

# THE VOLCANIC MASSIF OF BIQ'AT HAYAREAH (SINAI-NEGEV): A CASE OF POTASSIUM METASOMATISM<sup>1</sup>

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## ABSTRACT

On Biq'at Hayareah, an area 80 km<sup>2</sup> in size on the border between Sinai (Egypt) and the Negev (Israel), a sequence of late Precambrian alkali-rhyolites (lavas, tuffs, and ignimbrites) and their hypabyssal equivalents (rhyolite-porphyrries) are exposed. These rocks form part of the alkaline Katharina Province, representatives of which are found from the Indian Ocean to West Africa. About half the rocks of Biq'at Hayareah have undergone a mainly metasomatic alteration not recognizable in hand specimens. Chemically, the alteration is expressed by the almost total exchange of Na<sup>+</sup> by K<sup>+</sup>, and by the addition of about 3% silica and of a small amount of alumina; the trace element composition remained almost unaffected. Mineralogically, albite has been replaced by K-feldspar, and secondary quartz has crystallized while some primary quartz has been replaced by K-feldspar. It is concluded that the potash-metasomatism is the result of an interaction between the originally partly glassy rhyolites and hydrothermal solutions or, more probably, vapors.

## INTRODUCTION

Biq'at Hayareah (Valley of the Moon) is a plateau 800 m above sea level and about 80 km<sup>2</sup> in size, straddling the border between Sinai (Egypt) and the Negev (Israel) near the head of the Gulf at Eilat (fig. 1). The area has an almost dead drainage; half of it is covered by alluvial accumulations capped in places by a thin layer of loess. Above this plain rise steep-sided, sometimes conical hills, up to 2 km<sup>2</sup> in area and up to 100 m above the level of the plain. In the northern part of the area, immediately south of and parallel to the Themed Fault (fig. 1), these hills merge to form an almost continuous ridge, known as Jebel el Hamra (the Red Mountain) 13 km in length and about 1 km in width; its summits attain a height of 931 m, about 150 m above the surrounding plain. This ridge is built of rhyolitic volcanics, lavas, tuffs, and ignimbrites, which dip at 25° to almost 90° toward the E and ENE, i.e., in the direction of the Aravah Valley (African

Rift Valley) 12 km farther east. These dips result from a regional tilt which occurred in Neogene times in connection with the formation of the rift valley. During this tilt, the Precambrian rocks of Biq'at Hayareah were first exposed. Not all dips of the volcanics, however, are of tectonic origin. Individual lava flows and ignimbrite layers show strong pressure ridges which explain the steeper dips.

The inselbergs to the south of Jebel el Hamra consist mainly of the hypabyssal equivalents of the volcanics. This arrangement of hypabyssals in the south, volcanics in the north is due to the position of Biq'at Hayareah on the northern slope of the Precambrian massif.

The volcanic-subvolcanic massif of Biq'at Hayareah is part of the Young Volcanic Series of the Arabo-Nubian massif, which is known in the Negev as Volcano-Conglomeratic Complex (Bentor 1961) and in southern Sinai as the Katharina Volcanics. In many places – but not in Biq'at Hayareah – they are intruded by alkali-granites of exactly the same chemical composition. One granite of this group, the Iqna Granite, has been dated by the Rb-Sr method to 583 ± 23 m.y. (Bielski et al. 1979); the preceding volcanics can only be a few million years older.

<sup>1</sup> Manuscript received October 29, 1980; revised March 25, 1981.

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[Journal of Geology, 1981, vol. 89, p. 479–495]  
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0022-1376/81/8904-009 \$1.00

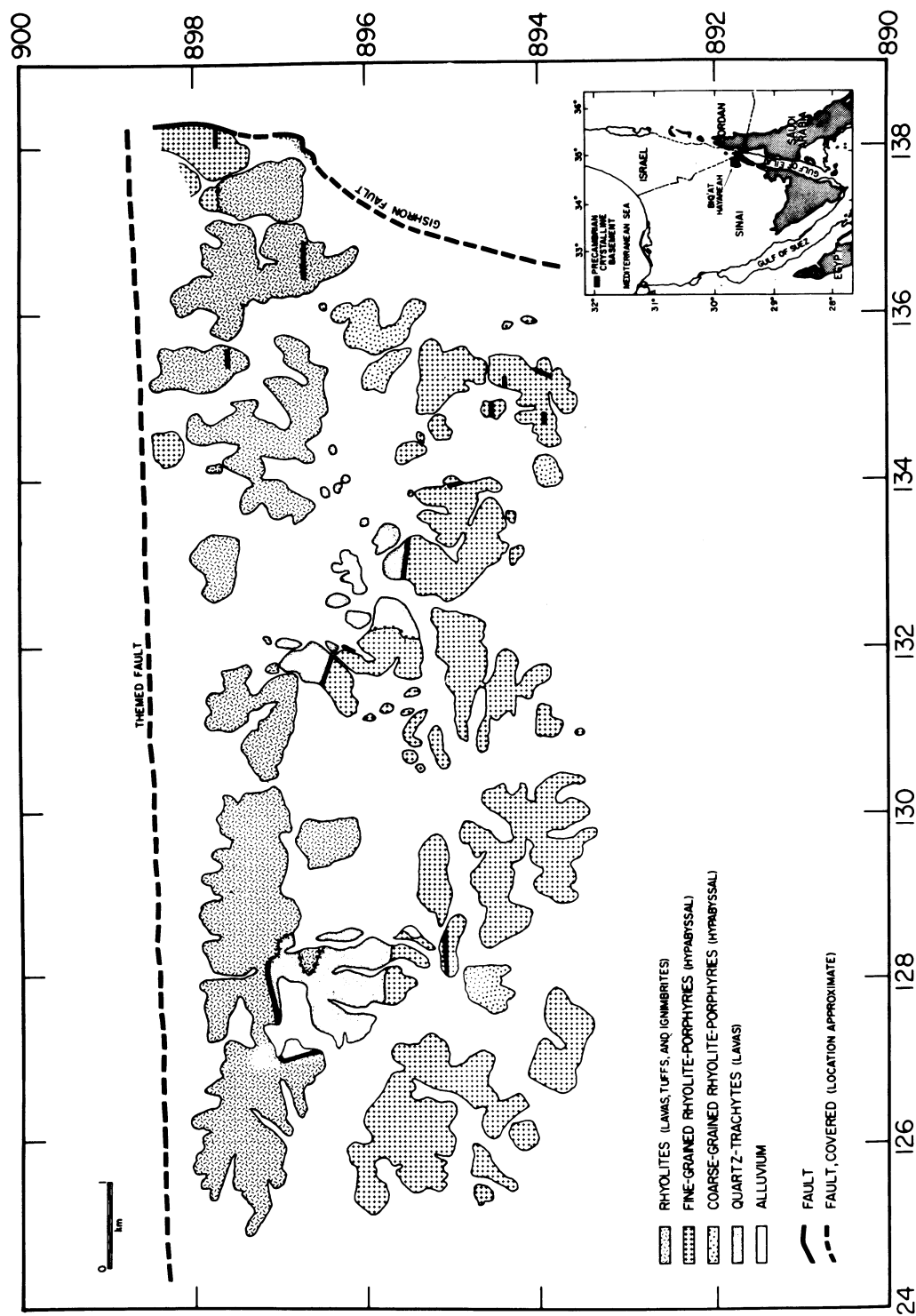


Fig 1. - Geological map of Biq'at Hayareh.

In addition to the hypabyssal alkali-rhyolite-porphyrries and their volcanic equivalents, another group of rocks occurs at Biq'at Hayareah accounting for 15–20% of the outcrops. These are orange-colored alkali-quartz-trachytic lavas and closely related dikes of bostonite. No undisturbed contacts between these lavas and the rhyolitic rocks are exposed, but, as the bostonite dikes cut all other rock units, the quartz-trachytes are the youngest igneous rocks of Biq'at Hayareah; they might well not even be of Precambrian age. In fact, we suspect them to be part of the early Cretaceous Ramon Province and thus unrelated to the main rock units of Biq'at Hayareah. As these rocks do not show the alteration characteristic of the earlier rocks, they will not be considered further in this paper.

#### METHODS

One-hundred seventy-five stained thin sections were examined under a petrographic microscope. Major elements were determined by atomic absorption spectrophotometry (except  $\text{SiO}_2$ , determined gravimetrically),  $\text{P}_2\text{O}_5$  by optical spectrophotometry and  $\text{CO}_2$  on the vacuum line. Trace elements were measured by neutron activation; the technique used is described by Perlman and Asaro (1969).

#### PETROLOGY

The rhyolitic extrusives are macroscopically dense, fine-grained, moderately porphyritic, frequently flow-banded rocks of gray, orange, brown or purple color. Pyroclastic rocks and ignimbrites can generally be distinguished from lavas only under the microscope. The hypabyssal rhyolite-porphyrries have a very similar appearance, but generally lack the fluidal texture, are frequently somewhat coarser grained, and more strongly porphyritic.

#### MINERALOGY AND TEXTURE

a) *Lavas*. — The lavas are all porphyritic alkali-rhyolites. They contain euhedral to subhedral *phenocrysts* of quartz, 1–3 mm across. Euhedral crystals dominate, and their

cross-sections are commonly perfect squares or somewhat distorted hexagons; some of the crystals are slightly corroded and show embayments or rounded corners. Some crystals show a faint mortar texture, attributed to the Tertiary-Quaternary rift valley faulting. Most lavas contain, in addition, phenocrysts of *perthitic alkali-feldspar*. The crystals are generally subhedral, stout-prismatic, simply twinned, slightly corroded, and measure 1–3.5 mm in length. Albite forms patches and strings in the K-feldspar and is more abundant along the periphery of the crystals than in their center. Albite is clear and colorless, whereas the K-feldspar is cloudy and contains tiny colorless as well as red-brown inclusions. The former are probably kaolinite, the latter hematite. Although kaolinite usually forms in an acid environment, it is known also as an alteration product of feldspar in contact with slightly alkaline hydrothermal solutions, e.g., in Yellowstone National Park (Honda and Muffler 1970). The elongate and skeletal hematite crystals are strongly aligned and give the K-feldspar a fibrous appearance. The amount of phenocrysts varies from 1–18%, and quartz is generally twice as abundant as feldspar (table 1). A few larger ore grains form aggregates of prismatic outlines, indicating the former presence of some mafic phenocrysts, probably amphibole.

The *matrix* shows a variety of textures. In many samples, it is granophyric and consists of anhedral, strongly pigmented crystals of K-feldspar .1–.3 mm across intergrown with smaller acicular to vermicular clear colorless quartz crystals and a few ore grains. Other lavas show a spherulitic ground-mass; the spherulites measure .1–1.5 mm and are composed of radial fibers of K-feldspar and quartz; the center consists generally of a mosaic of small (about 50  $\mu\text{m}$ ) anhedral equant crystals of K-feldspar. A final group of lavas exhibits a strongly flow-banded matrix which consists of an irregular aggregate of K-feldspar, quartz, and ore; the crystals have an average size of 50  $\mu\text{m}$ , and their boundaries are blurred. This type of matrix is interpreted as resulting from the

TABLE 1  
Phenocrysts (%) in Rocks of Biq'at Hayareah

	Quartz	Feldspar	Total	F/Qz
<i>Lavas</i>				
range	1.1–10.1	0–7.8	1.1–17.3	.50–1.05
average	4.8	3.3	8.1	.69
<i>Hypabyssal rocks</i>				
range	4.2–26.8	8.8–58.5	13.0–85.3	1.28–2.18
average	11.8	22.0	33.8	1.86

devitrification of an original glass; perlitic cracks, now filled in by iron oxides, are frequently still recognizable. The lavas have from 3 to 10% small, irregular vesicles, partly filled by secondary calcite and gypsum.

b) *Tuffs and Ignimbrites*. — These rocks differ from the lavas mainly by their pyroclastic textures. The tuffs were originally a mixture of glass shards and crystals of quartz and alkali-feldspars. These crystals are identical in shape and size to the phenocrysts of the lavas, but are generally broken. They reach a size of 4 mm and account for up to one-third of the total rock mass. A few fragments of country-rock, mainly quartzite, occur in some of the tuffs. The ignimbrites are rich in large collapsed pumices with frayed edges. The shards are moulded against each other or around the larger crystals, which are sometimes broken.

c) *Hypabyssal rhyolite-porphyries*. — The rocks considered to be hypabyssal differ from the lavas in the following features: (1) Although both groups of rocks carry the same types of phenocrysts, their amount in the hypabyssal rocks is four times higher than in the lavas (table 1) and accounts for up to 85.3% of the rock. (2) Whereas in the lavas quartz is more common than feldspar among the phenocrysts, this ratio is reversed in the hypabyssal rocks, which carry almost twice as much feldspar as quartz phenocrysts (table 1). (3) The hypabyssal rocks alone have preserved remnants of an original mafic mineral within the ore grain aggregates. This turns out to be an arfvedsonite, with a characteristic pleochroism from deep greenish-blue to light yellow. (4) The crystals composing the matrix are frequently larger

and measure up to .5 mm across. (5) Granophyric textures are more common in the hypabyssal rocks, spherulitic textures in the extrusives. Whereas spherulites form during devitrification, granophyric textures are not indicative of a unique origin. Barker (1970) as well as Schloemer (1964) have concluded that they can be formed as primary crystallization from melt or secondarily during devitrification. As in the rocks of Biq'at Hayareah, granophyres are clearly more common in the hypabyssal rhyolite-porphyries, including the unaltered rocks, than in the extrusive rhyolites; we suspect them to be of primary origin. (6) The hypabyssal rocks contain no vesicles.

Contacts with the country rocks are nowhere exposed; the hypabyssal nature of these rocks can therefore only be inferred from the massive nature of these rock bodies, which show no internal boundaries in contrast to the layered nature of the extrusives in which lava flow surfaces and tuff intercalation are easily observed. Moreover, the hypabyssal rocks commonly have a coarser matrix, are richer in phenocrysts, but devoid of vesicles.

Rhyolites, similar in composition and texture to the hypabyssal rhyolite-porphyries, but poorer in phenocrysts, also form numerous *dikes*.

#### CHEMICAL COMPOSITION

a) *Major Elements*. — The average major element composition of five unaltered rocks is given in table 2. To facilitate comparison, the chemical composition has been recalculated after deduction of the secondary minerals calcite and gypsum. As optical as

TABLE 2  
Major Element Composition and Niggli Parameters and Norms of Rhyolite(Porphyrries) of Biq'at Hayareah (on Calcite-Gypsum-H<sub>2</sub> O-free Basis)

	Chemical Composition		Niggli Parameters		Niggli Norm	
	Average of 5 Unaltered Rocks	Average of 8 Altered Rocks	Average of 5 Unaltered Rocks	Average of 8 Altered Rocks	Average of 5 Unaltered Rocks	Average of 8 Altered Rocks
SiO <sub>2</sub>	75.84 ± 1.63	77.73 ± .71	462.6	556.1	Q	42.25
TiO <sub>2</sub>	.25 ± .08	.18 ± .05	42.4	45.6	Or	48.68
Al <sub>2</sub> O <sub>3</sub>	11.73 ± .71	10.83 ± .70	18.4	17.0	Ab	2.03
Fe <sub>2</sub> O <sub>3</sub>	3.29 ± 1.10	2.67 ± .83	.2	.2	Cord	.95
FeO	.20 ± .09	.12 ± .05	39.0	37.3	Fe-Cord	1.12
MnO	.14 ± .17	.15 ± .19	.50	.96	Hm	1.94
MgO	.15 ± .10	.13 ± .11	.08	.07	Ru	.13
CaO	.05 ± .04	.05 ± .06	1.1	1.0	Ap	.06
Na <sub>2</sub> O	3.33 ± .43	.22 ± .14			Kaol	2.84
K <sub>2</sub> O	4.98 ± .81	7.89 ± .57	+ 205.1	+ 302.9	Total	100.00
P <sub>2</sub> O <sub>5</sub>	.03 ± .03	.03 ± .04				
Total	99.99	100.00				

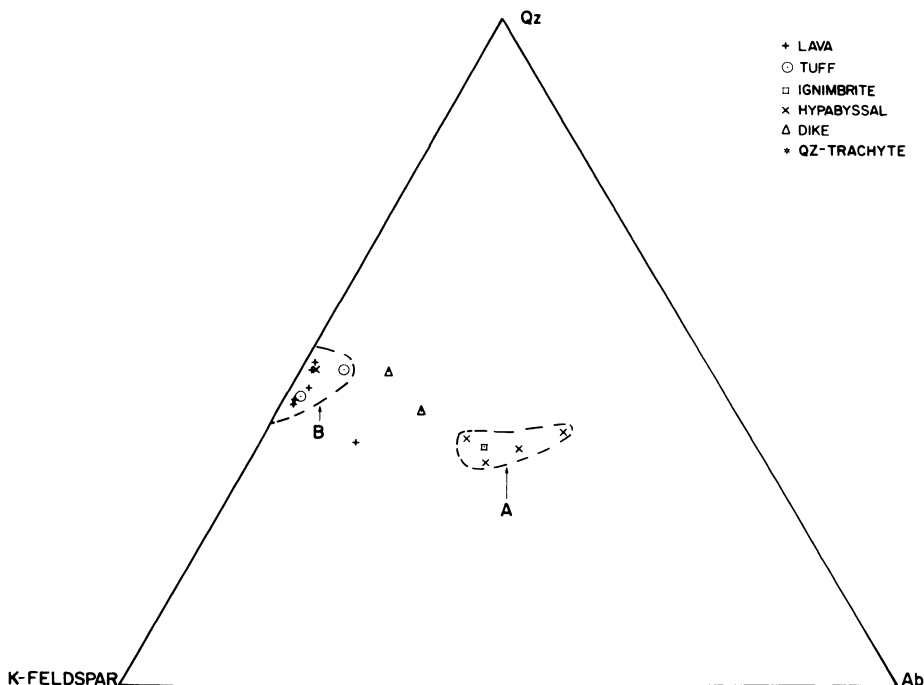


Fig. 2. — Normative quartz-K-feldspar-albite composition of rocks of Biq'at Hayareah. For explanation of fields A and B see text.

well as X-ray diffraction data of the plagioclase fraction of the perthite (extinction  $\perp(010) = 20.2^\circ$ , diffraction peak  $\bar{2}01 = 22.06^\circ$ ,  $002 = 27.96^\circ$ ) show it to be an ideally pure albite, and in the absence of any other potentially Ca-bearing mineral, all CaO, with the exception of the small amounts required by the apatite present, was calculated as calcite and gypsum.

The unaltered rocks form a homogeneous group of highly differentiated silica-rich (generally  $\geq 75\%$ ), CaO-poor ( $< 1\%$ ) rocks, all of the alkaligranitic magma type with no compositional differences between intrusive and extrusive rock types. They carry about 30% of each, normative K-feldspar and albite, and about 35% normative quartz (table 2 and field A in fig. 2). The matrix (table 3) is composed of about 65% feldspar and 35% quartz. The average feldspar of the total rock contains almost exactly equal amounts of K- and Na-feldspars, but the composition varies in individual rocks from

$Or_{38}Ab_{62}$  to  $Or_{58}Ab_{42}$  (table 3); as no albite seems to occur outside the perthite crystals, the latter are partly perthites and partly anti-perthites. The average composition of the matrix,  $Qz_{35.7}Or_{32.3}Ab_{32.0}$ , is well within the range of granophyres from different localities, studied by Barker (1970) and close to the temperature trough in the system Qz-Or-Ab- $H_2O$  (Tuttle and Bowen 1958).

The highly characteristic mineralogical and chemical composition of these rocks leaves no doubt that they are part of a very large magmatic province of late Precambrian age, which we call the Katharina Province after its type locality at Jebel Katharina in south-central Sinai. Rocks of this province, forming small high-level plutons, commonly intrusive into slightly earlier consanguineous volcanics, occur from the Indian Ocean (Socotra) through Saudi Arabia westward over the whole of North Africa, including Somalia and Ethiopia, and in West Africa

TABLE 3  
Modal Composition (%) of Rocks from Biq'at Hayareah

	Total Feldspar	Matrix	F/Qz
<i>Non-altered rocks:</i>			
range	Or <sub>37,7-57,8</sub> Ab <sub>42,2-62,3</sub>	Qz <sub>33,6-39,1</sub> Or <sub>23,0-37,7</sub> Ab <sub>27,6-37,9</sub>	1.56-1.97
average	Or <sub>50,1</sub> Ab <sub>49,9</sub>	Qz <sub>35,7</sub> Or <sub>32,3</sub> Ab <sub>32,0</sub>	1.80
<i>Altered rocks:</i>			
range	Or <sub>89,1-97,4</sub> Ab <sub>2,6-10,9</sub>	Qz <sub>39,2-50,5</sub> Or <sub>49,2-59,0</sub> Ab <sub>1,4-6,0</sub>	.98-1.42
average	Or <sub>95,9</sub> Ab <sub>4,1</sub>	Qz <sub>44,6</sub> Or <sub>53,1</sub> Ab <sub>2,3</sub>	1.23

TABLE 4  
Niggli Parameters of Rocks of the Katharina Province

	si	al	fm	c	alk	k	mg	qz
1	462.6	42.4	18.4	.2	39.0	.50	.08	+ 205.1
2	334.6	40.4	17.3	4.4	37.9	.50	.08	+ 83.0
3	474.0	42.2	14.7	3.4	39.7	.55	.05	+ 215.2
4	406.2	41.5	13.8	3.8	40.5	.43	.14	+ 143.0
5	529.1	39.7	17.4	2.0	40.9	.40	.05	+ 269.1
6	405.4	43.6	15.0	3.3	38.2	.19	.13	+ 151.6
7	455	45	13	2	39	.38	.04	+ 197
8	423.5	37.5	26.1	...	36.4	.42	.02	+ 177.4
9	325.7	40.0	13.7	4.3	42.1	.49	.08	+ 63.6
10	374	39.5	18.1	1.8	40.6	.36	.03	+ 114.9
11	411.0	39.9	14.3	3.8	41.9	.43	.08	+ 149.4
12	558.9	40.0	21.6	1.3	37.1	.42	.15	+ 309.7
13	387.9	40.9	13.2	5.8	40.1	.37	.54	+ 127.5
14	419.4	38.1	20.7	4.4	36.8	.40	.16	+ 172.2
15	432	43.4	12.1	2.8	41.7	.41	.14	+ 165.2
16	484.4	43.1	13.4	1.1	42.4	.41	.06	+ 214.8
17	309.3	41.1	16.1	1.5	41.3	.40	.08	+ 44.7

- 1 - Average unaltered alkali-rhyolite-(porphyry), Biq'at Hayareah, this paper.
- 2 - Average Sharm Granite, southern Sinai (Bentor et al. in preparation).
- 3 - Marha Granite, southern Sinai (Bentor et al. in preparation).
- 4 - Sahara Granite, southern Sinai (Bentor et al. in preparation).
- 5 - Riebeckite-granite, Socotra Is., Indian Ocean (Herrmann 1924).
- 6 - Dahamite (riebeckite-grorudite), Dahamis, Haghers Mountains, Socotra Island, Indian Ocean (quoted in: Washington 1917, p. 158, no. 66).
- 7 - Biotite-granite, Jebel Zeit, Eastern Desert of Egypt, (Schürmann 1942).
- 8 - Riebeckite-granite, E. Desert of Egypt, 23°45'N-34°40'E (Schürmann 1974).
- 9 - Hornblende-biotite-granite, S. of Yubdo, Wollega, Ethiopia (Comucci 1948).
- 10 - Grorudite, Uweinat, Libya (quoted in: Schürmann 1974).
- 11 - Hyperalkaline granite, Gara Adjemamaye, SE Ahaggar, Algerian Sahara (Boissenas et al. 1970).
- 12 - rhyolite, W. Adrar Ti-n Echeni, Ahaggar, Algeria (Lelubre 1952).
- 13 - Alkali-rhyolite, Jebel Sarhro, Tizin Tazazert, Anti-Atlas, Morocco (Cherotzky and Choubert 1973 p. 116, no. 316).
- 14 - Riebeckite-micro-granite, Gouré, Damergou, Mounio, Niger. (quoted in: Schürmann 1974).
- 15 - Riebeckite-granite, Fita, Dahomey (quoted in Schürmann 1974).
- 16 - Microgranite, Amboro, Nigeria (Bain 1934).
- 17 - Riebeckite-granite, Eken, Sungale, Cameroons (Hintze 1907).

at least as far south as Nigeria, a total area of about 20 million km<sup>2</sup>. The Niggli parameters of some rocks from different parts of this province are given in table 4 for comparison.

b) *Trace elements*. - The average concentration of 21 trace elements in five alkali-rhyolites and rhyolite-porphyries, obtained by Neutron Activation Analysis, is shown in table 5; again, there are no differences

between intrusive and extrusive rock types. The concentration of most elements is well within the range of many alkaline granites and rhyolites. The very low concentration of Ba is explained by the absence of any calcic phase in the rock. The low value for Cs (1.43 ppm) is difficult to explain, but shows again (Bentor et al. in prep.) that Cs does not follow Rb; the Rb/Cs-ratio in these

TABLE 5  
Trace Element Concentrations (ppm) in Rocks of  
Biq'at Hayareah

	Average of five unaltered rocks	Average of eight altered rocks
Cs	1.43 ± .61	1.37 ± .53
Rb	168 ± 17	214 ± 41
Ba	137 ± 104	293 ± 145
La	79.30 ± 27.90	65.99 ± 31.32
Ce	154.7 ± 32.7	166.7 ± 27.4
Nd	74.5 ± 23.8	60.3 ± 22.9
Sm	14.84 ± 3.65	14.64 ± 2.82
Eu	1.04 ± .35	.77 ± .15
Tb	2.41 ± .56	2.77 ± .25
Yb	6.52 ± 2.53	7.92 ± .60
Lu	1.00 ± .19	1.14 ± .08
Th	13.88 ± 3.19	16.17 ± 1.84
U	2.56 ± .92	3.05 ± .68
Hf	15.82 ± 3.67	19.70 ± 1.72
Co	1.40 ± 1.40	1.37 ± 1.01
Ni	19 ± 7	17 ± 4
Sc	1.46 ± 1.54	.36 ± .08
Cr	4.6 ± .5	4.7 ± 1.0
Sb	.65 ± .23	1.03 ± .71
As	3.4 ± 2.2	5.41 ± 3.08
Ta	2.48 ± .52	2.90 ± .28
Ni/Co	13.6	12.4
Cr/Ni	.24	.28
Ce/La	1.95	2.53
La/Eu	76.2	85.70
La/Yb	12.16	8.33
Th/U	5.42	5.30
K/Rb	246.1	306.1
Rb/Cs	117.5	156.2
Sb/As	.19	.19

rocks of Biq'at Hayareah is 117.5 instead of an expected value of about 40. The rather high content of Hf, and by implication of Zr, is a common feature of alkaline granites.

The REE-pattern is characteristically granitic (fig. 3) and similar to that of the standard granite NIM-G; the negative Eu-anomaly, though less pronounced than in NIM-G, is strong. This fact, in conjunction with the low initial  $^{87}\text{Sr}/^{86}\text{Sr}$ -ratio of  $.7028 \pm .0028$  determined for a rock of this province by Bielski et al. (1979), seem to indicate that these granitoids formed by fractional crystallization of a mantle-derived melt.

#### POTASSIUM METASOMATISM

Most lavas and tuffs and some hypabyssal rhyolite-porphyries have undergone an alteration which cannot be recognized in the field as the altered rocks look entirely fresh and undistinguishable from the original

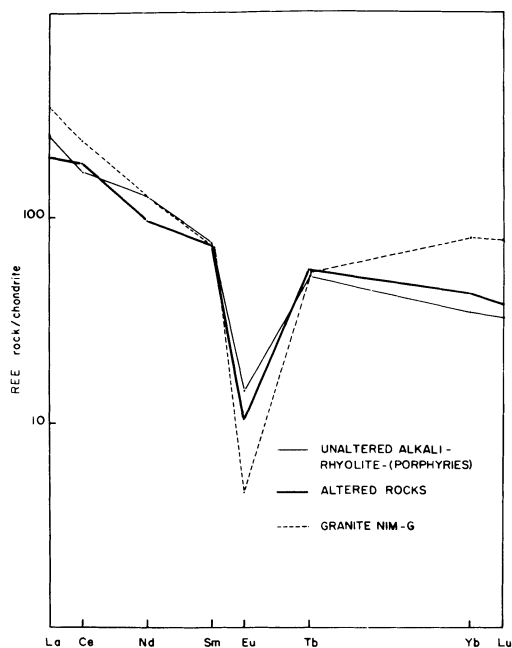


Fig. 3. — REE content of rocks of Biq'at Hayareah and of Standard granite.

ones. The alteration, however, affects the mineralogy of the rocks as seen under the microscope and is most conspicuous in their chemical composition.

Under the microscope, the following changes can be observed: 1) The phenocrysts of perthite, while preserving their characteristic morphology, have undergone a potash-metasomatism, transforming the albitic fraction into K-feldspar and thus obliterating entirely the perthite texture. 2) The rocks contain a new generation of quartz, concentrated preferentially in the empty spaces between spherulites and commonly forming almost continuous rims surrounding them. They also occur as linings of vesicles. These new quartz crystals measure up to 1 mm and are easily distinguished from the original quartz phenocrysts by their anhedral outlines. 3) The quartz phenocrysts, particularly the smaller ones, are partly replaced by K-feldspar; the latter forms narrow irregular ribbons within the quartz crystals extending perpendicularly



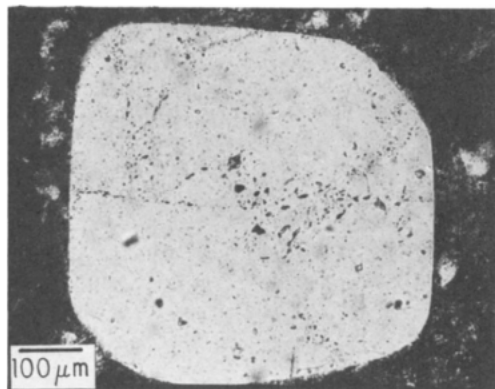


Fig. 4. — Quartz phenocryst in alkali-rhyolite-tuff, Biq'at Hayareah, sample B19A, crossed nicols.

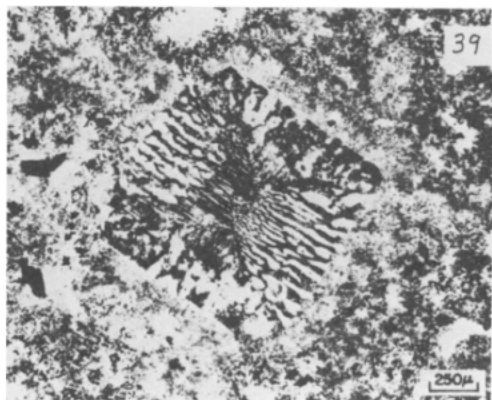


Fig. 5. — Quartz (white) phenocryst, partly replaced by K-feldspar (dark) in alkali-rhyolite, Biq'at Hayareah, sample C2, crossed nicols. Note that the form of the crystal is the same as in figure 4.

from the outer faces toward the center of the crystals, frequently causing an hourglass texture.

Granophyric textures are common in acid hypabyssal and volcanic rocks and quartz-K-feldspar intergrowths in which the whole aggregate shows crystalline outlines are not rare; they have been attributed to primary simultaneous intratelluric crystallization or even to post-eruptive growth (Barker 1970). In our case, however, we believe that they were formed by late-stage metasomatic replacement of quartz phenocrysts by K-feldspar. This conclusion is based on the observation that the outlines of these aggregates, almost perfect squares with slightly rounded corners, are identical to the highly characteristic ones of the quartz phenocrysts present in all these rocks including those carrying the granophyric megacrysts (figs. 4–7). 4) In some of the altered rocks small amounts of lithiophorite, identified by its X-ray pattern, have formed.

The most conspicuous of the corresponding chemical changes is the almost quantitative elimination of  $\text{Na}_2\text{O}$  and its replacement by  $\text{K}_2\text{O}$  (table 2). In these rocks the molar ratio  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  reaches the unusually high value of 96:4. This replacement proceeds very nearly in a 1:1 molar ratio, as the total molar alkali content

remains almost constant (alk = 39.0 in the original rocks against 37.2 in the altered ones), whereas  $\text{K}_2\text{O}$  increases from 4.98 wt % to 7.89 wt % (maximum value 8.64 wt %) and  $\text{Na}_2\text{O}$  diminishes from 3.33 wt % to .22 wt % (minimum value .14 wt %).

In the composition diagram of figure 2 the altered rocks plot in a clearly separate area B, shifted, as compared with the original rocks (area A), well to the left and very close to the Qz-K-feldspar joint. The intervening area is populated by three rocks in which the alteration process has not run to completion. Where complete, it leads to the formation of a rock group even more homogeneous than the unaltered rocks.

The quartz enrichment during alteration is expressed by an increase of the parameter si from 462.6 to 556.1, corresponding to an increase of  $\text{SiO}_2$  from 75.84% to 77.73% (table 2). The modest increase of the parameter al from 42.4 to 45.4 explains the quantitatively limited K-feldspathization of quartz. The excess  $\text{Al}_2\text{O}_3$  introduced leads also to the appearance of about 3% normative kaolinite; this mineral occurs in the mode as tiny inclusions in the K-feldspar, increasing their turbidity.

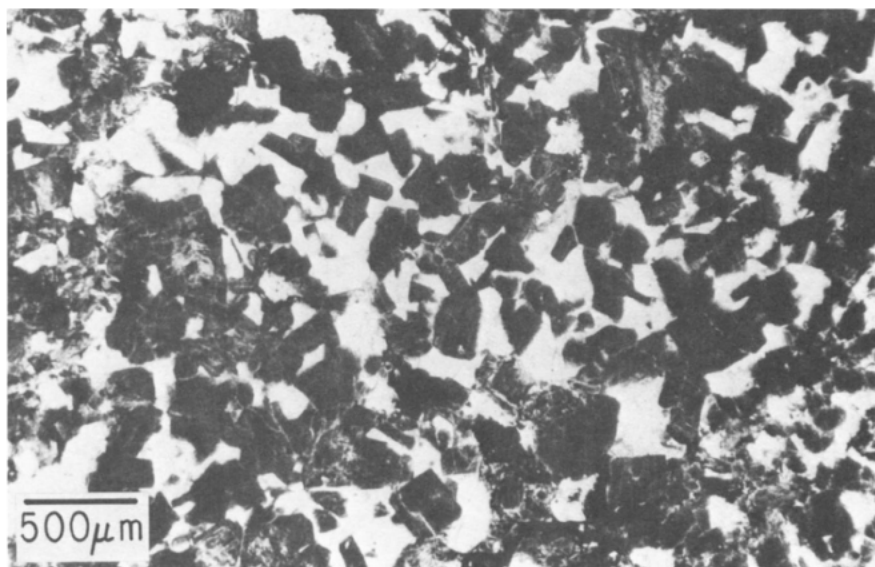


Fig. 6. – Granophyre, matrix of alkali-rhyolite-porphyry, Biq'at Hayareah, sample C7, crossed nicols (white: quartz; dark: K-feldspar).

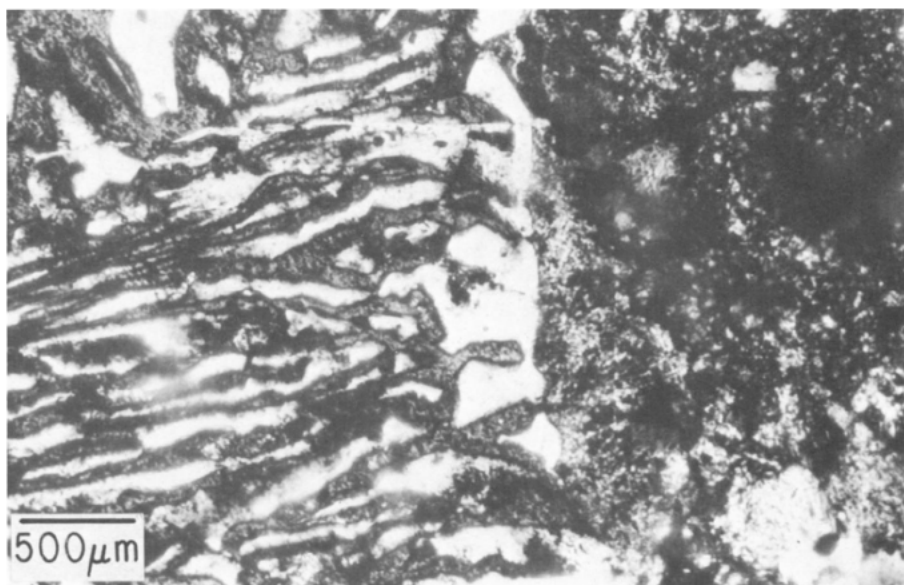


Fig. 7. – Granophyre formed through partial replacement of quartz phenocryst by K-feldspar in alkali-rhyolite, sample C2, Biq'at Hayareah, crossed nicols. Note that the primary granophyre of figure 6 is hackly and unoriented. The replacement granophyre of figure 7 is ribbon-like and oriented.

The overall result is the formation of rocks composed of about 50% normative Or, 40% Qz, and 2% Ab. The matrix of these rocks has an average composition of 55% K-feldspar and 45% quartz, and a F/Q = ratio of 1.23 versus a value of 1.80 for the unaltered rocks (table 3).

The general trace element pattern of the rocks remains essentially unchanged during the alteration process (table 5). Rb, Hf, Ta, Th, and possibly U, all late-stage magmatic elements, are slightly enriched, whereas Sc is depleted. The Rb-enrichment, however, is less than the proportional increase of K, the K/Rb-ratio increasing from 246 to 306. The fluid with which the original rocks reacted was thus depleted in Rb compared with the granitic melt, probably by large-scale prior crystallization of K-feldspar. The REE are generally unchanged. Three out of the 11 altered samples analyzed, however, have selectively lost 50–80% of their La-content (fig. 8). We cannot explain the mechanism of this La-depletion.

#### DISCUSSION AND CONCLUSIONS

The interest of the rhyolite-(porphyries) of Biq'at Hayareah lies in the high  $K_2O$  content (more than 7%) and the unusually high  $k$ -value (molar  $K_2O/Na_2O + K_2O$  ratio) of .96–.98 of about half the rocks. The problem of potash-rich rocks has been discussed since Niggli (1923), Bowen (1928, 1938), and Doggat-Terzaghi (1929, 1935) drew attention to their existence. Their genesis was originally explained by fractional crystallization, a reasonable explanation as long as the phase relations between K-feldspar and plagioclase were believed to be of the peritectic type. When, however, it was shown by Schairer and Bowen (1947) that the phase relations in the anhydrous granitic system are cotectic, such an explanation became difficult; it became untenable when it was shown later (see Luth 1976) that the relations are cotectic also in a hydrous granite system containing  $CO_2$  or not. Many granites and rhyolites have compositions near the thermal trough in the  $SiO_2$ -Or-Ab system, i.e., near  $Qz_{34}Or_{28}Ab_{38}$  and

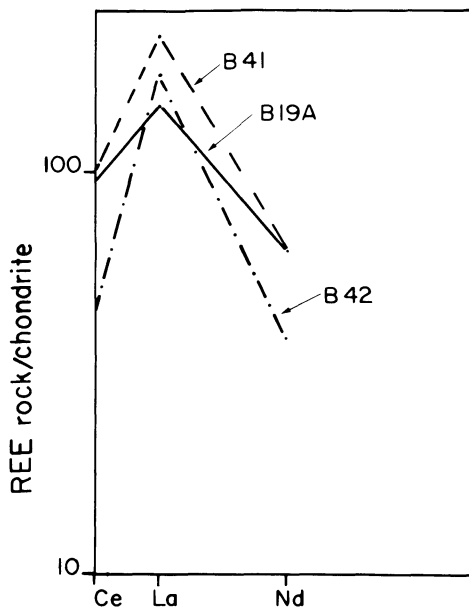


Fig. 8. — Ce- La- and Nd-content of altered alkali-rhyolites, Biq'at Hayareah. Note the Ce-deficiency.

are therefore unlikely to contain more than 5–6%  $K_2O$  and  $k$ -values higher than .5–.6, even taking into account the presence of some biotite (generally less than 5%) containing 6–9%  $K_2O$  with  $k \sim .9$ . Only on highly perfect crystallization fractionation could a granitic magma approach a composition of  $Ab_{20}Or_{45}Qz_{35}$  (Steiner et al. 1975), corresponding to a  $K_2O$ -content of 7.6%.

In the case of the rocks of Biq'at Hayareah the derivation of the high-potash rocks from a magma of similar composition is excluded in any case by the close relationships of these rocks with others of normal alkali-granitic composition ( $K_2O \sim 5\%$   $k = .50$ ). It is inconceivable that two independent magmas were intruded in the same area giving rise to rocks which, except for a large difference in the  $K_2O/Na_2O$  ratio and a slight difference in  $SiO_2$  content, are identical in mineralogical and chemical composition as well as in texture. For the same reason an origin of the high-K rocks from a

magma enriched in K by its derivation from K-rich zones in the mantle (biotite-pyroxenite?) or by later assimilation of such rocks is excluded. Such a hypothesis was appealed to by Bowen (1938) to explain the K-rich volcanics of the Western Africa Rift (see also Wones 1979).

The only way to understand the potash-rich rocks of Biq'at Hayareah is to assume that they are derived from a normal alkali-granitic magma, but underwent alteration during or after emplacement. Several authors (e.g., Noble 1970) recognized that peralkaline silicic magmas lose sodium during primary crystallization either by volatilization as halides (Kogarko et al. 1968) or by the formation of water-soluble compounds. This mechanism cannot explain the changes in alkali content in the rocks of Biq'at Hayareah for the following reasons: (1) These rocks are not peralkaline; (2) The alteration at Biq'at Hayareah has affected both, primarily crystallized hypabyssals as well as originally glassy volcanics; (3) Even in peralkaline magmas the sodium loss rarely reaches 10% whereas in the rocks of Biq'at Hayareah the average loss is 93%; (4) The mechanism does not account for the strong potassium gain.

It has been noted by many authors (e.g., Bowen 1928; Dogget-Terzaghi 1935) that most, if not all, high-K-rocks are, or were originally, glasses: obsidians, pitchstones, or perlites. Ideas concerned their post-depositional K-enrichment were recently reviewed by Stewart (1979) and are pertinent to the rocks of Biq'at Hayareah, as probably all the extrusives and at least some of the high-level hypabyssals were originally entirely or partly glassy, as indicated by a perlitic relict texture.

A K-enrichment of siliceous glasses can result from *leaching* by groundwater without concomitant devitrification. This mechanism was studied by Lipman (1965) and by Noble (1967) who found that hydrated glasses are depleted in  $\text{Na}_2\text{O}$  by .1–.4% and sometimes enriched in  $\text{K}_2\text{O}$  by up to .3% by ion exchange between groundwater and glass. This process cannot explain the origin of the high K-rocks of Biq'at Hayareah; it is

quantitatively insufficient and the small K-increase is only residual, while our rocks have had about 3%  $\text{K}_2\text{O}$  actually added. This is a very considerable quantity. Taking into account only the preserved volume of the almost entirely altered extrusives, the amount of  $\text{K}^+$  added is calculated to  $130 \times 10^6$  tons; this is more than a hundred times the amount of dissolved  $\text{K}^+$  carried yearly by the Mississippi River into the ocean (Leifeste 1971; Livingstone 1963). In addition, as pointed out by Noble (1967), the small K-enrichment caused by leaching is only transient and continued leaching leads to K-loss and some removal of silica.

*Devitrification* by groundwater or hydrothermal solutions is much more effective in changing the composition of an acid glass. Contrary to opinions frequently held, this process is rarely isochemical. The high mobility, particularly of the alkali metals, was convincingly shown by Ewart (1971) in his study on the devitrification (spherulite formation) of the Aratiatia rhyolite in New Zealand. He observed a strong fractionation of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  between spherulites and relict glass, as shown in table 6, no. 1 for one of his more extreme cases (sample 4).

This is a strong fractionation, but in this case it occurred over small distances only, as the total rock composition remained constant. A similar fractionation of alkalis between spherulites and relict glass was shown by Tanida (1961) in calc-alkaline rhyolites of Japan (table 6, no. 2).

In many instances, however, devitrification of acid glasses, particularly when induced by hydrothermal solutions, leads to major changes in total rock composition, affecting the glassy as well as the crystalline phases of the rock. The general trend is a metasomatic replacement of Na by K, an addition of  $\text{SiO}_2$  and  $\text{H}_2\text{O}$  and, more rarely, of small amounts of  $\text{Al}_2\text{O}_3$ , as well as an increase in the  $\text{Fe}^{3+}/\text{Fe}^{2+}$ -ratio. These changes have been observed in many places and were described, among others, by Coombs (1952) in rhyolite domes of the Columbia River Plateau in Washington (table 6, no. 3), by Bowen (1938) in a pitchstone

TABLE 6

[illegible]

from Turkana (Eastern African Rift, table 6, no. 4), by Simons (1962) in rhyolitic ignimbrites from Klondyke, Arizona (table 6, no. 5), by Terzaghi (1948) in rhyolites and obsidians of the Esterel, France (table 6, no. 6), by Anderson and Rodley (1915) in Tertiary "leidleite" (dacite) from Mull, Scotland (table 6, no. 7), and in much detail by Fenner (1936) (table 6, no. 8). This subject was more recently summarized by Macdonald (1975). All the authors attribute the chemical changes to K-metasomatism by hydrothermal solutions or vapors.

These observations agree with experimental results. Truesdell (1962, 1966) showed by the membrane electrode method that ion exchange between silicic glasses and dilute aqueous solutions is highly selective with a selectivity sequence  $2H^+ > 2K^+ > 2Na^+ > Ca^{2+} \geq Mg^{2+}$ . It follows that the solution causing a replacement of  $Na^+$  by  $K^+$  need not be either K-rich or characterized by a high K/Na-ratio. Thus, Fenner (1936) concluded that vitrophyres still exchange Na for K when in contact with aqueous solutions with a Na/K-ratio as high as 34, and Stewart (1979) quoting Hemley states that at ambient temperatures the partitioning of K into feldspars is so marked, that this element will be taken up preferentially from a solution containing Na and K in a ratio of 400.

The chemical changes presently taking place in Yellowstone National Park, particularly in the Upper Basin, by the interaction between glassy dacites and rhyolites and hydrothermal solutions were studied by Fenner (1936) and more recently by Honda and Muffler (1970), Keith and Muffler (1978), and Keith et al. (1978). These changes are very similar to those distinguishing the altered rhyolite(-porphyries) from the unaltered ones at Biq'at Hayareah. In both cases the major change is the large-scale K-metasomatism for Na, in both cases 2–3%  $SiO_2$  and small amounts of  $Al_2O_3$  are added to the rocks. Whereas in the Yellowstone rocks primary K-feldspar is generally sodic with a composition near  $Or_{53}Ab_{47}$ , the same as in the perthites of

the original Biq'at Hayareah rocks, the secondary K-feldspars have a composition  $Or_{96.3}Ab_{3.7}$  (Fenner 1936; Keith et al. 1978, p. A17), exactly that of the K-feldspars in the altered rocks of Biq'at Hayareah. In Yellowstone as at Biq'at Hayareah the paradoxical fact can be observed that simultaneously with the crystallization of secondary quartz some primary quartz crystals are partly replaced by K-feldspar. Fenner (1936, p. 308) attributes this feature to "second order instability" of quartz caused by "the crystallizing force of the growing orthoclase," but the true nature of this replacement is not really understood.

If the hydrothermal solutions are acid, alkalis are leached, and the altered nature of the rock is, in most cases, readily recognized by the presence of clay minerals, zeolites, or alunite and the dissolution of feldspars. Alteration by alkaline solutions, however, frequently leaves no obvious indications and the rocks are entirely fresh looking, as are those of Biq'at Hayareah. It is doubtful if, had no unaltered rocks been preserved here, the genesis of the high-potash rocks could have been deciphered.

The rhyolite(-porphyries) of Biq'at Hayareah are unique in two respects. First, this seems to be the first clear case in which this type of potash metasomatism has been observed in Pre-Cambrian rocks. Hydrothermal alteration of Precambrian acid volcanics has frequently been described. Bennet and Rose (1973) found loss of alkalies and gain of Mg in Archean felsic volcanics from Ontario, but no clear relationship to the hydrothermal mineralization of the area could be established. Anderson (1968) in his study of Precambrian silicic volcanics in Central Arizona found an increase in  $SiO_2$ ,  $Al_2O_3$ , MgO, and FeO in the hydrothermally altered rocks, but no systematic change in alkali-content. In no case was a K-enrichment observed. Second, and more important, the replacement of Na by K seems to be more extreme at Biq'at Hayareah than in any other locality so far described (table 6). The only comparable case we found in the literature is a quartz-

porphyry from the Kahusi Massif, Kivu (Western African Rift), described by Sorotchinsky (1934). This rock contains .32%  $\text{Na}_2\text{O}$  and 7.58%  $\text{K}_2\text{O}$ ,  $k = .94$ . Although Sorotchinsky described the intense hydrothermal activity affecting many rocks in the area, he attributed the high K-content to assimilation of alkali-rich rocks of the basement; Bowen (1938), however, suspected the high K-content to be the result of hydrothermal action.

Hydrothermal  $\text{K}^+$ -metasomatism for  $\text{Na}^+$ , entirely analogous to that at Biq'at Hayareah, seems, to judge from published chemical analysis (Bouladon and Youravsky 1955), to have affected alkali-rhyolites of the Tiouine area in the Central Anti-Atlas of Morocco. These rocks are very similar in composition to the alkali-rhyolites of Biq'at Hayareah, are of the same age and also belong to the Katharina Province. The data illustrating the successive stages of K-enrichment in the Moroccan rocks are shown in table 6 no. 9a-c.

Even the most strongly altered dacite and rhyolite glasses of Yellowstone Park have an average  $k$ -value of only .82, and in no case values higher than .85, against an average  $k$ -value of .96 in the rocks of Biq'at Hayareah. This difference is certainly connected with the observation of Fenner (1936), confirmed by Keith and Muffler (1978) and Keith et al. (1978), that even where hydrothermal alteration has gone to completion the original K-feldspar and plagioclase phenocrysts remained unaffected and the same is true in many other areas. A particularly well documented case of this kind was presented by O'Neil et al. (1973); these authors compared calc-alkaline dacites of Miocene age from the Bodie Mining District, Mono County, California with their hydrothermally altered equivalents. The average  $k$ -value of their unaltered rocks is .33 that of the hydrothermally altered ones is .65 (table 6, no. 10), but with one exception no altered rock shows a  $k$ -value  $> .90$ . The authors also determined  $\delta\text{O}^{18}_{\text{SMOW}}$ -values of both, phenocrysts, and whole rock. The  $\delta\text{O}^{18}$ -values of the latter decreased during alteration from

about  $+6.1\text{‰}$  to values of  $-.2$  to  $-1.3\text{‰}$ , corresponding to about 50% equilibration with the hydrothermal fluid; the phenocrysts practically preserved their magmatic  $\delta\text{O}^{18}$  of  $+5$  to  $+7\text{‰}$  (op. cit. p. 774). These data corroborate the refractory character of the phenocrysts during hydrothermal alteration in contrast to the glass and the microlites of the matrix, although O-exchange is certainly more difficult to achieve than cation exchange. Stewart (1979 p. 46) also states that K-metasomatism in glassy rocks is most complete when it affects the crystalline alkali-feldspars and not only those contained virtually in the glass. In the rocks of Biq'at Hayareah, perthite phenocryst up to 5 mm in size, and thus considerably larger than those occurring in the Yellowstone rocks, are entirely metasomatized. It appears that only in these cases can values of  $k > .90$  be attained.

It seems, thus, that an agent more effective than hydrothermal solutions is needed to produce total K-metasomatism. This could conceivably be granitic vapors. The alkali ion-exchange between vapor and feldspar phases has been studied by Orville (1963) for conditions corresponding to deep-level intrusions and by Fournier (1976) for hypabyssal and volcanic conditions. In Fournier's experiments feldspars of varying K/Na-ratios were brought into contact with .5 molar  $\text{KCl} + \text{NaCl}$  containing solutions with steam densities as low as  $.05 \text{ gm/cm}^3$  at temperatures of  $400\text{--}700^\circ\text{C}$  for periods of 10 to 48 days. It was found that the K-enrichment of the crystalline feldspars was very thorough. Feldspars with  $k = .24$  to  $.55$  in contact with solutions with  $k = .30$  to  $.50$  were converted to almost pure K-feldspar with  $k = .98$  to  $1.00$ . Within the temperature interval studied the replacement was more thorough at lower than at higher temperatures. A reaction of this type would easily explain the almost total replacement of  $\text{Na}^+$  by  $\text{K}^+$  in the rhyolite (-porphyries) of Biq'at Hayareah.

One final point should be made. The question whether K-metasomatism was achieved by hydrothermal solutions, by

vapors or even in a late stage deuteric reaction might be devoid of meaning, at least for rocks such as those of Biq'at Hayareah. As the unaltered rocks show, the magma from which they were derived was alkali-granitic. Luth and Tuttle (1969) showed that the addition of alkali to a calc-alkaline granitic melt spectacularly increases its capacity to dissolve water and concluded that for per-alkaline granitic magmas the transition from a magma to a hydrothermal solution might

well be continuous (op. cit. p. 513). It might thus be best to say that the K-metasomatism of these rocks is a result of pneumatolysis.

ACKNOWLEDGEMENTS. — We wish to express our thanks to Dr. I. Perlman and Dr. J. Yellin of the Department of Archeometry, Hebrew University, Jerusalem, who kindly offered to carry out the trace element determinations.

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