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# THE EFFECTS OF WEATHERING ON WHOLE-ROCK Rb-Sr AGES OF GRANITIC ROCKS

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ABSTRACT. Weathered granitic whole-rock samples were analyzed for Rb, Sr, and $Sr^{87}/Sr^{86}$ ratios to measure the effect of weathering on whole-rock Rb-Sr ages. Four weathered samples of the Cape Ann Granite, Massachusetts, average 10 percent younger than the age from the whole-rock isochron. Fourteen fresh samples of the Petersburg Granite, Virginia, do not define an isochron, but the average age of 7 weathered samples is 8 to 15 percent younger than the average age of the fresh samples.

Chemical analyses of 7 fresh and 6 weathered Petersburg Granite samples show that in the weathered zone Li and Ca are depleted by about 50 percent, and Na, Sr, and Mg are depleted by about 25 percent. Potassium shows essentially no depletion, whereas Rb is enriched by about 20 percent in the weathered samples. Rb/Sr ratios increase by approximately 70 percent in the weathered zone. The mobility of these elements is largely controlled by the mineralogy. Petersburg Granite is composed of quartz, K-feldspar, plagioclase, and biotite. The plagioclase in the weathered samples is extensively to completely altered, but the other minerals are essentially unaltered.

For Petersburg Granite, the minimum age and maximum $(Sr^{87}/Sr^{86})_0$ ratio are 460 m.y. and 0.7245, respectively. Assuming a $(Sr^{87}/Sr^{86})_0$ ratio of 0.705, the maximum age is 690 m.y. The Petersburg Granite is late Precambrian to early Paleozoic in age.

## INTRODUCTION

In collecting whole-rock samples for rubidium-strontium age measurements, the freshest material available is selected in order to avoid the possible deleterious effect of weathering. However, it sometimes is difficult or impossible to obtain samples that are completely free of alteration due to weathering. Goldich and others (1966) have suggested that even incipient weathering may lower whole-rock Rb-Sr ages.

Although there is little or no specific information on the effect of weathering on whole-rock Rb-Sr ages, some information is available on the effect of weathering on Rb-Sr mineral ages. Based on laboratory results, Kulp and Engels (1963) stated that biotite Rb-Sr ages could be lowered by exchange of Rb in groundwater for $Sr^{87}$ in the biotite. Zartman (1964) analyzed biotite from two samples of weathered Town Mountain Granite (Texas) and found the Rb-Sr ages to be only 10 percent lower than the Rb-Sr ages on fresh biotite. The Rb-Sr ages of microcline from the same granite were unaffected by the weathering. Goldich and Gast (1966) found that the Rb-Sr ages of biotite from the Morton Gneiss of Minnesota were lowered approximately 75 percent by weathering.

The effect of weathering on whole-rock Rb-Sr ages was studied by analyzing obviously weathered Cape Ann Granite (Massachusetts) and Petersburg Granite (Virginia). Fresh samples of the Petersburg Granite also were studied; fresh samples of the Cape Ann Granite were studied in a previous investigation (Bottino, ms). The Rb-Sr ages of the fresh and weathered samples were compared. In addition, other chemical analyses were made on Petersburg Granite samples to evaluate changes that took place in the rock during weathering (Bottino and Fullagar, 1968).

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## SAMPLE PREPARATION AND ANALYTICAL PROCEDURES

All whole-rock samples were prepared by grinding a 30 to 50 gram piece of rock. For Rb and Sr mass spectrometric analyses, the samples were dissolved in reagent grade HF and vycor-distilled $H_2SO_4$ and HCl acids; the solutions were passed through cation exchange columns in order to concentrate the Rb and Sr. Sr and Rb concentrations were measured by isotope dilution techniques or by X-ray fluorescence analyses of pellets made from powdered samples. Samples analyzed by isotope dilution were used as standards for the X-ray analyses. The Sr isotopic compositions were measured on separate unspiked solutions using a 12-inch radius of curvature solid-source mass spectrometer.

Separate solutions of fresh and weathered Petersburg Granite samples were analyzed quantitatively for Li, Na, and K, and semi-quantitatively for Mg and Ca by atomic absorption spectroscopy.

Thin sections of all specimens were studied, and modal analyses were made of selected thin sections.

## CAPE ANN GRANITE, MASSACHUSETTS

The Cape Ann Granite samples (Essex County, Massachusetts) are from outcrops located east of the Annisquam bridge, 0.4 mile beyond the second rotary on Massachusetts route 128 extension and on the eastern slope of Mount Ann. This granite is one of the alkaline granitic rocks of eastern Massachusetts. The granite was described by Clapp (1921), although he referred to it as the Quincy Granite from Cape Ann. Clapp states that the chief constituent is a microperthitic feldspar which occurs in medium to coarse rectangular grains. Quartz is interstitial to the large feldspar crystals. The mafic minerals are mainly katophorite and hedenbergite. Modal analyses made in our study indicate that the rock is approximately 60 to 70 percent microperthite, 20 to 35 percent quartz, and 5 to 10 percent mafic minerals.

The Cape Ann Granite was analyzed previously by Bottino (ms) for Rb, Sr, and Sr isotopic content. The five samples analyzed, which were collected during 1962, were selected on the basis of apparent freshness of the hand specimen and favorable Rb/Sr ratios as determined by X-ray fluorescence analyses. Using $\lambda_{Rb^{87}} = 1.39 \times 10^{-11}$ year$^{-1}$, these five samples give an age of 415 $\pm$ 10 m.y. ($2\bar{\sigma}$) with an initial $(Sr^{87}/Sr^{86})_N$ ratio of 0.707 $\pm$ 0.002 (fig. 1).

In order to determine the effect of weathering on the Rb-Sr age of the Cape Ann Granite, additional samples (ODC-203 through ODC-206) were collected during the summer of 1965. These samples came from the

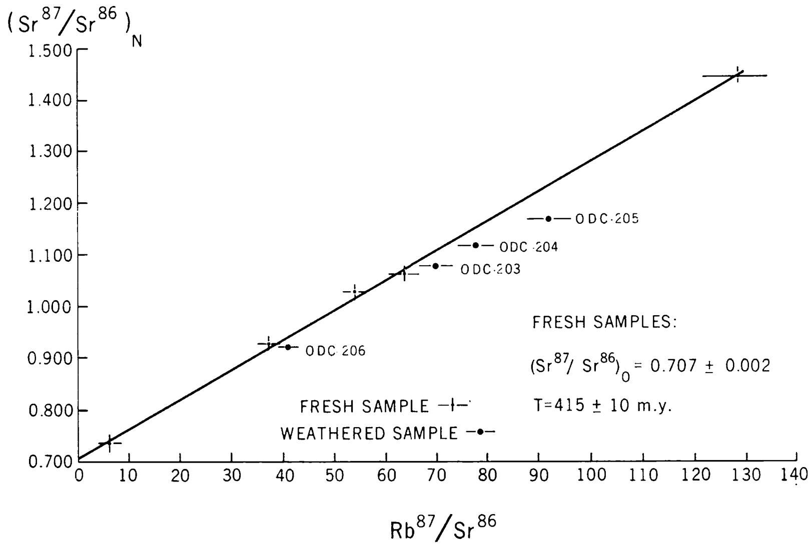


Fig. 1. Isochron for Cape Ann Granite, Massachusetts, plus analytical results for the weathered samples (ODC-203 to 206).

top of the outcrops and were those that showed the greatest amount of weathering. The four samples were weathered to approximately the same degree; the hand specimens were slightly friable, and thin sections of these samples showed considerable alteration of both the plagioclase in the microperthite and the mafic minerals.

The Rb-Sr analytical data for the weathered Cape Ann Granite samples are given in table 1, and the results are plotted in figure 1. The initial ratio established by the fresh samples was used to calculate the "ages" of the individual weathered samples. Ages of 379 m.y., 377 m.y., 358 m.y., and 372 m.y. are obtained for ODC-203 through ODC-206, respectively. The average age of 372 $\pm$ 10 m.y. ($2\bar{\sigma}$) for the four weathered samples is approximately 10 percent lower than the 415 m.y. age of the fresh samples.

### PETERSBURG GRANITE, VIRGINIA

Samples of the Petersburg Granite were collected by the writers during the spring of 1965 from the Trego Stone Corporation quarry. The quarry is located about 2 miles west of the town of Skippers, Greenville County, Virginia. Samples that appeared fresh in hand specimen were collected from near the ground surface down to depths of approximately 200 feet. Weathered samples were collected from the top to the bottom of the approximately 7 feet of weathered granite that overlies the fresh rock. The weathered rock is extremely friable and weak; the extent of
lite. Sample ODC-116, from the top of the weathered zone, is the most
the decomposition is such that the weathered rock is very nearly sapro-

TABLE 1

Cape Ann Granite and Petersburg Granite Rb-Sr analytical data

| Sample | Rb (ppm) | Total Sr (ppm) | Rb/Sr | $Rb^{87}/Sr^{86}$ | $Sr^{86}/Sr^{88}$ | $(Sr^{87}/Sr^{86})_N$ |
|---|---|---|---|---|---|---|
| ODC–203 | 103 | 4.41 | 23.36 | 70.08 | 0.1216 | 1.0763 |
| –204 | 114 | 4.42 | 25.79 | 77.65 | 0.1211 | 1.1139 |
| –205 | 126 | 4.14 | 30.43 | 92.07 | 0.1204 | 1.1658 |
| –206 | 98.3 | 7.09 | 13.86 | 40.96 | 0.1210 | 0.9190 |
| ODC–43 | 214* | 107* | 2.00 | — | — | — |
| –44 | 244 | 76.6 | 3.19 | 9.31 | 0.1190 | 0.7818 |
| –45 | 228 | 95.6 | 2.38 | 6.93 | 0.1201 | 0.7699 |
| –46 | 224* | 97.9* | 2.29 | — | — | — |
| –47 | 218 | 93.3 | 2.34 | 6.82 | 0.1198 | 0.7790 |
| –48 | 207 | 110 | 1.88 | 5.47 | 0.1202 | 0.7611 |
| –49 | 195* | 101* | 1.93 | — | — | — |
| –55 | 204* | 115* | 1.77 | 5.15 | 0.1202 | 0.7618 |
| –63 | 234* | 85.6* | 2.73 | 7.96 | 0.1197 | 0.7795 |
| –65 | 192 | 205 | 0.94 | 2.73 | 0.1191 | 0.7334 |
| | | | | — | 0.1200 | 0.7373 |
| –65 (leached) | — | — | — | — | 0.1195 | 0.7313 |
| –65 (filtrate) | — | — | — | — | 0.1200 | 0.9383 |
| –70 | 252* | 89.6* | 2.81 | 8.19 | 0.1212 | 0.7746 |
| –71 | 246* | 80.1* | 3.07 | 8.95 | 0.1194 | 0.7799 |
| –72A | 175* | 131* | 1.34 | 3.90 | 0.1214 | 0.7509 |
| | | | | — | 0.1205 | 0.7499 |
| –72B | 166* | 105* | 1.58 | 4.60 | 0.1206 | 0.7538 |
| –73 | 235* | 117* | 2.01 | 5.85 | 0.1206 | 0.7636 |
| –74 | 208* | 103* | 2.02 | 5.88 | 0.1213 | 0.7632 |
| –75 | 261* | 83.5* | 3.13 | 9.13 | 0.1221 | 0.7878 |
| –105 | 272* | 68.5* | 3.97 | — | — | — |
| –106 | 280* | 73.6* | 3.80 | 11.09 | 0.1200 | 0.7911 |
| –107 | 265* | 70.6* | 3.75 | — | — | — |
| –108 | 292* | 48.4* | 6.03 | 17.68 | 0.1198 | 0.8387 |
| –109 | 284* | 83.4* | 3.41 | — | — | — |
| –110 | 273 | 69.9 | 3.91 | 11.42 | 0.1202 | 0.7923 |
| –111 | 202* | 91.4* | 2.21 | 6.44 | 0.1190 | 0.7644 |
| –112 | 265* | 61.2* | 4.33 | — | — | — |
| –113 | 228 | 110.5 | 2.06 | 5.99 | 0.1202 | 0.7587 |
| –114 | 229* | 103* | 2.22 | — | — | — |
| –115 | 283 | 77.6 | 3.65 | 10.65 | 0.1194 | 0.7877 |
| –116 | 285 | 66.1 | 4.31 | 12.58 | 0.1202 | 0.7887 |

*X-ray analysis

friable of the analyzed samples. Fresh samples are numbered ODC-43 to ODC-75, and weathered samples are numbered ODC-105 to ODC-116.

The Petersburg Granite is a fine-grained rock varying in color from gray to pink. Modal analyses indicate that the rock is 30 to 40 percent quartz, 25 to 35 percent potassium feldspar, 25 to 35 percent plagioclase feldspar, and 5 to 10 percent biotite. (On the basis of these modal analyses the Petersburg Granite perhaps should be called a granodiorite or quartz monzonite.) Much of the potassium feldspar exhibits the crosshatch twinning characteristic of microcline. The plagioclase feldspar (albite) shows both polysynthetic twinning and albite twinning; some of the plagioclase crystals are zoned. The biotite generally is green-brown in color. Small veins of calcite are commonly visible in thin sections of both weathered and fresh specimens. The plagioclase crystals in the fresh specimens show slight alteration, with the greatest amount of alteration present in the center of the zoned crystals; the other minerals exhibit no alteration. The plagioclase in the weathered samples shows extensive to complete alteration; the other minerals are not appreciably different in appearance from those in the fresh specimens.

Twenty-one whole-rock samples were analyzed for Rb, Sr, and $Sr^{87}/Sr^{86}$ ratios (table 1). Seven of the samples are from the zone of decomposed granite; the other 14 samples are fresh. The results of these analyses are plotted in figure 2 with single $Sr^{87}/Sr^{86}$ measurements plotted as $\pm$ 0.003 and duplicates as $\pm$ 0.002. $Rb^{87}/Sr^{86}$ values are plotted as $\pm$ 5 percent if the analyses were by isotope dilution and $\pm$ 10 percent if they were made by X-ray fluorescence. Figure 2 shows a scatter in age values for the fresh samples (ODC-43 through 75). All but one of the weathered samples (ODC-116) lie within the age envelope of approximately 505 m.y. to 675 m.y. established by the fresh samples. The weathered sample outside the envelope (ODC-116) is from the top of the weathered zone immediately below a fossiliferous Miocene (?) unit. Using an initial $Sr^{87}/Sr^{86}$ ratio of 0.715, the ages of the 14 fresh samples are found to average 580 $\pm$ 30 m.y. ($2\bar{\sigma}$). The weathered samples average 495 $\pm$ 30 m.y. ($2\bar{\sigma}$) or about 15 percent lower than the average of the ages of the fresh samples. Figure 3 shows a plot of the distribution of these "ages".

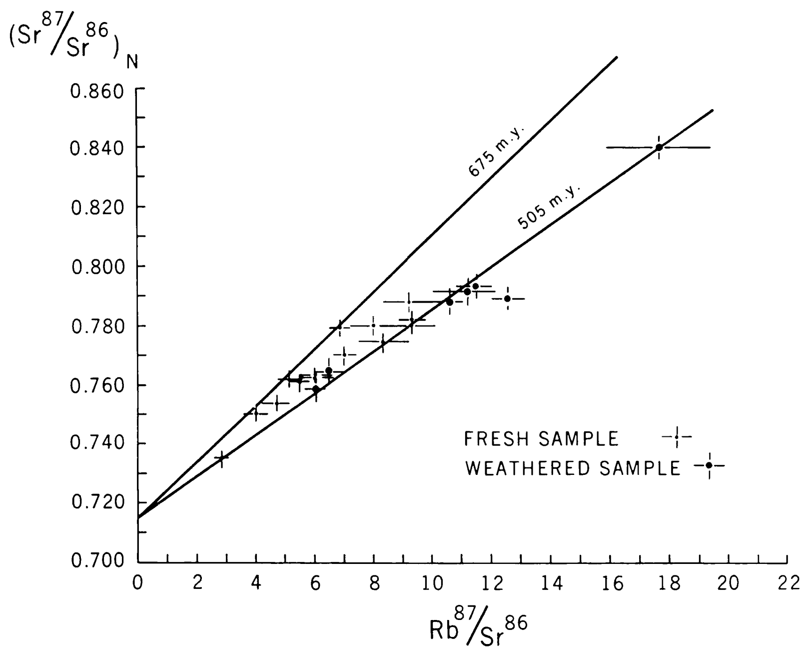


Fig. 2. Plot of $(Sr^{87}/Sr^{86})_N$ versus $Rb^{87}/Sr^{86}$ for all analyzed samples of Petersburg Granite.

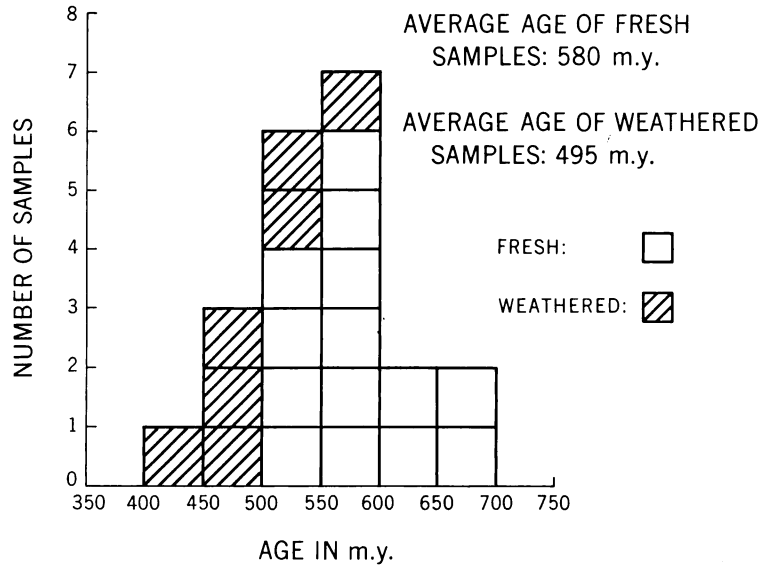


Fig. 3. Distribution of Rb-Sr ages of all Petersburg Granite samples.

Examination of the plot of $Sr^{87}/Sr^{86}$ versus $Rb^{87}/Sr^{86}$ (fig. 2) indicates that of the fresh samples two in particular show scatter, ODC-47 and ODC-65. If these two points were excluded from figure 2 a line with a slope corresponding to an age of approximately 460 m.y. could be drawn through the plot of the data for the fresh samples. Field relationships, hand specimens, thin sections, and the results of chemical analyses were studied for indications that samples from the Trego quarry represent more than one time of crystallization. Hand specimens of fresh samples were gray in color except for ODC-44 and ODC-45 which were pink due to the presence of pink K-feldspar. Field studies indicate that this pink color is related to fracturing and apparently is the result of alteration that proceeds outward from fractures: the wider the fracture (usually filled with quartz) the greater the thickness of the pink granite. The change from pink to gray granite is gradational. Thin section studies indicate that ODC-47 is similar to the rest of the specimens. Sample ODC-65 has the same mineralogy as the other samples, but it is considerably coarser grained. Zoning of plagioclase crystals is much more prominent in the thin section of this specimen than in others. Also, the biotite in ODC-65 is dark brown rather than green-brown as in all other specimens. Chemical analyses show that ODC-65 contains almost twice as much Sr as any other sample (table 1) and less K than any other fresh sample. Semi-quantitative analyses indicate that ODC-65 contains at least twice as much Ca as any other sample.

The thin section of ODC-65 showed significant amounts of carbonate minerals occurring in veins. Since these post-crystallization veins might contain Rb and Sr that could affect either or both the $Sr^{87}/Sr^{86}$

TABLE 2

Analytical data for 13 Petersburg Granite samples

| Element | Average content, 6 weathered samples | Average content, 7 fresh samples | Average, weathered/fresh |
|---|---|---|---|
| Li | 17 ppm | 36 ppm | 0.47 |
| Na | 1.7 percent | 2.3 percent | 0.74 |
| K | 3.5 percent | 3.6 percent | 0.97 |
| Rb | 261 ppm | 222 ppm | 1.18 |
| Sr | 77 ppm | 110 ppm | 0.70 |
| Rb/Sr | 3.39 | 2.02 | 1.68 |

ratio and the $Rb^{87}/Sr^{86}$ ratio, a sample of ODC-65 was leached with cold 0.4 N HCl for about 10 minutes (all visible reaction had ceased) to remove the soluble minerals. The unleached sample weighted 0.7615 g and the leached sample weighted 0.7041 g. Apparently 0.0574 g of the sample, or approximately 7.5 percent, was carbonate and other readily soluble minerals. The leached sample was dissolved, and the $Sr^{87}/Sr^{86}$ ratio of this sample was measured as well as that of the filtrate from the leached sample; the results were 0.7313 and 0.9383, respectively. Comparing the $Sr^{87}/Sr^{86}$ ratios of the whole-rock sample (0.7334) and the leached whole-rock sample (0.7313) indicates that the soluble vein material did not significantly affect the $Sr^{87}/Sr^{86}$ ratio of the whole-rock sample. The high $Sr^{87}/Sr^{86}$ of the filtrate (0.9383) suggests that the soluble vein minerals have a high Rb/Sr ratio but contain relatively little Rb and Sr. (If the radiogenic $Sr^{87}$ in the filtrate were preferentially leached from insoluble minerals in the whole-rock sample, the $Sr^{87}/Sr^{86}$ ratio of the leached whole-rock sample should be significantly lower than that of the unleached sample.)

In spite of the differences between the analyzed samples there is no significant evidence that there are granitic rocks of different age at the Trego quarry. However, it is of interest to consider Rb-Sr results on samples from a limited portion of the quarry. Samples ODC-70 through ODC-75 were collected within a few tens of feet of each other in the northwestern part of the quarry and approximately 15 to 35 feet below the contact between weathered and fresh rock; all weathered samples were collected almost directly above these samples. The analytical results for these samples are plotted in figure 4, and a visual best-fit line is drawn through these points. Using the $Sr^{87}/Sr^{86}$ initial ratio of 0.7245 determined by this line, the ages of the seven fresh samples average 460 $\pm$ 15 m.y. ($2\bar{\sigma}$). Using the same initial ratio, the average age of the seven weathered samples is 425 $\pm$ 25 m.y. ($2\bar{\sigma}$) or 8 percent lower than the age of the fresh samples. The distribution of these ages is shown in figure 5.

A $Sr^{87}/Sr^{86}$ ratio of 0.7245 for the Petersburg Granite 460 m.y. ago, as suggested by figure 4, might indicate that the rock is remelted crustal material. Another possibility, which is consistent with the scatter (fig. 2), is that this high $Sr^{87}/Sr^{86}$ initial ratio has been caused by rotation of an

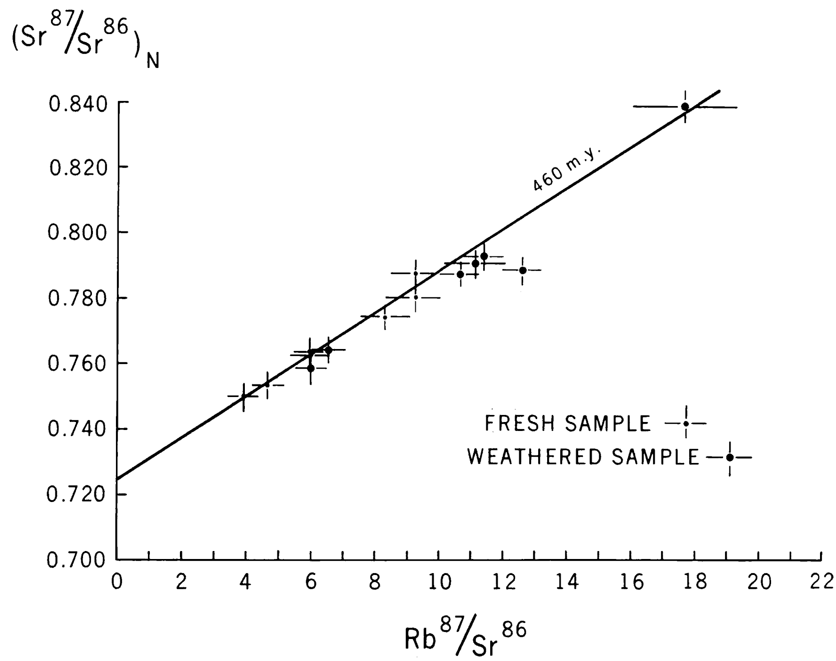


Fig. 4. Plot of $(Sr^{87}/Sr^{86})_N$ versus $Rb^{87}/Sr^{86}$ for Petersburg Granite samples from northwestern side of Trego quarry.

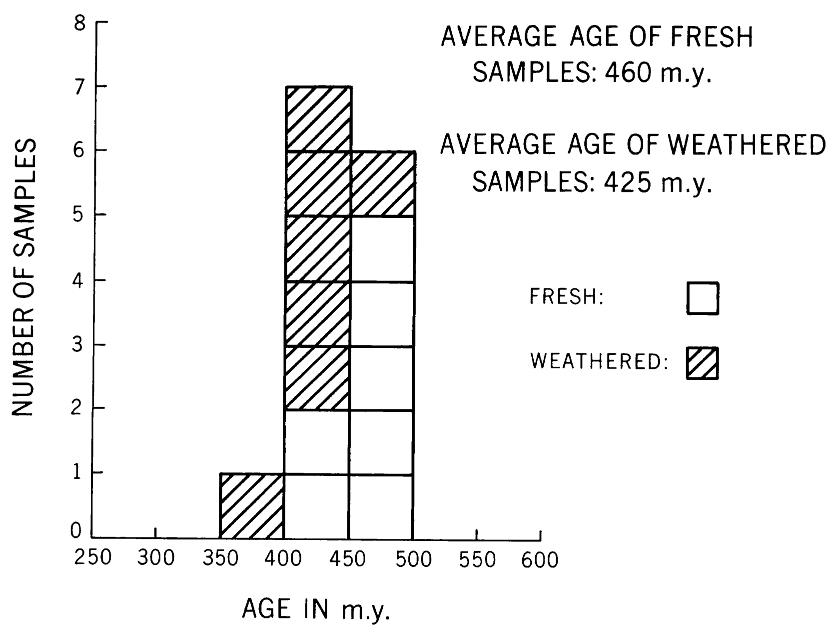


Fig. 5. Distibution of Rb-Sr ages of Petersburg Granite samples from northwestern side of Trego quarry.

isochron due to a post-crystallization disturbance of the Rb-Sr system; this would lower the age and raise the initial ratio. Even if the analyzed hand specimens have not remained closed systems with respect to Rb and Sr since crystallization, 460 ± 15 m.y. ($2\bar{\sigma}$) would be a minimum age for the Petersburg Granite. By assuming values for the $Sr^{87}/Sr^{86}$ initial ratio, maximum ages may be calculated for the Petersburg Granite if the rock unit has remained a closed system and if the measured average Rb/Sr ratio of approximately 2.1 (table 3) is representative of the closed system. If the $Sr^{87}/Sr^{86}$ initial ratio were 0.705, approximately 230 m.y. would have been required for the $Sr^{87}/Sr^{86}$ ratio to increase to 0.7245, and the rock would be 690 m.y. old. Initial $Sr^{87}/Sr^{86}$ ratios of 0.710 and 0.715 yield ages of 630 m.y. and 580 m.y., respectively. The Petersburg Granite apparently is no younger than early Paleozoic and no older than late Precambrian.

In addition to the Rb and Sr analyses by isotope dilution and X-ray fluoresence (table 1), seven fresh (ODC-44, 47, 48, 55, 63, 65, 72) and six weathered samples (ODC-106, 108, 110, 111, 113, 116) selected at random were analyzed by atomic absorption spectroscopy for Li, Na, and K (table 2). These analyses were made to establish the chemical changes that occurred as a result of the weathering. Li and Na are depleted in the weathered rock by approximately 50 percent and 25 percent respectively. K shows essentially no change, while Rb is enriched by about 20 percent. Sr is depleted by approximately 30 percent in the weathered rock. The average Rb/Sr ratio increases by about 70 percent in the weathered rock. Semi-quantitative results by atomic absorption spectroscopy for Mg and Ca on the above 13 samples indicate weathered rock/fresh rock ratios of approximately 0.75 and 0.55, respectively.

The distribution of elements in the fresh and weathered Petersburg Granite samples (table 2) reflects the mineralogy of this rock. The plagioclase in most of the weathered samples has undergone alteration resulting in a loss of Ca, Na, and Sr. Most of the K in the rock is in microcline and orthoclase which exhibit only very slight alteration in the weathered samples; the amount of K is approximately the same in both fresh and weathered samples.

Possible explanations for the increase of Rb in weathered samples are that this element may be trapped through a cation exchange mechanism on clay minerals produced by alteration of the plagioclase or adsorbed on other minerals. The increase of approximately 70 percent in the Rb/Sr ratio of weathered versus fresh samples with only a 10 percent lowering of the age probably is the result of the loss of non-radiogenic Sr from plagioclase due to weathering and the retention of the relatively radiogenic strontium in the K-feldspar and biotite. (The weathered samples are essentially whole-rock-minus-plagioclase samples.) Removal of non-radiogenic Sr from the whole-rock samples would raise both $Rb^{87}/Sr^{86}$ and $Sr^{87}/Sr^{86}$ ratios. Rb-Sr and K-Ar analyses on minerals separated from the Petersburg Granite may provide additional information on the effects of weathering on whole-rock ages.

TABLE 3

Summary of Rb and Sr analyses on Petersburg Granite samples

| Element | Average content, 12 weathered samples | Average content, 17 fresh samples | Average, weathered/fresh |
|---|---|---|---|
| Rb | 263 ppm | 218 ppm | 1.21 |
| Sr | 77 ppm | 106 ppm | 0.73 |
| Rb/Sr | 3.42 | 2.06 | 1.66 |

The Rb and Sr X-ray fluorescence and isotope dilution analyses are summarized in table 3. (Eighteen additional fresh samples were analyzed for approximate Rb/Sr ratios by sawing smooth surfaces on specimens and analyzing these surfaces by X-ray fluorescence. The 18 fresh samples have an average Rb/Sr ratio of approximately 2.3 which is close to the value of 2.06 given in table 3. These additional results support our belief that 2.06 is the approximate Rb/Sr ratio for the unweathered Petersburg Granite.) The average Rb/Sr ratios for the 13 samples selected for additional chemical analyses (table 2) are in good agreement with the data for all 29 samples (table 3). This agreement indicates that the 13 samples are representative of the larger sampling of the granite.

## CONCLUSION

Rb-Sr analyses of the Cape Ann Granite from Massachusetts and the Petersburg Granite from Virginia indicate that weathering readily visible in hand specimen has lowered the Rb-Sr whole-rock ages. However, the Rb-Sr whole-rock ages have been lowered only by approximately 10 percent. These results suggest that incipient weathering should not significantly affect the Rb-Sr whole-rock age of granitic rocks. If additional studies show that Rb-Sr whole-rock ages are consistently lowered by about 10 percent due to weathering, useful age data might be obtained on weathered granitic rock. Analyses of weathered granitic rocks would be especially useful in areas such as the southeastern United States where in places it is very difficult or impossible to obtain fresh samples.

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