A second occurrence of dalyite and the petrology of some ejected syenite blocks from São Miguel, Azores

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[Taken as read 9 March 1967]

Summary. Dalyite, $K_2ZrSi_6O_{15}$, occurs in the ejected syenite blocks of Serra de Agua de Pau (Lagoa do Fogo), São Miguel, Azores, in an assemblage sanidine–arfvedsonite–quartz–aegirine–fayalite–astrophyllite–dalyite–pyrrhite. Other blocks from the same locality contain biotite–zircon in place of astrophyllite–dalyite. A comparison made between the chemistry of one specimen of each type indicates that they may be related by paraeutectoid fractional crystallization.

THE ejected syenite blocks of Serra de Agua de Pau (Lagoa do Fogo), São Miguel, Azores, were first described in the last half of the nineteenth century (Hartung, 1860; Mügge, 1883; Osann, 1888) and have been studied occasionally since those times (Esenwein, 1928; Berthois, 1953). In March 1965, R.R.S. *Discovery* called at São Miguel in the course of a marine geological cruise, and the opportunity was taken to visit Serra de Agua de Pau and to collect a number of syenite blocks for comparison with the granite blocks of Ascension Island concurrently being studied (Cann, 1965).

Serra de Agua de Pau is a large volcano rising to about 1000 m, 15 km east of Ponta Delgada, the chief town of the island. Its caldera contains the lake, Lagoa do Fogo, which is usually cited as the source of the ejected syenite blocks. In fact blocks are also common in the layer of tuff that mantles the outer slopes of the volcano, and specimens up to 50 cm in diameter were found abundantly on a traverse from the hamlet of Remédios to the top of the mountain.

Alteration of the blocks. Two distinct processes of alteration appear to have affected many of the blocks subsequent to their initial consolidation. One, consisting of intense oxidation during ejection, turns the blocks brick-red or mud-coloured, and thin sections show the complete replacement of ferromagnesian minerals by iron oxides, which also penetrate between the feldspar grains. The other process seems to have

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been a mild, high temperature oxidation, and can only be followed in thin section. Aegirine has formed from sodic amphibole and usually takes the form of crystal clusters or stellate groupings that do not have an ortho-igneous texture. The originally homogeneous feldspar has been turned into a vein perthite, and the whole rock has been slightly crushed and granulated. This process must have occurred under plutonic conditions and at relatively high temperatures, presumably soon after the original consolidation of the rock, though it has not affected all of the specimens.

Petrography of the fresh blocks. The freshest rocks show on newly fractured surfaces large white platy feldspar crystals and brilliant black striated prisms of amphibole. Drusy cavities are abundant, and contain well-terminated crystals of feldspar, amphibole, and quartz, and small orange octahedra of pyrrhite. In thin section the feldspar is seen to be an optically homogeneous sanidine with thin rims of twinned triclinic feldspar. The amphibole shows intense absorption and considerable pleochroism, from yellow to a near-opaque dark green-blue, and is very similar in appearance to that from the freshest granites of Ascension Island, which chemical analysis has shown to be an arfvedsonite. It sometimes contains cores of fayalite, presumably a relic from the earliest stages of crystallization, and around the edges of the grains aegirine prisms are often found, probably indicating the onset of the high-temperature plutonic alteration that has more profoundly affected other specimens. Quartz occurs interstitially to the feldspar plates and appears to be concentrated near druses. Small octahedra of pyrrhite, yellow in thin section, are ubiquitous, and minute amounts of apatite are present.

The 12 specimens of the present collection may be divided into two groups by their content of other accessory minerals. Most of the rocks contain small flakes of brown biotite and prisms of zircon, but three specimens contain interstitial dalyite and rectangular crystals of astrophyllite. A third type of rock reported by Osann (1888), containing sodalite and lâvenite, was not represented.

Dalyite ($K_2ZrSi_6O_{15}$) was first described from the ejected granite blocks of Ascension Island by van Tassel (1952). More recently Fleet (1965) determined its crystal structure. It is a colourless mineral of moderate positive relief (β 1·590) and shows second order birefringence colours in thin section. It is triclinic, optically negative ($2V_\alpha$ 72°), and has two good cleavages intersecting at 73°. These features enable it to be readily distinguished optically from other minerals, and in the present

case the identification was confirmed by a powder photograph, which is identical with that of the type material.

This occurrence is only the second locality reported for dalyite, and the paragenesis is extremely like that of the first occurrence in Ascension Island. The feldspar and the ferromagnesian minerals of the two rock types are very similar, and both are marked by the presence of a pyro-chlore-group mineral. Both seem to represent slowly cooled equivalents of the most salic members of the volcanic rock series on the islands, though the slow cooling has been suddenly interrupted at a high enough temperature for the feldspar to remain an optically homogeneous sanidine, and for the druses to remain unfilled. However, while in Ascension Island dalyite is associated with aenigmatite in the arfved-sonite granites (Cann, 1965), in São Miguel it is accompanied by astro-phyllite, and the amount of quartz in the rock is much less in São Miguel than in Ascension.

Pseudomorphs after dalyite or vlasovite (Cann and Fleet, 1967), composed of graphic intergrowths of zircon and quartz, are not un-common in both occurrences. It is interesting that a similar intergrowth was found in a specimen of riebeckite–aegirine granite from the Kwaya River, Lireui Hills, Nigeria (Harker collection number 68618), although a search through Nigerian and many other peralkaline granites failed to reveal the presence of fresh dalyite or vlasovite. It would seem that during late magmatic stages of plutonic peralkaline granite or syenite crystallization, either alkalis are removed, to give the pseudomorphs, or the alkali zirconium silicates are hydrated (to elpidite, for example (Sabine, 1960)), and no fresh anhydrous alkali zirconium silicates remain except where the late stage processes are suddenly interrupted as in the present instance.

Chemistry of the syenite blocks. In order to examine the differences between the group of blocks containing biotite and zircon and that containing dalyite and astrophyllite, a typical specimen of each type was analysed. Table I shows the analyses and norms of these rocks, and also the two previous analyses of ejected blocks from Serra de Agua de Pau, one by Esenwein (1928) and one made for Lacroix by Raoult and published by Berthois (1953). All four analyses are extremely similar to one another: such variation as there is might mostly be caused by analytical errors. In all four analyses Σ *PRS* (the sum of normative or, ab, ne, and Q) is close to 90 %, and the normative feldspar composi-tion is close to $Or_{35}Ab_{65}$. Osann (1888) analysed feldspar from one of his blocks, and the composition ($Or_{37}Ab_{61}An_2$) compares closely with

TABLE I. Analyses of ejected syenite blocks

	1 (Berthois, 1953)	2 (Esenwein, 1928)	3 92801	4 92803
SiO_2	63·18	65·50	65·11	65·54
Al_2O_3	17·59	16·00	17·18	16·26
Fe_2O_3	1·27	2·50	1·33	1·72
FeO	1·62	2·14	2·16	2·23
MnO	0·32	0·20	0·22	0·28
MgO	0·57	0·22	0·07	0·05
CaO	1·30	0·91	0·76	0·45
Na_2O	6·75	5·91	7·37	7·38
K_2O	5·76	5·55	5·58	5·10
TiO_2	0·86	0·57	0·46	0·45
P_2O_5	0·22	0·31	0·03	0·02
H_2O+	0·27	0·38	0·15	0·23
H_2O-	0·11	0·09	0·00	0·00
Cl	0·27	—	—	—
	100·09	100·28	100·42	99·71
less O for Cl	0·12			
	99·97			
Rb*	—	—	220	354
Sr	—	—	21	3
Yt	—	—	71	136
Zr	—	—	995	1460
Q	—	8·2	—	3·0
or	34·1	32·8	33·0	30·1
ab	56·0	50·0	57·2	55·3
an	0·7	0·7	—	—
ne	0·6	—	0·1	—
ns	—	—	0·2	0·4
ac	—	—	3·8	5·0
wo	1·8	0·8	1·5	0·9
en	1·0	0·6	0·1	0·1
fs	0·8	1·3	1·6	3·9
fo	0·3	—	0·1	—
fa	0·2	—	1·8	—
mt	1·9	3·6	—	—
il	1·6	1·1	0·9	0·8
ap	0·5	0·7	0·1	0·0
halite	0·4	—	—	—
water	0·4	0·5	0·2	0·2
	100·3	100·3	100·6	99·7
ΣPRS	90·7	91·0	90·3	88·4
normative feldspar comp.	$Or_{36}Ab_{63}An_1$	$Or_{38}Ab_{61}An_1$	$Or_{35}Ab_{65}An_0$	$Or_{34}Ab_{66}An_0$

* Values for Rb, Sr, Yt, and Zr are in ppm and are based on values of Rb = 210 ppm, Sr = 245 ppm, Yt = 16 ppm, and Zr = 210 ppm for the standard granite Gl. Accuracy is about $\pm 3\%$ except for the Sr of 92803 which may be in error by 1 ppm.

the normative ones. This composition is very close to that of the thermal minimum on the Or–Ab join at low pressures.

Although two of the analyses have just undersaturated norms and two just oversaturated ones, this is probably not significant, as the presence in the actual rock of amphibole rather than the normatively calculated pyroxene will depress the normative quartz relative to the modal. On the other hand, it may be significant that analyses 1 and 2 show normative anorthite, while 3 and 4 show normative sodium metasilicate. In table I the analyses have been arranged in order of decreasing CaO, MgO, and TiO_2, all elements that decrease markedly in the last stages of fractionation. The decrease in all three elements is consistent in the four analyses. If this decrease is significant, then it is possible that the rock series becomes normatively peralkaline at a stage between analyses 2 and 3.

However, we are concerned here particularly with analyses 3 and 4, the first rock containing diagnostic biotite and zircon, the second dalyite and astrophyllite. Examination of these analyses shows no significant difference in major element content and gives no clue to the explanation of the difference between the rocks. Accurate values of four trace elements, Rb, Sr, Yt, and Zr were determined for these rocks by X-ray fluorescence analysis, using the method of Norrish and Chappell (Chappell, personal communication). These are set out in table I, and despite the closeness of major element composition, the trace elements show a considerable contrast. 92 803, the dalyite-bearing syenite, contains higher Rb, Yt, and Zr and lower Sr than 92 801. All of these differences are significant.

Thus, if, as seems plausible to assume in this case, the two rocks are related by fractional crystallization, a liquid of the composition of 92 801 must become about 50 % solid to yield a liquid of the composition of 92 803 if the subtracted solid contains no Yt. If, as is more likely, the subtracted solid contains some Yt, the degree of solidification would have to be even greater.

If this relationship is, in fact, correct, it is possible to explain it by postulating a modified form of eutectoid crystallization. Because the major elements contents of the two rocks scarcely differ, the composition in terms of major elements must be on a eutectoid point for the conditions concerned, so that the major element composition of the precipitated solid is the same as that of the liquid. However, the minor element content of the precipitated solid must have been very different from that of the liquid, and the trace element content of the liquid is changed

during crystallization. By observing the behaviour of the trace elements, then, the course of crystallization of a magma lying at a eutectoid point might be followed. Although signs of such behaviour may be found in published trace element contents of rock series (e.g. Nockolds and Allen, 1953 (in the Scottish Caledonian) and Wager and Mitchell, 1951 (in the Skaergaard intrusion)), analyses have neither been accurate enough nor sufficiently concentrated on similar end-stage rock types from the same series to confirm it. Further detailed investigation of such salic varieties is necessary in order to determine how useful such a concept of para-eutectoid crystallization is.

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