Ba, Rb and Cs in the Earth's Mantle

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

In 166 isotope dilution analyses of Ba, Rb, Cs on *fresh* basalts from mid-ocean ridges and oceanic islands, Ba/Rb and Cs/Rb ratios are nearly constant. From this, we conclude that Ba/Rb and Cs/Rb ratios are essentially constant in the present-day mantle in spite of large differences in the degree of source depletion or enrichment. As it appears improbable that these ratios could be both constant and non-primitive, we propose that they are representative of the primitive mantle and of the present-day crust-mantle system. We explain this uniformity of relative abundances as follows: the mantle is depleted by subtraction of a mobile phase such as a partial melt or an aqueous fluid. In either case, a significant amount of the mobile phase remains in the residue. Ba, Rb and Cs are among the most highly incompatible elements. Therefore the mobile phase cannot fractionate these elements relative to one another but retains the source ratios of Ba/Rb and Cs/Rb. Also, the amount of mobile phase remaining in the residue is enough to dominate the Ba, Rb and Cs concentrations in the residue. Consequently, neither the mobile phase nor the residue, nor any other portion of the mantle that may be enriched by addition of the mobile phase, will be changed in their relative abundances of Ba, Rb and Cs, even though the absolute abundances of these elements may change by orders of magnitude.

The primitive Ba/Rb = 11.3 and Cs/Rb = 12.6×10^{-3} lead to the following estimates for the primitive mantle: Ba = 6.9 ppm (taken from Jagoutz et al. [1]), Rb = 0.61 ppm and Cs = 7.7 ppb.

Assuming the earth has a chondritic Sr/Ba ratio of 3.08, we calculate a Rb/Sr ratio of 0.029 for the earth. This corresponds to a present-day $^{87}Sr/^{86}Sr$ of 0.7045. This value lies near the lower limit of the ratios estimated from the correlation of Nd and Sr isotopic abundances in oceanic basalts.

The Cs/Rb ratios is about a factor of ten lower than the C1-chondritic ratio and a factor of three lower than the lunar ratio. This low terrestrial Cs/Rb ratio should be matched by similar values in the continental crust. However, the large range of Cs/Rb ratios found in the crust prevent us from obtaining a meaningful mass balance.

Introduction

Estimating the relative and absolute abundances of elements in the earth's mantle is an aim of geochemistry in which much progress has been made in recent investigations (e.g. Jagoutz et al. [1], Sun [2]). Nevertheless, the abundances of highly incompatible trace elements are not well known by direct observations on mantle rocks or mantle-derived melts, because these elements are usually depleted by large and highly variable degrees. Therefore, these abundance estimates are strongly model dependent.

In this paper we draw attention to a substantial body of data, which indicates that, in contrast with the relationships among many other incompatible trace elements (e.g. K/Rb or Ba/La ratios), the ratios of Ba, Rb and Cs to each other are nearly constant in present-day, mantle-derived melts and are only weakly dependent on the absolute trace element concentrations in these melts. It appears that these elements are so highly incompatible that neither variable degrees of source depletion nor variable degrees of subsequent partial melting and fractional crystallization have affected their abundance ratios to a significant extent. If this is true, then these Ba/Rb and Cs/Rb ratios are representative of the bulk crust-mantle system. In conjunction with the "standard" assumption that the relative abundances of refractory elements are chondritic, so that the absolute terrestrial Ba and Sr abundances are known, these ratios may be used to estimate the absolute terrestrial Rb and Cs abundances and the terrestrial Rb/Sr ratio. These abundance estimates are therefore independent of the isotopic correlation of Nd and Sr, the so-called mantle array, which has been used by others to infer the bulk-earth Rb/Sr ratio and the Rb abundance.

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The Data

A preliminary survey of published abundance data of Ba, Rb and Cs in oceanic basalts (mid-ocean ridge and oceanic-island basalts) showed that these elements are often near or below the detection limit of instrumental neutron activation and X-ray fluorescence techniques and that Rb and Cs abundances can be seriously affected by alteration due to interaction with sea water or leaching by rainwater. In addition, basalts from continental and island arc environments are suspect, because some of them are known to have been contaminated by the crust (e.g. Carlson et al. [3]) or by subducted sediments (e.g. Magaritz et al. [4]; Kay [5], Whitford et al. [6]). We therefore restricted the data so as to include only isotope dilution analyses on fresh basalts dredged from mid-ocean ridges or collected from *historical eruptions* on oceanic islands. Unfortunately, this results in a severely restricted data base for oceanic islands. However, as we shall subsequently demonstrate, the alkalis appear to be so mobile in subaerial weathering environments that no alternative exists.

The resulting data set is biased in favor of the Atlantic ocean and the Galapagos region, but the available data from other areas assure at least a widely scattered geographic coverage and are consistent with the data from areas of good coverage. We also note that the samples we have included range in $^{87}Sr/^{86}Sr$ ratios from 0.7023 to 0.7043, about half the range observed in oceanic basalts.

All the data we are aware of are listed in Table 1. Most of these have been published and are shown for the reader's convenience. The results for the Galapagos Islands (analyses made by W. M. W. at the Carnegie Institution of Washington) and 13 new analyses of fresh MORB glasses obtained at MPI have not previously been published. Conventional log-log plots of K, Ba and Cs versus Rb (Fig. 1) show that Ba, Rb and Cs retain approximately constant ratios over a concentration range of 0.2 to 60 ppm Rb (i.e. a factor of 300). Hertogen et al. [17] and Schilling et al. [42] have previously noted the essentially constant Cs/Rb ratios in oceanic basalts. In contrast, the K/Rb ratio of about 400 at high concentrations increases to a limit of about 2000 at low concentrations. In addition, the scatter on the K vs. Rb plot is significantly greater than on the other two plots. This scatter is far outside the analytical error of isotope dilution analyses, which is less than 5% even when no attempt is made to control isotopic fractionation during the analysis. Thus, except for possible but rare "outliers" that may be caused by gross contamination or other uncontrolled errors, both the scatter and the trends are not artifacts of the analyses.

Figures 2, 3, and 4 show the ratios Rb/K, Ba/Rb and Cs/Rb plotted as functions of the Rb, Ba, and Cs concentrations respectively. The results of linear

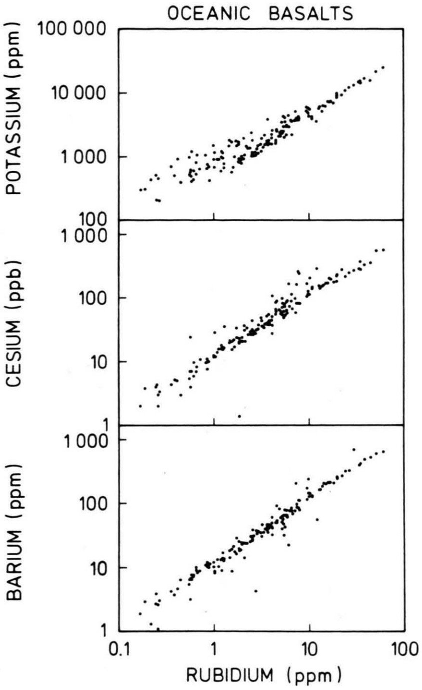

Fig. 1. Abundances of K, Cs, and Ba versus Rb in ppm, Cs in ppb, in fresh oceanic basalts (mid-ocean ridge and oceanic islands). All analytical data were obtained by isotope dilution analysis. For data and sources, see Table 1.

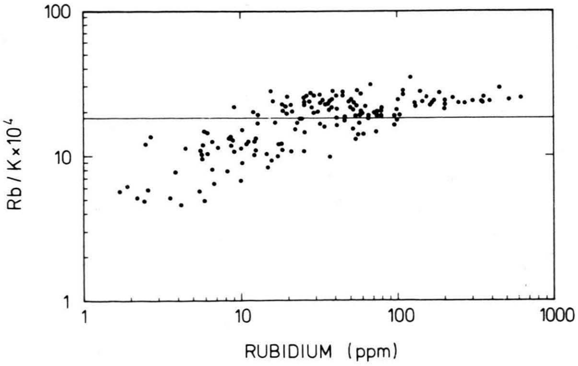

Fig. 2. Rb/K versus Rb (ppm) in fresh oceanic basalts. The horizontal line represents the arithmetic mean of the Rb/K ratios. *Correction added in proof:* Because of a drafting errors, all the Rb concentrations in Fig. 2 are to large by a factor of 10.

Table 1.

Sample No.	Ref.	K ppm	Rb ppm	Cs ppb	Ba ppm	Ba/Rb	Cs/Rb $\times 10^3$	Rb/K $\times 10^3$
MORB: Atlantic Ocean								
GLI-10	[7]	401	0.59	7	7.5	12.71	11.9	1.471
TRI00 26D10	[7]	398	0.45	3	6.3	14.00	6.7	1.131
TR100 23D10	[7]	300	0.17	2	1.9	11.18	11.8	0.567
GLI-7	[7]	637	0.72	11	8.6	11.94	15.3	1.130
TR100 13D11	[7]	4335	6.13	166	22.0	(3.59)	(27.1)	1.414
TR100 12D10	[7]	2546	4.13	108	41.0	9.93	(26.2)	1.622
TR138 11D1	[7]	887	1.00	12	10.0	10.00	12.0	1.127
TR138 9D2	[7]	600	0.62	6	7.4	11.94	9.7	1.033
TR138 8Di	[7]	739	0.87	10	10.00	11.49	11.5	1.177
CH13 PD-1-1	[7]	689	0.89	10	11.0	12.36	11.2	1.292
TR138 7D1A	[7]	900	1.09	14	13.0	11.93	12.8	1.211
TR138 6D1	[7]	985	1.23	16	13.0	10.57	13.0	1.249
TR138 5D1	[7]	1733	1.72	34	16.0	9.30	19.8	0.993
TR138 3D1	[7]	1761	3.65	39	46.0	12.60	10.7	2.073
TR138 2D3	[7]	563	1.56	21	19.0	12.18	13.5	2.771
TR138 1AD1	[7]	3505	12.20	295	55.0	(4.51)	(24.2)	3.481
TR138 1D1	[7]	3496	6.60	116	75.0	11.36	17.6	1.880
HU 9-4	[7]	3724	7.98	245	78.0	9.77	(30.7)	2.143
HU 47B-1	[7]	2527	4.65	91	53.0	11.40	19.6	1.840
CH43 104-18	[7]	4141	7.79	265	84.0	10.78	(34.0)	1.881
CH43 104-16	[7]	2546	4.13	108	41.0	9.93	(26.2)	1.622
TR154 14D1	[7]	2866	6.28	75	76.0	12.10	11.9	2.191
CH43 107-6	[7]	2062	4.91	66	81.0	16.50	13.4	2.381
TR154 13D1	[7]	1483	2.93	38	36.0	12.30	13.0	1.976
TR154 12D2	[7]	3610	7.13	98	76.0	10.66	13.7	1.975
AII32 12-8	[7]	4767	9.93	129	145.0	14.60	13.0	2.083
TR154 15D2	[7]	5081	9.60	107	114.0	11.88	11.0	1.889
TR154 16D3	[7]	1538	3.49	40	40.0	11.46	11.5	2.269
TR154 17D2	[7]	1021	2.63	30	31.0	11.79	11.4	2.576
TR154 18D2	[7]	815	1.84	20	25.0	13.59	10.9	2.258
TR154 19D3	[7]	1005	1.96	24	24.0	12.24	12.2	1.950
TR122 3D4B	[7]	927	2.08	31	24.0	11.54	14.9	2.244
TR122 3D9	[7]	678	1.61	22	21.0	13.04	13.7	2.375
TR154 7D1B	[7]	1046	2.81	32	37.0	13.17	11.4	2.686
TR154 20D3	[7]	4152	10.10	114	127.0	12.57	11.3	2.433
TR89 20D5	[7]	5855	9.58	172	170.0	17.75	18.0	1.636
TR89 30D10	[7]	2196	5.88	64	76.0	12.93	10.9	2.678
TR89 31D1	[7]	5616	9.92	113	238.0	(23.99)	11.4	1.766
TR154 8D1	[7]	5617	12.90	158	161.0	12.48	12.2	2.297
TR154 21D3	[7]	5059	14.00	154	184.0	13.14	11.0	2.767
TR154 10D3	[7]	9045	22.50	283	268.0	11.91	12.6	2.488
TR89 21D2	[7]	7194	17.10	202	212.0	12.40	11.8	2.377
TR89 21D3	[7]	7216	16.60	208	211.0	12.71	12.5	2.306
TR122 5D2	[7]	4121	10.90	143	127.0	11.65	13.1	2.645
TR122 5D4	[7]	3869	10.90	151	130.0	11.93	13.9	2.817
TR119 4D1B	[7]	2280	5.29	55	63.0	11.91	10.4	2.320
TR119 4D4	[7]	2605	4.60	89	91.0	19.78	19.3	1.766
521-4-3	[7]	2331	5.35	83	56.0	10.47	15.5	2.295
525-5-3	[7]	1012	2.53	27	30.0	11.86	10.7	2.550
527-6-1	[7]	2174	6.74	69	68.0	10.09	10.2	3.100
534-3-1	[7]	1589	3.74	39	46.0	12.30	10.4	2.354
AII73 10-19	[7]	1752	4.54	63	51.0	11.23	13.9	2.591
AII73 14-17	[7]	1130	2.94	33	36.0	12.24	11.2	2.602
AII73 16-2	[7]	1586	4.10	52	49.0	11.95	12.7	2.585
AII73 50-6	[7]	2088	5.12	57	57.0	11.13	11.1	2.452
TR119 6D3	[7]	1786	3.84	40	45.0	11.72	10.4	2.150
TR119 6D6	[7]	1315	2.84	33	33.0	11.62	11.6	2.160
TR119 7D1	[7]	6135	14.40	159	205.0	14.24	11.0	2.347
TR119 7D5	[7]	6077	15.30	173	203.0	13.27	11.3	2.518
V30 RD7 P10	[7]	3936	7.45	165	86.0	11.54	22.1	1.893
TR119 8D1	[7]	6858	18.50	180	207.0	11.19	9.7	2.698

Table 1 (continued).

Sample No.	Ref.	K ppm	Rb ppm	Cs ppb	Ba ppm	Ba/Rb	Cs/Rb $\times 10^3$	Rb/K $\times 10^3$
TR119 8D5	[7]	4983	7.30	59	205.0	(28.08)	8.1	1.465
TR123 1D6	[7]	1093	2.55	30	27.0	10.59	11.8	2.333
TR123 1D7	[7]	1141	2.56	32	26.0	10.16	12.5	2.244
TR123 4D5	[7]	444	0.26	2	1.1	(4.23)	7.7	0.586
TR123 4D7	[7]	427	0.22	1	1.3	5.91	(4.5)	0.515
TR123 5D1	[7]	488	0.58	1	6.5	11.21	(1.7)	1.189
TR123 5D3	[7]	515	0.56	7	6.4	11.43	12.5	1.087
A150 RD7	[7]	1198	1.22	17	8.8	7.21	13.9	1.018
A150 RD20	[7]	1199	0.59	7	6.3	10.68	11.9	0.492
P-1	[7]	1932	2.09	37	14.0	6.70	17.7	1.082
N-1	[7]	449	0.26	3	2.6	10.00	11.5	0.579
1-2	[8]	1986	5.59	80.1	78.0	13.94	14.32	2.817
56-2	[8]	1625	4.50	67.2	–	–	14.93	2.770
4519-34	[8]	5420	10.34	209.0	141.6	13.69	20.24	1.908
44-2-1	[8]	1685	1.56	15.8	8.63	5.52	10.11	0.928
III 327	[8]	813	0.66	7.0	9.94	15.06	10.61	0.812
III 273	[8]	963	0.55	5.3	5.37	9.75	9.62	0.572
AD5-5	[8]	560	0.57	24.5	3.10	5.44	(42.91)	1.019
AD5-18	[8]	1140	1.02	12.3	8.60	8.46	12.11	0.891
AD3-3	[8]	1780	1.48	21.6	13.9	9.40	14.61	0.831
VG-937	[9]	1057	0.68	–	8.19	12.04	–	0.643
VG-205	[9]	912	0.42	5.0	4.57	10.88	11.90	0.405
VG-367	[9]	597	1.20	18.0	13.10	10.92	15.00	2.010
VG-744	[9]	1151	1.25	15.5	13.75	11.00	12.40	1.086
VG-962	[9]	420	0.91	–	11.17	12.27	–	2.167
VG-965	[9]	643	0.85	11.0	10.30	12.12	12.94	1.322
VG-968	[9]	308	0.19	3.8	2.89	15.21	20.00	0.617
VG-192	[9]	700	0.36	4.4	4.19	11.64	12.22	0.514
MORB: Pacific Ocean: East Pacific Rise								
P6702	[8]	502	0.246	4.0	2.67	10.86	16.26	0.490
PD1P	[8]	430	0.619	9.7	7.1	11.47	15.69	1.440
AMPH 3M	[8]	900	1.124	16.0	10.1	98.98	14.23	1.250
AMPH 4M	[8]	500	0.389	5.2	3.72	9.56	13.36	0.778
VG-973	[9]	530	0.662	8.3	8.82	13.32	12.54	1.249
VG-875	[9]	1509	1.820	23.5	–		12.91	1.206
VG-798	[9]	1052	0.826	9.6	10.65	12.89	11.62	0.785
MORB: Pacific Ocean: Juan de Fuca Rise								
D10-SRH1	[8]	1671	1.842	20.5	19.45	10.56	11.13	1.103
D2-SRHA	[8]	2154	3.43	39.3	39.0	11.37	11.46	1.592
VG-768	[9]	207	0.25	4.3	3.84	15.36	17.20	1.208
D10-1	[9]	1439	1.47	20.1	18.0	12.24	13.67	1.022
KD11	[10]	1400	3.9	50	46.0	11.79	12.8	2.786
1154	[10]	1400	3.24	31	30.3	9.35	9.56	2.314
4Z	[10]	852	0.91	13	18.0	19.78	14.30	1.068
MORB: Pacific Ocean: Mariana Trough								
42-0	[11]	3420	5.24	99	39.5	7.54	18.89	1.532
46-0	[11]	4190	5.44	71	47.1	8.66	13.05	1.298
46-5	[11]	2350	2.52	45	25.8	10.24	17.86	1.072
46-11	[11]	3770	3.71	41	34.6	9.33	11.05	0.984
46-12	[11]	4005	5.62	75	42.3	7.53	13.35	1.403
MORB: Pacific Ocean: Galapagos Rise								
DS D-2A	[12]	605	0.575	4.0	6.57	11.43	6.96	0.950
DS D-3A	[12]	1173	2.75	28	4.21	(1.54)	10.18	2.344
DS D-1A	[12]	1957	4.13	37	31.9	7.72	8.96	2.110
ST7 17D-4	[12]	2470	5.5	49	31.5	5.73	8.91	2.227
CTW 6D-1	[12]	908	1.86	1.4	18.0	9.68	(0.75)	2.048
CTW 7D-1	[12]	200	0.27	3.4	3.0	11.11	12.59	1.350

Table 1 (continued).

Sample No.	Ref.	K ppm	Rb ppm	Cs ppb	Ba ppm	Ba/Rb	Cs/Rb $\times 10^3$	Rb/K $\times 10^3$
TR164 1D-2A	[12]	1342	2.41	30	24.9	10.33	12.45	1.796
TR164 2D-1	[12]	2520	5.26	72	50.6	9.62	13.69	2.087
TR164 3D-1B	[12]	880	1.93	21	18.5	9.59	10.88	2.193
TR164 4D-3B	[12]	983	1.66	17	17.3	10.42	10.24	1.689
TR164 5D-2	[12]	1058	2.14	21	23.6	11.03	9.81	2.023
CTW 9D-1	[12]	1770	2.56	28	38.0	14.84	10.94	1.446
TR164 6D-1	[12]	5980	13.11	144	162.5	12.40	10.98	2.192
TR164 6D-2	[12]	1453	2.22	34	23.9	10.77	15.32	1.528
TR164 7D-1	[12]	1358	2.44	27	29.8	12.21	11.07	1.797
TR164 8D-2	[12]	3430	5.73	54	65.0	11.34	9.42	1.671
TR164 9D-1	[12]	3600	6.52	89	84.1	12.90	13.65	1.811
TR164 27D-3	[12]	1927	3.21	37	45.7	14.24	11.53	1.666
TR164 26D-3	[12]	8940	20.1	236	246.0	12.24	11.74	2.248
TR164 26D-4	[12]	9500	19.9	225	250.0	12.56	11.31	2.095
TR164 25D-1	[12]	2340	5.06	58	58.8	11.62	11.46	2.162
TR164 25D-2	[12]	2890	5.44	62	64.3	11.82	11.40	1.882
TR164 24D-3	[12]	2065	5.12	60	59.5	11.62	11.72	2.479
CTW 10D-1	[12]	1540	3.66	40	42.6	11.64	10.93	2.377
TR164 10D-1	[12]	2930	5.89	88	64.1	10.88	14.94	2.010
TR164 11D-1	[12]	3030	5.83	86	77.1	13.22	14.75	1.924
TR164 12D-4	[12]	1557	3.12	50	34.5	11.06	16.03	2.004
TR164 23D-2	[12]	1712	4.49	57	49.7	11.07	12.69	2.623
TR164 13D-1	[12]	1562	3.75	55	40.3	10.75	14.67	2.401
TR164 14D-1	[12]	1598	3.61	53	38.3	10.61	14.68	2.259
TR164 15D-1G	[12]	770	1.98	21	22.5	11.36	10.61	2.571
TR164 15D-3	[12]	1568	3.82	44	41.0	10.73	11.52	2.436
TR164 16D-1	[12]	1386	3.33	35	34.8	10.45	10.51	2.403
TR164 17D-1	[12]	1576	4.10	45	41.9	10.22	10.98	2.602
DS D-8A	[12]	1216	3.19	45	30.2	9.47	14.11	2.623
DS D-5	[12]	672	1.29	36	12.5	9.69	(27.91)	1.920
TR164 20D-1	[12]	680	1.02	29	8.1	7.94	(28.43)	1.500
T6-372	[12]	1452	1.74	24	28.2	16.21	13.79	1.198
MORB: Indian Ocean								
5111-7	[8]	1480	1.00	12.5	11.82	11.80	12.50	0.677
CIRCE 93	[8]	1350	2.29	27.2	23.7	10.34	11.89	1.698
CIRCE104	[8]	770	1.29	16.8	13.44	10.40	13.03	1.678
CIRCE107	[8]	960	1.25	15.6	16.71	13.37	12.49	1.307
Hawaii: Kilauea, Mauna Ulu and summit eruptions								
Ave of 15 samples	[13]	3925	7.8	83	110.1	14.11	10.6	1.99
Kilauea rift (submarine)								
Ave of 4 samples	[14]	3920	7.96	83	109.5	13.75	10.4	2.03
Galapagos Islands								
Santiago								
E-20	[15]	3062.0	5.96	57	60.4	10.13	9.56	1.946
SH-75a	[15]	638.5	0.86	7.7	1.9	13.82	8.94	1.348
Fernandina								
F3N3	[15]	2235	4.10	28	59.8	14.59	6.83	1.834
F436	[15]	3679	7.44	82	96.1	12.92	11.02	2.022
Isabela								
ZOB6	[15]	7264	16.1	174	210	13.04	10.81	2.216
Azores								
Sao Miguel								
SM6	[16]	15440	45.1	362	525	11.64	8.03	2.921
SM12	[16]	21250	51.7	566	600	11.61	10.95	2.433

Table 1 (continued).

Sample No.	Ref.	K ppm	Rb ppm	Cs ppb	Ba ppm	Ba/Rb	Cs/Rb $\times 10^3$	Rb/K $\times 10^3$
Terceira								
T8	[16]	12780	30.2	276	691	(22.88)	9.14	2.362
Sao Jorge								
SJ6	[16]	15190	35.2	379	416	11.82	10.77	2.317
SJ8	[16]	11790	26.9	251	324	12.04	9.33	2.282
SJ18	[16]	14690	34.5	290	397	11.51	8.40	2.348
Pico								
P21	[16]	8385	20.0	183	257	12.85	9.15	2.385
P24	[16]	10630	24.4	220	317	12.99	9.02	2.296
P28	[16]	24740	61.7	580	645	10.45	9.40	2.494
Faial								
F14	[16]	16520	38.9	339	485	12.47	8.71	2.355
F33	[16]	14110	35.5	286	421	11.86	8.06	2.515

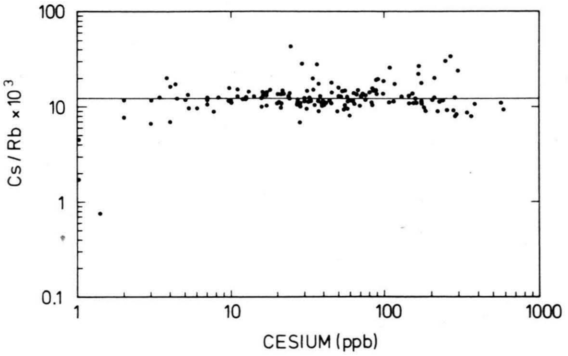

Fig. 3. Cs/Rb versus Cs (ppb) in fresh oceanic basalts. The horizontal line represents the arithmetic mean of the preferred Cs/Rb ratios (Table 2).

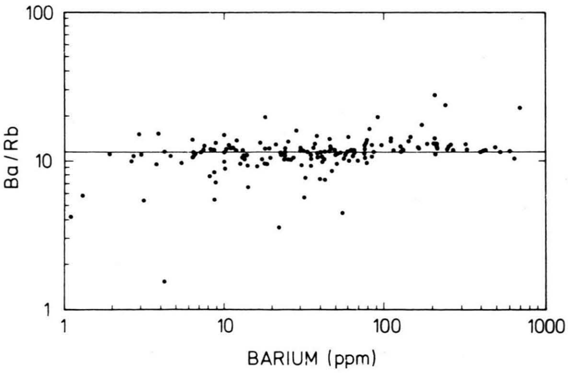

Fig. 4. Ba/Rb versus Ba (ppm) in fresh oceanic basalts. The horizontal line represents the arithmetic mean of the preferred Cs/Rb ratios (Table 2).

regression analyses of the ratios versus element concentrations are given in Table 2 for the entire set and several subsets which exclude outliers and restrict the sample to the Atlantic ocean, the Pacific ocean and 3 oceanic island groups, respectively. In each case, the numerator is chosen to represent the more highly incompatible element (such a plot will show a positive slope if there is a significant difference in degree or incompatibility and the samples are related to one another by an initially uniform source that was partially melted to different degrees: see discussion below).

These results show that Ba/Rb and Cs/Rb ratios are nearly uniform in oceanic basalts from different parts of the world and that these ratios are nearly independent of the absolute concentrations of these elements, which vary by more than two orders of magnitude. In contrast, the Rb/K ratio shows a clear dependence on concentration and varies by about a factor of five (an even more extreme example of this latter type of behavior is the Rb/Sr ratio, which varies by as much as a factor of 100 in MORB).

In computing the linear regressions from the data, a few outliers have been omitted from one of the regressions on the grounds that they are likely to represent altered samples or, in one or two cases, gross analytical errors. The omitted data are listed in parentheses in Table 1. Their inclusion changes the computed regressions and their uncertainties only marginally (see Table 2).

A more important question is whether any of the subsets of data are significantly different from the

Table 2. Mean Ratios and Linear Regression of Trace Element Ratios versus Concentrations.

Sample set	Ba/Rb	Ba/Rb versus Rb		Cs/Rb $\times 10^3$	Cs/Rb versus Cs	
	mean	slope	intercept	mean	slope	intercept
All oceanic basalts	11.60 ± 0.24	0.0079 ± 0.0019	10.96 (166 sa.) ± 0.27	13.06 ± 0.40	0.0035 ± 0.0041	12.79 (166 sa.) ± 0.51
Preferred samples	11.55 ± 0.17	0.0032 ± 0.0015	11.30 (159 sa.) ± 0.21	12.22 ± 0.23	− 0.0032 ± 0.0024	12.46 (155 sa.) ± 0.29
Preferred MORB	11.44 ± 0.19	0.0114 ± 0.0032	10.87 (142 sa.) ± 0.24	12.59 ± 0.24	0.0098 ± 0.0042	12.06 (137 sa.) ± 0.33
Atlantic MORB	11.66 ± 0.25	0.0130 ± 0.0037	10.92 (83 sa.) ± 0.31	12.80 ± 0.33	0.0107 ± 0.0051	12.13 (78 sa.) ± 0.45
Pacific MORB	11.11 ± 0.31	0.0063 ± 0.0065	10.85 (55 sa.) ± 0.41	12.31 ± 0.38	0.0060 ± 0.0085	12.03 (54 sa.) ± 0.55
Oceanic Islands	12.45 ± 0.30	− 0.0037 ± 0.0013	13.56 (17 sa.) ± 0.45	9.40 ± 0.28	0.001 ± 0.002	9.27 (18 sa.) ± 0.50

mean or from each other. For example, there is some indication that Ba/Rb (but not Cs/Rb) of Kilauean tholeiites is significantly higher than that ratio in other basalts of similar Ba concentration. Also, Ba/Rb and Cs/Rb ratios from Mariana trough samples appear to be low and high respectively, and Cs/Rb (but not Ba/Rb) of Azores basalts appear to be low. At the present time, we regard the data base to be inadequate for these differences to be resolved unequivocally. Instead, we focus attention on the fact that even if these ratios are not uniform, they are very similar indeed.

To show the effects of alteration, both submarine and subaerial, we have plotted Ba/Rb and Cs/Rb ratios of some altered rocks on Figure 5. The effects of submarine alteration have been discussed in the literature (e.g. Hart [18], Hart et al. [19]; Staudigel et al. [20], Verma, [21 a]), but the effects of subaerial alteration on the abundances of Ba, Rb and Cs have not received much attention. The set of data from Kohala, an extinct volcano on the island of Hawaii, taken from Feigenson et al. [22] is shown as an example. These authors argue that the alkali elements, but not barium, have been extensively leached out of the rock by very high rainfall on Kohala. This leaching causes the alkali abundances of Kohala tholeiites to be abnormally low (K as low as 500 ppm!) and the K/Rb, Cs/Rb and Ba/Rb to be extremely erratic. These data have convinced us that "absolute" sample freshness is a crucial criterion in the selection of data suitable for inclusion in Table 1.

We have not made an extensive survey of Ba, Rb, Cs abundances in continental rocks. Sun and Nesbitt [23] have estimated an upper crustal Cs/Rb = 33×10^{-3}. Heier and Brunfelt [24] have published values for lower crustal rocks from Norway, which average Cs/Rb = $(3.5 \pm 2.8) \times 10^{-3}$ for granulites, and $(1.0 \pm 0.6) \times 10^{-3}$ for mangerites. These widely varying data show that it is difficult, if not impossible, to obtain an accurate estimate of the alkali abundances of the bulk continental crust.

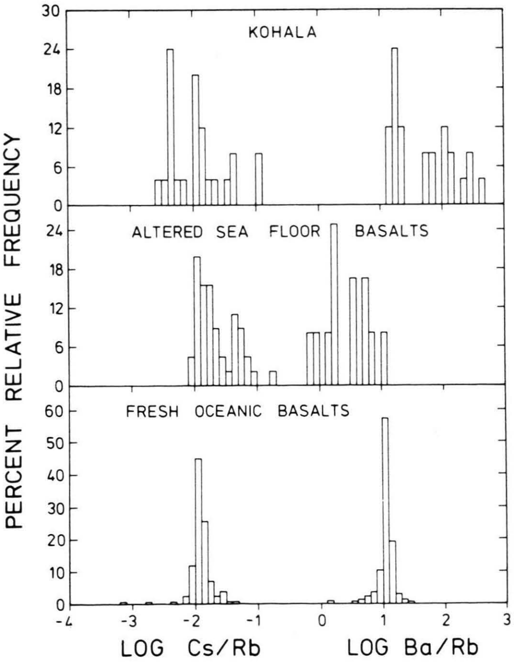

Fig. 5. Frequency distribution of Cs/Rb and Ba/Rb ratios in subaerially weathered basalts (Kohala, Feigenson et al. [22]), altered sea floor basalts (Hart [18]; Hart et al. [11], [19]); Philpotts et al. [20a]; Staudigel et al. [20b]; Verma [21], and fresh oceanic basalts (Table 1, all data).

Discussion

Nd and Sr isotope ratios indicate the mantle underlying the ocean ridges is severely depleted in highly incompatible elements (relative to the primitive mantle) and that the mantle source of the oceanic island basalts is either less depleted, primitive, or enriched. Samples included in Table 1 have Sr and Nd isotope ratios covering about half (the more depleted half) of the range of observed $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios in oceanic basalts. In view of this range of isotopic ratios and the extreme variability of the concentrations of the elements involved, the uniformity of the Ba/Rb and Cs/Rb ratios in fresh, mantle-derived basalts is remarkable. It appears therefore that processes of depletion (and enrichment) all lead to nearly uniform Ba/Rb and Cs/Rb ratios. This behavior clearly does not extend to ratios between Cs, Rb, and Ba on the one hand, and even slightly less incompatible elements such as K, U, or La, on the other. For example, Fig. 2 shows that the Rb/K ratios decrease significantly with decreasing concentrations. Hertogen et al. [17] noted similar behavior for Cs/U and Rb/U ratios, and Jochum et al. (unpublished data, 1982) also found a significant positive correlation between Th/U and Th concentration in fresh MORB glasses. Thus it appears that the significant, and concentration-dependent variations in the ratios between elements of differing incompatibility give way to constant, i.e. concentration-independent ratios, only in the case of the most extreme incompatibility (i.e. for Cs, Rb and Ba).

The only simple explanation that occurs to us (and does not require some kind of special pleading) is that these ratios are not significantly changed by the depletion and enrichment processes and have therefore retained their primitive-mantle values. For these ratios to be *both* non-primitive *and* uniform, some sort of homogenization event would have to be postulated to insure the uniformity after the initial fractionation event. Subsequently, new fractionation processes would have produced the great range in observed compositions (including two orders of magnitude of concentration levels plus substantial differences in the isotopic compositions of Sr, Nd and Pb), and these processes would have to be fundamentally different from the initial one in that they were no longer capable of fractionating Ba from Rb and Cs. We think that this scenario is too contrived to be plausible, and we favor the simple explanation, namely that, in the mantle, Ba, Rb and Cs were never fractionated in the first place.

Although our proposed explanation is very simple, the actual mechansim for achieving such uniformity in relative abundances of highly incompatible elements is not immediately obvious. The bulk partition coefficients of the crystal-melt or crystal-metasomatic fluid systems can hardly be expected to be identical for the three most incompatible elements known. Now, if the depletion of the mantle proceeds by *complete extraction* of melt or fluid, the depleted residue will retain an extremely small amount of highly incompatible elements. The ratios of these elements to one another (relative to their initial ratios) will be roughly the same as the ratios of their respective bulk partition coefficients. Therefore, complete extraction of a melt or other fluid will leave a residue that has extremely low concentrations and grossly non-primitive ratios of the highly incompatible elements. This mechanism is therefore inconsistent with the observed concentrations and ratios of Rb, Ba and Cs (see also Hanson [25]). On the other hand, the concentrations of the highly incompatible elements may be reduced by nearly arbitrary factors without affecting their *relative* abundances if the mantle is depleted by *partial* withdrawal of a melt or other fluid. Consider, for example, the case where two elements with bulk partition coefficients of $D_1 = 1 \times 10^{-3}$ and $D_2 = 1 \times 10^{-4}$ are extracted from a source in which the initial concentrations are $C_1 = C_2 = 1$. Then the ratio of concentrations in the melt will vary only between 0.99 and 1.0, if the degree of melting varies between 5 and 50 percent (at the same time the ratio in the solid residue will be $C_1/C_2 \simeq 10$ and the concentrations in the solid will be less than 2 percent of the original). If 10 percent of the melt remains in the residue and 90 percent is extracted, the remaining net residue will have only between 10 and 20 percent of the original concentrations in a ratio essentially identical to the ratio in the liquid phase. This is true because the 10 percent portion of the liquid completely dominates the contribution from the solid part of the residue, the latter being 15 percent or less of the total residue. This point has previously been discussed by Hanson [25] and is therefore not further elaborated here. The important point to remember is that this mechanism will prevent fractionation of the depleted residue so long as all the bulk partition coefficients involved are negligibly small relative to the degree of melting and as long as a sufficiently large amount of melt remains in the residue to overwhelm the amounts of trace elements remaining in the solid phases.

Ever since Gast [26] demonstrated that the earth's crust-mantle system is depleted in alkalis relative to alkaline earths (compared to chondritic abundances), the estimation of the terrestrial alkali abundances has been a subject of enduring interest. The most recent method employed has been to determine the bulk-earth Rb/Sr ratio using the negative correlation of $^{143}Nd/^{144}Nd$ versus $^{87}Sr/^{86}Sr$ ratios in mantle derived basalts, the so-called mantle array (DePaolo and Wasserburg [27]; O'Nions et al. [28]; Allègre et al. [29]). Assuming that the present-day terrestrial and the chondritic $^{143}Nd/^{144}Nd$ ratios are identical, these authors have used the linear mantle array to determine first the present-day $^{87}Sr/^{86}Sr$ ratio of about 0.7045 to 0.7050. With this value and the initial ratio of 0.699 at a time 4.6 Ga ago, the age equation can be solved for the Rb/Sr ratio of the crust-mantle system, yielding a value of Rb/Sr = 0.03. This method is theoretically and practically sound, if and only if the isotopic mantle array actually gives a valid estimate of the bulk-earth $^{87}Sr/^{86}Sr$ ratio. Although any number of models can be constructed which predict that the bulk earth $^{87}Sr/^{86}Sr$ should lie within the mantle array, there is no *a priori* ground for assuming it *must* lie within the mantle array.

In a recent paper (White and Hofmann [30]), we have shown, using a large number of new Nd and Sr isotopic analyses, that the mantle array is not linear but a rather diffuse data array with a weak negative correlation. These results indicate clearly, as has been known from Pb isotopic data for many years, that more than two components or end members contribute to the mantle array. Once this is realized and accepted, there is no longer any compelling reason to think that the bulk-earth composition must lie within this data field at all. Armstrong [31] has reached similar conclusions from a different starting point. All in all, we argued that the isotopic data can no longer be used to give an unequivocal estimate of the terrestrial Rb/Sr ratio. An independent method to estimate the terrestrial Rb/Sr ratio and Rb abundance is therefore useful even if the assumptions of that method are also open to question (as they most emphatically are).

Using our conclusion that the present-day, apparently uniform Ba/Rb and Cs/Rb ratios in the mantle are those of the primitive earth, we compute the terrestrial Rb and Cs abundances from the terrestrial Ba abundance given by Jagoutz et al. [1]. This Ba value is based on the assumption that the relative abundances of the refractory lithophile elements are the same in the terrestrial mantle and in C-1 chondrites, and on the finding that the compatible refractory elements Yb, Sc, Al and Ca are enriched in primitive terrestrial mantle xenoliths by a factor of about 1.4 relative to C1 chondrites. From the value of Ba = 6.9 ppm for the primitive terrestrial mantle, we obtain primitive mantle abundances of Rb = 0.61 ppm and Cs = 7.7 ppb. Because the K/Rb and K/Cs ratios are not uniform in terrestrial mantle-derived rocks, we cannot give an estimate of the K abundance with the same degree of confidence. However, borrowing the value of K/Rb = 350 from Sun [2], we find a value for K = 210 ppm.

Having a Ba/Rb ratio for the earth, we need only to decide upon an appropriate Sr/Ba ratio to calculate the Rb/Sr ratio of the earth. As both Sr and Ba are refractory elements, it is reasonable to assume that the earth's Sr/Ba ratio is chondritic. This ratio is, however, not as well constrained as we would like. Ba abundances in meteorites are surprisingly variable, leading to variations in Sr/Ba. Further, the number of high quality isotope dilution analyses of Ba are few, and simultaneous Sr-Ba determinations fewer. Thus Sr/Ba ranges from 2.1 in H5 to 3.91 in C1 (see compilation of Wedepohl [32], and Palme et al. [33]). We have chosen to use the average of six measurements on the meteorites Abee, Bruderheim, Forest City, and Leedy by Tera et al. [34] because these data represent high-precision, simultaneous isotope dilution measurements with exceptionally consistent results. The mean and standard deviation of these Sr/Ba ratios are 3.08 ± 0.08. From this we calculate $Rb/Sr = (Ba/Sr) \times (Rb/Ba) = 0.029$. This corresponds to a present-day $^{87}Sr/^{86}Sr = 0.7045$, which is at the lower limit of the range of values estimated from the Sr-Nd isotopic correlation for the mantle (see compilation by White and Hofmann [30].

The Cs/Rb ratio of the mantle derived rocks reviewed above is smaller than the chondritic ratio by about a factor of 10. If this ratio is indeed representative of the primitive mantle, then the silicate portion of the earth is even more severely depleted in Cs than in Rb or K. On the other hand, many upper crustal rocks have Cs/Rb ratios similar to chondrites. Because the crust contains a significant portion of the total alkalis (e.g. 50 ppm $\mathrm{Rb} \times 2.256 \times 10^{25}$ g crust $= 113 \times 10^{19}$ g Rb in the crust versus 0.6 ppm $\mathrm{Rb} \times 403.4 \times 10^{25}$ g crust plus mantle $= 242 \times 10^{19}$ g total Rb in crust plus mantle yields a fraction of 0.47 of the total Rb residing in the continental crust; mass estimates from Jacobsen and Wasserburg, [35]), the bulk crust should have a similar Cs/Rb ratio as the residual mantle if our interpretation is correct, i.e. if the residual mantle retains an unfractionated Cs/Rb ratio.

Therefore it is possible, in principle, to test our inferred value of $\mathrm{Cs/Rb} = 12 \times 10^{-3}$ for the bulk mantle-crust system by obtaining a representative Cs/Rb ratio for the bulk continental crust. Unfortunately, as we have noted above, Cs abundances in the crust are extremely erratic. For example, in the high-grade metamorphic rocks of Norway analyzed by Heier and Brunfelt [24], Cs/Rb ratios range from 0.34×10^{-3} to 19.2×10^{-3} in amphibolites, granulites and mangerites, whereas the K/Rb ratios range only from 160 to 1300. This corresponds to a variation by a factor of 56 for Cs/Rb versus a factor of 8 for K/Rb. This relationship is just the opposite of that found for the oceanic basalts. This may be the result of hydrothermal processes in the crust that transport certain elements such as U and Cs from the lower crust into the upper crust. The strong affinity of Cs for clay minerals adds further uncertainties to any estimate of Cs abundances in the crust.

Consequently we cannot use crustal Cs abundances except as a rough check for consistency with the mantle abundance. Using the estimates $(\mathrm{Cs/Rb})_{\mathrm{U.C.}} = 0.030$ (Sun and Nesbitt [23]), $(\mathrm{Cs/Rb})_{\mathrm{L.B.}} = 0.003$ (from Norwegian granulites of Heier and Brunfelt [24]), and $(\mathrm{Cs/Rb})_{\mathrm{T.C.}} = 0.012 = (\mathrm{Cs/Rb})_{\mathrm{mantle}}$ (this paper) for the upper crust, lower crust and total crust, respectively, and assuming similar Rb abundances in the upper and lower crust (as is indicated by the data of Heier and Brunfelt), the mass fraction of the upper crust is about 0.3. If the concentration and ratio estimates used in this mass balance are valid, most of the crustal Cs would reside in the upper 10 km of the crust, and Cs would in this respect be similar to the element uranium. We emphasize again that mass balance calculations based on crustal abundances cannot be closely constrained at present. Therefore, the similarity of upper crustal and chondritic Cs/Rb ratios does not strongly constrain the bulk-earth Cs/Rb ratio and is consistent with a much lower Cs/Rb ratio inferred from mantle derived basalts.

A comparison of published estimates of K, Rb, Cs and Ba in the terrestrial crust plus mantle (Table 3) shows surprisingly good agreement for the

Table 3. Published estimates for K, Rb, Cs, and Ba abundances in the terrestrial curst-mantle system.

Reference	K ppm	Rb ppm	Cs ppb	Ba ppm	K/Rb	Ba/Rb	Cs/Rb $\times 10^3$	Rb/Sr
Larimer [36]	193	0.62	13	7.9	310	12.6	21	0.035
Shaw [37]	160	0.59		5.5	270	9.3		0.022
Ganapathy and Anders [38]	252	0.86	88	7.7	290	8.8	102	0.032
Ringwood and Kesson [39]	286	0.85	31	8.4	335	9.9	37	0.035
Smith [40]	193	0.73	13	7.3	265	10.0	27	0.025
Sun and Nesbitt [23]	240	0.68	24	7.1	355	10.4	35	0.030
Jagoutz et al. [1]	260	0.81		6.9	320	8.5		0.029
Jacobsen and Wasserburg [35]	260	0.63		7.6	410	12.1		0.029
Sun [2]	230	0.66	8–17		350		12–26	0.030
This work		0.61	7.7	6.9[a]		11.3	12.6	0.029
C-1 Chondrite Orgueil (Palme et al. [33])	517	2.06	0.19	2.2	251	1.1	92	0.240

[a] This value, taken from Jagoutz et al. [1], is based on the assumption that terrestrial refractory element ratios are chondritic (using Ba/Sc in C-1 chondrites) and using the Sc abundance in primitive mantle xenoliths.

estimated Ba/Rb ratios with a rather narrow total range between values of 8.5 and 12.6. Because our best estimate of ~ 11.0 is in excellent agreement with these published values, we believe that our approach should also be valid for the Cs/Rb ratio, for which there is very poor agreement in the literature. Sun [2] has also pointed out that the terrestrial Cs/Rb ratio is poorly constrained to lie somewhere between 12 and 30×10^{-3}. Other authors simply use the chondritic ratio. Our results indicate that the silicate portion of the earth has a Cs/Rb ratio about a factor of ten lower than the chondritic value. The question whether the missing cesium was selectively volatilized and lost from the earth, or whether it found its way into the metallic core (Bukowinskii [41]) is interesting but cannot be answered from our results.

Acknowledgements

This work was inspired by the huge 1982 harvest of apples in Professor Klemm's orchard, which the senior author had the pleasure (and back ache) to help convert into great quantities of sweet cider. Truly sweet cider of uniformly high quality is obtained only if all the rotten apples are picked out first from each batch!

Reviews by and discussions with B. Dupré, H. Palme, P. J. Patchett, J.-G. Schilling, and H. Wänke did much to improve the manuscript. We tried – but failed – to come up with a terrestrial Cs/Rb ratio acceptable to our friends from cosmochemistry.

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Note added in proof:

While this paper was in press, we received communications from S. R. Hart and J.-G. Schilling with several useful comments and additional unpublished data (by Hart), which could not be included in the text. We did correct an error, pointed out by Schilling, in our discussion on the quantitative effects of retaining a portion of the melt in the residue. Schilling also called our attention to his published discussion on Rb/Cs and Rb/Ba ratios in basalts from the North Atlantic [42].