

Geochemical features of the rocks of the Great Tolbachik Fissure Eruption 1975–1976 in relation to petrogenesis

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A study has been made of the distribution in the rocks produced by the eruption of the major (Si, Al, Mg, Ca, Fe, Ti, Na, K, P) and minor (Rb, Li, F, B, Be, Ag, Nb, Ta, Zr, Hf, Ba, Sr, Ni, Co, Cr, V, Cu, Zn, Pb, Sn, Ga, Mo, Mn, Sc, As, Ge, Y, La, Ce, Nd, Yb) elements. The degree of detail involved and the accuracy of the methods used varied. The most detailed data were obtained for the major elements and also for Rb, Li, F, B, Be, P, Ti, Ni, Co, Cr, V, Cu, Zn, Pb, Sn and Ga; data on the remaining elements are so far only preliminary. The quantities of the major elements were determined by the usual methods of complete silicate analysis of the rocks in the chemical laboratory of the Institute of Volcanology of the DVNTs AN SSSR. The Na, K, Pb and Li contents were determined in the Vinogradov Institute of Geochemistry of SO AN SSSR (using flame photometry), as well as F, B, Be and Ag (by the quantitative spectrum method using special techniques evolved for F, B and Be by L. L. Petrov, and for Ag by V. A. Legeydo), Ba, Sr, La, Ce, Nd, Y and Yb (using quantitative X-ray spectroscopy), Sr, Mg, Ca and Al (using atomic absorption on the Perkin-Elmer 403 instrument), and Nb, Ta, Zr and Hf (using the spectrochemical method). The Ni, Co, Cr, V, Ga, Pb, Zn, Cu and Sn contents were determined by quantitative spectroscopy in the physical chemistry research laboratory of the Far East Geological Institute of the DVNTs AN SSSR. Preliminary data on the Ni, Co, Cr, V, Ag, Cu, Zn, Pb, Mo, Sn, Sc, Ga, Ge, Y, Zr, P, Ti, Mn, B and Nb contents were obtained using refined semi-quantitative spectrum analysis in the laboratory of the Geochemical Expedition of the Central Geophysical Trust (in the town of Aleksandrov). The As and Sb contents were also determined there, using a special technique of quantitative spectrum analysis. At the Institute

of Geochemistry of SO AN SSSR two determinations were made of the isotope composition of Sr from basalts of the eruption.

Mention must first be made of information published earlier (Volynets *et al.*, 1976a) on the petrochemical properties of the solid volcanic products of the eruption. As was noted there, all the rocks of the eruption correspond to basalts in their composition. And although in Yoder & Tilley's classification (1965) they are all placed in one group – that of the olivine–tholeiites, since they contain normative olivine and hypersthene – the basalts of the Northern and Southern Breakthroughs differ greatly in Al_2O_3 , MgO, CaO, K_2O , Na_2O , P_2O_5 and TiO_2 content. The MgO and CaO content is higher in the basalts of the Northern Breakthrough, whilst that of the other components is higher in the Southern Breakthrough (Table 1, Fig. 1). The difference in silica and iron oxide content in the two Breakthroughs is very small (0.6–0.7%), both being slightly higher in rocks of the Southern Breakthrough. Because of the sharp decrease in Mg content in the rocks of the Southern Breakthrough compared with the Northern, the former are much more ferruginous than the latter (50–60 at. %, as against 30–40%). The basalts of both Breakthroughs have a similar degree of iron oxidation (25–35 at. % for the vast majority of the rocks).

These very different basalts of the Northern and Southern Breakthroughs are united in the course of the eruption by the appearance of basalts of an intermediate composition (see Fig. 1). The latter occur mainly at the end of the Northern and beginning of the Southern Breakthroughs and over an extremely limited interval of time. The composition of the basalts of the Northern Breakthrough began to change only a week before it ceased activity (the Northern Breakthrough lasted a total of ten weeks). That of the basalts of the Southern Breakthrough (which lasted almost fifteen months) also changed radically only in the first week of the eruption, although over the next two months the composition gradually evened out. One must also remember that the volumes of the intermediate basalts are quite small, comprising only 5–10% of the volume of rocks from each Breakthrough.

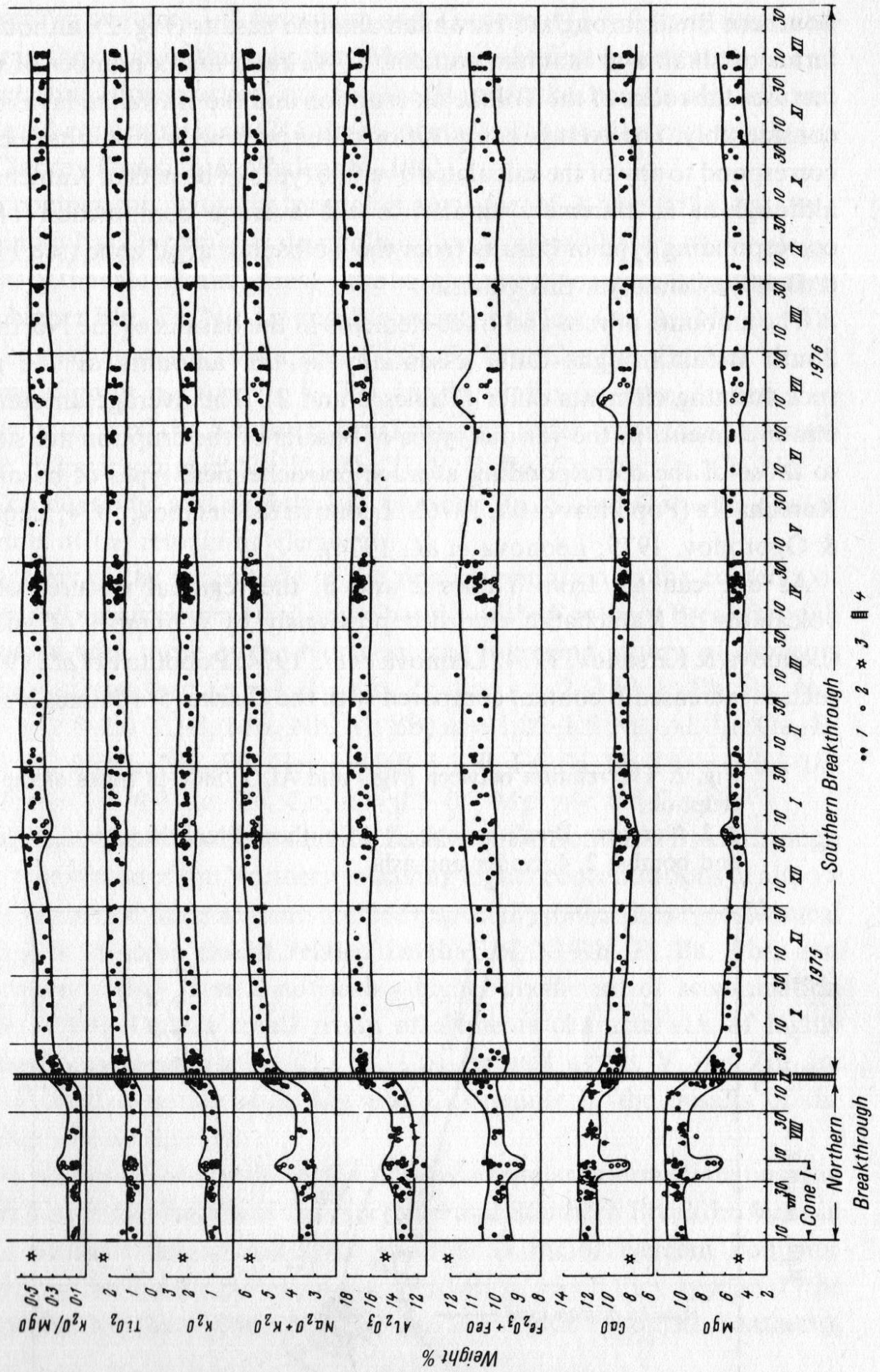
According to the classification scheme offered earlier for Quaternary basalts of Kamchatka (Volynets *et al.*, 1976b), the basalts of the Northern Breakthrough are of the magnesian type with moderate alkalinity and the basalts of the Southern Breakthrough are of the aluminous subalkaline type. In terms of the ratio of MgO to $\text{Al}_2\text{O}_3/\text{SiO}_2$ the basalts of the Northern Breakthrough are similar to Hawaiian tholeiites, those of the

Table 1. Average chemical composition of basalts from the Tolbachik eruption of 1975–76

Oxides	Northern Breakthrough		Southern Breakthrough		
	Predominant lava types (7 July 75–10 Sept. 75)	Intermediate lavas from the end of the Northern Break-through (11–15 Sept. 75)	Intermediate lavas from the first days of the Southern Break-through (18–24 Sept. 75)	Intermediate lavas from the start of the eruption (25 Sept.–30 Nov. 75)	Predominant lava types (1 Dec. 75–9 Dec. 76)
SiO ₂	49.76 49.18–50.91	50.02 49.46–50.74	50.30 49.58–50.76	50.90 50.20–51.46	50.69 49.72–51.88
TiO ₂	1.02 0.83–1.10	1.30 1.10–1.59	1.51 1.31–1.78	1.70 1.45–1.85	1.66 1.30–1.95
Al ₂ O ₃	13.48 12.10–14.22	15.32 13.83–16.35	16.62 16.02–17.07	16.83 16.12–17.30	17.10 15.91–18.60
Fe ₂ O ₃	3.06 2.08–4.86	3.47 2.22–4.87	3.14 2.03–5.09	3.42 2.74–4.46	3.55 1.49–6.01
FeO	6.99 5.48–8.19	6.88 5.72–7.47	6.95 5.11–7.61	7.05 5.82–7.56	6.99 4.78–8.79
MnO	0.16 trace–0.21	0.17 0.15–0.18	0.18 0.13–0.20	0.17 0.17–0.21	0.17 0.08–0.22
MgO	9.88 9.21–10.66	7.69 6.21–8.83	6.44 5.74–6.95	5.39 4.42–6.26	4.87 3.83–5.83
CaO	11.60 10.46–12.34	9.83 9.12–10.53	9.20 8.67–9.75	8.74 8.06–9.17	8.65 7.84–9.42
Na ₂ O	2.44 2.18–2.75	3.14 2.83–3.96	3.30 3.09–3.52	3.36 3.21–3.72	3.60 3.24–3.97
K ₂ O	1.03 0.84–1.44	1.62 1.36–1.89	1.83 1.75–2.02	1.99 1.85–2.19	2.10 1.88–2.40
P ₂ O ₅	0.25 0.16–0.37	0.35 0.27–0.40	0.40 0.20–0.52	0.40 0.13–0.57	0.53 0.42–0.68
H ₂ O ⁺	0.13 0.00–0.68	0.09 0.00–0.43	0.02 0.00–0.19	0.06 0.00–0.20	0.06 0.00–0.39
H ₂ O ⁻	0.18 0.00–0.34	0.11 0.00–31	0.19 0.00–0.34	0.25 0.00–0.50	0.11 0.00–0.46
<i>n</i>	21	11	8	14	85

n is the number of analyses for calculation of the average analysis. The numerator gives the average content for basalts, the denominator the range of content in individual samples.

Fig. 1. Variation of chemical composition of rocks during eruption. 1, lavas, bombs; 2, ashes; 3, cinders from summit crater of Ploskiy Tolbachik; 4, pause between eruptions of the Northern and Southern Breakthroughs. Black circle with dot, data from atomic absorption method. Remaining signs, results of bulk silicate analysis.



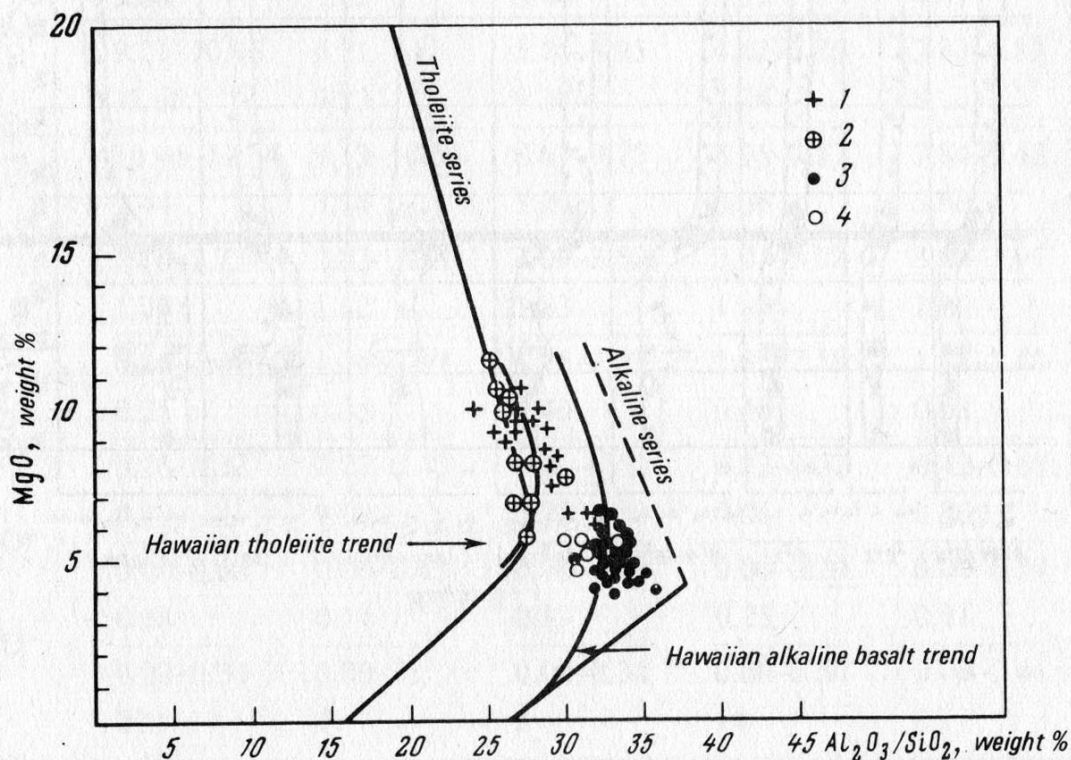
Southern Breakthrough to Hawaiian alkaline basalts (Fig. 2), although in terms of alkali and titanium content, K/Na ratio and a number of other features the rocks of the Tolbachik eruption and the Hawaiian lavas differ considerably. The average composition of the intermediate basalts does not correspond to any of the calculated average types of basalts of Kamchatka, although it is extremely similar to the average composition of the corresponding type of basalts from the Tolbachik areal zone (see Flerov & Bogoyavlenskaya, this volume).

The amounts of rare and trace elements in the basalts of the North and South Breakthroughs differ essentially as the amounts of the main rock-forming elements differ (Tables 2 and 3). The average amounts of minor elements in the various types of basalts of the eruption are similar to those of the corresponding average petrochemical types of basalts of Kamchatka (Popolitov *et al.*, 1976b; Leonova & Kirsanov, 1974; Leonova & Ogorodov, 1975; Leonova *et al.*, 1974).

As one can see from Tables 2 and 3, the regional features of the volcanites of Kamchatka recorded previously by a number of authors (Leonova & Kirsanov, 1974; Leonova *et al.*, 1974; Popolitov *et al.*, 1976a), such as increased B content compared with the Clarke (5–10 times higher),

Fig. 2. The relation between MgO and Al_2O_3/SiO_2 in rocks of the eruption.

1–2, Northern Breakthrough; 3–4 Southern Breakthrough; 1, 3, lavas and bombs; 2, 4, cinder and ash.



a lower Nb content (3–5 times less) and Ti content (1.3–2 times less), also occur in the rocks of this eruption. Moreover, the first quantitative As and Sb determinations carried out for the Kamchatka basalts also showed increased concentrations (2–5 times greater) of these elements relative to the Clarke (Turekian & Wedepohl, 1961).*

In comparison with the predominant type of Kamchatka basalts – aluminous basalts of moderate alkalinity (or, to use a different terminology, basalts of the calc-alkalic series) – the basalts of the Northern Breakthrough have higher Mg, Cr, Ni, Ag and B contents and less Cu, Be, Nb and Ta, with similar amounts of Ca, Fe, Ti, Sr, P, Mn, Co, La, Ce, Nd, Y and Yb and slightly less Al, Na, K, Rb, Li, Ba, F, Pb, Sn, Mo, Zn and V.

The basalts of the Southern Breakthrough differ from this dominant basalt in having higher Na, K, Rb, Ti, P, B, Be, Cu, Nb, La, Ce, Nd, Y and Yb contents, and slightly less Mg, Ca, Zn, V and Co, with similar amounts of the remaining elements.

In terms of the magnitude of the relative variation in the contents of major and minor elements (n) in the basalts of the Southern Breakthrough compared with those of the Northern, the following groups of elements can be distinguished: $n > 3$ Hf, Rb, Zr, La; $n = 2-3$ K, P, Pb, Ba, Nd, Be; $n = 1.5-2.0$ Ti, B, Mo, Nb, Y, Yb; $n = 1.25-1.5$ Na, Al, Li, Ga, F; $n = 1.1-1.25$ Cu, Mn, Sb, Ge; $n = 0.9-1.1$ Si, Fe, Sn, Sr, Ta; $n = 0.8-0.9$ Sc, V; $n = 0.7-0.8$ Ca, Zn, Co; $n = 0.5-0.7$ Mg; $n < 0.5$ Cr, Ni.

It follows from the above that the basalts of the Southern Breakthrough differ from those of the Northern in having higher concentrations of almost all the minor and trace elements studied (especially those whose geochemical history is to some extent related to that of K–Rb, P, Ba, Pb), and consequently they have a noticeably higher coefficient of accumulation (Shaw, 1969). Only a small group of elements characteristic of highly magnesian types of rocks (Cr, Ni, Co), as well as Sc, V and Zn, are concentrated (together with Mg and Ca) mainly in the basalts of the Northern Breakthrough.

The basalts of intermediate type occupy a regular intermediate position in relation to the basalts of the Northern and Southern Breakthroughs in terms of their minor and trace as well as major element contents. Moreover, during the period of the eruption in which they appeared (the end of the Northern Breakthrough and the beginning of the Southern),

* Data in the authors' possession on the Sb content in intermediate–acidic Quaternary lavas of Kamchatka, obtained independently by the neutron activation method, are also 5–10 times higher than the Clarke.

Table 2. Content of minor elements in basalts of the Tolbachik eruption from results of refined semiquantitative analysis

Elements	Northern Breakthrough		Southern Breakthrough			Holocene
	Predominant mass of rocks 5 July–10 Sept. 75 (43)	Intermediate varieties 11–15 Sept. 75 (12)	Intermediate varieties 18–24 Sept. 75 (31)	Intermediate varieties 24 Sept.–30 Nov. 75 (27)	Predominant mass of rocks 1 Dec. 75–9 Dec. 76 (55)	Megaplagiophyre lavas of the Tolbachik zone of cinder cones (9)
1	2	3	4	5	6	7
Cu	160 50–300	160 120–300	230 100–400	210 100–400	340 150–500	200 100–400
Zn	230 80–800	170 120–250	210 100–400	200 120–300	270 200–600	180 120–250
Pb	2.5 2.0–3.0	4 2.0–6.0	5 2.0–10.0	4.5 4.0–20	7 4.0–15.0	7 3.0–15.0
Ni	55 20.0–100.0	40 30.0–80.0	40 20.0–80.0	35 20.0–50.0	35 20.0–60.0	30 20.0–40.0
Co	25 8.0–50.0	20 12.0–40.0	20 10.0–40.0	20 12.0–30.0	23 12.0–40.0	20 8.0–30.0
Cr	390 150–1000	300 200–400	270 120–500	210 150–400	160 100–300	130 60–250
V	230 80–400	220 150–300	280 120–500	260 200–400	260 200–600	250 200–500
Mo	0.5 0.3–0.8	0.6 0.4–1.0	0.7 0.3–2.0	0.9 0.6–1.5	1.0 0.6–1.5	1.0 0.3–1.5
Ag	—	0.08 0.08–0.08	0.07 0–0.1	0.05 0–0.4	0.08 0.08–0.6	0.08 0–0.12
Mn	1100 100–1500	950 600–1200	950 500–1500	950 600–1200	1300 1000–1500	950 600–1000
As	5 2.0–15	4 3.0–8.0	4 3.0–6.0	5 3.0–15.0	5 3.0–20.0	3 2.0–4.0
Sb	0.4 0.0–3.0	1.7 0.0–8.0	1.4 0.0–6.0	2.3 0.0–5.0	1.5 0.0–6.0	1.2 0.0–4.0
Sn	1.5 0.0–3.0	1.7 1.0–4.0	1.1 0.0–5.0	1.3 1.0–3.0	2.6 2.0–5.0	2.0 1.0–5.0
Sc	9 0.0–12.0	10 8.0–12.0	8 0–12.0	10 8.0–12.0	8 8.0–10.0	8 8.0–10.0
Ti	1700 500–8000	2100 500–3000	1900 1000–4000	1900 1500–5000	3900 40–6000	2800 2000–5000
Nb	0.02 0.0–8.0	2 0.0–8.0	0.5 0.0–8.0	1.2 0.0–8.0	2.2 0.0–8.0	1.0 0.0–8.0
Y	8 8.0–10.0	10 8.0–12.0	9 8.0–10.0	9 8.0–15.0	10 8.0–12.0	9.0 8.0–12.0

Table 2. (cont.)

Elements	Northern Breakthrough		Southern Breakthrough			Holocene
	Predominant mass of rocks 5 July– 10 Sept. 75 (43)	Intermediate varieties 11–15 Sept. 75 (12)	Intermediate varieties 18–24 Sept. 75 (31)	Intermediate varieties 24 Sept.– 30 Nov. 75 (27)	Predominant mass of rocks 1 Dec. 75– 9 Dec. 76 (55)	Megaplagio- phyre lavas of the Tolbachik zone of cinder cones (9)
l	2	3	4	5	6	7
Zr	$\frac{70}{50-80}$	$\frac{75}{60-100}$	$\frac{70}{50-100}$	$\frac{70}{50-80}$	$\frac{80}{50-100}$	$\frac{75}{60-100}$
P	$\frac{1400}{600-2000}$	$\frac{2700}{300-4000}$	$\frac{3700}{1000-6000}$	$\frac{3100}{2500-6000}$	$\frac{5400}{2000-8000}$	$\frac{3200}{2000-5000}$
Ge	$\frac{1.0}{0.0-2.0}$	$\frac{0.9}{0.8-1.0}$	$\frac{1.1}{0.0-2.0}$	$\frac{0.8}{0.0-2.0}$	$\frac{1.3}{1.0-2.0}$	$\frac{0.8}{0.0-1.2}$
Ga	$\frac{11}{6.0-15.0}$	$\frac{12}{8.0-20.0}$	$\frac{14}{8.0-25.0}$	$\frac{11}{6.0-20.0}$	$\frac{19}{12.0-30.0}$	$\frac{9}{6.0-20.0}$
B	$\frac{25}{12.0-30.0}$	$\frac{30}{15.0-40.0}$	$\frac{30}{15.0-60.0}$	$\frac{25}{20.0-50.0}$	$\frac{60}{30.0-100.0}$	$\frac{35}{20.0-50.0}$

Numbers in brackets are the number of analyses made; content of elements in g/t. Numerator is average content of minor element; denominator is range from minimum to maximum content.

the amounts of these elements generally changed uniformly from those typical of magnesian basalts with moderate alkalinity to ones typical of subalkaline aluminous basalts (see Figs 1 and 3). Correspondingly, the dispersions of the amounts of the individual elements in the basalts of intermediate composition greatly exceed (by 1.5–3 times) those for the predominant mass of rocks of each Breakthrough.*

Appreciable differences can also be observed in the composition of basalt samples of the intermediate stage collected during a single day of the eruption. Thus, whereas in those from one day's eruption of the Northern Breakthrough the variations in Na content do not exceed 0.15–0.18%, K 0.08–0.10%, Rb 1–2 g/t, B 3–10 g/t, F 100–150 g/t, Be 0.3–0.5 g/t, and MgO 1.0–1.3%, in basalts of the last day's eruption of this Breakthrough the variations in Na content attain 0.3%, K 0.4%, Rb 7 g/t, B 20 g/t, F 420 g/t, Be 1 g/t, and MgO 2.6%. For the purposes of comparison we should point out that during the first two months of the eruption of the Northern

* This does not apply to F, B and H₂O⁺, whose behaviour during the eruption is examined in a separate paper.

Table 3. *Content of minor and rare elements in basalts of the Tolbachik eruption*

Elements	Northern Breakthrough		Southern Breakthrough		
	Predominant lava types (7 July 75–10 Sept. 75)	Intermediate lavas from the end of the eruption (11–15 Sept. 75)	Intermediate lavas from the first days of the eruption (18–24 Sept. 75)	Intermediate lavas from the start of the eruption (25 Sept. 75–30 Nov. 75)	Predominant lava types (1 Dec. 75–9 Dec. 75)
1	2	3	4	5	6
Na	1.87 (68)	2.27 (15)	2.54 (18)	2.67 (19)	2.71 (136)
	1.62–2.18	2.04–2.58	2.35–2.80	2.38–2.76	2.48–3.40
K	0.75 (68)	1.31 (17)	1.49 (18)	1.60 (19)	1.75 (136)
	0.66–0.86	1.00–1.60	1.40–1.57	1.52–1.68	1.66–2.21
Rb	11.6 (56)	23.7 (7)	31.4 (11)	40.0 (15)	46.5 (94)
	10–14	20–30	27–35	31–50	38–60
Li	9.8 (56)	12.4 (7)	13.7 (11)	15.1 (14)	15.7 (81)
	4.5–23.0	8–16	10–19	11–21	10–48
F	285 (65)	350 (19)	350 (22)	310 (27)	405 (147)
	150–560	190–680	180–540	250–500	110–830
B	34 (72)	43 (19)	57 (22)	56 (27)	60 (167)
	19–48	20–57	20–85	45–66	40–99
Be	0.67 (75)	1.1 (19)	1.4 (23)	1.3 (27)	1.5 (167)
	0.45–1.30	0.70–1.90	1.0–2.2	0.90–1.70	0.80–2.60
Ba	330 (15)	440 (4)	535 (7)	535 (6)	870 (11)
	280–360	420–470	430–600	450–690	570–1100
Sr	315 (16)	425 (5)	410 (8)	470 (6)	325 (11)
	220–450	300–530	240–530	360–570	240–450
Ni	120 (28)	78 (10)	71 (11)	41 (10)	52 (50)
	55–182	40–125	36–130	26–55	24–100
Co	42 (28)	32 (10)	31 (11)	29 (10)	31 (50)
	30–57	24–42	25–45	23–35	20–46
Cr	265 (28)	195 (10)	145 (11)	120 (10)	102 (48)
	160–460	100–430	85–200	57–190	38–210
V	250 (28)	220 (10)	225 (11)	170 (10)	210 (50)
	150–320	150–310	158–300	93–240	93–320

Table 3. (cont.)

Elements	Northern Breakthrough		Southern Breakthrough		
	Predominant lava types (7 July 75– 10 Sept 75)	Intermediate lavas from the end of the eruption (11–75 Sept. 75)	Intermediate lavas from the first days of the eruption (18–24 Sept. 75)	Intermediate lavas from the start of the eruption (25 Sept. 75– 30 Nov. 75)	Predominant lava types (1 Dec. 75– 9 Dec. 75)
1	2	3	4	5	6
Ga	<u>12 (28)</u>	<u>11 (10)</u>	<u>12 (11)</u>	<u>12 (10)</u>	<u>16 (50)</u>
	7–20	5–19	5.5–22	6–19	7–28
Pb	<u>2.7 (28)</u>	<u>3.2 (10)</u>	<u>4.4 (11)</u>	<u>3.5 (10)</u>	<u>5.9 (50)</u>
	0–5	0–6	2–7	2–6	0–12
Zn	<u>75 (27)</u>	<u>52 (10)</u>	<u>58 (10)</u>	<u>45 (10)</u>	<u>59 (50)</u>
	42–91	28–110	36–79	36–63	30–100
Cu	<u>145 (28)</u>	<u>140 (10)</u>	<u>170 (11)</u>	<u>155 (10)</u>	<u>175 (50)</u>
	100–220	110–190	110–240	110–190	110–290
Sn	<u>3.3 (28)</u>	<u>2.2 (10)</u>	<u>3.1 (11)</u>	<u>2.4 (10)</u>	<u>3.3 (50)</u>
	1–5	1–4	1–9	1–4	1–5
Ag	<u>0.15 (51)</u>	<u>0.13 (7)</u>	<u>0.15 (9)</u>	—	—
	0.08–0.25	0.11–0.16	0.12–0.19		
F	<u>0.11 (29)</u>	<u>0.16 (15)</u>	<u>0.18 (10)</u>	<u>0.18 (18)</u>	<u>0.24 (74)</u>
	0.07–0.16	0.12–0.19	0.13–0.23	0.14–0.25	0.17–0.34
Ti	<u>0.61 (22)</u>	<u>0.78 (11)</u>	<u>0.90 (8)</u>	<u>1.02 (11)</u>	<u>1.0 (72)</u>
	0.50–0.66	0.66–0.95	0.79–1.07	0.87–1.11	0.64–1.38
Nb	<u>2.7 (10)</u>	<u>2.9 (5)</u>	<u>4.8 (3)</u>	<u>3.2 (4)</u>	<u>4.7 (20)</u>
	1.0–5.8	1.0–4.3	2.3–7.0	2.2–5.5	2.6–7.0
Ta	<u>1.1 (6)</u>	<u>0.5 (5)</u>	<u>1.2 (3)</u>	<u>0.7 (4)</u>	<u>1.0 (8)</u>
	0.4–1.9	0.3–0.7	1.0–1.6	0.3–1.4	0.5–1.5
Zr	<u>70 (10)</u>	<u>145 (5)</u>	<u>239 (4)</u>	<u>175 (4)</u>	<u>231 (20)</u>
	10–143	70–188	125–362	165–200	125–330
Hf	<u>1.0 (9)</u>	<u>3.6 (5)</u>	<u>3.3 (4)</u>	<u>4.3 (4)</u>	<u>5.5 (20)</u>
	0.2–2.0	2.0–4.2	2.8–4.6	3.4–6.0	3.3–8.0
La	<u>≈ 10 (3)</u>	—	—	—	<u>30 (8)</u>
	~ 10–10				25–33

Table 3. (cont.)

Elements	Northern Breakthrough		Southern Breakthrough		
	Predominant lava types (7 July 75–10 Sept. 75)	Intermediate lavas from the end of the eruption (11–15 Sept. 75)	Intermediate lavas from the first days of the eruption (18–24 Sept. 75)	Intermediate lavas from the start of the eruption (25 Sept. 75–30 Nov. 75)	Predominant lava types (1 Dec. 75–9 Dec. 75)
1	2	3	4	5	6
Ce	< 30 (3)	—	—	—	43 (8)
Nd	< 30– < 30 ≈ 10 (3)	—	—	—	20–50 23 (8)
Y	5–15 24 (3)	—	—	—	20–30 43 (8)
Yb	23–25 2.6 (3)	—	—	—	41–45 4.6 (8)
K/Na	2.2–2.9 0.40	—	—	—	4.3–5.0 0.65
K/Rb	0.34–0.48 645	0.58 550	0.59 475	0.60 400	0.55–0.71 375
Ba/Sr	540–740 1.05	435–615 1.04	435–505 1.30	435–500 1.14	315–475 2.68
Nb/Ta	0.73–1.83 2.5	0.9–1.24 5.8	0.8–1.41 4.0	0.8–1.57 4.6	1.42–3.80 4.7
Zr/Hf	1.5–4.5 70	3.3–8.6 40	4.4–5.0 72	3.9–7.7 41	3.2–7.3 42
Ni/Co	13–116 2.85	34–50 2.4	37–129 2.3	33–48 1.4	30–51 1.7
V/Ni	1.6–4.4 2.1	1.6–3.3 2.8	1.4–3.2 3.2	1.0–1.8 4.1	1.1–2.2 4.0
La/Yb	1.3–3.2 3.8	1.5–5.0 —	2.3–5.6 —	3.4–7.5 —	2.5–5.9 6.5
	3.4–4.5	—	—	—	6.0–7.7

Na, K, F, Ti contents in weight %, other elements in g/t. Numerator, average content of element (in brackets the number of analyses used in calculating average); denominator, variation in content of element in individual samples from minimum to maximum.

Breakthrough the variations in the content of these elements were: Na 0.56%, K 0.2%, Rb, 4 g/t, B 30 g/t, F 410 g/t, Be 0.9 g/t and MgO 1.5%. Intermediate basalts of the first few days of the eruption of the Southern Breakthrough display a similar tendency. Thus basalts of the intermediate stage of the eruption, as distinct from the overwhelming mass of extremely homogeneous basalts of the Northern and Southern Breakthroughs, are characterised by an heterogeneous (non-equilibrium) composition. It should, however, be emphasised that the composition of the basalts from the last day of the eruption of the Northern Breakthrough is practically identical to the average composition of those from the first day of the eruption of the Southern Breakthrough.

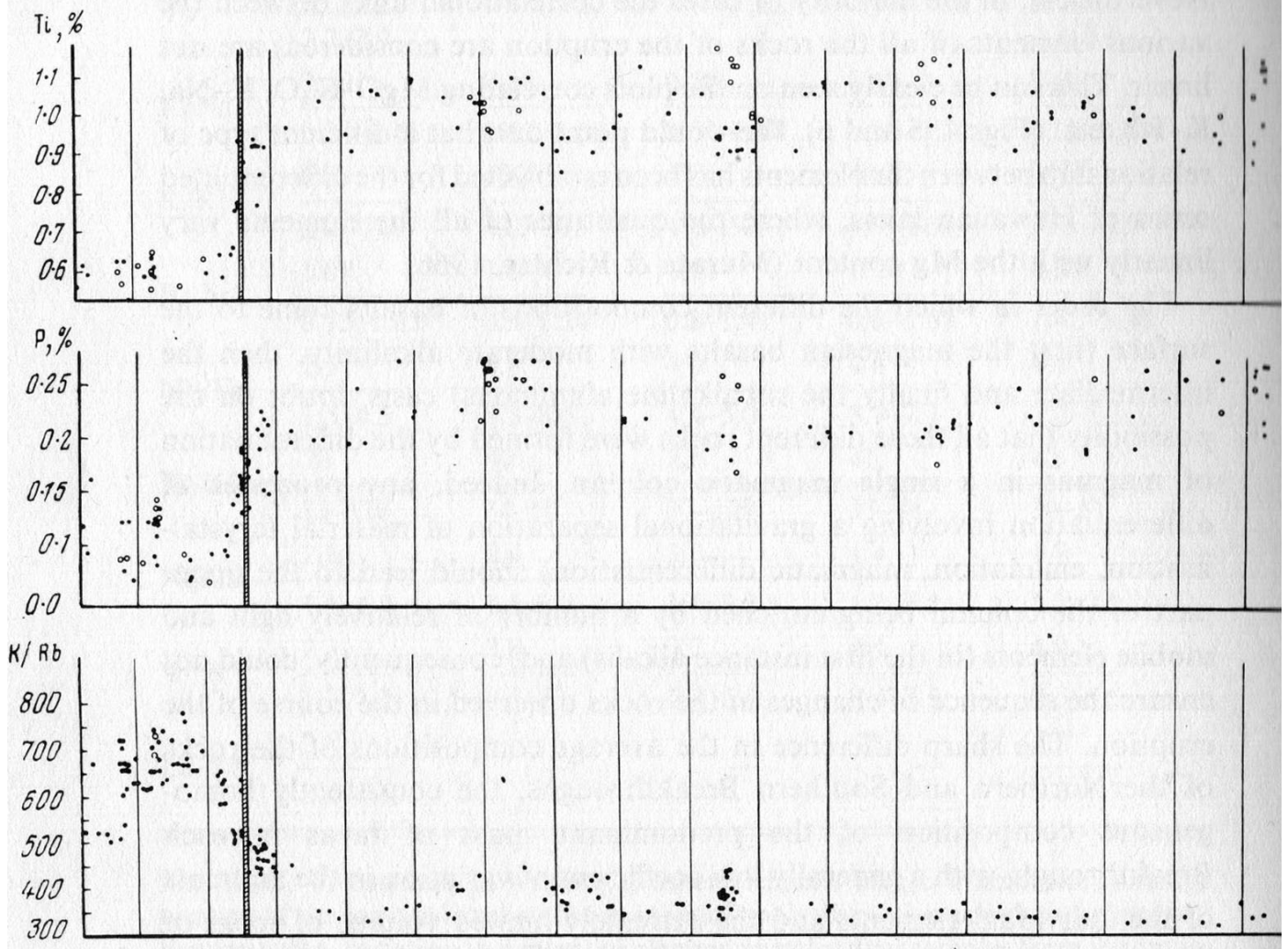
As a result of the substantial difference in the composition of the basalts of the Northern and Southern Breakthroughs and the very small variations in the concentrations of their individual elements, the plots of the main mass of rocks of the Northern and Southern Breakthroughs give isolated clusters on the various petro-geochemical diagrams. However, these clusters are united by the presence of basalts of intermediate composition. Nevertheless, in the majority of cases the correlational links between the various elements (if all the rocks of the eruption are considered) are not linear. This can be clearly seen on the plots correlating MgO–K₂O, K–Na, K–Rb, etc. (Figs 4, 5 and 6). We would point out that a different type of relationship between the elements has been established for the differentiated series of Hawaiian lavas, where the quantities of all the elements vary linearly with the Mg content (Murata & Richter, 1966).

The order in which the different compositions of basalts come to the surface (first the magnesian basalts with moderate alkalinity, then the intermediate and finally the subalkaline aluminous) casts doubt on the possibility that all these different rocks were formed by the differentiation of magmas in a single magmatic column. Indeed, any processes of differentiation involving a gravitational separation of material (crystallisation, emanation, magmatic differentiation) should lead to the upper part of the column being enriched by a number of relatively light and mobile elements (in the first instance alkalis) and, consequently, could not ensure the sequence of changes in the rocks observed in the course of the eruption. The sharp difference in the average compositions of the rocks of the Northern and Southern Breakthroughs, the consistently homogeneous composition of the predominant mass of lavas in each Breakthrough, with a generally low coefficient of variation in the amounts of the individual elements and the extremely limited volume of rocks of the intermediate composition – all this suggests that the primary melts of

the Northern and Southern Breakthroughs were independent. However, this does not dispose of the question of whether the different types of basalts could have been formed by processes of differentiation of a single primary magma in a relatively deep magma chamber (or chambers). This is a question that requires special discussion.

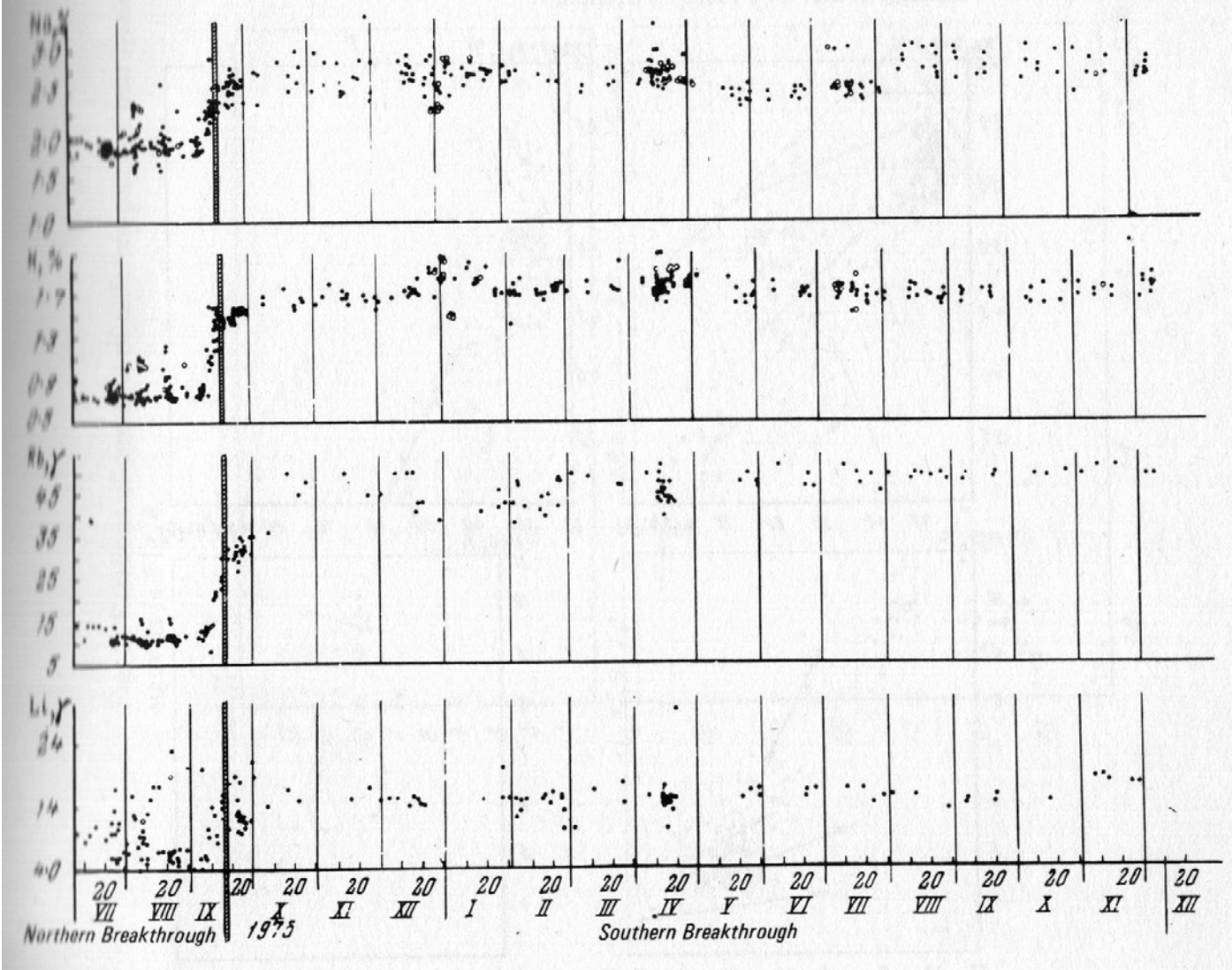
According to the most widely held opinion, the main cause of the variety in magmatic rocks is the crystallisation differentiation of magmatic melts. Let us examine how legitimately this hypothesis can be applied to the Tolbachik eruption. In accordance with the chemistry of the rocks, the phases immediately below the liquidus of the basalts of the Northern Breakthrough are olivine and clinopyroxene, and of the Southern Breakthrough mainly plagioclase. The groundmass of the basalts of the Northern Breakthrough, by comparison with their overall composition, is accordingly

Fig. 3. Variation of the Ti, P, Na, K, Rb and Li content and K/Rb ratios in rocks of the eruption.
1, lavas and bombs; 2, ashes; 3, pause between eruptions of the Northern and Southern Breakthroughs.



enriched with Al, alkalis, Ti, P, etc., and the groundmass of the basalts of the Southern Breakthrough is enriched with Mg, Fe, K, Ti, P, etc. This can also be clearly seen from the graphs in Figs. 4, 5 and 6. The compositions of the groundmass of rocks show the possible directions of shifts in the composition of the melts should crystallisation differentiation occur. It follows that if there is in principle a possibility that melts similar to the Southern Breakthrough basalts originated from crystallisation differentiation of magma corresponding to the basalts of the Northern Breakthrough, then the reverse is impossible. Theoretically, it is even easier to obtain melts of the Southern Breakthrough basalt type from melts with the composition of the intermediate basalt. In this case, the basalts of the Northern and Southern Breakthroughs could have formed a complementary pair, in which the basalts of the Northern Breakthrough would

Fig. 3. (cont.)



have been a cumulative series and the basalts of the Southern Breakthrough a residual melt.

The likelihood of all the types of rocks of the eruption originating in the crystallisation differentiation of a single primary melt corresponding to the basalts of the Northern Breakthrough or to intermediate basalts, can be assessed with the aid of some simple calculations, using the data presented in Tables 1–3, as well as data on the compositions of the

Fig. 4. Relations between contents of alkalis, MgO and Al_2O_3 in rocks of the eruption.

I, lavas and bombs; II, ash. Dots, rocks of the Northern Breakthrough; Crosses, rocks of the Southern Breakthrough. Arrows indicate direction and magnitude of the alteration in composition in paired values (bulk composition of the rock – composition of its ground mass). In constructing the arrows, as well as the authors' own material, use was made of data from Kirsanov & Ponomarev (1974) for the aluminous subalkaline basalts of the last eruptions of the summit crater of Ploskiy Tolbachik.

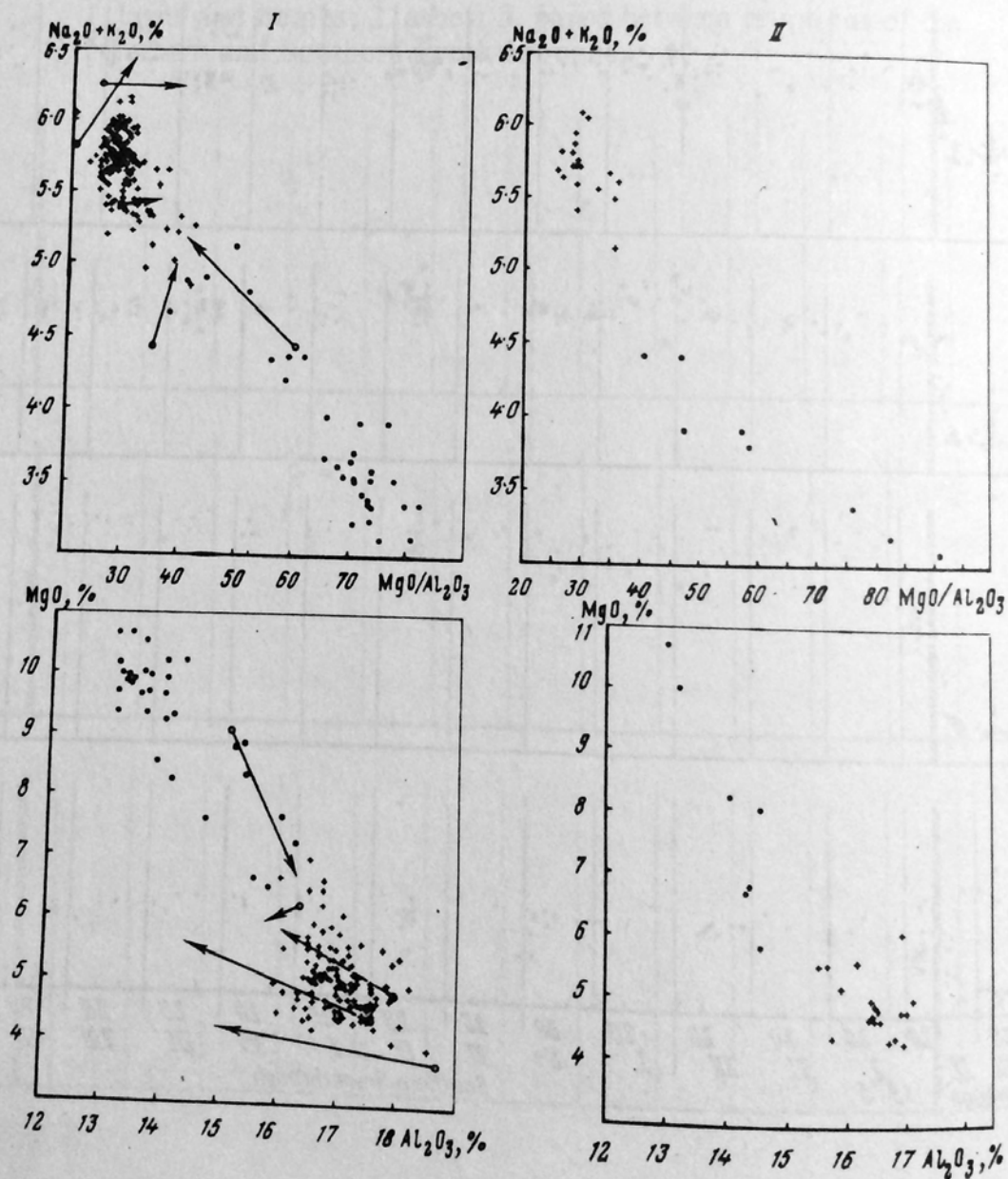
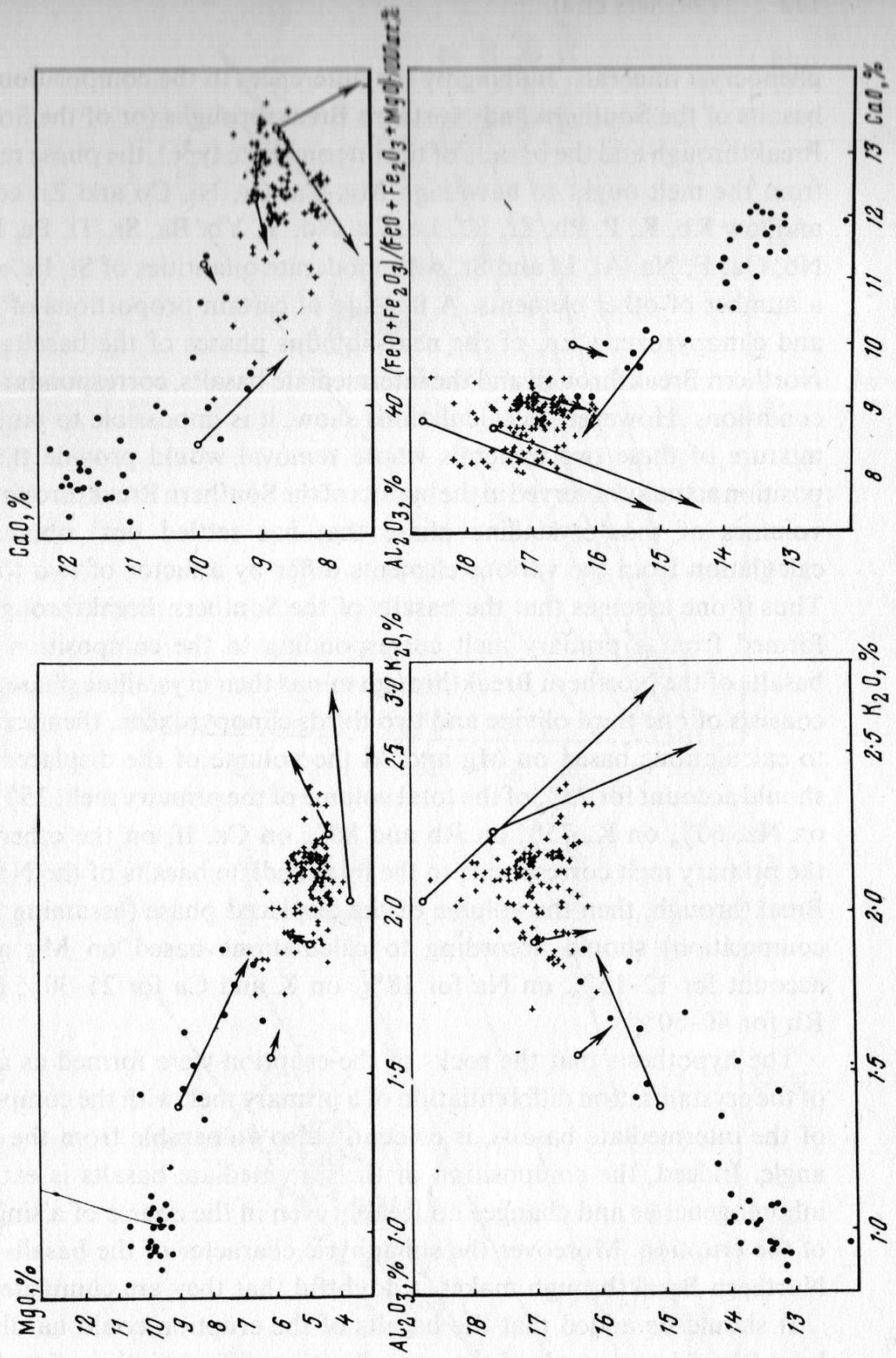


Fig. 5. Relations of contents of different pairs of petrogenic elements in rocks of the eruption. Conventional signs as in Fig. 4.

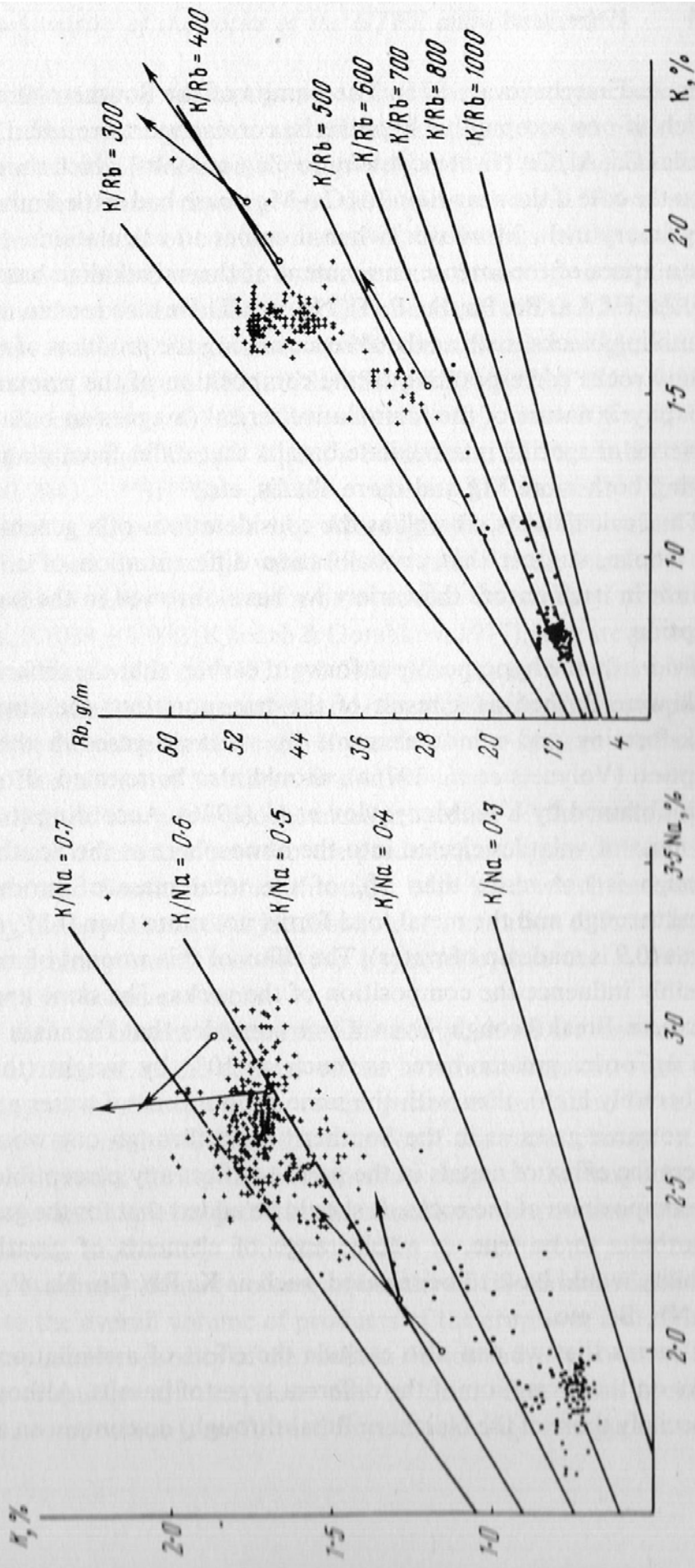


phenocryst minerals. Judging by the differences in the composition of the basalts of the Southern and Northern Breakthroughs (or of the Southern Breakthrough and the basalts of the intermediate type), the phase removed from the melt ought to have high Mg, Ca, Cr, Ni, Co and Zn contents and low Rb, K, P, Pb, Zr, Hf, La, Ce, Nd, Y, Yb, Ba, Sr, Ti, Be, B, Mo, Nb, Ga, F, Na, Al, Li and Sr, with moderate quantities of Si, Fe, As and a number of other elements. A mixture of certain proportions of olivine and clinopyroxene, i.e. of the near-liquidus phases of the basalts of the Northern Breakthrough and the intermediate basalts, corresponds to these conditions. However, as calculations show, it is impossible to pinpoint a mixture of these two minerals whose removal would provide the composition actually observed in the basalts of the Southern Breakthrough – the volumes of the 'crystalline phase that has settled out' obtained by calculation from the various elements differ by a factor of two to three. Thus if one assumes that the basalts of the Southern Breakthrough were formed from a primary melt corresponding to the composition of the basalts of the Northern Breakthrough minus their crystalline phase, which consists of one third olivine and two thirds clinopyroxene, then according to calculations based on Mg and Al the volume of the displaced phase should account for 25% of the total volume of the primary melt, 35% based on Na, 60% on K, 75% on Rb and 80% on Ca. If, on the other hand, the primary melt corresponds to the intermediate basalts of the Northern Breakthrough, then the volume of the displaced phase (assuming similar composition) should according to calculations based on Mg and Al account for 12–15%, on Na for 18%, on K and Ca for 25–30% and on Rb for 40–50%.

The hypothesis that the rocks of the eruption were formed as a result of the crystallisation differentiation of a primary melt with the composition of the intermediate basalts, is evidently also vulnerable from the logical angle. Indeed, the composition of the intermediate basalts is extremely inhomogeneous and changes noticeably even in the course of a single day of the eruption. Moreover the subaphyric character of the basalts of the Northern Breakthrough makes it doubtful that they are cumulates.

It should be added that the basalts of the eruption could hardly have been formed as a result of the crystallisation differentiation of a primary melt that corresponded to the composition of the plagiobasalts (or aluminous basalts of moderate alkalinity, in our terminology) – i.e. the most widespread type of Quaternary basalt on Kamchatka – as a number of authors assumed earlier for similar types of rocks (Yermakov, 1971;

Fig. 6. Relations of contents of K and Na and K and Rb in rocks of the eruption. Conventional signs as in Fig. 4.



Sirin & Timerbayeva, 1971). The basalts of the Southern Breakthrough, which, if one accepts this hypothesis, correspond to residual melts, have similar Ca, Al, Cr, Ni, etc. contents to plagiobasalts, which should not have been the case if the near-liquidus Ca–Mg phase had settled out of this kind of primary melt. Moreover, when it comes to calculations, the problem again arises of the intense enrichment of the subalkaline basalts with K, Rb, Zr, Hf, La, Ba, Pb, Be, P, Ti, Nb, etc. There also remain many logical stumbling blocks, such as the absence among the products of the eruption of any rocks corresponding to the composition of the primary melt, the subaphyric nature of the 'cumulative series' (magnesian basalts) and the presence of specific intermediate basalts that differ from plagiobasalts in having both more Mg and more alkalis, etc.

Thus calculations, as well as the considerations of a general nature set out above, suggest that crystallisation differentiation of a single melt cannot in itself ensure the variety we have observed in the basalts of the eruption.

Evidently the hypothesis put forward earlier, that the different types of rock were formed as a result of the transport into the atmosphere of rock-forming and minor elements by volcanic gases in the course of eruption (Volynets *et al.*, 1976a), should also be rejected, if one uses the data obtained by I. A. Menyaylov *et al.* (1976). According to these data, the mass of volatiles ejected into the atmosphere at the Southern Breakthrough is not more than 1% of the total mass of products of the Breakthrough and the metal load forms not more than 0.1% of the mass of gas (0.9 is made up of water). The efflux of this amount of metal cannot possibly influence the composition of the rocks. The same applies to the Northern Breakthrough. Even if one concedes that the mass of volatiles was an order greater here, as much as 10% by weight (this figure is deliberately high), then with the same proportions of water and metal in the volcanic gases as in the Southern Breakthrough one would still not expect the efflux of metals in the gases to effect any perceptible change in the composition of the rocks. It should be added that for the gas transport hypothesis to be true, a whole range of elements of greatly differing mobility would have to be released, such as K, Rb, Cu, Na, P, Ti, Al, Ba, Zr, Nb, Be, etc.

It seems that we can also exclude the effect of assimilation of crustal rocks on the formation of the different types of basalts. Although basalts (especially those of the Northern Breakthrough) do contain an appreciable

amount of inclusions of volcanogenic–sedimentary, siliceous rocks and occasional inclusions of granites and peridotites, there is no noticeable incorporation of xenoliths, even if completely melted, and the xenolith–basalt boundaries remain clear-cut and distinct in all cases. The absence of any noticeable traces of contamination of the basalts of the eruption by crustal rocks is also borne out by data on the Sr isotope composition (analyses carried out in the Institute of Geochemistry of SO AN SSSR by G. S. Plyusnin and G. P. Sandemirova): Northern Breakthrough, sample A₇B₁, lava from 1 August 1975, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7041$, $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ where the K content = 0.76‰, Rb = $12 \times 10^{-4}\%$, Sr = $300 \times 10^{-4}\%$; Southern Breakthrough, sample A₄₀B₃, a bomb from 22 September 1975, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7043$, $^{86}\text{Sr}/^{88}\text{Sr} = 0.1196$ where K content = 1.48‰, Rb = $31 \times 10^{-4}\%$, Sr = $300 \times 10^{-4}\%$. Although the $^{87}\text{Sr}/^{86}\text{Sr}$ values are slightly higher than the average value for this ratio for the basalts of the Klyuchi volcano and the intermediate–acidic Quaternary rocks of Kamchatka, 0.7034 ± 0.002 (Khedzh & Gorshkov, 1977), they are generally close to the average value of 0.7035 ± 0.0005 (Khedzh & Gorshkov, 1977) for volcanites of the Pacific Ocean belt and oceanic islands. The main point, though, is that the value for this ratio is practically the same in the basalts of both the Northern and Southern Breakthroughs.

Thus analysis of the petro-geochemical properties of the rocks of the eruption reveals differences between the predominant types of basalts of the Northern and Southern Breakthroughs of a kind which cannot be explained by the hypothesis of crystallisation or emanation differentiation of a single primary melt, nor by the hypothesis that the latter was contaminated by basement rocks.

The fact that the basalts of intermediate composition are restricted to the period at the end of the activity of the Northern Breakthrough and the beginning of the Southern (i.e. to the period of transition from one type of basalt to another during the eruption); the rapid change in the composition of rocks during this intermediate stage of the eruption; the comprehensive and stable range of these intermediate-composition varieties, from magnesian moderately alkaline basalts to aluminous subalkaline basalts; the extremely limited volume of basalts of this intermediate type in relation to the overall volume of products of the eruption; and, finally, the conspicuous heterogeneity of the rocks in this period, even over a single day of the eruption – all this leads one to think that these rocks of intermediate composition were formed from the mixing of magmatic melts

corresponding to the basalts of the Northern and Southern Breakthroughs.* Such an hypothesis is also supported by features of the mineralogical composition of the intermediate-composition basalts, such as the presence of generations of olivines that are similar in composition to those of both the Northern and Southern Breakthroughs, and the fact that the lavas of this stage contain individual megacrystals of plagioclase which are characteristic of basalts of the Southern Breakthrough.

The data presented above and the critical analysis of the various petrogenetic conceptions lead to two important conclusions: firstly, that the melts which were the sources of basalts of the Northern and Southern Breakthroughs were to some extent independent, and secondly that the rocks of intermediate composition were formed by the mixing of these two initial melts. These conclusions do not contradict the geophysical data obtained at the eruption.

Thus according to seismological data (Fedotov *et al.*, 1976a; Fedotov, 1976), in the earthquake swarm that preceded the formation of the Northern Breakthrough the epicentres of the deepest earthquakes were at depths of 20–30 km, and as time passed they were observed to shift upwards. But the earthquakes which preceded the formation of the Southern Breakthrough were near the surface (depth of epicentres 0–5 km). These observations enabled Fedotov and his co-authors (Fedotov, 1976; Fedotov *et al.*, 1976a) to assume that the source of the basalts of the Northern Breakthrough lay at sub-crustal depths, and that of the basalts of the Southern Breakthrough within the upper part of the crust. The presence of crustal subsurface magma chambers seems to be confirmed by seismic and gravimetric data (Balesta *et al.*, 1976), which show that in the region of the eruption within the upper zones of the crust there are parts where the seismic waves are attenuated and there is a gravitational anomaly, interpreted by these authors as shallow magma chambers.

Thus the interpretation of geophysical evidence gives grounds for supposing that the basalts of the Northern and Southern Breakthroughs came to the surface from magma chambers situated at different depths. This accords well with petrological data indicating a certain independence of the basalts of the two Breakthroughs. Moreover, the very presence of chambers at different depths creates the pre-conditions for the mixing of magmatic melts during the eruption, when the deep magmatic melt is rising

* Hypothetical mixing of magmatic melts was successfully used by T. L. Wright & R. S. Fiske (1971) to account for the compositions of rocks from a series of eruptions in the rift zone of Kilauea.

and on its way meets the crustal reservoir of magma (the intermediate chamber). The action of the deep melt could be the impulse that causes magma to erupt from the crustal reservoir, and the nature of the interaction of the melts is reflected in the compositional features of the rocks of the eruption's transitional stage (the end of the Northern and the beginning of the Southern Breakthrough).

If one assumes that the change in the composition of basalt samples collected chronologically during the transitional stage reflects the mixing of the two magmatic melts in the course of the eruption, it follows that kinetic methods can be used to evaluate the constants of the rates of interchange of the various elements between the two types of melt. Results of the calculation (Table 4, Fig. 7) of diffusion for spherical volumes (Lykov, 1967) show that this process can be satisfactorily described in terms of a mechanism of diffusional mixing of components. The values of the constants of the rates of interchange for K, Na, Ca, Mg, Al, Ti, P, Rb, Li and Be coincide within limits of error and furnish a single constant value for D/r^2 of $5.4 \times 10^{-8} \text{ s}^{-1}$.

The existence of a single constant of rate of interchange for different chemical elements seems at first sight unexpected, since it is well known from experiments that in silicate melts at temperatures of 1100–1250 °C there is a great difference in the diffusion coefficients of the elements involved. However, we also know that in crystalline silicate structures the

Table 4. *Values of constants for the rate of diffusion exchange between various components during mixing*

Element	D/r^2 (24 h ⁻¹)	(D/r^2) (mean)
K	0.0042 ± 0.0016 (24)	
Na	0.0055 ± 0.0029 (23)	
Ca	0.0065 ± 0.0032 (17)	
Mg	0.0046 ± 0.0030 (18)	
Al	0.0059 ± 0.0037 (16)	0.0047 ± 0.0028 (172), 24 h ⁻¹
Ti	0.0032 ± 0.0016 (14)	$5.4 \times 10^{-8} \pm 3.2 \times 10^{-8} \text{ s}^{-1}$
P	0.0028 ± 0.0012 (17)	
Rb	0.0024 ± 0.0010 (16)	
Li	0.0065 ± 0.0054 (10)	
Be	0.0054 ± 0.0040 (17)	

In brackets, the number of analyses. D/r^2 is a constant consisting of diffusion coefficient D , and a characteristic dimension r (the radius of the sphere registering the diffusion flow).

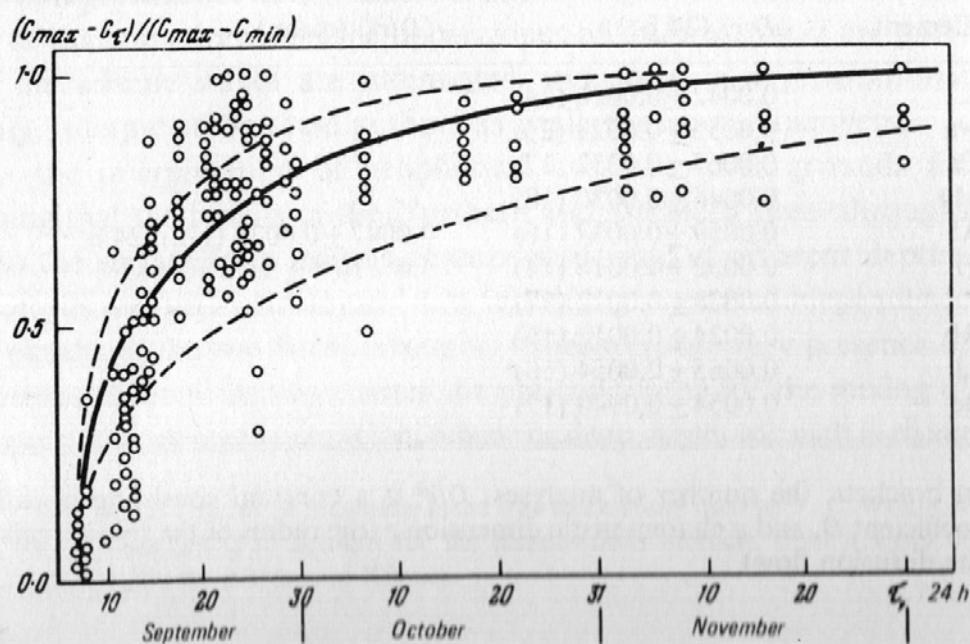
displacement of the mobile components can be held back by the displacement of other components with higher activation energies for diffusion. Therefore the results of our calculation could indicate that at least one of the basalt melts had a quasi-crystalline structure at the time of mixing.

The change in the F and B contents, which do not fit into the general pattern of change in the petrogenic and minor element contents, is evidence that at the mixing stage the volatile components behaved independently of the assumed structure of the melt, i.e. it confirms the presence of fluid during the interaction of the two melts.

On the basis of the D/r^2 constant calculated, it is possible to estimate the values of r . Assuming that the diffusion coefficient of the element limiting the mobility of the other components in the coalescing melts could have values from $n \times 10^{-6}$ cm²/s to $n \times 10^{-12}$ cm²/s, then for r we obtain values in the range of 10 cm to 0.01 cm. This result is in itself interesting, since it implies considerable mechanical intermixing of the melts in the process of coalescence.

Altogether, a kinetical analysis of the mixing of the basalt melts produces the following characteristics for a geochemical model of the Great Tolbachik Fissure Eruption. Initial conditions consisted of the

Fig. 7. Alteration in the relative concentrations of K, Na, Ca, Mg, Al, Ti, P, Rb, Li and Be in basalts in the mixing stage. Continuous curve, theoretical dependence corresponding to the diffusion constant $D/r^2 = 5.4 \times 10^{-8}$ s⁻¹; Broken curve, measurement error ($\Delta = \pm 3.2 \times 10^{-8}$ s⁻¹); Circles, empirical data.



existence of two basalt melts of different composition (of which at least one had a quasi-crystalline structure), and of a fluid which, among other things, contained F and B. Conditions during the mixing were that there was some degree of contact between the mechanically intermixed basalt melts. The mixing mechanism was a diffusional exchange of components, limited by the rate of displacement of one of the chemical elements (with maximum diffusion activation in these conditions) in the quasi-crystalline structure of the melt.

In conclusion, it is important to emphasise that within the Holocene Tolbachik regional zone of cinder cones the association of moderately alkaline magnesian basalts and aluminous subalkaline basalts is consistently reproduced in the individual volcanic centres. The characteristics of the change in composition and facies of the rocks in the course of the activity of such centres are similarly reproduced: first the magnesian then the aluminous basalts come to the surface, in the former pyroclastics predominate over lavas, in the latter it is the other way round. All this indicates that eruptions like the Great Tolbachik Fissure Eruption of 1975–76 are not random processes, and consequently testifies in favour of the proposed model.

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