# On the electrolysis of molten basalt

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*Summary.* The effects to be expected from the interaction of possible electric currents at depth with bodies of basaltic magma have been investigated experimentally. Trough-shaped molten specimens were produced in the surface of basalt blocks by heating from above; the melts were electrolysed and the products analysed chemically.

Si, Al, Ti, P, $Fe^{2+}$, and probably $Fe^{3+}$ are concentrated towards the anode, apparently in the form of drifting lattice remnants; oxygen gas is liberated. Na, K, Ca, Mn, and Mg ions concentrate towards the cathode.

Relatively to basalt, the cathodic product is an alkaline and femic rock with normative nepheline and a more acid plagioclase. The anodic rock is distinctly calc-alkaline and salic, with normative quartz and a plagioclase that is more basic. The precise 'rock-type' developed depends on the amount of electricity passed, but the trends are distinct. In that increasing basicity and alkalinity (cathodic rocks) are accompanied by both increasing Na/K and $Mg/(Fe^{2+}+Fe^{3+})$ ratios (which ratios decrease with decreasing basicity and alkalinity) the electrolytic series developed from a basalt magma appears to have few counterparts among natural rocks.

THE idea is entertained that terrestrial electricity might constitute a factor, either general or local, in the development of magmas. Were electric currents to pass through natural magmas, which are electrolytes, then chemical changes can be expected that would be of petrological importance. Experiments have been begun to investigate the effects of electrolysis on artificially melted igneous rock samples, and the initial results are presented here.

Lyell (1835) discussed the electrical and magnetic properties of the earth with his customary skill and foresight; he queries on p. 369 as to: 'How far subterranean electric currents may possess the decomposing power of the voltaic pile. . . .'

Doelter (1905) gives the following startling statement on p. 146 of his book: 'Was die Elektrolyse als Ursache der Differentiation anbelangt, so haben einige Versuche, die ich ausführte, wohl ergeben, dass eine solche möglich ist, es trat an den Elektroden eine Trennung von eisenreichen und eisenarmen Magmen ein; und dies deutet darauf hin, dass die Ursache in der elektrolytischen Dissoziation zu suchen sei.'

To the author's knowledge little modern work on rock electrolysis has been carried out although there exists an important body of information concerning the electrolysis of artificially prepared silicates; the latter was performed mainly by Bockris and his school, and is summarized by Bloom and Bockris (1959). Coster (1948, p. 197) gives analyses of material liberated at the negative electrode during electrolysis of two glassy basalts at 500 and 900 °C. No material was deposited on the positive electrode. In that the total material liberated was 'much in excess' of that expected from the number of coulombs passed, and in that the experiments were carried out in the solid state the conduction mechanism of which is apparently not ionic, the results add little to our understanding of magmatic electrolysis. However, a gross transfer of material from the positive to the negative side was established by weighing the two halves before and after the experiment. Noritomi (1958) studied the electrolysis of a basaltic andesite at temperatures below the melting point, and a gross gain of material was found on his negative side. Spectroscopic analysis of a deposit found on the negative electrode after an experiment at 680 °C—there being no deposit on the positive electrode—showed the Si and Al lines as having a relatively strong intensity; at 868 °C the Na, Ag, and Pb lines were relatively strong. In a third experiment performed at 895 °C the two halves of the specimen were analysed chemically; the negative side was found to be relatively enriched in $Al_2O_3$, CaO, MgO, and $Na_2O$, and the positive side relatively enriched in $SiO_2$, $Fe_2O_3$, and $K_2O$.

A survey of many relevant experiments conducted mainly on artificial glasses is given by Eitel (1954, pp. 197–214, 1338–1384; 1965, pp. 100–116, 472–487).

### *Possible sources of electricity in association with magmas*

When the geologist talks of electric currents in the earth he may be referring to any of three distinct phenomena: electric currents postulated in the earth's core in explanation of the main magnetic field (Rikitake, 1966); galvanic electricity generated in wet rocks containing different metals; or electric currents measurable at the earth's surface (Garland, 1960; Vozoff *et al.*, 1964). The first two kinds of electric currents will not affect magmas at their depth of formation; the third type is not of terrestrial origin, being induced by an incoming wind of ionized hydrogen (Cahill, 1965).

It is more reasonable to attribute any natural electrolytic effects to the action of local currents arising in association with the magma itself. The local nature is emphasized, for if electrolysis be indeed a petrological factor, then—as will be brought out in the sequel—it has only occurred locally, or temporarily. It would accordingly be a special combination of geological circumstances leading to the generation of electricity, which could pre-determine the petrological developments controlled by electrolysis. Four possible sources for local currents arising in association with the magma itself may be suggested:

*The magneto-hydro-dynamic effect* (M.H.D.). This is the formation of an electric current in liquid conductors moving through a magnetic field. Lord Kelvin in the last century was able to measure the current produced in this manner by the River Thames flowing east–west across the local magnetic field. Indeed, a water velocity in the sea of only five knots can induce a field as strong as the telluric field measurable on the continental surface (Longuet-Higgins *et al.*, 1954). M.H.D. effects would be expected to arise in magmas in motion through the earth's magnetic field.

*The Nernst effect.* This is the generation of a current in a static conductor subjected to a magnetic field whilst heat passes along the conductor. It would be expected to be operative in cooling magmas having a temperature gradient.

*The Seebeck effect.* When electrical conductors are joined in circuit, electricity will flow if there is a temperature gradient across the circuit. Noritomi (1955) has measured the 'thermo-e.m.f.' of quartz, perthite, and some metallic minerals when subjected to a temperature gradient: the current measured is largely controlled by the type of conductivity exhibited by the mineral and Noritomi's results cannot be extrapolated to hot rocks or magmas for which direct experiments are required.

*The Galvanic cell effect.* Eitel (1954, pp. 228–236; 1965, pp. 139–162) cites many experiments involving silicates in which appreciable voltages are achieved, culminating in 330 mV measured by Esin *et al.* on a $CaO–Al_2O_3–MgO–SiO_2$ slag cell (Eitel, 1965, pp. 141–143). Silicates of differing composition are held in contact at an elevated temperature and if the circuit is closed a current will flow. The author has measured 20 mV in a granite–basalt molten contact at 1350 °C, the voltage tending to increase with temperature but falling to only 1 mV at 1150 °C. This effect might be expected to be operative at the contacts of igneous rocks against country rocks of different chemical composition.

The quantitative importance of the above effects is unknown for natural magmas. At all events, high temperature is a necessary prerequisite for the development of any appreciable currents because silicate conductivities rise exponentially with rising temperature, and each of the effects enumerated is stronger with increasing conductivity. Solid basalt at 200 °C, for instance, has a conductivity only some $10^{-6}$ that of the melt at 1200 °C; the published rock conductivity data have been summarized by Keller (1966). It is suggested that each of the enumerated generative effects is probably a weak source of current acting alone, and different effects may cancel each other. Occasionally, however, a favourable rare combination could lead to the local production of current sufficiently strong to effect electrolysis in the time available. If electrolysis occurs in nature, accordingly, it is probably a localized phenomenon; the natural analogues of the electrolysed specimens described hereunder do not fall in the category of 'common' rocks.

### *Experimental methods*

*Specimens.* Two separate basalts were used as specimens. The Calton Hill basalt, from Derbyshire, England, was electrolysed in a preliminary experiment, only the alkalies being analysed. A description and analysis of this rock are given by Hamad (1963). The main experiments were carried out on the Golani basalt, collected some 300 m north of the Golani road junction, Lower Galilee, Israel. Under the microscope the Golani basalt is seen to be an alkali olivine basalt. It is fine-grained and intergranular with small olivine and titanaugite phenocrysts. The olivine phenocrysts show hypidiomorphic outlines with narrow iddingsite rims around which an outer rim of fresh olivine is sometimes seen; the 2V is effectively 90°. The pyroxene phenocrysts are idiomorphic and zoned, showing textbook hour-glass structures; the cores in many sections are clearly xenocryst fragments for they show the typical 'cauliflower' structures so typical throughout the area of xenolithic pyroxene at the nodule edge. The groundmass consists of plagioclase, zoned from $An_{85}$–$An_{75}$ probably having slender alkali feldspar rims; titanaugite; equant idiomorphic ore crystals; and a colourless almost isotropic mesostasis too fine to resolve.

*Specimen preparation.* The specimens used were in all cases the natural basalt sawn to brick size. An elongated trough was melted in the top surface of the rock: the specimen thereby served as its own crucible with the object of preventing contamination of the melt. The specimens were heated from above, the electrolysing current being carried by platinum electrodes inserted at either end of the trough.

A trough shape was chosen for the melt in order to minimize mixing of electrolytic products by convection; this arrangement also favoured the recovery of specimens a few grams in weight from each of the regions—

anode, middle, and cathode. The trough length is about 14 cm, and its width $1\frac{1}{2}$ cm; the cross-section is hemispherical and about 3 mm deep.

The Calton Hill rock was melted directly as it stood, but the Golani specimens splintered explosively, even if carefully oven-dried and preheated. The difficulty was overcome by grinding out a trough and filling it with powdered rock, for the powder melted smoothly.

*Heating.* At first a brick oven was built, heated by a Globar, or combination of Globars (silicon-carbide resistance rods) held horizontally over the specimens. However there were difficulties in attaining a controllable temperature high enough to melt the basalt along a narrow zone whilst maintaining the rest of the specimen appreciably cooler. A radical improvement was effected by the use of a Line Heater (Research Incorporated); this is a silica-enclosed tungsten element suspended at one focus of a water-cooled aluminium mirror of elliptical section. The heat is reflected in a concentrated manner along a line, and melting of the basalt can be effected in minutes, as against hours by the former method. No oven is necessary, moreover, the heater standing directly on the specimen unenclosed (or suspended above it); it is possible to observe the melt directly, even whilst the highest temperatures are being maintained; with the aid of a darkened mirror, electrodes can be adjusted whilst an experiment is under way. Indeed, without this facility of open observation the issue of gas during electrolysis might have passed unnoticed.

Both Globars and Line Heater limit the attainable temperature to some 1400 °C. Electrolysis was effected using a 1200-watt Line Heater overloaded to $2\frac{1}{4}$ kW to give temperatures in the range 1250 to 1300 °C; under these conditions the lamps had a life of some three hours. Temperatures were measured using platinum-rhodium thermocouples and a pyrometer.

*Electrolysing current.* The Calton Hill basalt was electrolysed with a welder-like Mallory generator giving 25V. This was replaced for the Golani basalt electrolyses by a rectifying bridge attached to the output of a Variac transformer; 200 V were used. No coulometer was present in the circuit, the number of coulombs passed being estimated from the record of current readings.

### *Experimental results*

The first experiment was electrolysis of the Calton Hill basalt for 16 hours at over 1300 °C; an estimated 2000–3000 coulombs were passed. The results are:

| | *Before electrolysis (from Hamad, 1963)* | *Anode specimen* | *Middle specimen* | *Cathode specimen* |
|---|---|---|---|---|
| $Na_2O$ % | 2·72 | 1·21 | 2·29 | 3·06 |
| $K_2O$ % | 1·16 | 1·07 | 1·18 | 1·31 |
| | 3·88 | 2·28 | 3·47 | 4·37 |
| Na % | 2·02 | 0·90 | 1·70 | 2·27 |
| K % | 0·96 | 0·89 | 0·98 | 1·09 |
| | 2·98 | 1·79 | 2·68 | 3·36 |

Not revealed by these analyses is the loss of gas that takes place at the anode: small bubbles could be seen emerging from the top of the melt around the platinum anode electrode. The gas is certainly an electrolytic product for the emission ceases within seconds of switching off the current, and is resumed at once when the circuit is closed. It is assumed that the gas is oxygen, for no other anionic constituent occurs in basalt in sufficient quantity to supply gas to the degree observed. Oxygen has been reported as a product of the electrolysis of silicates by Bockris, Kitchener, and Davies (1951, 1952).

The experiment was then repeated with the object of making full silicate analyses of the products. A Golani basalt specimen was melted and electrolysed as before except that the changed circuitry permitted a higher amperage to be delivered and the electrolysis was run for a shorter period. An estimated 1500–2500 coulombs were passed during 3½ hours. A third run was made on another Golani basalt block through which an estimated 2300–4300 coulombs were passed. For this run the powder was heated as a ridge upon the flat basalt surface rather than in a trench: the viscosity suffices to maintain the molten ridge and the arrangement favours recovery of larger specimens.

Analytical results are given in table I. Because the heating in air causes severe oxidation of the basalt, a blank specimen was prepared, which underwent the same heat treatment as the first electrolysed Golani specimen (3½ hours). The analysis of this rock is labelled 'oxidized rock' in the tables (O in the figures) and serves as a standard against which the composition of the electrolytic derivatives will be compared. Fig. 1 presents the results as variation diagrams, the oxides being plotted against ($Na_2O+K_2O$).

As oxygen is being lost from the anode during electrolysis, the analytical results have been recalculated in table II to show the weight of the cation portion alone, which is included in each oxide value of the standard analysis. The same treatment was adopted by Nockolds in his geochemical surveys (Nockolds and Allen, 1953, 1954, 1956); a cationic

TABLE I. The Golani basalt: analysis before and after electrolysis. in wt. %

| | Original rock | Oxidized rock | *With ca. 2000 coulombs* | | | *With ca. 3500 coulombs* | | |
|---|---|---|---|---|---|---|---|---|
| | | | *Anode* | *Middle* | *Cathode* | *Anode* | *Middle* | *Cathode* |
| *Analysis no.* | 19 | 21 | 22 | 23 | 24 | 6 | 7 | 8 |
| *Code in figures* | R | O | A | M | C | $\bar{A}$ | $\bar{M}$ | $\bar{C}$ |
| $SiO_2$ | 44·73 | 45·37 | 46·37 | 45·78 | 45·17 | 48·71 | 45·77 | 40·89 |
| $Al_2O_3$ | 14·68 | 14·84 | 15·99 | 14·43 | 14·54 | 15·52 | 30·44 | 28·49 |
| $Fe_2O_3$ | 5·99 | 10·56 | 10·34 | 9·83 | 8·87 | 9·95 | | |
| FeO | 6·31 | 2·10 | 2·64 | 2·69 | 1·90 | 2·96 | n.d. | n·d. |
| MnO | 0·15 | 0·16 | 0·15 | 0·16 | 0·17 | n.d. | n.d. | n.d. |
| MgO | 7·52 | 7·68 | 7·39 | 7·57 | 7·86 | 7·50 | 7·75 | 8·06 |
| CaO | 10·69 | 10·73 | 10·40 | 10·74 | 11·34 | 9·48 | 10·75 | 11·54 |
| $Na_2O$ | 3·24 | 3·22 | 1·69 | 3·46 | 4·71 | 0·58 | 2·76 | 7·90 |
| $K_2O$ | 1·17 | 1·22 | 1·09 | 1·22 | 1·29 | 0·93 | 0·95 | 1·33 |
| $P_2O_5$ | 1·12 | 1·12 | 1·16 | 1·11 | 1·06 | 1·18 | n.d. | n.d. |
| $CO_2$ | 0·10 | 0·13 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| $H_2O^+$ | 1·12 | 0·01 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| $H_2O^-$ | 0·71 | 0·10 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Cl | 0·18 | 0·10 | 0·49 | 0·18 | 0·35 | nd.. | n.d. | n.d. |
| $TiO_2$ | 2·74 | 2·73 | 2·78 | 2·76 | 2·74 | 3·00 | 2·52 | 2·48 |
| Cl corr. | −0·04 | −0·02 | −0·10 | −0·04 | −0·08 | — | — | — |
| | 100·41 | 100·05 | 100·39 | 99·89 | 99·92 | 99·81 | 100·94 | 100·69 |
| $Fe_2O_3/(FeO+Fe_2O_3)$ | 0·49 | 0·83 | 0·80 | 0·79 | 0·82 | 0·77 | — | — |

*Norms (C.I.P.W.)*, calculated water- and $CO_2$-free; $Fe_2O_3/FeO$ ratios adjusted to equal that of 'Original rock'

| | | | *With ca. 2000 coulombs* | | | *With ca. 3500 coulombs* | | |
|---|---|---|---|---|---|---|---|---|
| | *Original rock* | *Oxidized rock* | *Anode* | *Middle* | *Cathode* | *Anode* | *Middle* | *Cathode* |
| *Analysis no.* | 19 | 21 | 22 | 23 | 24 | 6 | 7 | 8 |
| *Code in figures* | R | O | A | M | C | Ā | M̄ | C̄ |
| Apatite | 2·69 | 2·69 | 2·76 | 2·66 | 2·52 | 2·82 | | |
| Halite | 0·29 | 0·16 | 0·16 | 0·29 | 0·57 | — | | |
| Ilmenite | 5·28 | 5·22 | 5·21 | 5·27 | 5·22 | 5·74 | | |
| Magnetite | 8·82 | 8·66 | 8·89 | 8·61 | 7·36 | 8·89 | | |
| Orthoclase | 7·01 | 7·29 | 6·46 | 7·29 | 7·63 | 5·57 | | |
| Albite | 24·02 | 24·18 | 13·64 | 24·86 | 17·10 | 4·93 | | |
| Anorthite | 23·06 | 22·92 | 33·33 | 21·00 | 16·16 | 37·20 | | |
| Woll } Diopside | 9·76 | 9·71 | 4·54 | 10·52 | 13·92 | 0·95 | | |
| En } Diopside | 7·69 | 7·66 | 3·55 | 8·32 | 11·40 | 0·76 | | |
| Fs } Diopside | 0·98 | 0·96 | 0·49 | 1·02 | 0·82 | 0·08 | | |
| En } Hypersthene | — | — | 14·93 | — | — | 18·02 | | |
| Fs } Hypersthene | — | — | 2·07 | — | — | 1·74 | | |
| Forsterite | 7·93 | 8·10 | — | 7·43 | 5·78 | — | | |
| Fayalite | 1·11 | 1·11 | — | 0·99 | 0·46 | — | | |
| Quartz | — | — | 4·01 | — | — | 13·36 | | |
| Nepheline | 1·36 | 1·36 | — | 1·76 | 11·02 | — | | |
| | 100·00 | 100·02 | 100·04 | 100·02 | 99·96 | 100·06 | | |
| Normative colour index | 44·3 | 44·1 | 42·4 | 44·8 | 47·5 | 39·0 | | |
| An content of plagioclase | 49·0 | 48·7 | 71·0 | 45·8 | 48·6 | 88·3 | | |
| Or/total feldspar | 13·0 | 13·4 | 12·1 | 13·7 | 18·7 | 11·7 | | |

Analyses 19–24: Mrs. Z. Shohat; analyses 6–8: Mrs. O. Amit, M.Sc.

presentation would seem the more suitable for all cases in which oxygen saturation is not established.

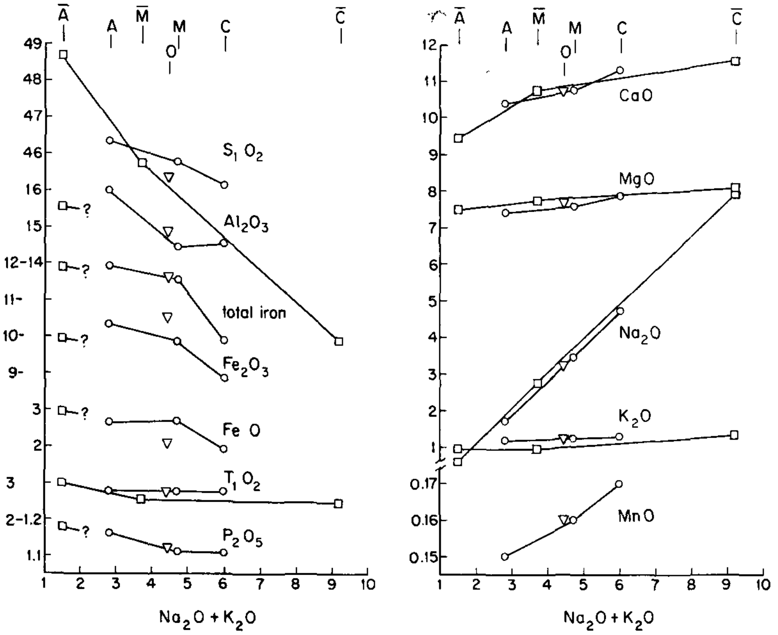

FIG. 1. Golani basalt and its electrolysed derivatives plotted as oxides against ($Na_2O+K_2O$), the most variable constituents. For key see legend to fig. 3 (p. 1118).

## *Interpretation of the results*

In that electrolysis occurs it appears certain that the conductive mechanism in the melt is essentially ionic; this may not be the case for solid basalt, especially at lower temperatures. However, the conductivity data are far from unambiguous in their interpretation: see Tozer (1959) for a discussion of this rather confused matter.

Perusal of the analyses reveals that certain oxides are enriched at the anionic side, others at the cathodic side of the trough. The 'middle' specimens, except for $Al_2O_3$ and FeO, are always intermediate to the anodic and cathodic compositions, and are satisfactorily close to the 'oxidized rock' composition (table I and fig. 1). It should be pointed out that as each specimen includes material lying along $2\frac{1}{2}$–3 cm of the trough length, there was presumably a concentration gradient along each of them prior to their crushing for analysis; and the gross differences

TABLE II. The analyses of table I expressed as weight of cations (in grams) per 100 gram rock, calculated on a water- and chlorine-free basis

| | Original rock | Oxidized rock | With ca. 2000 coulombs | | | With ca. 3500 coulombs | | |
|---|---|---|---|---|---|---|---|---|
| | | | *Anode* | *Middle* | *Cathode* | *Anode* | *Middle* | *Cathode* |
| *Analysis no.* | 19 | 21 | 22 | 23 | 24 | 7 | 7 | 8 |
| *Code in figures* | R | O | A | M | C | $\bar{A}$ | $\bar{M}$ | $\bar{C}$ |
| Si | 20·91 | 21·21 | 21·67 | 21·40 | 21·11 | 22·77 | 21·39 | 19·11 |
| Al | 7·77 | 7·85 | 8·46 | 7·64 | 7·70 | 8·21 | — | — |
| $Fe^{3+}$ | 4·19 | 7·39 | 7·23 | 6·88 | 6·20 | 6·96 | — | — |
| $Fe^{2+}$ | 4·90 | 1·63 | 2·05 | 2·09 | 1·48 | 2·30 | — | — |
| Mn | 0·12 | 0·12 | 0·12 | 0·12 | 0·13 | — | — | — |
| Mg | 4·54 | 4·63 | 4·46 | 4·57 | 4·74 | 4·52 | 4·67 | 4·86 |
| Ca | 7·64 | 7·67 | 7·43 | 7·68 | 8·10 | 6·78 | 7·68 | 8·25 |
| Na | 2·40 | 2·39 | 1·25 | 2·57 | 3·49 | 0·43 | 2·05 | 5·86 |
| K | 0·97 | 1·01 | 0·90 | 1·01 | 1·07 | 0·77 | 0·79 | 1·10 |
| Ti | 1·64 | 1·64 | 1·67 | 1·65 | 1·64 | 1·80 | 1·51 | 1·49 |
| P | 0·49 | 0·49 | 0·51 | 0·48 | 0·46 | 0·52 | — | — |
| Total | 55·57 | 56·03 | 55·75 | 56·09 | 56·12 | 55·06 | unknown | unknown |

between the composition of smaller samples taken from each electrode region would certainly be greater than the values given here.

The general behaviour is summarized in table III, which expresses the enrichment or depletion of each cation relative to its value in the oxidized rock (middle specimen in the case of Calton Hill). If a particular cation occurs to the extent of $x$ % in the oxidized rock then the enrichment is expressed in table III as $(x-y)/y\times 100$ %; a negative value indicates depletion in that cation relative to its concentration in the oxidized rock. It will be seen that the second Golani specimen, which received the most current, in every case shows enrichment in the same sense as the first specimen, and the enrichment degree is usually greater—more markedly so for the more mobile ions.

TABLE III. Cation behaviour on electrolysis of basalt melts. Enrichment (positive numbers) and depletion (negative numbers) expressed as percentages relative to values in the 'oxidised rock' (analysis 21).

| | | *Anode enrichment* (%) | | | *Cathode enrichment* (%) | | | |
|---|---|---|---|---|---|---|---|---|
| *Ion* | *Ionic** *radius* | A(22) | $\bar{A}$(6) | Calton Hill | C(24) | $\bar{C}$(8) | Calton Hill | *Ion-oxygen attraction** |
| $P^{5+}$ | 0·35 | +4·1 | +6·1 | — | −6·1 | — | — | 3·58 |
| $Si^{4+}$ | 0·42 | +2·2 | +7·4 | — | −0·5 | −9·9 | — | 2·64 |
| $Ti^{4+}$ | 0·68 | +1·8 | +9·8 | — | 0 | −9·1 | — | 2·00 |
| $Al^{3+}$ | 0·51 | +7·8 | +4·6 | — | −1·9 | — | — | 1·80 |
| $Fe^{3+}$ | 0·64 | −2·2 | −5·8 | — | −16·1 | — | — | 1·56 |
| $Mg^{2+}$ | 0·66 | −3·7 | −2·4 | — | +2·4 | +5·0 | — | 1·02 |
| $Fe^{2+}$ | 0·74 | +25·8 | +41·1 | — | −9·2 | — | — | 0·94 |
| $Mn^{2+}$ | 0·80 | 0 | — | — | +8·3 | — | — | 0·89 |
| $Ca^{2+}$ | 0·99 | −3·1 | −11·6 | — | +5·6 | +7·6 | — | 0·75 |
| $Na^{+}$ | 0·97 | −47·7 | −82·0 | −47·1 | +46·0 | +145·2 | +33·5 | 1·46 |
| $K^{+}$ | 1·33 | −10·9 | −23·8 | −9·2 | +5·9 | +8·9 | +11·2 | 1·06 |
| $Fe^{t}$† | — | +2·9 | +2·7 | — | −14·9 | — | — | — |

* Ionic radii taken from Handbook of Chemistry and Physics, 46th edition, 1965–66 The Chemical Rubber Company, Cleveland, Ohio).

† $Fe^{t} = Fe^{3+} + Fe^{2+}$).

Na and K are the most mobile ions, Na more so than K; the behaviour of iron is anomalous and will be discussed later.[1] Even if all the electrons were born by oxygen[2] it is sufficient that only one cation species should move to the cathode for the relative proportions of all the other metals to fall in a cathode specimen analysis, and to rise in the anode analysis. Apparent enrichment at the anode, therefore, might mean only that the cation concerned, having not moved towards the cathode, now finds

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[1] In view of the low MnO concentrations, the apparent high mobility (+8·3 % in analysis 24) is not given much weight.

[2] i.e. not carried by ions containing metals.

itself more concentrated than formerly; the establishment of an anode enrichment is accordingly of little value in interpreting what has happened.

However, a positive enrichment of cations in the cathode specimen (postive percentages in table III) indicates real movement. It is thus established that there is a migration of Na, K, Ca, Mn, and Mg towards the cathode.

Considering these 'cathodic' cations, the true mobility of which is not in doubt, it might have been expected that within a particular valency group the smaller ions would be the more mobile. This is the case for sodium and potassium, but not for the divalent ions. Bockris, Ignatowicz, and Tomlinson (1952) studied both the conductivity and electrolysis of many molten silica–oxide binary mixtures; as the result of their comprehensive and careful work they have developed a plausible model which is tentatively adopted with slight adaptations, although the true picture is probably more complex. The ions are classified on the basis of what is here termed their 'ion-oxygen attraction',[1], $I$, into what may be termed lattice-trapped ions and lattice-free ions. With a high $I$ value the ion remains bound in a broken, negatively charged lattice; this is the case here for Al, Ti, P, and, of course, Si. Low $I$ values grant the ions freedom to respond to the attraction of the cathode, and such ions are mobile. Amongst the divalent ions the order of mobility is then the inverse of that expected from the ionic radius alone; this order is reasonably close to that observed (table III) except for ferrous ion. For the univalent ions, however, the ion–oxygen attraction is now so low as to be negligible, and the effect of the radius becomes dominant; sodium accordingly leads potassium in its mobility.

The iron data are puzzling: there is a total gross $Fe^t$ drift towards the anode[2] but this is accompanied by a decreasing valency (higher $Fe^{2+}$ value). The anodic specimens would have been expected to undergo the reaction $Fe^{2+} \rightarrow Fe^{3+} + e$, but the opposite appears to be the case. In the work of Bockris *et al.* (1952) both $Fe^{2+}$ and Mg occupy an intermediate position in the ion–oxygen attraction scale. It appears likely that most of the $Fe^{2+}$ in the basalt experiment is oxidized on heating to $Fe^{3+}$ and migrates in this lattice-trapped trivalent state towards the anode; but the anomalous formation of ferrous iron is a phenomenon requiring further study and it is premature to offer explanations; a

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[1] $I = 2z/(r_i - r_o)^2$, where $z$ is the ionic charge, $r_i$ the ionic radius, and $r_o$ the radius of the oxygen ion.

[2] The symbol $Fe^t$ is used for $(Fe^{2+} + Fe^{3+})$.

degree of electronic conduction may be involved. It is hoped that experiments in hand using an inert atmosphere will help to clarify this point.

Bockris, Kitchener, and Davies (1952) have shown that oxygen is released from most synthetic silicate melts in an amount strictly equivalent to the current passed. However, they have argued that the oxygen most probably stems from a reaction such as $SiO_4^{4-} \rightarrow SiO_2+O_2+4e$ rather than by the direct release of oxygen. The implication is that Ti, Al, P, and Si (and perhaps $Fe^{3+}$) are effectively bound in complex ions, which must actually migrate towards the anode. Such a behaviour can also be expected on the basis of the known tendency of these ions to form complex anions.

### *Petrological applications*

C.I.P.W. norms of the Golani specimens are given in table I. Analyses 7 and 8 are unfortunately incomplete, and direct knowledge as to the cathode development under the stronger electrolysis is lacking. In each norm calculation the ferrous–ferric ratio has been adjusted to that obtaining in the original rock (analysis 19); calculations with uncorrected oxide values give strikingly different norms having higher magnetite values, some hematite, and consequent excess of free quartz. Examination of the norm reveals the following main features in the electrolytic products, relative to the original rock (alkaline olivine basalt):

The anodic rock is quartz-bearing, more salic, and its plagioclase is more basic; it is distinctly calc-alkaline in character. These features are more pronounced in specimen $\bar{A}$ (analysis 6). The rock may be regarded in general terms as quartz dioritic with basic plagioclase.

The cathodic rock is nepheline-bearing, more femic, and its plagioclase is more acidic; it is distinctly alkaline in character, and in general terms may be regarded as theralitic.

The anodic rocks are slightly iron enriched (fig. 3) relative to the parent rock, and the cathodic specimen has a correspondingly depleted iron–magnesium ratio. However, as discussed in the former section, the behaviour of iron is not understood, nor can its distribution be extrapolated to conditions under which the specimen would not be oxidized by heating in air. Future work in non-oxidizing environments may well lead to a revision of some conclusions presented here. However, in that the electrolysed rocks are in a lower state of oxidation than the non-electrolysed O specimen, the analyses with respect to iron are taken at their face value in the sequel. The calc-alkaline (anodic) derivative is accordingly considered as showing concomitant iron enrichment, whereas the alkaline (cathodic) rock becomes magnesian relative to the parent magma.

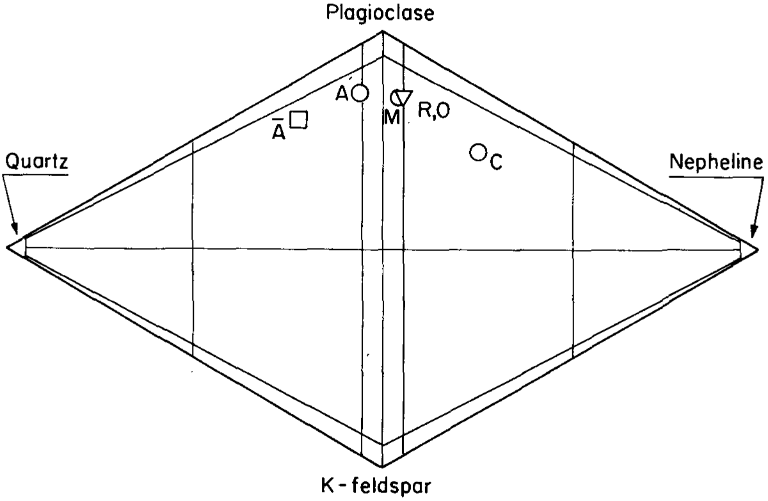

FIG. 2. Golani basalt and its electrolysed derivatives plotted in a Johannsen double triangle; the components are normative. For key see legend to fig. 3.

The normative mineral compositions are plotted on a Johannsen double triangle in fig. 2. As it is probable that more, or less, electrolysis would lead to a composition lying at different points along the general trends R–C and R–A–Ā (or their extension) there is little advantage in translating the particular compositions of these points into closely defined rock types; it is rather the trend involved that is of interest.

In fig. 3 the cationic sodium, potassium, and calcium values are plotted. The Golani analyses fall along a single straight line, which line is less regular if oxide values are used. The laws controlling the behaviour of each ion on electrolysis are presumably unchanged by the passage of a larger current, provided that the composition is not so drastically altered that a component be completely removed from any part of the system. Trends observable on mild electrolysis can accordingly be expected to be maintained, to an enhanced degree, with stronger electrolysis. Accordingly the straightness—or rather uniformity—of the line joining the experimental points permit the prediction that stronger electrolysis would cause a yet greater spread between the new 'A' and 'C' specimens without altering the direction of the trend.

Fig. 3 shows further that the increase in total alkalis in the cathode specimen (relative to the original and oxidized rocks) is accompanied by a prominent increase in the Na/(Na+K) values. In the anodic rock, conversely, not only is the total amount of alkalies reduced but the Na/(Na+K) ratio decreases to such an extent that in specimen Ā (analysis 6) the K content actually exceeds that of Na. The same tendencies are shown by the Calton Hill specimens, the analyses of which are projected along the Na–K boundary.

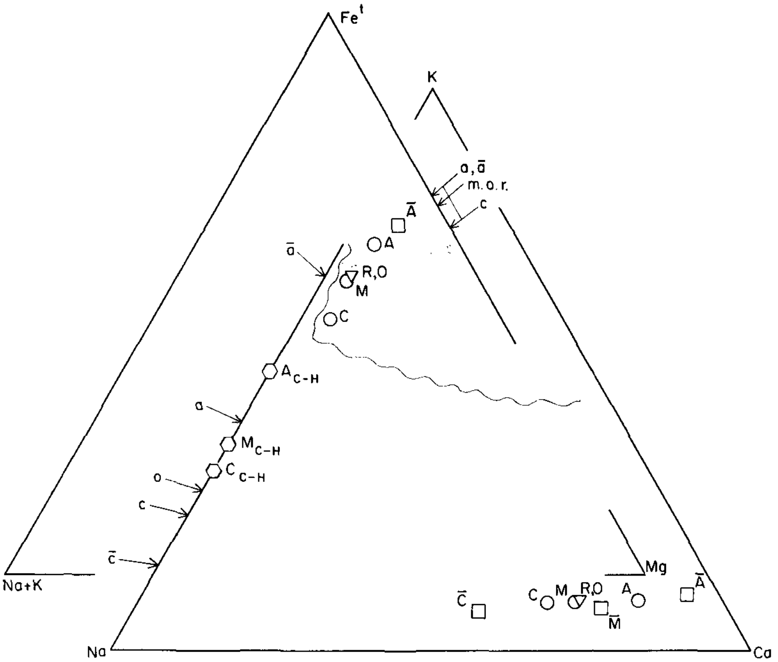

FIG. 3. Golani and Calton Hill basalts and their electrolysed derivatives plotted in AFM and Na–K–Ca diagrams (cationic values). Golani basalt: ▽, R, original rock (anal. 19) and O, oxidized rock (anal. 21); ○, A, anodic rock (anal. 22), M middle rock (anal. 23), and C cathodic rock (anal. 23), all with 2000 coulombs; □, Ā, anodic rock (anal. 6), M̄, middle rock (anal. 7), and C̄, cathodic rock (anal. 8), all with *ca.* 3500 coulombs. The Na/(Na+K) and Fe/(Mg+Fe$^t$) values are marked by arrows. Calton Hill basalt (Na/(Na+K) projections only): ⬡, A$_{C-H}$, anodic rock, M$_{C-H}$, middle rock, and C$_{C-H}$, cathodic rock, all with *ca.* 2500 coulombs.

Further illustration of the electrolytic process is given in the cationic A–F–M diagram included in fig. 3. The analyses fall on a smooth curve.

the cathodic and anodic specimens lying at the extremes. The available points do not permit an accurate prediction of the extension of the curve with stronger electrolysis yet its shape cannot be far removed from a straight line; were this not so the accompanying trends of alkali enrichment (*impoverishment*) and $\mathrm{Fe^t/(Mg+Fe^t)}$ impoverishment (enrichment) would not be maintained. It follows that were a melt that is electrolysed to have had a composition other than that of O, the general course of its development can reasonably be expected to be similar to that of basalt provided that the same components are involved with no gross differences in their abundance. Thus, for igneous rocks other than basalt the electrolytic products should fall along, or close to, a line passing through the original composition in such a manner that the cathodic product shows a simultaneous (Na+K) enrichment together with depletion in the $\mathrm{Fe^t/(Mg+Fe^t)}$ ratio when plotted in an AFM triangle. Similarly a (Na+K) enrichment will be seen in the Na–K–Ca diagram, with increasing Na/(Na+K) for the cathodic product; the anodic product should fall on, or close to, the straight line joining the cathodic and original compositions.

Fig. 4 repeats the plots of fig. 3 with the addition of the three Hawaiian lava series, the tholeiite-, alkaline-, and the Oahu ultra-alkaline-series; the data were taken from the analyses recalculated by Nockolds and Allen (1954, 1956). In the AFM diagram the group of alkali olivine basalts lying along the line *c–d* fulfil the conditions for an electrolytic origin from an original lava situated midway along the line. 'Anodic', 'middle', and 'cathodic' points are appropriately marked in the figure; it will be noted that not only are the 'cathodic' lavas alkali-enriched, but their $\mathrm{Fe^t/(Mg+Fe^t)}$ values are depleted relative to the 'anodic' lavas. The alkali olivine basalts of line *a–b*, on the other hand, cannot constitute an electrolytic series. For although the lavas near the point *b* appear 'cathodic' relative to those near the point *a*, they (the 'cathodic') are more iron-enriched than are the 'anodic' lavas. The Skaergaard-type differentiation is similarly at variance with the electrolytic trend, its increasing alkalinity being accompanied by increasing $\mathrm{Fe^t/(Mg+Fe^t)}$ values.

Having noted that basalt electrolysis produces normatively alkaline rocks as its cathodic product it is of interest to examine in the AFM diagram of fig. 4 whether the Oahu ultra-alkaline rocks are amenable to an 'electrolytic' explanation. The supplementary anodic products might well be the tholeiites at the top of the line passing through a potential 'middle' rock such as the indicated tholeiite (line *e–f*). However, when the Hawaiian rocks under discussion are examined in the

Na–K–Ca diagram (fig. 4) these conjectures fall. The lines *a–b*, *c–d*, and *e–f* are still clearly recognizable, and their Na/(Na+K) values have been marked along the Na–K edge of the triangle. The line *a–b* had already been eliminated as an electrolytic trend on the basis of its iron behaviour; its Na/(Na+K) behaviour is similarly unsuitable. In the line *c–d* the

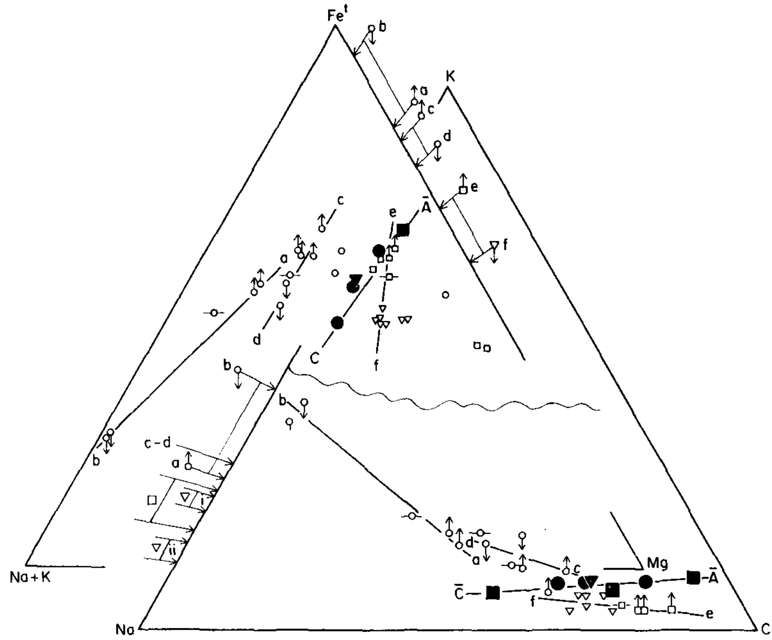

FIG. 4. The diagram of fig. 3 to which analyses of Hawaiian lavas have been added: ○, alkali olivine basalts (Nockolds and Allen, 1954, Table II); □, tholeiites, Kilauea (Nockolds and Allen, 1956, Table 28); ▽, ultra-alkaline lavas, Oahu (Nockolds and Allen, 1954, Table 13). Lines *a–b*, *c–d*, *e–f*, Ā–C, Ā–C̄ explained in the text. The $Fe^t/(Mg+Fe^t)$ and Na/(Na+K) values of each Hawaiian trend-line are marked by arrow-heads. Lavas having apparent 'anodic' affinities in the AFM diagram are marked by upward pointing arrows, those having apparent 'middle' affinities by horizontal ticks, and those having apparent 'cathodic' affinities by downward pointing arrows. The same lavas are similarly marked in the Na–K–Ca diagram.

'anodic' and 'cathodic' rocks have reversed Na–K relationships to those of the Ā–C̄ experimental trend. The tholeiites of the line *e–f* lie favourably with respect to the ultra-alkaline rocks of group ii (lying below the line *e–f* in the Na–K–Ca diagram); but the ultra-alkaline rocks of group i (lying above the line *e–f* in the Na–K–Ca diagram) are more potassic than the postulated 'anodic' tholeiites, and again an electrolytic origin cannot be maintained for these rocks.

It may be concluded that the chemistry of the Hawaiian lavas is not compatible with the idea that their evolution has been controlled by the electrolysis of a basaltic magma. It would furthermore be pretentious at this stage to claim for any common igneous rock associations a chemistry analogous to that of the experimental electrolytic series. However, were rarer rocks of electrolytic origin to exist, then the results presented here should provide a criterion for their distinction.

Nothing has been said of the loss of oxygen observed during electrolysis. Osborn (1962) has pointed out the contrasted courses of development that can be followed by crystallizing basalt magmas having different degrees of oxygen pressure. Electrolysis would evidently provide a mechanism for such a variation in the oxygen content.

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