

## On the electrolysis of basalt, II: experiments in an inert atmosphere

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**SUMMARY.** The recently described electrolysis of molten basalt (Oppenheim, 1968) gave indefinite results with regard to the behaviour of iron. Repeating the experiments in an inert atmosphere has shown that ferric iron moves towards the anode, and ferrous iron to the cathode. All metallic ions of valency three and more are now seen to be concentrated towards the anode, with relative enrichments in decreasing order:  $\text{Fe}^{3+}$ , P, Ti, Si, and Al; and oxygen gas is released at the anode. Metals of valency one and two are concentrated towards the cathode with relative enrichments in decreasing order: Na,  $\text{Fe}^{2+}$ , K, Ca, Mn, and Mg.

The series expected to be differentiated within a magma consequent upon its electrolysis is redefined. The absence of natural analogues suggests either the non-operation of suitable electric currents within magmas, or the destruction of their effects by convection, fractional crystallization, or both. An electrolytic process is feasible at the mantle-core boundary, leading mainly to deposition of iron on the core and release of oxygen upwards.

THE effects of electrolysing molten basalt were recently described (Oppenheim, 1968) but the results were not clear with regard to the iron distribution in the differentiated melt. The experiments have been repeated using a protective atmosphere of argon. The new results indicate a revised ferrous-ferric distribution and consequent modification of some former conclusions concerning the nature of the electrolysed magma series.

*Experimental procedure.* Only the changes in procedure relative to the earlier experiments are mentioned here; fuller details will be found in the 1968 paper.

Powder was prepared from a new specimen of the Golani basalt. A ridge of powder served as the specimen, spread along the top of a supporting block of the same basalt. Heating was effected from above, using the elongated image-furnace as before. The furnace was suspended above the specimen, both the furnace and basalt block being enclosed in a large asbestos-lined wooden box into which all leads are passed through drilled inserts. The specimen is amenable to lowering and raising by screwed supports operated from outside the box. Argon is fed directly into the furnace top, the mirror-halves being separate units; the furnace is so built that a steady purging stream of gas may be directed along a median line directly on to the specimen below. The enclosing box is not gas-tight, and a continuous stream of argon was used. The furnace length is 15 cm, and the specimen ridge was 13–14 cm long. It appears that the gas protection is not satisfactory at the furnace ends, but oxidation was effectively precluded within the inter-electrode range of 11 cm.<sup>1</sup>

<sup>1</sup> The prevention of atmospheric oxidation is evidenced by the  $\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$  figures

The electrolysing current was again passed at 200 V, using a variac and half-wave silicon-diode rectifying bridge; ripple-smoothing was not used. Temperatures were in the range 1250–1350 °C. Two separate runs were made. In the first, the inter-electrode distance was 11 cm; the current passed was estimated from the readings of a domestic kWh instrument installed at the AC end of the electrolysing circuit. In the second run the inter-electrode distance was reduced to 10 cm, and a copper-sulphate coulometer added in series with the DC circuit. It is estimated that 3000 coulombs were passed in the first run during 2½ hours; and some 4800 coulombs in the second run during 10½ hours.

It is doubtful whether the coulomb figures are more reliable than  $\pm 10\%$  for the first run, and  $\pm 5\%$  for the second. However, in view of the 'pre-electrode' dilution noted below, and in view of the non-representation inherent in interpreting compositional gradients using gross specimens weighing some 3 g, this degree of accuracy would appear satisfactory.

*Experimental results.* The analyses of specimens from the anode, middle, and cathode regions for each specimen are presented in table I, together with their calculated norms. Cationic (oxygen-free) values are given in table II. Some trace-elements were determined by atomic-absorption spectroscopy, and the results are included in table I. The two 'middle' values for zinc are inconsistent, and zinc has not been included in the plots of fig. 2; as zinc-oxide is used for cleaning the mirrors at intervals during an experimental run it is most likely that contamination has occurred.

In the earlier reported runs (1968) the electrodes were emplaced virtually at the ends of the molten trough, 14 cm apart. In the new runs this distance was reduced, with the following advantages:<sup>1</sup> restriction of electrolysis to the more uniformly heated central part of the molten ridge, the ensuring of a better protection of the specimen by the admitted argon, and reduction of the cell resistance, permitting a stronger electrolysing current to pass.<sup>2</sup> However, the new arrangement involved the formation of two molten zones at either end of the molten pool, beyond the electrodes: these terminal pools are referred to as the 'pre-electrode' areas, and their presence has proved undesirable. The melt could be observed during electrolysis, and it was seen that oxygen bubbles also arose beyond the anode, i.e. from the pre-anode region close to the electrode.

Pre-anode and pre-cathode specimens of the second run have been analysed, and the results are included in table I. These analyses strongly suggest that some of the

table I. In the earlier work it was seen that this ratio is 0.49 in the original rock, but 0.83 in a melt exposed to the atmosphere for three hours. The 'middle' specimen values given here are close to that of the original rock, and the anode and cathode values differ systematically around it. Only in the 'pre-cathode' and 'pre-anode' specimens are high ferric:ferrous ratios found.

<sup>1</sup> Undue shortening of the cell incurs the risk of convective mixing, as well as stirring by the oxygen bubbles as they are discharged; and the use of larger specimens is advantageous in that there is ample material for full chemical analyses.

<sup>2</sup> The reduction in the resistance is directly proportional to the reduction in the trough length; but a shortening of the trough length also decreases the liquid volume by a similar factor. The efficacy of the electrolysing current, i.e. the number of coulombs passed per gram sample, accordingly increases by a factor proportional to the square of the decrease in trough-length.

TABLE I. *The Golani basalt: analyses and C.I.P.W. norms of the electrolysed derivatives. Anal. Mrs. Z. Shohat*

Anal. Code	With c. 3000 C				With c. 4800 C				With c. 4800 C				
	Anode	Middle	Cathode	Pre-anode	Pre-cathode	Anode	Middle	Cathode	Pre-anode	Pre-cathode	Anode	Middle	Cathode
SiO <sub>2</sub>	184	185	186	179	183	184	185	186	180	181	180	181	182
Al <sub>2</sub> O <sub>3</sub>	47.90	46.09	45.20	47.74	44.10	2.82	2.69	2.49	3.09	2.82	3.09	2.82	2.82
Fe <sub>2</sub> O <sub>3</sub>	15.70	15.61	14.95	15.24	14.62	5.37	5.11	5.04	5.13	4.86	5.13	4.86	4.55
FeO	8.85	6.72	3.66	9.54	8.31	3.15	9.63	5.26	7.13	8.71	7.13	8.71	6.14
MnO	3.36	5.28	7.30	2.16	2.06	6.68	0.03	—	1.69	—	1.69	—	—
MgO	0.16	0.17	0.18	0.15	0.18	6.68	7.18	7.79	5.79	6.85	5.79	6.85	7.52
CaO	7.16	7.53	7.91	6.39	7.42	14.63	25.02	10.02	7.87	25.23	7.87	25.23	2.88
Na <sub>2</sub> O	10.01	10.81	11.82	8.77	11.02	31.72	23.15	13.88	35.50	25.01	35.50	25.01	4.42
K <sub>2</sub> O	1.73	3.49	5.08	0.92	6.38	4.24	9.47	15.54	—	8.44	—	8.44	19.05
TiO <sub>2</sub>	1.13	1.23	1.34	1.04	1.31	3.66	8.18	10.81	—	6.62	—	6.62	13.44
P <sub>2</sub> O <sub>5</sub>	2.83	2.71	2.68	2.53	2.42	—	—	3.44	—	0.90	—	0.90	3.97
	1.19	1.14	1.06	1.28	1.14	14.17	—	—	16.11	2.50	—	2.50	—
f*	100.02	100.78	101.18	98.82	98.96	—	—	—	—	—	—	—	—
Ni	0.72	0.56	0.33	0.58	0.80	—	7.30	6.06	—	6.75	—	6.75	3.95
Co	190	184	171	166	144	—	—	2.13	—	1.02	—	1.02	0.89
Cr	65	73	75	59	65	6.94	—	—	16.55	—	—	—	—
Sr	252	254	249	266	209	—	2.30	17.59	—	—	—	—	30.03
Cu	1132	1219	1288	912	1089	—	—	—	0.83	—	—	—	—
Zn†	67	83	93	60	67	100.06	100.06	100.05	99.69	100.05	99.69	100.05	99.66
Li	135	134	122	182	144	—	—	—	—	—	—	—	—
	8	17	25	2	22	—	—	—	—	—	—	—	—

Normative  
colour index  
An content of  
plagioclase, %  
Or/total  
feldspar, %

\* Fe<sub>2</sub>O<sub>3</sub>/(FeO+Fe<sub>2</sub>O<sub>3</sub>) † Values not plotted, contamination probable.

electrolytic products have intermingled with the adjacent non-electrolysed pre-electrode material. Nearly all the oxides in the pre-electrode specimens have a value intermediate between that of the adjoining electrolysed specimen and that of the middle melt; the pre-cathode  $K_2O$  and  $P_2O_5$  values are exceptional in that they are more extreme than those of the adjacent cathode specimen itself. This pre-cathode dilution is regrettable, for in its absence the current passed in both runs would have given yet more contrasted compositions than those recorded here. Discussion will be restricted to the inter-electrode region.

TABLE II. *The analyses of table I expressed as weight of cations (in grams) per 100-g rock, after analyses recalculated to 100 %. Also given is the cation behaviour on electrolysis of basalt melts; enrichment (positive numbers) and depletion (negative numbers) expressed as percentages relative to values in the corresponding 'middle' analysis*

Anal. Code	With c. 3000 C			With c. 4800 C			Anode enrichment (%)		Cathode enrichment (%)	
	184 a	185 m	186 c	180 ā	181 m̄	182 c̄	a	ā	c	c̄
Ion										
P <sup>5+</sup>	0.52	0.49	0.46	0.57	0.52	0.52	+6.1	+9.6	-0.1	-5.9
Ti <sup>4+</sup>	1.70	1.61	1.59	1.62	1.53	1.44	+5.6	+5.9	-1.2	-5.9
Si <sup>4+</sup>	22.38	21.37	20.88	23.69	21.57	20.21	+4.7	+9.8	-2.3	-7.4
Fe <sup>3+</sup>	6.19	4.66	2.53	4.63	4.20	2.96	+32.8	+10.2	-45.7	-29.5
Al <sup>3+</sup>	8.30	8.20	7.82	8.70	8.11	7.59	+1.2	+7.3	-4.6	-6.4
Fe <sup>2+</sup>	2.61	4.07	5.60	3.79	4.83	5.39	-35.9	-21.5	+37.6	+11.6
Ca <sup>2+</sup>	7.15	7.67	8.35	6.34	7.64	8.33	-6.8	-17.0	+8.9	+9.0
Mn <sup>2+</sup>	0.12	0.13	0.14	0.11	0.14	0.14 (5)	-7.7	-22.8	+7.7	+5.1
Mg <sup>2+</sup>	4.32	4.51	4.72	3.90	4.54	4.62	-4.2	-14.1	+4.7	+1.8
Na <sup>+</sup>	1.28	2.57	3.72	0.69	2.21	5.11	-50.2	-38.6	+47.7	+131.2
K <sup>+</sup>	0.94	1.01	1.10	0.81	0.96	1.05	-6.9	-15.6	+8.9	+9.4
Fe <sup>t</sup>	55.51 8.80	56.29 8.73	56.91 8.13	54.85 8.42	56.25 9.03	57.36 8.35	+0.8	-6.8	-6.9	-7.5

*Interpretation of the results.* The relative degree of enrichment or depletion for each element relative to the composition of the middle specimen is summarized in table II. The behaviour formerly determined for each ion is confirmed, i.e. ions of valency three and higher move towards the anode, whilst ions of valency one and two move towards the cathode. Amongst the divalent ions the order of enrichment is now Fe, Ca, Mn, Mg; accordingly the 'ion-oxygen attraction' hypothesis formerly adapted from Bockris does not appear to be applicable to the rock melt.

Fig. 1 shows the oxide variations plotted against  $(Na_2O+K_2O)$ , the most variable constituents. The curves are strikingly similar to those of fig. 1 in the 1968 paper, except for the iron values. In the presence of argon there is a pronounced tendency for ferric iron to become concentrated towards the anode, and for ferrous iron to migrate towards the cathode. The original rock (non-electrolysed) has been added to the curves of fig. 1, and it is seen that these points in some cases fall slightly aside of the curves; this is presumably because of inhomogeneity between different specimens

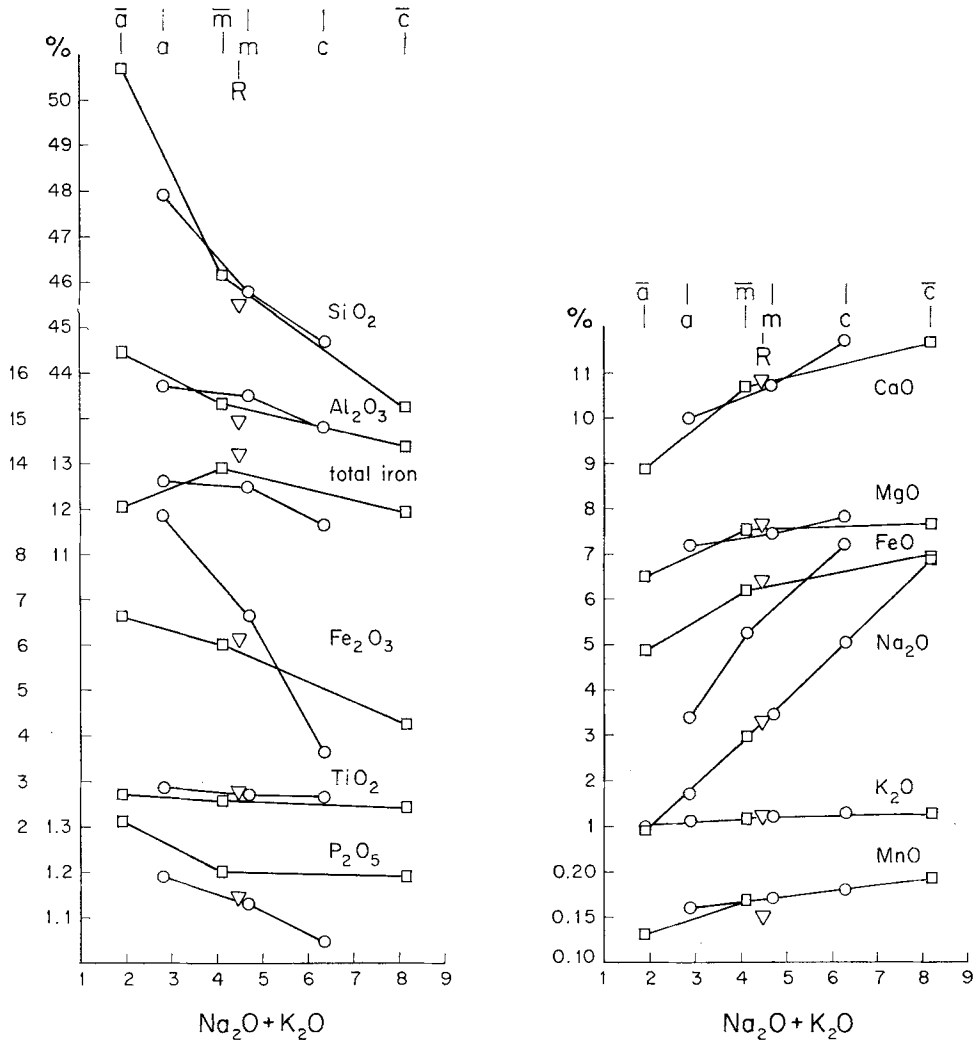


FIG. 1. Golani basalt and its electrolysed derivatives plotted as oxides against  $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ , the most variable constituents. The values plotted are those of table I after reduction to 100%.  $\circ$ —first run,  $\square$ —second run,  $\nabla$ —the original rock (analysis 19 in table I, Oppenheim, 1968).

taken from a single quarry. Calculation of the enrichment or depletion has been made relative to the middle members of each run.

Enrichment factors are not calculated for the trace-elements, but the general trends confirm those ascertained for the major elements, i.e. attraction to the anodic or cathodic end of the cell is determined by the ion's valency. Nickel showed opposing trends in the two runs, and there is probably an analytical error.

The degree of attraction of the ferrous and ferric components to their respective electrodes is almost equal, although the ferrous iron may have a slight advantage (see table II and fig. 2). Analysis of the non-electrolysed rock gives  $\text{Fe}_2\text{O}_3$  5.99%,

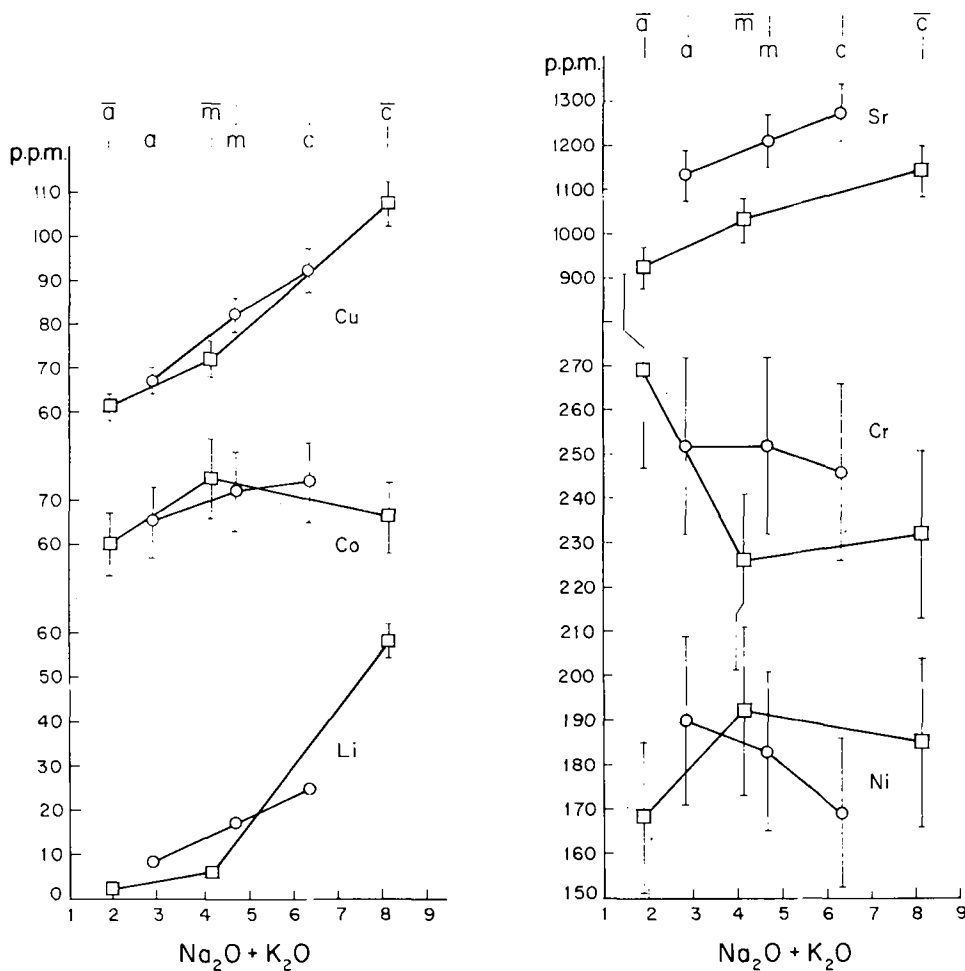


FIG. 2. Some trace constituents of electrolysed Golani basalt, plotted against  $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ . The values used are those of table III reduced by the factor used to bring the table I totals to 100%. The maximum inaccuracy inherent in the analytical method is indicated for each determination, but these ranges are probably pessimistic by a factor of  $1\frac{1}{2}$ -2.  $\circ$ —first run,  $\square$ —second run.

$\text{FeO}$  6.31%, i.e. the two oxides are present in approximately equal amounts. The Golani basalt accordingly shows little variation in its total iron content after electrolysis, but this feature is to be regarded as fortuitous in consequence of a special original composition. In silicates having the more usual dominance of  $\text{FeO}$  over  $\text{Fe}_2\text{O}_3$ , the

ferrous–ferric differentiation will necessarily involve a total gross iron concentration in the cathodic derivative, and a corresponding depletion in the anodic fraction.

For convenience in discussion it is proposed to use the terms ‘catholith’ and ‘anolith’ with the following meanings: a catholith is a rock that crystallizes from the cathode-region of an electrolysed melt; an anolith is a rock that crystallizes from the anode-region of an electrolysed melt. A further term ‘mediolith’ may be used to

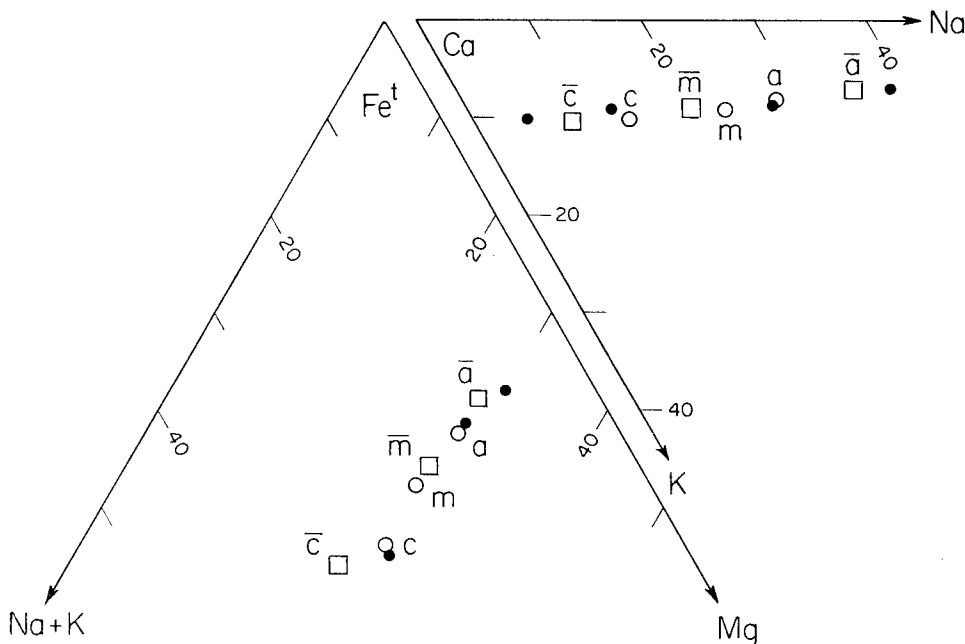


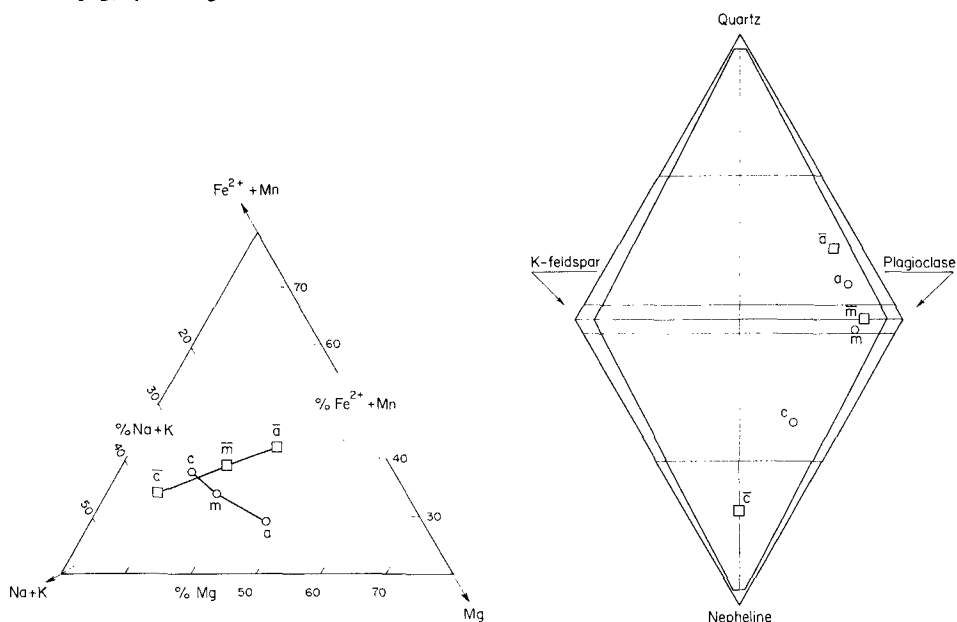
FIG. 3. Electrolysed Golani basalt derivatives plotted in AFM ( $F = Fe^t$ ) and Na–K–Ca diagrams (cationic values of table II). ○—first run, □—second run, ●—anolites and catholites from fig. 3 in Oppenheim, 1968.

indicate a rock that has crystallized from the middle portion of an electrolysed melt; its characteristic is that it is of virtually unchanged composition and represents the parent liquid. The corresponding liquids, prior to their crystallization, may simply be referred to as anolitic, mediolitic, or catholitic liquids.

Fig. 3 shows the alk– $Fe^t$ –Mg, and Na–Ca–K diagrams<sup>1</sup> of the former paper in which the new analyses have been plotted; the former trends are confirmed. The alk–( $Fe^{2+} + Mn$ )–Mg diagram of fig. 4 is new: the trend shown by each run is somewhat different, presumably because the  $\bar{c}$  rock has a stronger enrichment in alkalis relative to the  $Fe^{2+}$  enrichment than is the case for the  $c$  rock. The new results permit completion of the Johannsen diagram previously drawn, to include the more extreme catholitic composition (fig. 5). The electrolytic process involves not only the movement of ions towards the electrodes but also the discharge of anions and cations,

<sup>1</sup>  $Fe^t = Fe^{2+} + Fe^{3+}$ .

electrons being received at the cathode and given out at the anode. As noted, oxygen gas is released at the anode, the process schematically being  $2O^{2-} \rightarrow O_2 + 4e^-$ . An equivalent weight of metal will simultaneously be precipitated at the cathode by reactions such as  $Na^+ + e^- \rightarrow Na$ ,  $Fe^{2+} + 2e^- \rightarrow 2Fe$ ; but no metal can be precipitated at the anode notwithstanding the concentration there of those metallic ions having valency 3, 4, and 5.



FIGS. 4 and 5: Fig. 4 (left). Electrolysed Golani basalt derivatives plotted in a (Na+K)-(Fe<sup>2+</sup>+Mn)-Mg diagram. ○—first run, □—second run. Fig. 5 (right). Electrolysed Golani basalt derivatives plotted in a Johansen double triangle; the components are normative. ○—first run, □—second run.

Consideration of the number of coulombs passed permits calculation of the weight of oxygen liberated, and estimation of the metallic fraction deposited on the cathode. The weight of oxygen liberated is  $8 \times 3000/96500$  for the first run, and  $8 \times 4800/96500$  g for the second run, i.e. 0.25 and 0.40 g respectively. If the mono- and divalent ions are weighted in accordance with the catholytic enrichments appropriate to each run (table II), the composition of the metal deposited at the cathode will be:

First run (3000 C)

grams	Fe 0.29	Mn 0.06	Mg 0.01(5)	Ca 0.05	Na 0.28	K 0.10	Total 0.79
%	37	7	2	6	36	12	100

Second run (4800 C)

grams	0.10	0.04	0.01	0.06	0.90	0.11	1.22
%	8	3	1	5	74	9	100

Under the experimental conditions the free metal probably alloys itself in part with



the platinum wire constituting the cathode. This is believed to be the reason for the ease with which the cathode leads have 'burned out' in the course of experiments. The cathode wire recovered after the second run, however, had increased in weight by only 0.10 g, i.e. one tenth of the calculated deposited mass. On the other hand, a greasy, olive-green material, distinctly non-stony and non-metallic in appearance, was found surrounding the cathode, and it had exuded 0.8 cm around it beyond the specimen; some of this material was also found at the base of the solidified glass immediately below the cathode. A spectrographic analysis kindly performed by Y. Brenner and A. Starinsky at the Israel Geological Survey revealed the following elements: Al, Ba, Ca, Co (tr.), Cu, Fe (much), K, Li (tr.), Mg, Mn, Na (much), Ni (tr.), Si, Ti, V, and Zn.

The manner in which the free metals are disposed within the catholith remains to be clarified. If they are included within the cathode specimen collected for analysis then they have apparently been reoxidized during the grinding stage; otherwise the analysis total would be seriously in excess of 100 %.

*Geological considerations.* The motivation for this work was the determination of whether the interaction of natural electric currents in their passage through magma might constitute a petrogenetic factor. There can be no doubt that were electric currents (having a voltage exceeding the decomposition potentials of magmatic constituents) to pass unidirectionally through magma then electrolysis would occur.

It may be pointed out that the differentiation resulting from electrolysis of a magma would be significant for two reasons. The compositions attained would firstly be striking in that the electrolytic trend is an unusual one. The second consideration is common to any mechanism that affects a magma whilst it remains in the liquid state, in contrast with processes involving cooling and crystallization; for differentiation of a liquid will permit relatively large proportions of the original material to attain an extreme composition, in contrast to the effects of fractional crystallization by means of which any extremity in differentiated composition is attained at the expense of quantity.

In the absence of direct evidence for or against the existence of such currents at the depths of magma formation it is pertinent to compare the results of the experimental electrolysis of basalt with the known compositions of igneous rocks. Although the parent composition so far electrolysed is restricted to basalt it is probable that other igneous silicate melts would show qualitatively similar changes. The reason for this is that each constituent ion reacts to electrolysis primarily in accordance with its valency; and adopting a parent silicate liquid in which only the proportions of the ions are changed should not affect their behaviour. Table III sets out the expected properties of an electrolytic series. The mineralogy is given in terms of minerals that would crystallize from catholithic and anolithic liquids under plutonic conditions; the experimental liquids all solidified to glasses.

The author knows of no igneous rock group the members of which exhibit the above properties. It would be tempting to regard such basic alkaline rocks as malignite, melteigite, or uncomphagrite as catholiths; the difficulty is in finding corresponding

anolithic rocks with which the 'catholiths' could be grouped in a single genetic series. The required anoliths would require high silica, a low alkali content, and a  $K_2O/Na_2O$  ratio approaching or exceeding unity. Anolithic properties may perhaps be recognized in kimberlite, according to the following quotation: 'For a rock of such basicity, it [kimberlite] contains unusually high amounts of  $K_2O$ ,  $Al_2O_3$ ,  $TiO_2$ ,  $CaO$ ,  $CO_2$ ,  $P_2O_5$ ,  $H_2O$ , and  $SO_3$ . Compared with other ultrabasic rocks it has a low Mg/Fe ratio, but unusually high K/Na and  $Fe^{3+}/Fe^{2+}$  ratios' (Dawson, 1967).

It would appear that the question originally posed as to the efficacy of natural electric currents to affect the development of magmas can be answered in the negative.

TABLE III. *The electrolysed magma series. The properties indicated are relative to those of the parent melt*

*Silica-rich members: anoliths*

*Silica-poor members: catholiths*

*Chemically*

Oxidation state higher; enriched in  $Fe_2O_3$ ,  $TiO_2$ ,  $P_2O_5$ ,  $Al_2O_3$ , and other atoms of valency higher than two;  $Na_2O/K_2O$  decreased; gross depletion in total iron unless  $Fe^{3+} \geq Fe^{2+}$  in parent liquid.

Oxidation state lower; enriched in  $Na_2O$ ,  $FeO$ ,  $K_2O$ ,  $CaO$ ,  $MnO$ ,  $MgO$ , and other mono- and di-valent atoms;  $Na_2O/K_2O$  increased; gross enrichment in total iron unless  $Fe^{3+} \geq Fe^{2+}$  in original liquid.

*Mineralogically (estimated)*

More saturated minerals (quartz, amphiboles, etc.); plagioclase more basic; lower proportion of melanocratic minerals; melanocratic minerals will show decreased FeO/MgO, together with increased  $Fe_2O_3$ ; minerals expected are such as hematite, epidote, cordierite, andradite.

More undersaturated minerals (feldspathoids, melilites, olivine, etc.); plagioclase more acid, unless much nepheline; higher proportion of melanocratic minerals; melanocratic minerals will have higher FeO/MgO, and reduced  $Fe_2O_3$ ; FeO/MgO will increase as  $SiO_2$  decreases.

This conclusion does not imply the non-existence of currents in the regions of developing magmas, for it is possible that the expected electrolytic effects are hidden by the simultaneous play of stronger forces—gravity in the main—, which produce opposed geochemical trends; and the action of convection in a magma chamber would destroy electrically formed compositional gradients.

It is more reasonable to expect significant electric manifestations at the core-mantle boundary in association with the phenomena responsible for the earth's magnetic field. The effects consequent upon such a process would be mainly the precipitation of iron (and possible growth of the core) together with a simultaneous transfer of oxygen to higher levels in the earth. These processes are being discussed separately.

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