ated media, although analysis showed that leaves formed late in the lifetime of the plant were more highly deuterated than older leaves. As a test plant, tobacco suffered from the disadvantage that the range of available deuterium concentrations is limited, no higher plant having yet been grown in a completely deuterated medium (*10*). For these reasons, a more closely controlled experiment was devised, employing unicellular algae adapted to life in pure D_2O.

Completely deuterated *Chlorella vulgaris,* which had been mass cultured in heavy water for several years (*11*), was used to inoculate media of 75 percent and 99.6 percent D_2O composition; the hydrogen form of the same strain was used to inoculate media of 0, 25, and 50 percent D_2O concentrations. Flask cultures with media of these concentrations were grown on a shaker with conditions of illumination, gas flow, and agitation made as identical as possible for all cultures, as it has been shown that the conditions of growth of an algal culture may significantly change the apparent carbon isotopic fractionation factor (*4*). Cultures were aerated with a gas mixture composed of 95 percent nitrogen and 5 percent carbon dioxide. Under the wide range of deuterium concentrations used, the growth rates for the various cultures were widely different. Therefore, cultures were harvested, not after a specified time, but when an arbitrary cell density had been attained [$(3 \pm 0.5) \times 10^8$ cells/ml]. Growth times varied from 22 to 27 days.

After harvest, the cells were burned and the deuterium content and carbon isotopic ratios were determined. The deuterium content of the lyophilized cells did not correspond to the concentrations of deuterium in the media, owing to isotopic fractionation during metabolism. The lower group of points in Fig. 1 shows the results of the *Chlorella* experiments. The δ values in this case indicate enrichment relative to the initial isotopic content of the feed gas. The enrichment shown by the H_2O control culture was $\delta = -22.88$ per mil, in good agreement with the value of $\delta = -25.8$ per mil reported by Abelson and Hoering (*4*) for the closely related organism *Chlorella pyrenoidosa* under similar growth conditions.

That both curves of Fig. 1 have about the same slope suggests that a similar mechanism may be responsible in both cases for the observed isotopic fractionations. The observed δ values for tobacco, while covering only slightly more than one-half the range of deuterium concentrations, show a variation equal to that found throughout the range of plant species, as tabulated by Craig (*3*).

In our opinion the change in fractionation shown by deuterated organisms is most likely a consequence of widespread changes in the cell, and the present data do not allow interpretation in terms of kinetic isotope effects on specific chemical reactions.

ROBERT A. UPHAUS
JOSEPH J. KATZ

*Argonne National Laboratory,
9700 South Cass Avenue,
Argonne, Illinois 60439*

References and Notes

1. A. O. Nier and E. A. Gulbranson, *J. Am. Chem. Soc.* **61**, 697 (1939).
2. F. E. Wickman, *Geochim. Cosmochim. Acta* **2**, 243 (1952).
3. H. Craig, *ibid.* **3**, 53 (1953).
4. P. H. Abelson and T. C. Hoering, *Proc. Natl. Acad. Sci. U.S.* **47**, 623 (1961).
5. R. Park and S. Epstein, *Geochim. Cosmochim. Acta* **21**, 110 (1960).
6. ———, *Plant Physiol.* **36**, 133 (1961).
7. E. Flaumenhaft *et al., Intern. Rev. Cytol.* **18**, 313 (1965); J. J. Katz and H. L. Crespi, *Science* **151**, 1187 (1966).
8. Studies on tobacco were undertaken as part of a larger program in collaboration with M. I. Blake and F. T. Crane of the departments of Pharmacy and Pharmacognosy, University of Illinois, Chicago.
9. H. L. Crespi and J. J. Katz, *Anal. Biochem.* **2**, 274 (1961).
10. R. A. Uphaus *et al., J. Pharm. Sci.* **54**, 202 (1965); M. I. Blake, F. A. Crane, R. A. Uphaus, J. J. Katz, *Lloydia* **27**, 254 (1964).
11. H. F. DaBoll, H. L. Crespi, J. J. Katz, *Biotechnol. Bioeng.* **4**, 281 (1962).
12. Work performed under the auspices of the AEC. We thank O. Van Hook for mass spectrometer determinations.

3 October 1966

■

Fractionation of Potassium/Rubidium by Amphiboles: Implications Regarding Mantle Composition

Abstract. *We show that the rubidium in amphiboles is generally depleted with respect to potassium. The K:Rb ratios of 50 analyzed amphiboles range from 100 to 5000, averaging 1120. This fractionation effect holds for potassium concentrations ranging from 0.05 to 1.5 percent. The K:Rb ratios of abyssal tholeiites do not place unambiguous limits on the K:Rb ratio of the upper mantle, since partial melting of a mantle material such as amphibole peridotite would produce a liquid with a K:Rb ratio higher than that in the initial material. Large-scale mineralogic control of distributions of trace elements in the mantle could produce trends with depth that are the reverse of trends normally attributed to differentiation processes.*

Interest in use of the K:Rb ratio as a geochemical tracer was revived by the demonstration (*1*) that the K:Rb ratio of terrestrial rocks is not invariant but may vary significantly as a function of geologic process. Many papers have since discussed variations in the K:Rb ratio of rocks and their possible interpretation (*2–5*). Perhaps the most interesting was the finding (*2*) that oceanic abyssal basalts exhibit K:Rb ratios ranging from 475 to 1830, compared to the value of 240 that is believed to characterize continental igneous rocks (*6*).

We shall now discuss the role of mineralogy with respect to K/Rb fractionation. In particular, we show that amphiboles strongly discriminate against rubidium, and that amphiboles from most geologic occurrences have above-normal K:Rb ratios.

Ratios ranging from 400 to 1400 have been determined for amphibole peridotites from Saint Paul Rocks, with the amphibole content and K:Rb ratio varying sympathetically (*7*). Ratios as high as 2800 can also be derived from data published in connection with the K-Ar dating of amphiboles (*8*). While a preferential exclusion of rubidium from the amphibole structure is suggested by such data, a more convincing demonstration can be found in analyses of coexisting minerals (Table 1).

The mineral assemblages of both

Table 1. Potassium-rubidium data for coexisting phases (*9*). TQ2: metamorphic aureole, Tinaquillo, Venezuela. B65: Baltimore gneiss, Woodstock Dome, Maryland.

Mineral	K		Rb (ppm)	K/Rb
	ppm	Percent		
	TQ2 (*10*)			
Hornblende	465		0.196	2400
Pyroxene	89.4		.134	670
Plagioclase	274.		.972	280
	B65 (*11*)			
Hornblende		1.260	13.95	902
Pyroxene		0.0781	3.21	243
Plagioclase		.951	27.8	342

Table 2. Potassium-rubidium data for hornblende-biotite pairs (*9*). References to published biotite data appear in parentheses.

Sample	Source	Rock type	Biotite		Hornblende	
			K (%)	K/Rb	K (%)	K/Rb
B4	Maryland (*12*)	Gneiss	7.82	125	1.31	1350
B15	Virginia (*14*)	Gneiss	7.30	100	1.66	540
B16	Pennsylvania	Gneiss	7.64	180	1.48	1410
B21	Maryland (*12*)	Granodiorite	6.55	180	2.05	300
P20	Pennsylvania (*14*)	Gneiss	7.17	180	1.32	810
Sk	New York (*14*)	Granite	7.88	65	1.68	465
CG	New Hampshire	Granite	6.33	35	1.67	100
SA15	Saudi Arabia	Gneiss	4.87	155	0.544	1000
LS42b	Michigan (*13*)	Gneiss	6.70	65	.730	450
LS43a	Michigan (*13*)	Gneiss	3.55	290	.760	1900
LS53	Michigan (*13*)	Quartz diorite	5.24	210	.974	520
LS125	Wisconsin (*13*)	Amphibolite	3.76	65	.368	405
3089	Ontario (*15*)	Gneiss	6.37	125	1.29	850
942a	Venezuela	Gneiss	6.89	470	1.38	2090

rocks are metamorphic, so that equilibration of the trace elements between phases has presumably occurred. The relative depletion of rubidium in both hornblendes is striking, with the K:Rb ratio of the hornblende being 4 to 8 times higher than that of the coexisting pyroxene and plagioclase. Furthermore, this phenomenon does not depend strongly on alkali concentration, since the Tinaquillo hornblende has a lower potassium content than has any amphibole we have measured and the Baltimore gneiss hornblende is well above average in potassium content.

It would be most interesting in these two instances to know whether the K:Rb ratios of the bulk rocks are normal or not. While we did not analyze any total rocks during this study, from modal data for these samples (*10, 11*) we can estimate the K:Rb ratio of the bulk rocks. If one allowed for a K:Rb ratio of 200 to 500 for the small amount of K-feldspar in sample B65, the whole-rock K:Rb ratio would be in the range 350 to 500—just slightly above the continental rock average. For TQ2, the bulk-rock K:Rb ratio derived from modal data is about 900—well above normal.

Another suite of samples for which we have partitioning data are the hornblende-biotite pairs listed in Table 2. Because of the variety of rock types involved in this suite, these pairs do not necessarily represent equilibrium-fractionation data; yet it is clear that the hornblendes are again characterized by high K:Rb ratios, with fractionation factors ranging from about 2 to 10. Some of the lower fractionation values may be attributable to incomplete separation of the biotite and hornblende during preparation, as with B21 in which the hornblende separate contains about 8 percent biotite; correction for this impurity would raise the K:Rb ratio of this hornblende to about 400. Hornblende sample CG also has a low K:Rb ratio, but this may reflect rather the very highly differentiated nature of the granite from which it came than imperfect separation of the biotite and hornblende.

Because of the well-known tendency for micas to concentrate rubidium (*13, 16*), the K:Rb ratio of the bulk rock may be expected to lie somewhere between those of the biotite and the hornblende, depending in detail on the relative proportions of biotite and amphibole and on the presence of other K-rich phases such as K-feldspar. A compilation of data on biotite–K feldspar pairs shows that the K:Rb ratio of K-feldspar averages about 5 times the K:Rb ratio of biotite (*17*); this estimate, together with the modal data available for the rocks of Table 2, allows a crude calculation of the total-rock K:Rb ratios, which range from 100 to 600, averaging about 300. The generally high K:Rb ratios for the amphiboles thus represent real fractionation in comparison with either the biotite or the total-rock K:Rb ratios; the apparent fractionation factors average about 5 and 4 in comparison with biotite and the total rock, respectively.

Finally, in Table 3 we give K-Rb data for a number of amphiboles for which no coexisting-mineral data are available; again the prevalence of high K:Rb ratios in the amphiboles is striking, with the ratio of 5000 from sample 80827 being the highest value so far recorded.

There are 50 K-Rb analyses of amphiboles listed in Tables 1–3; the average K:Rb ratio is 1120, the average concentrations of K and Rb being 0.73 percent and 15 ppm, respectively. The K:Rb ratios are plotted in Fig. 1 as a function of the potassium content of the amphibole; there is no marked cor-

Table 3. Potassium-rubidium data for amphiboles (*9*). All samples other than those identified by footnotes are hornblende.

Sample	Source	Rock type	K (%)	Rb (ppm)	K/Rb
G15	N. Carolina	Gneiss	0.51	13.0	390
3426*	Ontario	Gabbro	.087	2.05	425
3136	New Brunswick	Granite	.506	10.3	490
4068	Colorado	Amphibolite	1.00	9.84	1020
1021	New York	Amphibolite	1.40	19.7	710
247	New York	Amphibolite	1.30	9.57	1360
R1-13†	Colorado	Pegmatite	1.17	29.7	395
R-15-6†	Colorado	Granite	1.12	25.6	440
R-21-8†	Colorado	Pegmatite	1.04	19.4	540
328a	Dom. Republic	Tonalite	0.359	1.36	2640
B92	Dom. Republic	Amphibolite	.054	0.53	1010
Pr57b	Puerto Rico	Amphibolite	.301	3.07	980
B27f	Dom. Republic	Hornblendite	.160	1.41	1135
B60	Maryland	Meta-gabbro	.208	2.76	755
B68	Maryland	Amphibolite	.512	5.14	1000
B69	Maryland	Amphibolite	.483	7.50	645
A76	Finland	Meta-gabbro	.259	0.703	3700
80827*	Austria	Skarn (?)	.0244	.049	5000
H1	Bavaria	Amphibolite	.408	3.87	1055
H2	Bavaria	Diorite	.867	15.8	550
H4	Bavaria	Amphibolite	.575	10.94	530
H5	Bavaria	Meta-gabbro	.176	1.51	1170
A38	Colorado	Gneiss	.393	1.70	2300
RHB-9-54	Michigan	Meta-pyroxenite	.472	21.4	220
RHB-120-52	Michigan	Basic pegmatite	.088	< 0.34	> 2600
HJ20A52	Michigan	Amphibolite	.303	1.47	2060
HJ68-55	Michigan	Meta-gabbro	.173	1.73	1000
HJ63-55	Michigan	Amphibolite	.580	6.24	930
SG	Minnesota	Granite	.487	6.76	720
SA1	Saudi Arabia	Granodiorite	.956	47.8	200
SA4	Saudi Arabia	Diorite	.409	2.92	1400
SA7	Saudi Arabia	Charnockite	.937	9.78	960
SA8	Saudi Arabia	Granite	.398	2.88	1380

* Actinolite. † Riebeckite.

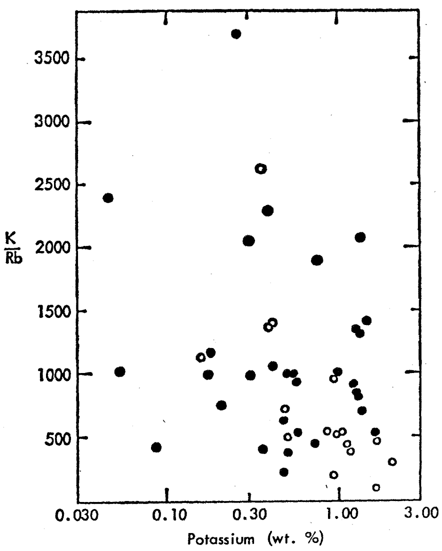

Fig. 1. Potassium : rubidium ratios and potassium contents of amphiboles. Open circles, igneous samples; solid circles, metamorphic samples.

relation between K:Rb ratio and potassium content as might be expected if the potassium content of the amphibole reflected the relative position of the host rock with respect to differentiation history. The K:Rb ratio generally tends to decrease with increasing differentiation (*1–5*). Our samples represent a very heterogeneous population of rock types, however, and any real trends to be expected in Fig. 1 may be obscured for this reason.

We feel that the above-mentioned data may have a particular bearing on the anomalously high K:Rb ratios reported in abyssal tholeiites (*2*, *4*). Gast (*2*) and Engel and Engel (*3*) state that the K:Rb ratio of the mantle must be at least as high as that in the tholeiites that are derived from it, and that the upper mantle therefore is chemically more like achondritic (K:Rb > 1000) than chondritic (K:Rb ~ 300) meteorites. The ambiguity of this approach can be easily shown by adopting a mantle model such as Ringwood's (*18*), which has an amphibole peridotite as the stable assemblage in the uppermost mantle. Cogent arguments in favor of amphibole as a phase in the upper mantle have been presented (*19*).

The melting relations of amphibole peridotite are essentially unknown; it is likely however that the hydrous phase will be one of the earliest to melt, perhaps incongruently (*20*). The liquid produced by partial melting of an amphibole peridotite would then contain most of the alkalis originally in the amphibole. In the case of the Saint Paul Rocks peridotite, the K:Rb ratio of this early liquid would not only exceed 1000, but it would also be greater (more "primitive" appearing) than the K:Rb ratio of the material from which it was derived. Clearly, the K:Rb ratios of abyssal tholeiites cannot be used a priori to set lower limits on the K:Rb ratio of the tholeiite-source regions.

So far we have considered only closed-system partitioning between the minerals of a given assemblage; we may also speculate on the large-scale effects of partitioning between assemblages. Ringwood's pyrolite model, for example, proposes an upper amphibole-peridotite layer that transforms at depth to peridotite or garnet peridotite (*18*). Any equilibration of trace elements between these layers would result in an upward transfer of potassium relative to rubidium, resulting in a higher K:Rb ratio in the uppermost mantle than in the deeper regions. Similar effects may exist for other trace elements such as Sr, U, Th, and Pb, all of which figure prominently in discussions of mantle composition. If Rb were relatively impoverished in the upper mantle, the Rb:Sr ratio of the mantle might even increase with depth, invalidating one of the main arguments against a chondritic earth model (*21*). Clearly, compositional models for the mantle, based on trace-element data from derived material such as basalt, must recognize the very real control that mineralogy can have on trace-element chemistry.

STANLEY R. HART*
L. T. ALDRICH
Department of Terrestrial Magnetism,
Carnegie Institution of Washington,
Washington, D.C.

References and Notes

1. P. Lessing, R. W. Decker, R. C. Reynolds, Jr., *J. Geophys. Res.* **68**, 5851 (1963).
2. P. W. Gast, *Science* **147**, 858 (1965).
3. A. E. J. Engel, C. G. Engel, R. G. Havens, *Bull. Geol. Soc. Amer.* **76**, 719 (1965).
4. M. Tatsumoto, C. E. Hedge, A. E. J. Engel, *Science* **150**, 886 (1965).
5. W. H. Taubeneck, *J. Geophys. Res.* **70**, 475 (1965); B. Gunn, *ibid.*, p. 6241; A. M. Stueber and V. R. Murthy, *Science* **153**, 740 (1966).
6. S. R. Taylor, L. H. Emeleus, C. E. Exley, *Geochim. Cosmochim. Acta* **10**, 224 (1956).
7. S. R. Hart, Geol. Soc. Amer. Ann. Meeting 77th 1964 Program, p. 86; ——— and G. R. Tilton, in preparation.
8. S. R. Hart, *J. Geophys. Res.* **66**, 2995 (1961); R. H. Steiger, *ibid.* **69**, 5407 (1964).
9. Potassium and rubidium determinations were made by isotope-dilution techniques similar to those described (*8*). Analytic uncertainty for potassium is 2 percent or less; for rubidium it is 5 percent, except at the lower levels of concentration at which it may approach 10 percent.
10. Separated minerals donated by H. H. Hess. TQ2 mode: 45 percent hornblende, 28 percent pyroxene (dominantly clinopyroxene), 25 percent plagioclase (An 70), and 2 percent ores.
11. Mode for B65 [from (*12*)]: 45 percent plagioclase (An 30), 37 percent hornblende, 9 percent diopside, 4 percent microcline, 2 percent epidote, 2 percent sphene, and traces of quartz and apatite.
12. G. W. Wetherill, G. R. Tilton, G. L. Davis, S. R. Hart, C. A. Hopson, *J. Geophys. Res.* **71**, 2139 (1966).
13. L. T. Aldrich, G. L. Davis, H. L. James, *J. Petrology* **6**, 445 (1965).
14. G. R. Tilton, G. W. Wetherill, G. L. Davis, M. N. Bass, *J. Geophys. Res.* **65**, 4173 (1960).
15. H. W. Fairbairn, P. M. Hurley, W. H. Pinson, *Proc. Geol. Assoc. Can.* **12**, 41 (1960).
16. K. Heier and J. A. S. Adams in *Physics and Chemistry of the Earth* (Pergamon, New York, 1963), vol. 5, pp. 255–381.
17. See (*13*) for data and discussion of K:Rb ratios in micas and feldspars.
18. A. E. Ringwood, in *Advances in Earth Science*, P. M. Hurley, Ed. (M.I.T. Press, Cambridge, Mass., 1966, pp. 357–99; D. H. Green and A. E. Ringwood, *J. Geophys. Res.* **68**, 937 (1963).
19. E. R. Oxburgh, *Geol. Mag.* **101**, 1 (1964).
20. F. R. Boyd, in *Researches in Geochemistry*, P. H. Abelson, Ed. (Wiley, New York, 1959), pp. 377–96.
21. P. W. Gast, *J. Geophys. Res.* **65**, 1287 (1960).
* Present address: Department of Earth Sciences, University of California, San Diego, La Jolla.

24 October 1966

Phenotypic Variations among Chloroplasts of a Single Cell

Abstract. *Some normal-looking chloroplasts of a* Nitella *cell do not incorporate carbon dioxide into substances insoluble in cold acid. The distribution of such chloroplasts among the rows of normal organelles indicates that the defect is not due to a genetic mutation but probably represents a physiological stage in the development of the organelles.*

The presence within a single cell of diverse types of mitochondria or plastids is considered good evidence for the existence of an independent genetic system in these organelles (*1*). Hagemann (*2*) described mixed cells, containing green and white plastids, in border regions between green and white areas of leaves of variegated plants. Avers *et al.* (*3*) demonstrated differences within the population of mitochondria of a single yeast cell by the diamine cytochemical test for cytochrome oxidase (*4*). They found that only some of the mitochondria gave a positive reaction for activity of cytochrome oxidase. Ogawa and Barrnett (*5*) showed differences among the mitochondria of cells from rat heart by use of tetrazolium salts. The accumulation of formazan crystals over