted together with kaolinite as a possible basis for comparison.

Initial experiments had shown that slime-particles approaching 4 μ in diameter were most likely to respond to the test, and the slime available was accordingly fractionated to meet this requirement.

Fig. 4 shows the transmission-patterns (powder photographs) for (a) unaltered pargasite, (b) dialysed pargasite, and (c) kaolinite. Between (a) and (b) there is a noticeable difference—best observed in the original negatives. Unfortunately, the patterns are not clear enough for exact measurements of the Kikuchi rings, which are more numerous in the dialysed fraction (b) than in the unaltered pargasite. Mr. Robins's interpretation of the difference is that the slime particles 'contain on their surface a *microcrystalline*, non-orientated layer of material which is not pargasite'. Thus there is warrant for entertaining the possibility that the particles of unaltered pargasite may be coated by a 'protective' film, which may be 'colloidal' but is definitely 'crystalline'. Unfortunately, the limited amount of evidence obtainable did not warrant a more precise identification, or even discussion of possible relationship to kaolinite—the only 'clay' species tested.

Conclusions.

Short-period electrodialysis·of the common rock-forming minerals selected induced chemical changes which suggest partial or complete collapse of

[1] B. Chalmers and A. G. Quarrell, The physical examination of metals, 1941, vol. 2, pp. 212–213.

crystal-structures. Colloidal end-products identified include those which, under appropriate natural conditions, could integrate to 'crystalline colloids' belonging to the 'clay' species.

The indecisive character of the results obtained, in tentative test-work necessarily restricted to the bare minimum, may be attributable to either (a) the relatively small mass of residual colloid produced, i.e. the shallowness of the superficial layer actually dialysed, or (b) the fact that the time- and TP-factors operative during the consolidation and reconstitution of natural clayey sediment could not be experimentally conditioned.

The large amount of water used in these experiments tends to maintain the amorphous colloid state. Presumably, this excess of water must be removed if the integration of these colloids to some specific crystalline species is to be expected. Moreover, some proportion of the excess (OH)-groups must also be removed by heat, or by pressure, or by both, so that the Al- and Si-atoms can be brought within effective range of each other and induced to combine chemically.

Removal of the excess of water is a simple matter: one merely filters it off, or removes it by centrifugation: but even the air-dried residue still contains an excess of water and/or (OH)-groups. The production of crystalline colloids is not likely to be conditioned merely by rapid heating, or even by heating at 'low' temperatures—possibly much below 105° C.

Considerations based on the environment in which 'crystalline colloids' occur in nature, particularly in soils and stratiform clays, suggest that these crystalline bodies arise by dehydration processes involving a very large time-factor, normal rock-temperatures, and conditions of *gradually* increasing pressure such as would be induced by slow burial of sediments beneath a gradually increasing load of later sediments. These natural conditions seem to be expressed by the thermodynamic equation, $\Delta P \times \Delta V = \Delta T$, which relates both gradual increase of pressure and gradual reduction of volume to modest increments of energy in the form of heat, operative over a long period.

The author makes grateful acknowledgement to Dr. A. Brammall, Mr. J. G. C. Leech, Mr. F. A. Bannister, Dr. Brian Mason, and Mr. W. G. H. Robins for valuable assistance particularized on pp. 137 and 138 of this paper.

EXPLANATION OF PLATE XIII.

X-ray powder photographs. Figs. 1–3 (Mr. F. A. Bannister and Dr. Brian Mason) taken with unfiltered copper-radiation, and figs. 4–6 (Mr. F. A. Bannister) taken with unfiltered iron-radiation, in a cylindrical camera, diameter 6 cm.

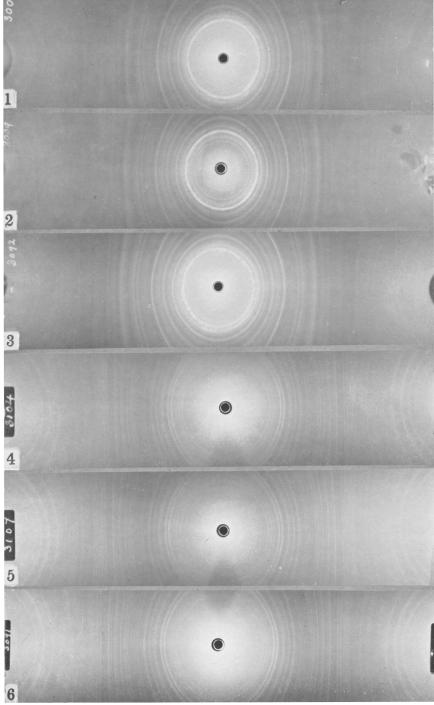FIG. 1. Orthoclase, dialysed slime, fine fraction.
FIG. 2.   ,,   ,,   coarse fraction.
FIG. 3.   ,,   fresh mineral, locality unknown.
FIG. 4. Hastingsitic hornblende, dialysed slime, fine fraction.
FIG. 5.   ,,   ,,   ,,   coarse fraction.
FIG. 6.   ,,   ,,   fresh mineral, County quarry, Malvern, Worcestershire.

Plate XIII

Tha Hla: Electrodialysis of Silicates