

K, Rb, Cs, Sr and Ba Contents and Sr Isotope Ratios of Ocean Floor Basalts

S. R. Hart

Phil. Trans. R. Soc. Lond. A 1971 **268**, 573-587

doi: 10.1098/rsta.1971.0013

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

K, Rb, Cs, Sr and Ba contents and Sr isotope ratios of ocean floor basalts

BY S. R. HART

*Department of Terrestrial Magnetism, Carnegie Institution of Washington,
Washington, D.C. 20015*

Reliable analyses of K, Rb and Cs in dredge basalts require samples which show no petrographic evidence of alteration minerals and which have H_2O^+ contents less than 0.7%. Very fresh glass samples usually have H_2O^+ levels of 0.1 to 0.2%, and this probably represents the primary level of H_2O in most submarine basalt magmas.

A dredge haul containing both basalt and andesite was studied for major element and trace element variations. The major elements were consistent with a differentiation model involving crystallization of plagioclase, olivine, clinopyroxene and titanomagnetite. This differentiation had little effect on Sr concentration and on K/Rb and K/Cs ratios; these parameters are thus especially useful in studying mantle chemistry and partial melting processes.

Twenty-eight unaltered dredge basalts were analysed, with K/Rb ratios varying from 360 to 1350. K contents of most samples, after correction for high level (shallow) differentiation processes, fall in the range 500 to 1200 parts/ 10^6 . A comparison of unaltered basalts from 'fast-spreading ridges' and 'slow-spreading ridges' shows that K, Rb, Cs and Sr contents and K/Rb, K/Cs and Rb/Sr ratios are identical for both environments, while Ba contents and $^{87}Sr/^{86}Sr$ ratios may be significantly different. Thus mantle chemistry appears to be largely decoupled from the dynamic processes of plate movement. It is shown that submarine ridge basalts have lower $^{87}Sr/^{86}Sr$ ratios than the basalts of the oceanic islands, suggesting an early depletion of parts of the mantle in the dispersed elements.

Average values for 15 samples from 11 different ridge localities: K = 1160 parts/ 10^6 ; Rb = 1.11 parts/ 10^6 ; Cs = 0.016 parts/ 10^6 ; Sr = 135 parts/ 10^6 ; Ba = 10 parts/ 10^6 ; K/Rb = 1060; K/Cs = 70000; Rb/Sr = 0.0082; $^{87}Sr/^{86}Sr$ = 0.70265.

INTRODUCTION

Submarine or dredge basalts show many unusual trace element characteristics of importance to an understanding of their magmatic derivation process and of the geochemistry of the mantle source regions. Interpretation of trace element data in these rocks is complicated by two problems: (a) recognition of deuteritic and alteration effects superposed during or after crystallization, (b) distinction of crystal fractionation effects from partial melting and source composition effects. The low K and Ba contents and high K/Rb and K/Cs ratios which characterize dredge basalts are now well established as primary features (Engel, Engel & Havens 1965; Gast 1965; Hart 1969; Philpotts, Schnetzler & Hart 1970). However, variability of these trace element parameters is considerable, and it is important to evaluate the contributions of alteration, differentiation, and mantle source chemistry to this variability.

The strong depletion of the large 'dispersed' elements (K, Rb, Cs, Sr, Ba, U, Th) in dredge basalts has been ascribed to their derivation from a mantle which has undergone previous differentiations or extractions of liquid and consequent depletion in the dispersed elements (Tatsumoto 1966; Tatsumoto, Hedge & Engel 1965; Gast 1968*a, b*; Bence 1966). Dispersed element models which derive dredge basalts by a single-stage process without explicit consideration of prior mantle events have also been proposed (Griffin & Murthy 1969; Hart & Aldrich 1967). The development of trace element heterogeneities in the mantle during a multi-stage evolution process may be studied by using the radiogenic tracer isotopes of strontium and lead. Heterogeneities which develop early in Earth's history, such as those indicated by the lead isotope study of Tatsumoto (1966), might be expected to play a role in the dynamics of

plate motion during sea-floor spreading. Thus, the variations in the dispersed elements of dredge basalts should be searched for possible relationships to parameters such as spreading rate.

ALTERATION EFFECTS

Various aspects of the effects of sea-water alteration on a number of the trace elements in dredge basalts has been described already in some detail (Hart 1969; Hart & Nalwalk 1970; Philpotts *et al.* 1970). A summary of these results for three typical samples is presented in figure 1, where trace element concentrations in altered margins of dredge fragments are compared with the concentrations in the fresher interiors. The elements are arranged in figure 1

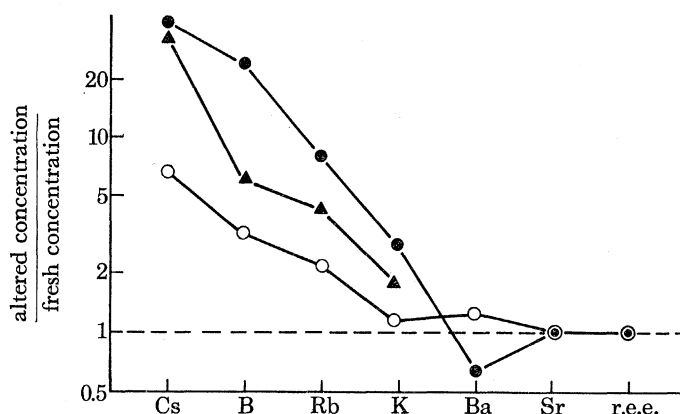


FIGURE 1. Comparison of alteration effects for seven elements in altered margins relative to less altered interiors of three dredge basalt fragments. Boron data from unpublished study of A. J. Erlank. ●, AD 5-18; ▲, AD 2-1; ○, AD 3-3.

in order of relative susceptibility to alteration, with caesium being most easily altered and the rare earth elements least easily altered. Clearly there is a fair degree of regularity to the order in which different elements are affected by sea-water alteration. Also, the size of the effect shown by the trace elements is qualitatively related to the visual degree of alteration of the individual specimens. The margin of AD 2-1 has a high H_2O^+ content (0.8%), shows obvious brown coloration, and contains alteration minerals which are clearly evident petrographically. AD 5-18 has a somewhat lower H_2O^+ content (0.58%) and shows a dark gray rim with only faint brown coloration but in which the alteration minerals are again petrographically quite obvious. These altered margin zones would be classed as middle stage 3 alteration in the classification of Hart & Nalwalk (1970). AD 3-3, on the other hand, shows no obvious petrographic signs of alteration and has a rather 'normal' H_2O^+ content (0.53%). Except for a very subtle colour change in sawn cross-section, this sample appears megascopically and microscopically unaltered. I am sure most geochemists would accept AD 3-3 as a 'fresh' sample, yet barium and the alkali metals have undergone significant alteration.

Because of the extreme susceptibility of the large alkalis to alteration, it is difficult to establish criteria for distinguishing altered from unaltered samples. H_2O^+ contents may be the most useful criteria, as I have so far found that all samples with $H_2O^+ < 0.3$ to 0.4% contain essentially unaltered alkalis. There are many samples however with H_2O^+ contents as high as 0.6 to 0.7% which also appear to contain unaltered alkalis, but which would normally have to be rejected for lack of criteria which demonstrate this unaltered character. In general,

geochemists must assume the burden of proving that samples which they deal with are fresh and unaltered with respect to the analyses they perform.

I have found that the freshest glass from dredge basalts invariably has H_2O^+ contents of 0.1 to 0.2%. I believe this value is characteristic of the primary basalt magmas and that higher values represent either concentration during crystallization and deuteric processes, or later additions by exchange with sea water or water-rich sediments. Moore demonstrated in a detailed study (Moore 1965) of Hawaiian submarine tholeiites that their primary water content was probably on the order of 0.5%—this value should not be applied to submarine ridge basalts, however, because their general depletion in the dispersed elements probably extends to a depletion in H_2O^+ as well. It is interesting to note that the freshest sea floor basalts have $\text{H}_2\text{O}^+/\text{K}_2\text{O} \sim 1$ and that while Hawaiian tholeiites have higher concentrations of both elements, the ratio $\text{H}_2\text{O}^+/\text{K}_2\text{O}$ is again approximately unity.

As shown in figure 1, the studies of Philpotts *et al.* (1970) show that the concentrations of strontium and the rare earth elements are relatively insensitive to sea-water alteration, at least up through stage 3 alteration. Hart & Nalwark (1970) found that strontium may undergo serious isotopic exchange with sea water at stage 4 and it is probable that the rare earths will begin to show effects at this high level of alteration also. For example, rare earth element analyses have been reported by two groups for the same sample (GE 160), but the analyses are significantly different (Philpotts *et al.* 1970; Kay, Hubbard & Gast 1970). The samples also have different K_2O and H_2O^+ contents, so may represent differently altered portions of a single fragment. The heavy rare earths are identical in both samples, whereas the most altered sample (stage 4) has notably higher Ce, Nd and Sm concentrations (and higher Sr and Ba concentrations also). In considering high precision analyses of strontium isotope ratios, it should also be recognized that minor but significant changes in $^{87}\text{Sr}/^{86}\text{Sr}$ may take place in dredge basalts at alteration levels well below those discussed above.

DIFFERENTIATION EFFECTS

There are several approaches which can be used in understanding the behaviour of trace elements during differentiation. With adequate data on the partition coefficients of various elements between minerals and silicate melts, trace element changes during differentiation can be calculated directly using various crystal fractionation models. Several recent papers have made important contributions to the data on partitioning of the dispersed elements, using both laboratory equilibration techniques and comparison of element concentrations between phenocrysts and groundmass in natural samples (Iiyama 1968; Griffin & Murthy 1969; Philpotts & Schnetzler 1970; Schnetzler & Philpotts 1970; Onuma, Higuchi, Wakita & Nagasawa 1968). Alternatively, the more classical approach may be used of studying trace element variations in natural differentiation series. With the finding of basalt and andesite together in a single dredge haul from the East Pacific Rise (Amphitrite 3, Scripps Institution of Oceanography), a comparison of these approaches is now possible.

Puzzling discrepancies have been apparent in trace element analyses of various Amphitrite 3 samples (Frey, Haskin, Poetz & Haskin 1968; Bence 1966). I have determined the major element chemistry of thirteen fragments from this dredge and a histogram of the results, shown in figure 2, clearly demonstrates the presence of both basaltic and andesitic rock types. The andesite is clearly calc-alkaline in nature and has a Peacock alkali-lime index of about 60. This

similar to the andesites in Al_2O_3 ; however, it has a higher content of FeO and TiO_2 than either the tholeiite or the andesite groups. The basalts and the andesites may both exhibit glassy surfaces, although the andesites generally are found as thin fracture-bounded plates. Even these latter, however, show only very fine grained variolitic and arborescent textures, demonstrating that they were cooled very rapidly. Aside from occasional olivine microphenocrysts and a few large rounded crystals of plagioclase, phenocrysts are relatively sparse. (One plagioclase grain in an andesite sample gave a micro-probe composition of An 69.) All samples appear very fresh, with no petrographic evidence of alteration and with only minor surface and crack coatings and fillings.

TABLE 1. AMPHITRITE 3 DIFFERENTIATION MODEL

	tholeiite (7)	andesite (5)	computed‡
SiO_2	50.1	58.1	57.8
Al_2O_3	15.8	13.4	13.3
FeO†	8.9	10.6	11.6
MgO	8.3	2.9	3.2
CaO	12.2	7.1	7.9
Na_2O	2.5	4.3	4.8
K_2O	0.10	0.54	0.24
$\text{H}_2\text{O}^\ddagger$	0.16	1.02	0.42
TiO_2	1.4	1.7	1.7
Sr	115	106§	105
Ba	13	39§	30

() Number of analyses averaged.

† Total iron calculated as FeO.

‡ By subtracting 30% An 80, 22% Cpx, 8% olivine and 2.3% titanomagnetite from tholeiite average.

§ from Philpotts *et al.* 1970.

|| Average of eight East Pacific Rise basalts.

The average compositions of the tholeiite group and the andesite group are given in table 1. A computed 'model andesite' is also shown in table 1, calculated from the tholeiite composition by subtraction of 30% plagioclase (An 80), 22% clinopyroxene (using analysed tholeiite pyroxene composition of Muir & Tilley 1964), 8% olivine (Fo 85) and 2.3% titanomagnetite. This differentiation scheme is obviously not unique and a better fit might perhaps be obtained by using the least-squares technique of Bryan, Finger & Chayes (1969); it is sufficient, however to show that the andesite composition can be derived in a relatively simple way from the tholeiite composition. It is interesting to note that Kay *et al.* (1970) concluded that the minor compositional variations found among dredge basalts could be explained by crystallization of plagioclase and olivine in proportions of about 4:1, essentially the same proportions derived from the computation of table 1. It is possible that the clinopyroxene enters into the crystallization scheme only after more extreme degrees of crystallization than those described by Kay *et al.* (1970).

The only elements whose distributions are difficult to reconcile with this simple differentiation model are K_2O and H_2O^+ , both of which are concentrated in the andesite by a factor of two more than the model would predict. All attempts to fit these two elements into a model based solely on crystal-liquid equilibria have been unsuccessful. I am forced to conclude that some form of concentration mechanism involving partitioning and transfer in a vapour phase is required. (This applies to the trace elements Rb and Cs as well.)

The K/Rb–K/Cs relations of six samples from Amphitrite 3 are shown in figure 3. The K/Cs ratios in the tholeiites and andesites are very similar, lying in the range 55 000 to 75 000. The intermediate sample 3J has a distinctly lower K/Cs ratio (40 000). While 3J appears as fresh as the other samples, Cs is so sensitive to alteration that there are no reliable criteria to prove that this sample is unaltered. The K/Rb data are more clearcut, and show that this ratio is essentially unaffected by differentiation (of the type proposed in table 1). The maximum variation in K/Rb is 15% over a range in K content of more than a factor of 5.

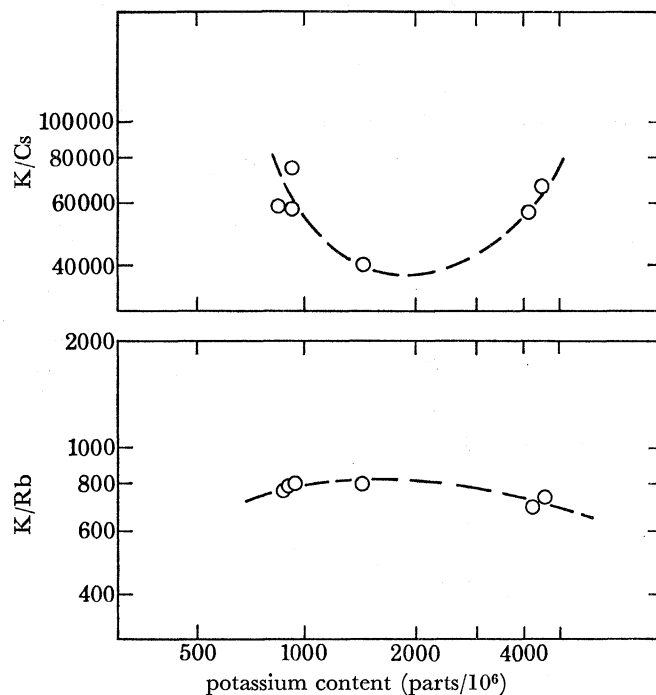


FIGURE 3. K/Rb and K/Cs against K content in basalt–andesite dredge suite from Amphitrite 3, Scripps Institution of Oceanography.

Consideration of partition coefficient data strongly supports this observed decoupling of K/Rb ratio from the differentiation process. The K/Rb partition coefficients for plagioclase, clinopyroxene and olivine reported by Philpotts & Schnetzler (1970), coupled with a fractional crystallization model (using the mineral abundances shown in table 1) predict a K/Rb ratio in the andesite only 5% lower than that in the tholeiite starting melt. This is largely a result of the fact that both K and Rb are strongly partitioned into the melt. I have already noted above, however, that a crystal fractionation scheme (either equilibrium or fractional) which satisfies the major elements is insufficient to produce the observed H_2O^+ and K_2O^+ concentration factors; thus the K/Rb–K/Cs relation may involve other mechanisms in addition to simple crystal–liquid equilibria. For example, if concentration takes place by a vapour transport mechanism, then the K/Rb–K/Cs ratios would be dependent in detail on the nature of the liquid–vapour equilibria as well.

Gottfried, Greenland & Campbell (1968) studied K/Cs relations in two continental diabase–granophyre suites and found in one suite (Dillsburg) rather scattered data which they ascribed to possible action of fluid rich phases. The other suite (Great Lake) showed a decrease in K/Cs of about a factor of two, accompanying a change in K by a factor of 3 to 4, and a change

in the mafic index ($\Sigma \text{FeO}/\Sigma \text{FeO} + \text{MgO}$) from 40 to 95 %. The variation of K in the Amphitrite 3 samples is larger than that in the Great Lake suite, but with a smaller change in mafic index (50 to 80 %) and with no significant change in K/Cs ratio. The Great Lake differentiation was clearly more extreme than Amphitrite 3, as in its later stages it involved a more sodic plagioclase (which has a great ability to fractionate K/Rb according to Philpotts & Schnetzler (1970)) as well as other alkali-bearing minerals. The difference in K/Cs behaviour between the Amphitrite suite and the Great Lake suite is thus not surprising.

The results for Sr and Ba in table 1 show that the concentrations of these elements in the andesite can be well accounted for by the simple crystal-liquid differentiation model. The Sr partition data for plagioclase of Philpotts & Schnetzler (1970) appears to be strongly dependent on composition; using their value for an An 80 plagioclase initially led to a higher concentration of Sr in the andesite than in the tholeiite. This behaviour of strontium partitioning in plagioclase is in conflict with Iiyama's results (1968) which show essentially no compositional dependence for Sr distribution between plagioclase and potassium feldspar. Iiyama also showed, however, that the limit of ideal solution for Sr in calcic plagioclase is surprisingly low (~ 32 parts/ 10^6 at An 100, > 310 parts/ 10^6 at An 50), suggesting the possibility that the Sr in the calcic plagioclases reported by Philpotts & Schnetzler (1970), (250 to 1000 parts/ 10^6) exceeds ideal solution limits. Therefore, for the strontium calculation of table 1 I have used a distribution coefficient of 2.07, which is an average for five plagioclases (Philpotts & Schnetzler 1970) in the composition range An 81 to An 46 (the two most calcic plagioclase, An 87, An 97, have been excluded on the premise that their partition coefficients are too low). Because barium is strongly partitioned into the melt relative to calcic plagioclase and clinopyroxene ($D < 0.2$) the differentiation calculation is relatively insensitive to possible uncertainties in the values used for the distribution coefficient.

The rare earth elements in one of the Amphitrite 3 andesites have been reported by Frey *et al.* (1968) and in the andesite no. PD 3B by Philpotts *et al.* (1970). Both analyses show a large depletion anomaly for europium (35 to 40 %), which is qualitatively consistent with crystallization and removal of substantial quantities of plagioclase. Philpotts *et al.* (1970) have shown how the europium behaviour of a number of dredge basalts, including the Amphitrite 3 andesite, can be interrelated in terms of a simple fractional crystallization model involving plagioclase.

The trace element parameters which are useful in 'seeing through' differentiation effects are thus the K/Rb ratio, perhaps the K/Cs ratio, and Sr concentration. Both K, Rb, Cs and Ba concentrations are strongly affected by differentiation. Ba apparently does not follow the alkalis particularly well during differentiation, as it can be modelled by crystal-liquid equilibria, whereas the alkalis seem to require some additional concentration mechanism such as vapour transport. Thus the K/Ba ratio will show some dependence, and the K/Sr ratio a large dependence, on the differentiation processes which are known to modify the compositions of dredge basalts (Miyashiro, Shido & Ewing 1969; Kay *et al.* 1970).

K/Rb-K/Cs RELATIONS

Samples which contain less than 0.7 % H_2O^+ and show no obvious petrographic evidence of alteration (stage 1 or stage 2 in the classification of Hart & Nalwalk 1970) are considered fresh enough to yield K and K/Rb data which is within 10 % of the primary value. Data for these samples is given in table 2 and plotted in figure 4. The above criteria may not be stringent

enough to insure unaltered Cs values however, and the low K/Cs ratios for several of the samples (AD 5-5, 92543, A 150-RD 7, A 150-RD 8) is quite probably a reflexion of incipient alteration effects in these samples. (The corresponding effect on the K/Rb ratio in these samples would be some 30 %, and in fact the latter three samples have somewhat low K/Rb ratios of 760, 760 and 660. A. J. Erlank has recently called my attention to the presence of alteration minerals in these three samples.) In general, the K/Cs ratios are quite variable, with the freshest samples generally falling in the range 50 000 to 125 000. There is no obvious relation between K/Cs and K content. Note that the two continental high-alumina basalts have K/Cs ratios (35 000 and 45 000) somewhat lower than most of the dredge basalts.

TABLE 2. K, Rb, Cs AND H₂O⁺ IN ABYSSAL VOLCANICS

sample number	ridge and location reference	K	Rb	Cs	H ₂ O ⁺ %	K/Rb	K/Cs
		parts/10 ⁶					
Amph 1-PDIP	E.P.R. (1, 8)	430	0.619	0.00969	0.10	700	44 700
Amph 4A	E.P.R. (2, 8)	500	0.389	0.0052	0.16	1 286	96 200
AD 5-5	M.A.R. (1, 9)	560	0.571	0.0244	0.63	980	22 800
Amph 4B	E.P.R. (2, 8)	593	0.439	0.0078	0.17	1 350	76 000
Tionesta 1	C. (12)	719	0.468	0.0204	0.33	1 536	35 200
Amph 3C	E.P.R. (1, 8)	844	1.131	0.015	0.19	746	57 000
127-ML-295	C. (11)	852	0.612	0.0195	0.16	1 392	43 700
Amph 1-DIC	E.P.R. (1, 8)	890	0.776	0.0072	0.37	1 148	123 800
92543	M.A.R. (3)	894	1.176	0.0528	0.51	760	16 930
Amph 3M	E.P.R. (1, 8)	900	1.127	0.016	0.19	798	56 200
Amph 3-PD3	E.P.R. (1, 8)	910	1.138	0.01241	0.10	800	73 100
A 150-RD7-BX1	M.A.R. (3)	930	1.226	0.0523	0.50	760	17 800
A 150-RD8-BX2	M.A.R. (3)	1 039	1.576	0.066	0.47	660	15 700
AD 5-18	M.A.R. (1, 9)	1 140	1.016	0.01231	0.44	1 120	92 800
5111.7	C.R. (4)	1 146	0.993	0.018	0.58	1 154	62 000
DIOA-I	J.F.R. (7)	1 401	1.422	0.014	0.19	985	100 000
Amph 3J	E.P.R. (1, 8)	1 426	1.814	0.036	0.43	786	39 600
AD 2-1	M.A.R. (1, 9)	1 480	1.505	0.01500	0.71	980	99 000
Chain 44-2-1	M.A.R. (5)	1 530	1.530	—	0.52 (5)	1 000	—
56-2H	M.A.R. (6)	1 625	4.504	0.067	—	360	24 200
56-2	M.A.R. (6)	1 638	4.78	—	0.43	343	—
D10-SRH 1	J.F.R. (7)	1 671	1.842	0.0205	0.15	907	81 500
AD 3-3	M.A.R. (1, 9)	1 780	1.479	0.0216	0.56	1 200	82 400
1-2	M.A.R. (6)	1 986	5.59	~ 0.08	0.12 (6)	355	~ 25 000
D2-SRHA	J.F.R. (7)	2 046	1.860	~ 0.04	0.35	1 100	~ 49 000
D2-SRHE	J.F.R. (7)	2 370	3.00	0.0296	0.55	790	80 100
Amph 3G	E.P.R. (1, 8)	4 416	6.36	0.08	1.13	694	55 000
Amph 3-PD 3B	E.P.R. (1, 8)	4 560	6.30	0.070	0.91	725	65 000

References: (1) Hart 1969; (2) Engel & Engel 1963; (3) Muir & Tilley 1966; (4) Cann & Vine 1965; (5) Melson, Thompson & Van Andel 1968; (6) Aumento 1968; (7) W. G. Melson, personal communication; (8) Bonatti 1967; (9) Engel & Engel 1964*a*; (10) Kay, Hubbard & Gast 1970; (11) Yoder & Tilley 1962; (12) D. Gottfried, personal communication.

Ridges: E.P.R., East Pacific Rise; M.A.R., Mid-Atlantic Ridge; J.F.R., Juan de Fuca Ridge; C.R., Carlsberg Ridge; C., Continental.

The K/Rb data appears to fall in two groups; a main group with K/Rb ratios in the range 700 to 1350, and three analyses with K/Rb ratios of only 350. These latter samples (56-2, 1-2) are near the Confederation Peak area on the mid-Atlantic ridge (Aumento 1968) and are particularly interesting because they do not show the depletion of Rb, Cs and Ba that characterizes most other submarine ridge basalts. (Kay *et al.* (1970), have recently reported a very similar analysis of a basalt from the Gorda ridge.) Two different fractions of glass were analysed from

56–2; glass was also analysed from 1–2. Microprobe studies of 1–2 show that the potassium is very homogeneously distributed, both in the glass zone and in the variolitic zone, and that the sample is completely free of ‘hot spots’ which would be indicative of incipient alteration. There can be no doubt that the high Ba contents (Aumento 1968) and the low K/Rb and K/Cs ratios are a primary feature of these two samples. If the depleted character of the dispersed elements in most dredge basalts is taken as evidence of prior extraction episodes in the mantle source region, then these anomalous samples may be viewed as deriving from a relatively primitive ‘unextracted’ mantle region.

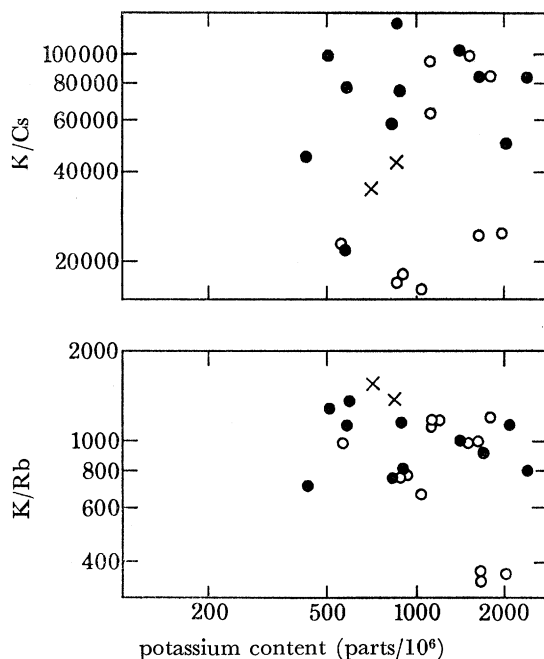


FIGURE 4. K/Rb and K/Cs against K content for unaltered dredge basalts from various oceanic ridges. ●, Fast spreading ridges; ○, slow spreading ridges; ×, continental high-alumina.

The main body of K/Rb data in figure 4 appears to show no dependence on K content. This is clearly at variance with the trend of decreasing K/Rb with increasing K content proposed by Gast (1965) and reiterated by Kay *et al.* (1970). If the two low K/Rb samples are included, then such a trend would be suggested also by figure 4. However, the trend outlined by Kay *et al.* (1970) is drawn so as to exclude their one fresh low K/Rb sample. I believe the other low K/Rb samples which they use to define their trend are a result of sea-water alteration, as proposed earlier (Hart, 1969). The exact nature of the ‘primary’ K/Rb trend is very important, as it will strongly confine the types of models used to explain the general depletion of dispersed elements in the sub-ridge mantle. Until now only the gross features of this depletion have been used; however, careful sampling and precise analytical work can probably bring many of the second-order relations of these dispersed element concentrations to bear on possible mantle-evolution models.

The K/Rb against K trend outlined by Kay *et al.* (1970) is based on much questionable data, so cannot be accepted as of any primary significance. They include seven samples which either have high H_2O^+ contents ($> 1.2\%$) or which they describe as altered. These tend to concentrate

in the low K/Rb region of their 'trend' envelope. They have excluded four apparently fresh samples from the envelope. They have included eight unpublished analyses for which no data, water content or description is given. Of the earlier analyses of Gast (1965) which Kay *et al.* (1970) plot, D 3 with a K/Rb of 1400 is clearly in disagreement with all my Amphitrite 3 samples (K/Rb \sim 800); D 4 with a K/Rb of over 1800 disagrees both with their later D 4 analyses and with my two D 4 analyses (K/Rb \sim 1300), and the two low K/Rb points of Gast (1965) are from dredge hauls from which most samples are somewhat altered (A 150–8 and A 150–20). Sample GE 160, which Kay *et al.* (1970) note as altered, is nevertheless plotted on their figure and included in their trend envelope. This sample strongly influences the trend as it is the lowest K/Rb sample in the envelope. Of the 39 values plotted in their figure, only 12 have published descriptions and H₂O⁺ contents by which they can be judged as unaltered. In addition, their data are plotted on a log–linear diagram with a four times vertical exaggeration which greatly accentuates the apparent K/Rb variation of the data. While Kay *et al.* (1970) do not use the data of the K/Rb figure in any detailed way, it is nevertheless unfortunate that they have permitted such a haphazard presentation of geochemical data.

An examination of the data of figure 4 shows that most of the samples of high K content also have high Σ FeO/MgO ratios, suggesting that these samples have undergone some degree of differentiation. The low K samples invariably have Σ FeO/MgO ratios of around unity; the two low K/Rb samples also have Σ FeO/MgO ratios very near unity. The increase of K content with increasing Σ FeO/MgO is somewhat larger than would be predicted from a simple differentiation model involving crystallization of plagioclase and olivine in 4:1 proportions. This may again relate to an alkali concentration mechanism involving vapour transfer. In any event, as a first approximation the data can be normalized according to the simple crystal–liquid differentiation scheme (holding K/Rb constant), and this normalization reduces the variation in K content of these dredge basalts considerably. Applying this technique to nine fresh samples of Kay *et al.* (1970) as well as to sixteen samples of figure 4 for which chemical analyses are available results in a clustering of the main high K/Rb group of samples into the range 500 to 1200 parts/10⁶ of K. This probably more nearly represents the primary alkali levels of these basalts as derived from the mantle, and emphasizes again the extreme constancy in composition of these submarine ridge basalts.

The low K/Rb samples (56–2 and 1–2), with Σ FeO/MgO of 1.03 and 1.05, are essentially unchanged by the normalization. This low group, including KD 11 of Kay *et al.* (1970), averages 1670 parts/10⁶ of K and K/Rb \sim 360. The main group, after normalization, averages \sim 800 parts/10⁶ of K and K/Rb \sim 950. These two averages define a trend of decreasing K/Rb with increasing K which I believe most closely represents the mantle evolution processes involved in generation of submarine ridge basalts. It is interesting to note that the highest K/Rb sample yet reported (P 6702 of Kay *et al.* 1970) has a K/Rb of 2030 and K content of 450 parts/10⁶ and is colinear with the above two group averages on a log–log figure such as figure 4. This trend is shifted considerably in the direction of lower K contents and has a somewhat steeper slope than the trend envelope of Kay *et al.* (1970).

REGIONAL TRACE ELEMENT VARIATIONS

It is clear from table 2 that there are substantial variations in the alkali metals in dredge basalts, both within a single dredge and on a wider geographic scale. Many of these variations, especially in the element concentrations, may be due in part to high-level differentiation effects. Variations in ratios, such as K/Rb, are difficult to account for in this way. In the five cases where more than one fragment was analysed from a single dredge, it is apparent that K/Rb is not even uniform in a single dredge, though the range is generally much smaller than that between different dredges. These variations could arise in several ways. First, the suboceanic mantle is demonstrably heterogeneous (Gast, Tilton & Hedge 1964; Tatsumoto 1966) and thus may yield basaltic melts which reflect this heterogeneity. Secondly, the partial melting process itself may be variable, either due to different degrees of partial melting or to the effects of partitioning among different mineral assemblages. Griffin & Murthy (1969) have shown that, while it is difficult to generate variable K/Rb ratios from an amphibole peridotite by different degrees of partial melting, addition of minor amounts of phlogopite is quite effective in this regard.

TABLE 3. DATA ON COMPOSITE SAMPLES FROM MID-OCEAN RIDGES

	K	Rb	Cs	Sr	Ba	K/Rb	K/Cs	Rb/Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
slow-spreading ridges†									
Mid-Atlantic, Carlsberg 7 samples, 6 localities	1260	1.16	0.018	140	7.8	1080	69000	0.0083	0.70277‡
fast-spreading ridges‡									
East-Pacific, Juan de Fuca 8 samples, 5 localities	1060	1.06	0.015	131	13.2	1040	71000	0.0081	0.70248‡
difference (%)	20	10	25	7	50	4	3	2	0.045

All element concentrations in parts/10⁶.

† Samples AD 5-5, AD 5-18, AD 2-1, AD 3-3, Chain 44-2-1, 5111.7, GE 159.

‡ Samples Amph 1-PDIP, Amph 3-PD3, DIO-SRH 1, DIOA-I, Amph 1-DIC, Amph 4A, Amph 4B, D2-SRHA.

§ Values normalized to 86/88 = 0.1194 and relative to E and A standard value of 0.70810.

To what extent are mantle heterogeneities and/or variations in partial melting processes related to plate dynamics? While the quantity and geographic coverage of fresh samples is hardly adequate to settle this problem, I have assembled my samples into two composites: one representing six localities on ridges of slow (normal) spreading rates, and one representing five localities on ridges with high spreading rates. The alkali data on these composites was obtained from table 2; the Sr and Ba data were determined on actual sample mixtures. Table 3 shows a summary of these data. Considering the small numbers of samples involved and the large individual variations in concentrations, it is clear that the K, Rb, Cs and Sr concentrations are indistinguishable in basalts from the two types of ridges. The Ba data seem rather different in the two composites, but in the absence of values on the individual samples this cannot be evaluated statistically. The ratios K/Rb, K/Cs and Rb/Sr are almost identical in the two composites, and well within the standard errors of the mean (for K/Rb, for example, the standard errors are 3% for the 'slow' composite and 7% for the 'fast' composite). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, while clearly distinct analytically, are nevertheless very similar; again, in the absence of individual values for all the samples, this small difference cannot be evaluated statistically. These data

clearly show that mantle chemistry, while variable, is very effectively decoupled from the dynamic processes involved in plate movement. In so far as U and Th levels can be inferred from the alkali metal contents, then it would appear that the gross level of radioactivity in the upper mantle is also unrelated to plate dynamics.

MANTLE EVOLUTION OF STRONTIUM

There is considerable disagreement between the two strontium isotope analyses reported in table 3 and other values reported previously in the literature. Tatsumoto *et al.* (1965) obtained an average value for three mid-Atlantic Ridge samples of 0.7024 and for two East Pacific Rise samples of 0.7016. Evidence from other published papers of these authors suggest that their values are generally systematically low and, to be compatible with the E and A Sr standard reported in table 3, should be raised by about 0.001. This correction would bring their Pacific value into line with the 'fast' composite value; their Atlantic value, however, ends up considerably higher than that of the 'slow' composite. Gast (1967) reported three values for Atlantic dredge samples (0.7032 average) and three values for Pacific dredge samples (0.7030 average). Both of these averages are higher than the values in table 3, though there is, unfortunately, no way to compare them in an absolute sense as Gast (1967) did not report a value for the Sr standard. Bence (1966) analysed four Atlantic basalts (0.7035 average) and seven Pacific dredge basalts (0.7034 average) along with a carefully controlled value for the Sr standard which is the same as that used as a basis in table 3. Bence's basalt values should be directly comparable then with the composite values of table 3—however, it is clear that they are systematically higher by 0.0008. As each composite contains three samples from dredges also analysed by Bence (1966), it seems unlikely that these isotope ratio differences can be attributed to sampling variations or differences in state of alteration. Most of Bence's analyses were calculated from spiked runs and it is possible that some of the discrepancy arises from this approach. (For example, two of the three dredge basalts which were analysed unspiked gave values ~ 0.0008 lower than values calculated from the spiked runs.) I feel that the Sr isotopic analyses in table 3 should supplant previous values for dredge basalts, partly because the samples were carefully picked for freshness and partly because the samples were run, along with the Sr standard, under conditions of ultra-high precision.

An accurate Sr isotopic value for dredge basalts is necessary if meaningful comparisons are to be made with basalts of the oceanic islands. Bence (1966) concluded from his study that alkali basalts from oceanic islands have very similar Sr isotopic ratios to dredge basalts, and suggested that similar mantle source materials might supply both magma types. Gast (1968) has stressed the necessity for deriving dredge basalts from a mantle depleted in the dispersed elements relative to that from which alkali basalts are generated. If the depletion event(s) has occurred at a much earlier time, as advocated by Tatsumoto (1966) then Sr developed in the depleted mantle should be less radiogenic than that in 'undepleted' mantle and dredge tholeiites would be expected to be less radiogenic than alkali basalts. The new Sr isotope values of table 3 show that this is in fact true. The average Sr of oceanic islands is about 0.7036, for both alkali basalt and tholeiitic basalt. The lowest well-documented value for a single island is for Iceland (Moorbath & Walker 1965) where 12 basalts average 0.7029 (relative to Sr standard of table 3). Other islands range considerably higher, as for example, Hawaii, where analyses tabulated by Gast (1967) average 0.7043. Thus, while there is a real variation of Sr isotope ratio between

different islands, all islands appear to show higher values than the dredge basalt average of 0.7026 (table 3). I believe this strongly argues for generation of dredge basalts from a mantle source region which has undergone depletion of the dispersed elements, especially Rb, Cs and Ba, at some time considerably earlier in the Earth's history. If the K/Rb ratio of basalts is used as an index of relative depletion, then it appears that the depletion factor is about 2 to 3 times. I infer from this that the Rb/Sr ratio of the mantle region from which submarine ridge basalts are generated is a factor of 2 to 3 lower than that in the 'undepleted' mantle regions. This difference has existed for relatively long times, and may have been produced in a single episode (Tatsumoto 1966), in multiple-episodes (Gast 1968) or essentially continuously (Hart & Brooks 1970).

I am indebted to F. Aumento, A. E. Engel, A. J. Erlank, W. G. Melson, D. Gottfried, H. S. Yoder, and the Scripps Institution of Oceanography for supplying the dredge samples used in this work. The microprobe studies were carried out with the generous assistance of C. Haddidiacos; P. E. Hare made available the gas chromatograph on which water analysis was performed. Invaluable assistance in mass spectrometry was provided by K. Burrhus. The boron data were kindly made available from an unpublished study carried out by A. J. Erlank.

APPENDIX. ANALYTICAL TECHNIQUES

The procedures used for K, Rb and Cs are as described by Hart (1969) and Hart & Nalwalk (1970). Accuracy for these elements is in the range 1 to 3%. Most Sr concentrations were determined by X-ray fluorescence ($\sim 5\%$), a few were done by isotope dilution ($< 1\%$). Sr isotope ratios were determined on a 23 cm 60° mass spectrometer fitted with a thick lens z-focusing source patterned after that of Dietz (1959) and Wasserburg, Papanastassiou, Nenow & Bauman (1969). This instrument features a fully automatic digital data acquisition system. Samples were run on single Ta filaments, and Faraday collection of 50 to 70 spectra was sufficient to produce normalized 87/86 ratios with 95% confidence limits of ± 0.0001 . The E and A SrCO₃ standard, measured repeatedly, gave a value of 0.70812 ± 0.00001 (standard error).

Major element concentrations were determined on the M. A. C. microprobe at the Geophysical Laboratory, using small fragments composed either of glass or very fine variolitic groundmass. Counting was carried out for 10 to 100 s during manual beam scanning of the sample. Both analysed basalts and synthetic materials were used as standards.

A gas chromatograph (F and M carbon-hydrogen-nitrogen analyser, model 185) was used to determine H₂O⁺ contents. Samples were preheated at 110 °C, and the water released between this temperature and 1050 °C was determined. Sensitivity of this technique was about 100 parts/10⁶, and blank levels were generally 200 to 300 parts/10⁶. Precision at levels above 0.5% is about ± 5 to 10%. Accuracy may be somewhat poorer as primary standards for H₂O are difficult to document.

REFERENCES (Hart)

- Aumento, F. 1968 The Mid-Atlantic Ridge near 45° N. II. Basalts from the area of Confederation Peak. *Can. J. Earth Sci.* **5**, 1–21.
- Aumento, F. 1969 Diorites from the Mid-Atlantic Ridge at 45° N. *Science, N.Y.* **165**, 1112–1113.
- Bence, A. E. (1966). The differentiation history of the earth by rubidium-strontium isotopic relationships. In *Variations in isotopic abundances of strontium, calcium, and argon and related topics* (ed. P. M. Hurley), M.I.T. 1381–14. Fourteenth Ann. Prog. Rep. pp. 35–78.
- Bonatti, E. 1968 Mechanisms of deep-sea volcanism in the South Pacific. In *Researches in geochemistry* (ed. P. H. Abelson), pp. 453–491. New York: John Wiley.
- Bryan, W. B., Finger, L. W. & Chayes, F. 1969 Estimating proportions in petrographic mixing equations by least-squares approximation. *Science, N.Y.* **163**, 926–927.
- Cann, J. R. & Vine, F. J. 1966 An area on the crest of the Carlsberg Ridge: petrology and magnetic survey. *Phil. Trans. Roy. Soc. Lond. A* **258**, 198–217.
- Dietz, L. A. 1959 Ion optics for the V-type surface ionization filament used in mass spectrometry. *Rev. scient. Instrum.* **30**, 235–241.
- Engel, A. E. J. & Engel, C. G. 1964*a* Composition of basalts from the Mid-Atlantic Ridge. *Science, N.Y.* **144**, 1330.
- Engel, A. E. J. & Engel C. G. 1964*b* Igneous rocks of the East Pacific Rise. *Science, N.Y.* **146**, 477.
- Engel, A. E. J., Engel, C. G. & Havens, R. G. 1965 Chemical characteristics of oceanic basalts and the upper mantle. *Bull. geol. Soc. Am.* **76**, 719–734.
- Frey, F., Haskin, M. A., Poetz, J. A. & Haskin, L. A. 1968 Rare earth abundances in some basic rocks. *J. geophys. Res.* **73**, 6085–6098.
- Gast, P. W. 1965 Terrestrial ratio of potassium to rubidium and the composition of earth's mantle. *Science, N.Y.* **147**, 858–860.
- Gast, P. W. 1967 Isotope geochemistry of volcanic rocks. In *Basalts*, pp. 325–358. New York: Interscience.
- Gast, P. W. 1968*a* Upper mantle chemistry and evolution of the earth's crust. In *The history of the earth's crust* (ed. R. A. Phinney). Princeton University Press.
- Gast, P. W. 1968*b* Trace element fractionation and the origin of tholeiitic and alkaline magma types. *Geochim. cosmochim. Acta* **32**, 1057–1086.
- Gast, P. W., Tilton, G. R. & Hedge, C. E. 1964 Isotopic composition of lead and strontium from Ascension and Gough Islands. *Science, N.Y.* **145**, 1181–1185.
- Gottfried, D., Greenland, L. P. & Campbell, E. Y. 1968 Variation of Nb-Ta, Zr-Hf, Th-U and K-Cs in two diabase-granophyre suites. *Geochim. cosmochim. Acta* **32**, 925, 947.
- Griffin, W. L. & Rama Murthy, V. 1969 Distribution of K, Rb, Sr and Ba in some minerals relevant to basalt genesis. *Geochim. cosmochim. Acta* **33**, 1389–1414.
- Hart, S. R. 1969 K, Rb, Cs contents and K/Rb, K/Cs ratios of fresh and altered submarine basalts. *Earth Planet. Sci. Lett.* **6**, 295–303.
- Hart, S. R. & Aldrich, L. T. 1967 Fractionation of potassium/rubidium by amphiboles: implications regarding mantle composition. *Science, N.Y.* **155**, 325–327.
- Hart, S. R. & Brooks, C. 1970 Rb–Sr Mantle Evolution Models. *Yb. Carnegie Instn Wash.* no. 68.
- Hart, S. R. & Nalwalk, A. J. 1970 K, Rb, Cs and Sr relationships in submarine basalts from the Puerto Rico Trench. *Geochim. cosmochim. Acta* **34**, 145–155.
- Iiyama, J. T. 1968 Experimental study of the distribution of trace elements between two feldspars. 1. Distribution of Rb, Cs, Sr and Ba at 600° C. *Geochem. Int.* **5**, 433–442.
- Kay, R., Hubbard, N. J. & Gast, P. W. 1970 Chemical characteristics and origin of oceanic ridge volcanic rocks. *J. geophys. Res.* **75**, 1585–1613.
- Melson, W. G., Thompson, G. & van Andel T. H. 1968 Volcanism and metamorphism in the mid-Atlantic Ridge, 22° N latitude. *J. geophys. Res.* **73**, 5925–5941.
- Miyashiro, A., Shido, F. & Ewing, M. 1969 Diversity and origin of abyssal tholeiite from the mid-Atlantic Ridge near 24° and 30° north latitude. *Contr. miner. Petrology* **23**, 38–52.
- Moorbath, S. & Walker, G. P. 1965 Strontium Isotope Investigation of Igneous Rocks from Iceland. *Nature, Lond.* **207**, 837–840.
- Moore, J. G. 1965 Petrology of deep-sea basalt near Hawaii. *Am. J. Sci.* **263**, 40–52.
- Muir, I. D. & Tilley, C. E. 1964 Basalts from the northern part of the rift zone of the mid-Atlantic Ridge. *J. Petrology* **5**, 409–434.
- Muir, I. D. & Tilley, C. E. 1966 Basalts from the northern part of the mid-Atlantic Ridge. II. *J. Petrology* **7**, 193–201.
- Onuma, N., Higuchi, H., Wakita, H. & Nagasawa, H. 1968 Trace element partition between two pyroxenes and the host lava. *Earth planet. Sci. Lett.* **5**, 47–51.
- Philpotts, J. A. & Schnetzler, C. C. 1970 Phenocryst-matrix partition coefficients for K, Rb, Sr and Ba. *Geochim. cosmochim. Acta* **34**, 307–322.

SEA FLOOR BASALTS: TRACE ELEMENTS

587

- Philpotts, J. A., Schnetzler, C. C. & Hart, S. R. 1970 Submarine basalts: Some K, Rb, Sr, Ba and rare-earth data bearing on their alteration, modification by plagioclase, and possible source materials. *Earth Planet. Sci. Lett.* **7**, 293–299.
- Schnetzler, C. C. & Philpotts, J. A. 1970 Partition coefficients of rare-earth elements between igneous matrix material and rock-forming mineral phenocrysts. II. *Geochim. cosmochim. Acta* **34**, 331–340.
- Tatsumoto, M. 1966 Genetic relations of oceanic basalts as indicated by lead isotopes. *Science, N.Y.* **153**, 1088–1093.
- Tatsumoto, M., Hedge, C. E. & Engel, A. E. J. 1965 Potassium, rubidium, strontium, thorium, uranium and the ratio of strontium-87 to strontium-86 in oceanic tholeiitic basalt. *Science, N.Y.* **150**, 886–888.
- Wasserburg, G. J., Papanastassiou, D. A., Nienow, E. V. & Bauman, C. A. 1969 A programmable magnetic field mass spectrometer with on-line data processing. *Rev. scient. Instrum.* **40**, 288–295.
- Yoder, H. S. & Tilley, C. E. 1962 Origin of basalt magmas: An experimental study of natural and synthetic rock systems. *J. Petrology* **3**, 342–532.