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Halogens in the Mantle Beneath the North Atlantic [and Discussion]

J.-G. Schilling, M. B. Bergeron, R. Evans and J. V. Smith

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Halogens in the mantle beneath the North Atlantic

By J.-G. Schilling, M. B. Bergeron and R. Evans
Graduate School of Oceanography, University of Rhode Island,
Kingston, R.I. 02881, *U.S.A.*

F, Cl and Br contents of tholeiitic volcanic glasses dredged along the Mid-Atlantic Ridge from 53° to 28° N, including the transect over the Azores Plateau, are reported. The halogen variations parallel those of $^{87}Sr/^{86}Sr$, La/Sm or other incompatible elements of varying volatility. The latitudinal halogen variation pattern is not obliterated if only Mg-rich lavas are considered. Variations in extent of low-pressure fractional crystallization or partial melting conditions do not appear to be the primary cause of the halogen variations. Instead, mantle-derived heterogeneities in halogens, with major enrichments in the mantle beneath the Azores, are suggested. The Azores platform is not only a 'hotspot' but also a 'wetspot', which may explain the unusually intense Azores volcanic activity. The magnitude of the halogen and incompatible element enrichments beneath the Azores appear strongly dependent on the size of these anions and cations, but independent of relative volatility at low pressure. The large anions Cl and Br behave similarly to large cations Rb, Cs and Ba, and the smaller anion F similarly to Sr and P. Processes involving crystal and liquid (fluid and/or melt), CO_2 rather than H_2O dominated, seem to have produced these large-scale mantle heterogeneities. Geochemical 'anomalies' beneath the Azores are no longer apparent for coherent element pair ratios of similar ionic size. Values of such 'unfractionated' coherent trace element ratios provide an indication of the mantle composition and its nature before fractionation event(s) which produced the inferred isotopic and trace element heterogeneities apparently present beneath the North Atlantic. The relative trace element composition of this precursor mantle does not resemble that of carbonaceous chondrites except for refractory trace element pairs of similar ionic size. It is strongly depleted in halogens, and to a lesser extent in large alkali ions Rb and Cs relative to refractory Ba. These relative depletions are comparable within a factor of 5 to Ganapathy & Anders's estimates for the bulk Earth, with the exception of Cs. There is also evidence for removal of phosphorus into the iron core during its formation. With the exception of San Miguel, alkali basalts from the Azores Islands appear to have been derived from the same mantle source as tholeiitic basalts from the ridge transect over the Azores Platform but by half as much degree of partial melting. The Azores subaerial basalts seem to have been partly degassed in Cl, Br and F, in decreasing order of intensity. A working model involving metasomatism from release of fluids at phase transformation during convective mantle overturns is proposed to explain the formation of mantle plumes or diapirs enriched in larger relative to smaller halogen and other incompatible trace elements. The model is *ad hoc* and needs testing. However, any other dynamical model accounting for the 400–1000 km long gradients in incompatible trace elements, halogens and radiogenic isotopes along the Mid-Atlantic Ridge should, at some stage, require either (1) some variable extent of mixing or (2) differential migration of liquid relative to crystals followed by re-equilibration (or both), as a diffusion controlled mechanism over such large distances is clearly ruled out, given the age of the Earth.

INTRODUCTION

It is increasingly evident that volatiles in the mantle may affect rheological properties, melting conditions and composition of melts generated in the mantle (see, for example, Goetze 1977; Mysen 1977; Eggler & Holloway 1977; Wyllie 1977*a*, *b*). Upward percolation of fluids could also affect the isotopic composition of upper zones of the mantle by re-equilibrating during the ascent. Release of fluids could occur at phase transitions during mantle convection, not only beneath island arcs as suggested by Fyfe & McBirney (1975) and Mysen (1978*c*), but also beneath hotspots and ridges. Recent rare earth partitioning experiments between crystal and fluids at high pressure also indicate that significant fractionation between trace element pairs can occur during processes involving crystal and H_2O or CO_2 rich fluids (Mysen 1978*a*, *b*; Flynn & Burnham 1978). The fractionations are of similar magnitude to those involving crystals and melts. Thus, fluid percolation in the mantle may also affect the distribution and fractionation of incompatible trace elements, including parent/daughter element ratios such as Rb/Sr, U/Pb, Th/Pb and Sm/Nd; and as a result with time, radiogenic isotopes as well. Evidence for the generation of trace element and isotopic heterogeneities in the mantle by metasomatism has been widely discussed for regions beneath continents (e.g. by Lloyd & Bailey 1975), but not for oceanic areas. Though it is clear that volatiles can have important effects in the mantle, their nature and magnitude are far less certain. These effects critically depend on the absolute and relative abundances of volatiles in the mantle, which are mostly unknown in comparison with more refractory trace elements and isotopes. Estimates of volatile abundances in the mantle are difficult to make because magmas or rocks rising from the mantle tend to lose their volatiles by outgassing at shallow depth, whereas volcanic gases tend to be contaminated by meteoritic fluids. Furthermore, the extent of fractionation occurring among volatiles during outgassing remains poorly understood. The study of volatiles contained in glassy basalts quenched under different hydrostatic pressures in the oceans is offering new opportunities. The approach was pioneered by Moore (1965) along the submarine extension of the Kilauea Iki rift on the eastern flank of the island of Hawaii, where he showed that water in tholeiitic lavas begins effervescing significantly only above approximate 500 m depth of water (*ca.* 50 bar†). This critical depth was theoretically predicted by McBirney (1963). Basaltic glasses collected from deeper than 500 m contained excess radiogenic argon suggesting incomplete or no degassing (Dalrymple & Moore 1968). Subsequent studies along the Reykjanes Ridge and extension over Iceland have shown that not only H_2O, but S (Moore & Schilling 1973), Se (Unni & Schilling 1976), and Cl and Br (Unni & Schilling 1978*a*) are also drastically degassed at approximately the same 500 m critical depth. The degassing of S, Se, Cl and Br seems to occur regardless of whether solubility of these volatiles in the melt is, or is not, exceeded at the prevailing temperatures of eruptions (110–1250 °C). For example, solubility of S is probably exceeded under such conditions, but not Cl and Br because of their comparatively lower abundance (Haughton *et al.* 1974; Katsura & Nagashima 1974; Iwasaki & Katsura 1967). A distinction must be made between major and trace volatiles, as their distribution in the mantle may be affected by different factors. For example, the above results suggest that H_2O and possibly CO_2 and $SO_2(H_2S)$ effervescing from magmas may act as a fluxing agent for other trace volatiles. Significant fractionation among volatiles can occur during low pressure outgassing of magmas even for a chemical group as closely related as the halogens.

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† 1 bar = 10^5 Pa.

Unlike Cl and Br, F variation in submarine basalts from the Reykjanes Ridge–Iceland profile indicates that this element is not appreciably degassed in basalts erupted above 500 m (Rowe & Schilling 1979). The distinction probably reflects the smaller anionic size of F relative to Cl and Br, which is also reflected in the ability of F to substitute for OH$^-$ molecules in silicate melts and minerals (see, for example, Carmichael *et al.* 1974; Burnham 1975; Mueller & Saxena 1977).

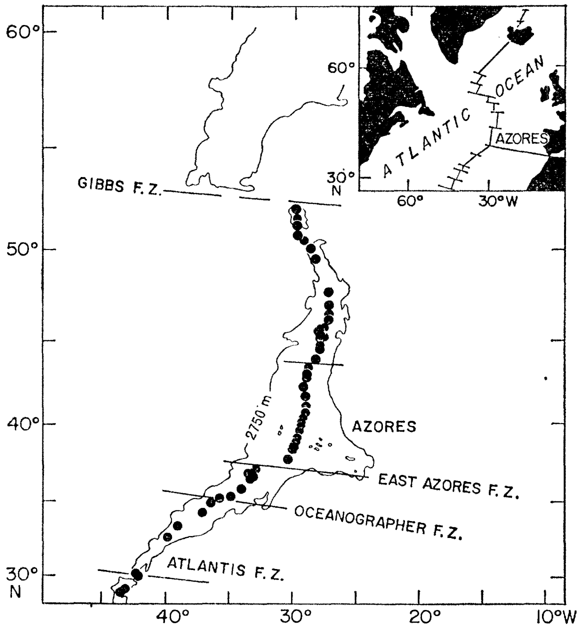

FIGURE 1. Location of Mid-Atlantic Ridge basalts studied. Dredged stations occupied mostly with R/V *Trident* (see table 1 for exact locations). The 2750 m contour outlines the Mid-Atlantic Ridge and the Azores Platform.

The contrasting behaviour between F and Cl (or Br) in igneous rocks and magmas is also readily apparent from experiments on partitioning between silicate melts and aqueous fluids. F preferentially partitions into the melt, whereas Cl concentrates preferentially in the fluid phase (Burnham 1967; Kilinc & Burnham 1972). Analyses of fresh subaerial igneous rocks should therefore more nearly represent the original F content of magmas (Carmichael *et al.* 1974). So far, no attempts have been made to use such contrasting behaviour among halogens to study mantle evolution.

In this report we focus on the contents of F, Cl and Br in glassy margins and pillow interiors of tholeiitic basalts erupted along the crest of the Mid-Atlantic Ridge (M.A.R.) from 52° to 29° N. There are two main reasons for selecting this particular segment of the ridge (figures 1 and 2).

First, the ridge elevation varies from 1100 m below sea level over the Azores platform transect to some 4000 m north or south. Since the entire profile is well below the 500 m critical depth of degassing, no appreciable degassing of Cl, Br (and F) would be expected judging from the results obtained previously along the Reykjanes Ridge–Iceland profile (Unni & Schilling 1978*a*; Rowe & Schilling 1979). With a few exceptions over the Azores Platform and at 35° N, vesicularity of the erupted basalts along the entire profile is less than 10 %, whereas near Iceland vesicularity reaches up to 50 % above 500 m depth (Moore & Schilling 1973). A reasonable postulate would then be that any fractionation between the small F and large anion Cl and Br may indeed reflect other processes of fractionation than preferential outgassing. Such processes are likely to be fractional crystallization during lava ascent, partial melting in the mantle, and fluid or melt percolation in the mantle resulting from mantle convection.

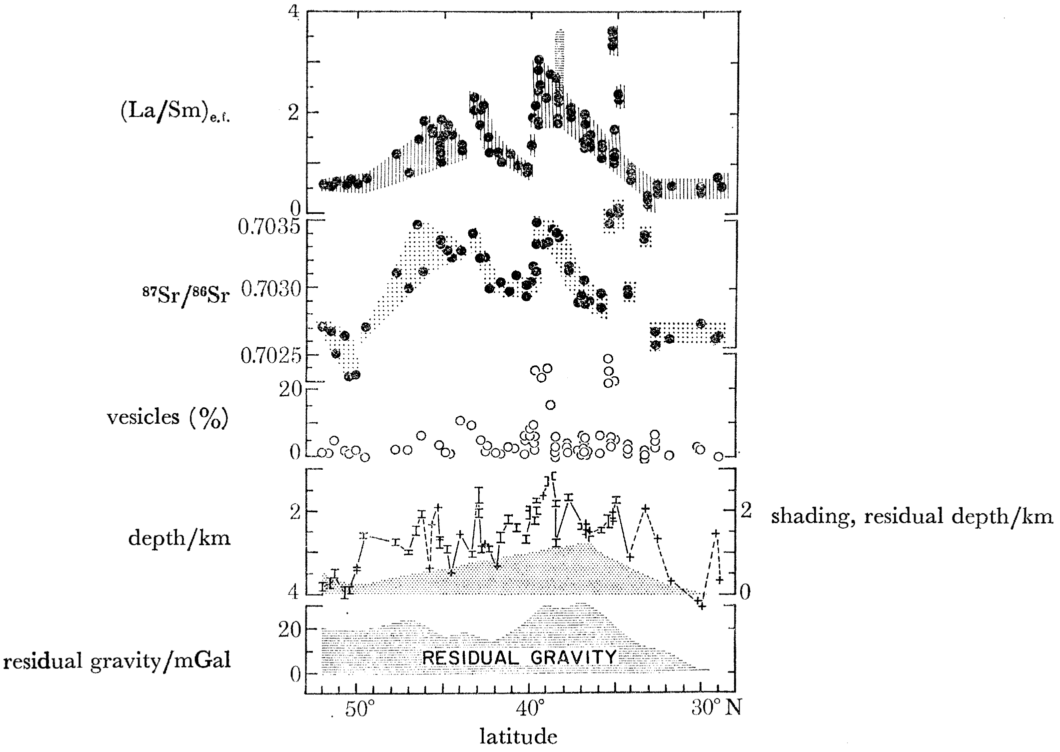

Figure 2. Comparison of La/Sm (Schilling 1975*a* and unpublished) $^{87}Sr/^{86}Sr$ (White & Schilling 1978), volume percentage vesicles of mid-Atlantic basalts studied with depth of recovery, and residual depth and gravity anomalies along the profile (Cochran & Talwani 1977). The La/Sm ratios are normalized to chondrites. Vertical and stippled area emphasizes the general geochemical trend, and the horizontally patched field is for the La/Sm range observed in the Azores Island alkali basalts studied.

Secondly, the elevation of the Mid-Atlantic Ridge axis and the free-air gravity field over the ridge are highly anomalous north of 32° N (Sclater *et al.* 1975; Cochran & Talwani 1977, 1978). Major positive residual gravity and depth anomalies occur north of 32° N. The largest of these residual anomalies coincide with the Azores Platform which is also the locus of unusually extensive volcanism (figures 1 and 2). Basalts erupted along this segment of the M.A.R. in the North Atlantic are also unusually enriched in trace elements and radiogenic strontium (figure 2). The major gradients in residual gravity and elevation north of 32° N up to the Azores, is also paralleled by major gradients in $^{87}Sr/^{86}Sr$, La/Sm and large ion lithophile element (l.i.l.e.) ratios (Schilling 1975*a*; White *et al.* 1976; White & Schilling 1978). Although the geochemical evidence clearly indicates major heterogeneities in the mantle beneath this segment of the North Atlantic ridge, the causes of these geochemical and geophysical anomalies and associated gradients remain subject to interpretation and are currently intensely debated (Schilling 1973*a*, *b*, 1975*a*; O'Hara 1973, 1975, 1977; Flower *et al.* 1975; Sigvaldason 1974; O'Nions & Pankhurst 1974; O'Nions *et al.* 1976; Langmuir *et al.* 1978; Nelson & Dasch 1976; Hoffman & Hart 1978; Pankhurst 1977; White *et al.* 1976; White & Schilling 1978). The

Table 1. F, Cl and Br concentrations (micrograms per gram) and $H_2O + 110$ °C in Mid-Atlantic Ridge tholeiitic basalts and Azores alkali basalts

sample	latitude, N	longitude, W	depth[1] m	vesicularity (vol. %)	glasses F	glasses Cl	glasses Br	pillow interiors F	pillow interiors Cl	pillow interiors Br	Mg no.[9]	$H_2O + 110$ °C (% by mass)
Mid-Atlantic Ridge[2]												
N-1	28° 53.0′	43° 20.0′	3658	0.1	326	21	0.10	85	—	—	68.3	0.25
P-1	29° 04.0′	43° 01.0′	2213	—	—	—	—	155	63	—	63.9	0.44
A150-20	30° 01.0′	42° 04.0′	4280	2.2	—	—	—	170	36	—	58.8	0.31
A150-7	30° 04.0′	42° 16.0′	4144	2.9	—	—	—	140	31	—	64.6	0.37
A150-RD-8	31° 49.0′	42° 25.0′	3700	0.4	—	—	—	160	34	—	63.5	0.36
TR123 5D-3	32° 27.4′	39° 52.1′	2700	3.8	225	57	0.11	165	—	—	57.3	0.12
TR123 4D-7	33° 22.2′	39° 04.8′	1950	—	522	64	0.24	80	—	—	69.5	0.24
TR123 1D-5A	34° 13.9′	37° 07.6′	3100	1.4	210	67	0.16	145	—	—	62.2	0.31
TR119 8D-1	34° 56.3′	36° 36.7′	1750	22.5	—	—	—	350	397	—	64.4	0.57
V30 RD7-10	35° 08.0′	35° 44.0′	2130	—	—	—	—	210	256	—	—	—
V30 RD8-P1	35° 09.0′	35° 44.0′	2135	3.1	—	—	—	145	116	—	70.0	0.39
V30 RD8-P2	—	—	—	3.3	—	—	—	—	205	—	58.1	0.54
TR119 7D-5	35° 20.0′	34° 54.0′	2250	22.0	—	—	—	444	284	—	70.8	0.26
TR119 7D-sg	—	—	—	—	550	403	0.90	—	—	—	—	—
TR119 6D-3A	35° 50.2′	34° 10.8′	2450	2.6	—	—	—	164	—	—	60.9	0.38
TR119 6D-10	—	—	—	—	270	74	0.16	—	—	—	—	—
AII73 50-13-6	36° 28.6′	33° 38.3′	2561	1.5	—	—	—	—	116	—	62.6	0.23
AII73 16-5-2	36° 42.7′	33° 17.3′	2598	5.4	314	112	0.25	220	—	—	61.2	0.17
AII73 10-2-19	36° 45.0′	33° 18.0′	2300	1.3	—	—	—	165	300	—	64.4	0.21
TR119 4D-1	36° 50.7′	33° 13.7′	2375	3.5	—	—	—	205	150	—	60.1	0.35
TR119 4D-3B	—	—	—	—	—	—	—	—	190	—	70.2	—
TR119 4D-sg	—	—	—	—	375	213	0.46	—	—	—	—	—
TR122 5D-5	37° 43.6′	31° 28.2′	1650	3.8	—	—	—	255	346	—	54.8	0.58
TR89 22D-1[3]	38° 25.3′	30° 27.0′	2775	—	—	—	—	375	31	—	—	—
TR89 22D-4	—	—	—	—	—	—	—	—	51	—	57.3	1.86
TR89 22D-5	—	—	—	—	—	—	—	—	63	—	58.8	0.37
TR89 21D-1	38° 26.0′	30° 21.4′	2775	5.9	560	632	1.39	564	528	—	55.5	0.73
TR89 21D-2	—	—	—	1.0	—	—	—	—	571	—	53.2	0.73
TR89 21D-3	—	—	—	3.1	—	—	—	—	583	—	53.9	0.79
TR154 10D-3	38° 41.9′	30° 11.4′	1150	26.4	547	774	1.76	509	667	—	58.6	0.47
TR154 21D-3	38° 53.3′	30° 02.9′	1305	15.6	410	394	0.93	324	—	—	65.9	0.35
TR154 8D-1	39° 11.9′	29° 56.8′	1630	23.8	495	387	0.94	339	—	—	60.5	0.64
TR89 30D-2-3	39° 37.9′	29° 44.4′	2025	3.7	388	166	0.31	344	—	—	66.2	0.51
TR89 30D-5	—	—	—	—	—	158	0.33	—	—	—	69.2	0.30

TABLE 1 (*cont.*)

					glasses			pillow interiors				
sample	latitude, N	longitude, W	depth[1] m	vesicularity (vol. %)	F	Cl	Br	F	Cl	Br	Mg no.[9]	H_2O+110 °C (% by mass)
Mid-Atlantic Ridge[2]												
TR89 30D-10	—	—	—	—	—	151	0.34	—	—	—	68.2	0.28
TR89 31D-1	39° 37.6′	29° 42.3′	1750	12.3	—	—	—	490	94	—	68.8	0.56
TR89 31D-3	—	—	—	26.0	—	—	—	500	664	—	53.5	0.72
TR154 20D-3	39° 45.7′	29° 41.2′	2225	9.4	335	295	0.79	—	—	—	63.7	0.39
TR154 7D-2	39° 56.1′	29° 40.1′	1950	—	215	122	0.29	—	—	—	—	—
TR154 6D-1	39° 57.1′	29° 39.9′	2100	—	—	—	—	180	179	—	62.6	0.35
TR122 3D-sg	40° 13.9′	29° 35.4′	2675	—	175	70	0.24	—	—	—	—	—
TR154 19D-2	40° 44.6′	29° 15.2′	2430	—	265	67	0.17	—	—	—	—	—
TR154 18D-2	41° 10.7′	29° 18.3′	2225	3.0	149	53	0.14	75	—	—	69.3	0.26
TR154 17D-2	41° 40.4′	29° 15.7′	2625	—	260	104	0.28	—	—	—	64.6	0.39
CH82 29-1	41° 55.0′	29° 13.0′	3320	1.0	—	—	—	165	179	—	61.6	0.22
TR154 16D-3	42° 23.1′	29° 24.1′	2895	3.1	239	159	0.36	140	—	—	67.6	0.43
CH82 35	42° 31.0′	29° 15.0′	2790	1.1	—	—	—	215	208	—	66.6	0.52
TR154 15D-2	42° 47.5′	29° 21.6′	2925	2.4	—	—	—	279	201	—	61.0	0.14
AII32 11-116	42° 57.1′	29° 14.0′	2075	—	—	—	—	170	106	—	—	—
AII32 12-8	42° 57.4′	29° 10.6′	1878	—	—	—	—	334	289	—	—	—
TR154 12D-1	43° 22.4′	28° 58.9′	3040	—	339	267	0.64	254	—	—	—	—
TR154 13D-2	44° 00.0′	28° 23.6′	2560	—	199	106	0.25	—	—	—	—	—
CH43 107-6	44° 34.0′	28° 09.2′	3480	0.7	—	—	—	185	203	—	65.9	0.60
TR154 14D-2	44° 49.2′	28° 02.6′	2925	—	—	—	—	214	—	—	—	—
TR154 14D-4	—	—	—	—	295	223	0.66	—	—	—	—	—
CH43 104-16	45° 11.0′	27° 54.0′	2790	3.5	—	—	—	—	137	—	66.0	—
CH43 104-17	—	—	—	—	—	—	—	105	69	—	80.7	—
CH43 104-59	—	—	—	—	—	—	—	150	148	—	70.8	—
HU 56-3	45° 13.0′	28° 00.0′	3360	—	—	—	—	155	221	—	65.8	—
HU 56-4	—	—	—	—	—	—	—	135	218	—	66.6	0.41
HU 9-4	45° 21.0′	28° 02.0′	1960	—	—	—	—	175	271	—	—	—
HU 9-7	—	—	—	—	—	—	—	—	232	—	—	—
HU 1-2	45° 39.0′	28° 09.0′	2340	—	—	—	—	180	299	—	—	—
TR138 1D-2	46° 13.9′	27° 23.4′	2068	6.3	394	218	0.50	174	—	—	70.4	0.47
TR138 1AD	46° 31.6′	27° 29.1′	2475	—	—	—	—	285	32	—	60.0	0.36
TR138 2D-3	47° 03.1′	27° 21.0′	2975	2.0	225	61	0.18	—	—	—	69.2	0.23
TR138 3D-1	47° 46.6′	27° 38.4′	2740	2.0	—	120	0.37	155	107	—	69.0	0.46
TR138 5D-sg	49° 31.4′	28° 32.2′	2587	—	245	37	0.09	—	—	—	—	—
TR138 6D-1	50° 02.6′	28° 56.0′	3370	1.8	319	28	0.09	180	—	—	60.6	0.33
TR138 7D-1	50° 27.5′	29° 25.4′	3880	1.0	190	26	0.06	—	—	—	68.2	0.34
CH13 PD-1-1	50° 44.0′	29° 52.0′	3980	—	—	—	—	130	26	—	66.7	—
TR138 8D-1	51° 16.6′	30° 09.0′	3500	4.7	210	20	0.06	—	—	—	66.4	0.28
TR138 9D-2	51° 33.3′	29° 55.4′	3710	0.9	200	15	0.05	140	—	—	63.1	0.23
TR138 11D-1	52° 04.0′	29° 57.0′	3800	0.7	289	23	0.06	120	—	—	62.4	0.27

Table 1 (*cont.*)

sample	latitude, N	longitude, W	depth[1] m	vesicularity (vol. %)	glasses F	glasses Cl	glasses Br	whole rock F	whole rock Cl	whole rock Br	whole rock Mg no.[9]	whole rock H_2O+110 °C (% by mass)
Azores Islands												
F-14	Faial	—	—	—	—	—	—	704	504	1.65	61.1	0.09
F-33	—	—	—	—	—	—	—	658	452	1.76	65.8	0.17
FL-20	Flores	—	—	—	—	—	—	583	618	1.61	68.8	0.27
G-2	Graciosa	—	—	—	—	—	—	425	93	—	65.3	—
G-4	—	—	—	—	—	—	—	415	390	1.67	69.9	—
P-21	Pico	—	—	—	—	—	—	513	132	0.69	73.7	0.21
SMA-2	Santa Maria	—	—	—	—	—	—	760	513	1.56	75.4	0.53
SM-2A	Sao Miguel	—	—	—	—	—	—	590	416	1.36	68.3	0.14
SM-28	—	—	—	—	—	—	—	628	30	—	58.0	—
TR89 11GC[4]	38° 50.3′	27° 39.2′	2295	—	955	444	0.90	—	—	—	—	—
standards[5]												
AGV-1 (Andesite)	—	—	—	—	—	—	—	390	100	—	—	—
recommended[6]	—	—	—	—	—	—	—	435	110	—	—	—
BCR-1 (Basalt)	—	—	—	—	—	—	—	428	59	0.08	—	—
1σ	—	—	—	—	—	—	—	—	±0.7	±0.01	—	—
recommended[6]	—	—	—	—	—	—	—	470	50	0.15	—	—
BR (Basalt)	—	—	—	—	—	—	—	988	—	—	—	—
1σ	—	—	—	—	—	—	—	±35	—	—	—	—
recommended[7]	—	—	—	—	—	—	—	1000	—	—	—	—
JB-1 (Basalt)	—	—	—	—	—	—	—	320	172	0.55	—	—
1σ	—	—	—	—	—	—	—	—	—	±0.02	—	—
recommended[8]	—	—	—	—	—	—	—	390	175	0.5	—	—

[1] Median depth of recovery.

[2] Sample identification includes ship (A, Atlantis; CH, Chain; HU, Hudson; TR, Tridnnt; V, Vema), cruise number, station number and sample number. Sg indicates a composite of loose glass chips from one dredge haul.

[3] Metamorphosed to greenschist facies (unusually low value compared with neighbouring stations suggest hydrothermal removal of Cl but not F).

[4] Gravity core from seamount in Terceira Trough northwest of Terceira Island.

[5] Cl and Br from Unni & Schilling (1978*a*, *b*).

[6] Flanagan (1973).

[7] Roubalt *et al.* (1970).

[8] Ando *et al.* (1971).

[9] Mg no. = 100 Mg/(Mg+Fe^{2+}), atomic.

phenomenon remains a major unanswered problem in geology, unaccounted for simply by the theory of sea-floor spreading. Unusual processes occurring within the mantle itself rather than the lithosphere are probably the cause of such phenomenon. The role that volatiles may have played in this phenomenon remain to be investigated.

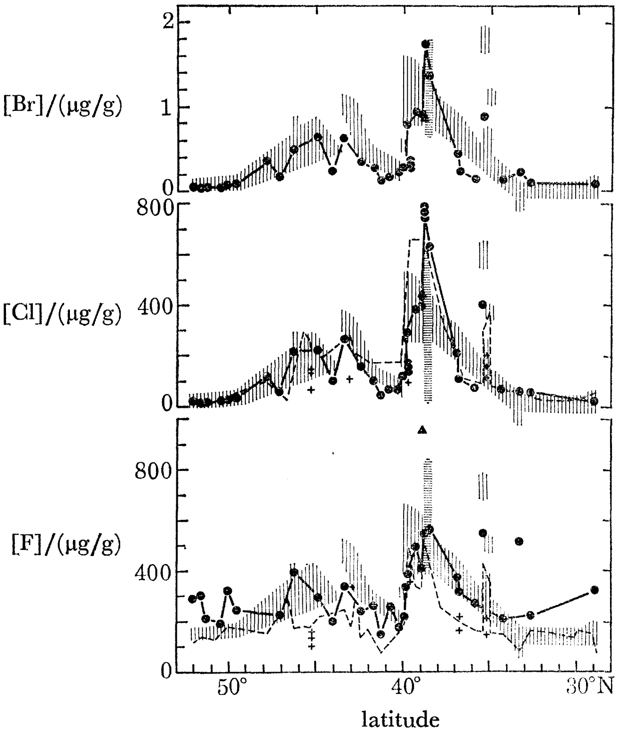

FIGURE 3. Br, Cl and F concentration variations along the Mid-Atlantic Ridge. Black dots and heavy lines are for glasses. Broken lines connect values from pillow interiors (variolitic zone mostly). Crosses are stations unconnected by lines for clarity. Horizontally hatched areas are halogen contents for the Azores Island alkali basalts. The 'camel-back' La/Sm variation pattern of figure 1 is shown for reference (vertical hatched field). Triangle is glassy basalt TR89 11gc collected in the Terceira Trough.

METHODS OF ANALYSIS AND RESULTS

Table 1 lists the concentrations of F, Cl and Br in the basalts studied. Whenever possible, both glass rims and pillow interiors from each dredged station were analysed.

The Cl and Br contents of the lavas were determined separately by two high-precision neutron activation techniques (Unni & Schilling 1978*b*, *c*). F analyses were obtained by using essentially the ion-selective electrode method described by Bodkin (1977). Precision and accuracy of the three methods can be estimated from the replicate analyses of JB-1 and BCR-1 rock standards in table 1. Freshest crushed fragments of both glass rim and interior of pillows (variolitic zone mostly) were hand-picked under the microscope, ultrasonically cleaned with ultrapure distilled water and dried. The process of crushing, picking and cleaning was repeated as needed. The clean fragments were ground in an agate mortar to 50–75 μm for further analyses. To overcome possible Cl contamination by sea salt evaporated within microcracks of the pillow interiors, the powders were further ultrasonically cleaned with ultrapure distilled water. The method has been tested thoroughly to demonstrate that only NaCl is removed by this technique but not appreciable Cl intrinsic to the lava (Unni & Schilling 1978*a*). This latter step was judged unnecessary for F because of its low concentration in sea water and in view of the freshness of the rocks. The Cl content of the glasses and pillow interior from the same sample are usually comparable, whereas consistently higher F values are found in glassy rims relative to the interior of the pillow. Possible explanations are discussed by Rowe & Schilling (1979).

The procedure used for the subaerial Azores island basalts is the same as for the glasses. Bulk compositions of the M.A.R. basaltic pillow interiors are reported in Schilling *et al.* (1980), the M.A.R. glasses by Sigurdsson & Schilling (1979) and those from the islands by White *et al.* (1979). The M.A.R. samples are invariably tholeiitic (either quartz or olivine normative), with the exception of two unusual stations (TR119 7D and TR123 4D). Lavas from station TR119 7D and TR123 4D are, respectively, alkalic (nepheline normative) and picritic in composition. The island basalts all contain nepheline in the CIPW norms and are therefore classified as alkali basalts according to the scheme of Yoder & Tilley (1962).

F, Cl and Br variations along the M.A.R. profile

The variation of F, Cl and Br content of the glasses along the M.A.R. shows the same general trend as the variation in $^{87}Sr/^{86}Sr$, or La/Sm ratios (figure 3). This is true despite the fact that vesicularity may be as high as 25 % over the Azores platform. Previously reported, l.i.l.e. variations show similar trends to F, Cl and Br (e.g. K, Rb, Cs) or refractory elements (e.g. La, Ba) (White & Schilling 1978; Schilling *et al.* 1980). This suggests first that probably no significant degassing of F, Cl and Br has taken place, and secondly that the gross F, Cl and Br patterns along the ridge are probably a mantle source characteristic. However, this does not mean that partial melting in the mantle and fractional crystallization during magma ascent have not affected the absolute content of F, Cl and Br from that of its mantle source. The mere fact that these basalts contain phenocrysts does indicate that fractional crystallization has indeed been operative. Furthermore, variations of major elements, phenocrysts (type and abundance) and content of compatible elements such as Ni and Cr along the profile also indicate that fractional crystallization operated to variable extents. Variation in the extent of partial melting along the ridge is more difficult to evaluate. However, since the $^{87}Sr/^{86}Sr$ ratio is unlikely to fractionate during these two magmatic processes, the similarity of the F, Cl and Br variation to that of $^{87}Sr/^{86}Sr$ and La/Sm along the profile would not be expected had the degree of partial melting and extent of fractional crystallization been highly variable and randomly distributed along the ridge axis. The combined effect of fractional crystallization and partial melting on the content of the three halogens can be evaluated by looking at covariations with the FeO/(FeO + MgO) ratio as an index of fractionation for these two processes (figure 4). Two geographical sampling populations were considered separately: (1) the ridge basalts over the Azores Platform which are characterized by high $^{87}Sr/^{86}Sr$ and La/Sm ratios; and (2) those characteristic of the so-called ‘normal’ ridge segments as south of 34° N and north of 49° N featuring low $^{87}Sr/^{86}Sr$ and La/Sm ratios (figure 2) (see Schilling (1975*b*) for definition of the term). Both glasses and pillow interiors were considered separately. Two distinct covariation trends corresponding to the two populations are clearly distinguished in the glasses for each of the three halogens. At equal FeO/(FeO + MgO), the F, Cl and Br content over the Azores Platform is also clearly higher than along the two normal ridge segments, thus suggesting two distinct mantle sources. Though we emphasize that the absolute F, Cl and Br contents of these basalts are not equal to that of their mantle source, we suggest that the *relative* F, Cl and Br variations along the ridge reflect a grossly similar pattern in the mantle source of these basalts beneath the ridge. Variation of concentration ratios among the three halogens along the ridge will further support our contention as we shall see later.

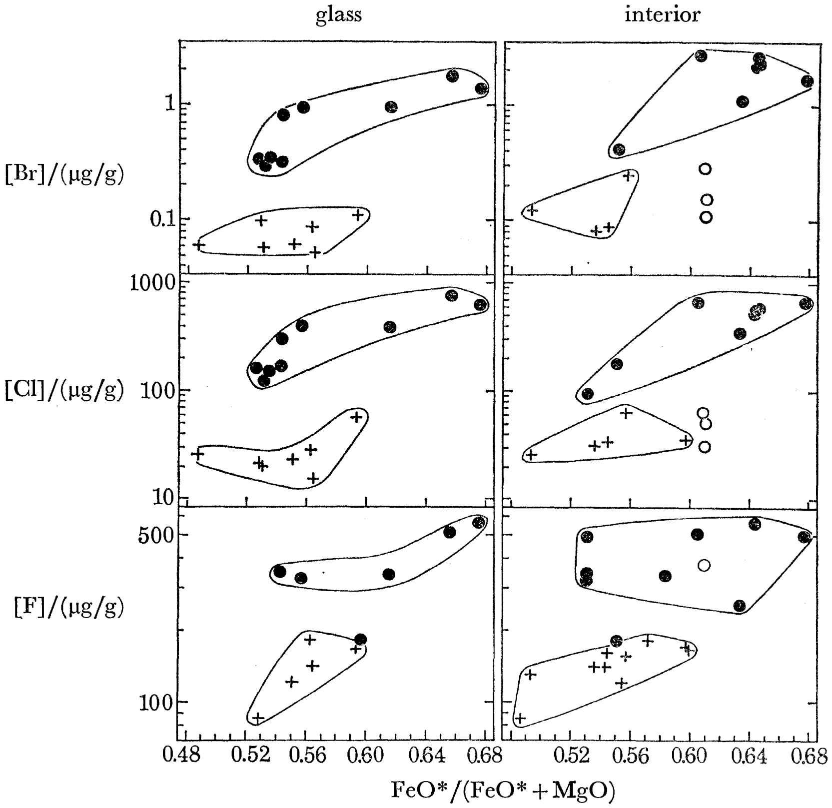

FIGURE 4. Halogens versus FeO*/(FeO*+MgO) of M.A.R. glasses and pillow interiors for the ridge transect over the Azores Platform (filled circles), and the two normal ridge segments from 28° to 33° N and 49° to 52° N (crosses). Note the systematically higher halogen contents of the Azores group. Open circles are metamorphosed M.A.R. basalts from station TR89 22D belonging to the Azores group. Both Cl and Br seem to have been hydrothermally leached out, but not F.

Table 2 shows that on the average the F, Cl and Br content of the Azores mantle is probably enriched by respectively 1.7–2.7, 11–12 and 10–14 relative to the l.i.l.e.-depleted asthenosphere source of M.A.R. basalts south of 33° 30′ N or north of 49° N· These enrichments represent probably minimum values because of the slightly higher content of vesicles in the lavas over the Azores transect (figure 2). The water content of these M.A.R. basalts is also significantly higher over the Azores platform than along the two normal ridge segments ($H_2O^+ = 0.52 \pm 0.17\%$ (1σ) and $0.33 \pm 0.12\%$ (1σ), respectively). This suggests that the Azores region is not only a 'hotspot' but also a 'wetspot'. Smaller volatile enrichments are observed beneath the 43–46° N region. The two unusual localities near 35° N are also noted (stations TR119 7D and TR123 4D).

Table 2. Average concentrations of Mid-Atlantic Ridge basalts and Azores Islands basalts with relative enrichments

	glasses			pillow interiors										
	F	Cl	Br	F	Cl	Br	La	K	Rb	Cs	Sr	Ba	P	Ti
A†	421 ±124	342 ±231	0.79 ±0.53	389 ±131	454 ±221	1.84 ±0.84	15 ±7	5230 ±2302	12.0 ±5.0	0.15 ±0.07	231 ±106	163 ±69	1110 ±389	9550 ±2550
B‡	251 ±54	29 ±13	0.08 ±0.02	144 ±28	38 ±14	0.13 ±0.08	3.0 ±0.8	940 ±470	1.0 ±0.5	0.01 ±0.01	102 ±11	10 ±4	605 ±156	8620 ±1480
C§	— —	— —	— —	586 ±118	350 ±210	1.47 ±0.36	40 ±10	12000 ±3900	30.0 ±12.5	0.31 ±0.14	620 ± 96	435 ±122	2441 ±517	16480 ±3230
A/B	1.7	11.8	9.9	2.7	11.9	14.2	5.1	5.5	12.0	12.0	2.3	16.3	1.8	1.1
C/A‖	(1.4)	(1.0)	(1.9)	1.5	0.8	0.8	2.6	2.3	2.5	2.1	2.7	2.7	2.2	1.7

† A is for average and 1σ for 20 Mid-Atlantic Ridge tholeiitic basalts from the Azores transect (37–40° N) for either glasses or interiors of pillows.

‡ B is for average and 1σ for 16 Mid-Atlantic Ridge tholeiitic basalts from two normal ridge segments (28–33° N and 49–52° N).

§ C is for average and 1σ for 18 alkali basalts from the Azores Islands. Glass not available except for TR89 11GC from seamount in Terceira Trough.

‖ Halogen glass ratio is for island alkali basalt/M.A.R. glass from Azores transect.

Factors affecting F, Cl and Br fractionation in the mantle

For the sake of a more direct comparison, the relative variation of Cl/F, Br/F and Br/Cl ratios along the ridge are shown in figure 5*a*. There enrichment factor ratios were normalized to their values in sample TR 138 11Dg (a basalt typical of normal ridge segments as defined by Schilling 1975*b*). The up-to-tenfold progressive Cl/F and Br/F enrichment of the ridge basalts over the shallow Azores Platform convincingly rules out the possibility of preferential Cl and Br outgassing at shallower depth. The two trends are just the opposite of the variations observed on the Reykjanes Ridge and Iceland above 500 m, where the Cl/F and Br/F ratios drop by about a factor of ten owing to intense vesiculation and outgassing of Cl and Br (Rowe & Schilling 1979). The Azores geochemical anomaly disappears for the ratio of Br to Cl, which are two large anions of similar size ($r_{\mathrm{Cl}} = 1.81$ Å† and $r_{\mathrm{Br}} = 1.95$ Å). On the other hand, the ratios of larger to smaller anions Cl/F and Br/F, ($r_{\mathrm{F}} = 1.36$ Å) retain the characteristic ^{87}Sr/^{86}Sr 'camel back' pattern (figure 2). L.i.l.e. ratios of variable ionic size show the same pattern as for the halogens (compare figure 5*a* with figure 5*b*–*d*). The Cs/Rb enrichment ratio ($r_{\mathrm{Cs}} = 1.64$ Å, $r_{\mathrm{Rb}} = 1.47$ Å), or Rb/Ba ($r_{\mathrm{Ba}} = 1.36$ Å), remains nearly equal to unity and constant along the profile. On the other hand, the greater the difference in ionic radius of the element pair, the more pronounced is the characteristic 'camel-back' pattern (e.g. Rb/Sr, Ba/Sr). It appears that the cationic or anionic radius is a determining factor in controlling the characteristic camel-back pattern, whereas relative volatility and valency are apparently not. For example, the ratio of two large ions of similar size and volatility such as Cs/Rb show the same constancy along the ridge as for two large ions of similar size but distinct

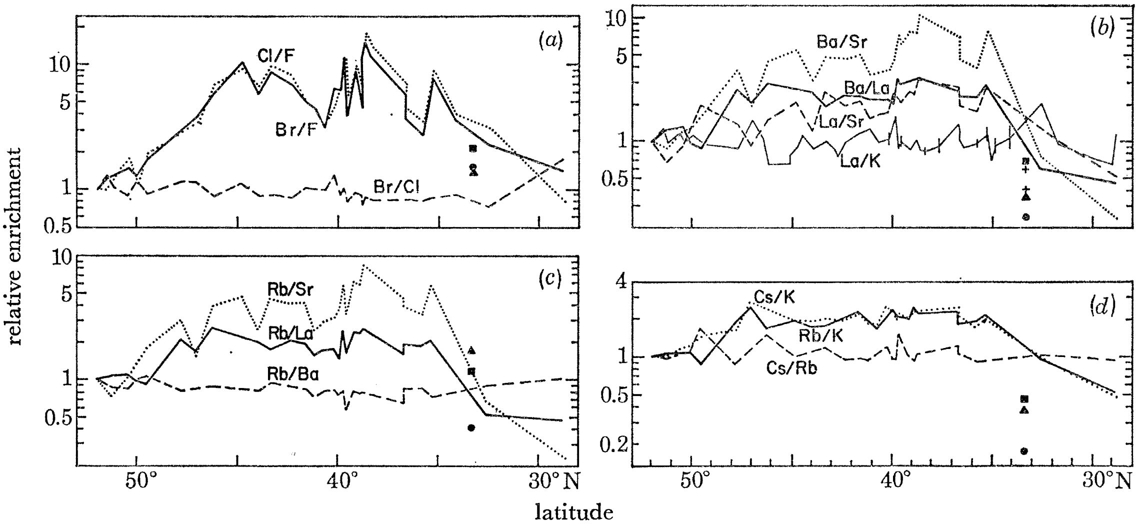

Figure 5. Halogen and l.i.l.e. enrichment factor ratio (e.f.) variation along the M.A.R. The ratios are normalized to values in sample TR138 11D [e.f. = $(\mathrm{Cl/Br})_{\mathrm{sample}}/(\mathrm{Cl/Br})_{\mathrm{std}}$]. Note the lack of variation for cations or anions of similar size. Region between 32° N and 29° N lacks data points (see figure 3), and N-1 glass from 28° N is altered and of poor quality. Station singled out by symbols are for the picrites from station TR123 4D (+, La/Sm; ● corresponds to ratios joined by solid lines, ▲ to ratios joined by dashed lines, and ■ to ratios joined by dotted lines).

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† 1 Å = 10^{-10} m = 10^{-1} nm.

volatility and charge such as Rb/Ba or La/K. Rb^+ and K^+ are mildly volatile whereas Ba^{2+} and La^{3+} are highly refractory and have different valencies.

Our postulate is further emphasized by comparing ratios of the three halogens with l.i.l.e. of different size, charge, electropositivity and volatility (figure 6*a–c*). There is practically no fractionation for F/P and F/Sr along the ridge, suggesting that F behaves similarly to P_2O_5 and Sr in the mantle beneath the region (figure 6*c*). F is the smallest anion of the halogen series, whereas this is also true of Sr and P_2O_5 within the l.i.l.e. series. F is progressively more depleted in the Azores mantle source relative to large l.i.l.e., the greater these ions are. The characteristic 'camel-back' pattern is now inverted since F is a smaller ion than the denominator elements considered. Again Rb, Ba and Cs, the largest ions of the l.i.l.e., are fractionated to a similar extent relative to F. In contrast, the large halogen anions Cl and Br show no fractionation relative to the largest cations of the l.i.l.e. series, Rb, Ba and Cs (figure 6*a*, *b*). In other words, during mantle fractionation processes, whatever such processes may have been, the largest volatile halogens behaved similarly to the largest l.i.l.es, and the smallest halogens similarly to the smallest l.i.l.es. Figure 7*a* further illustrates the effect of ionic or anionic size on the relative enrichment of the halogens and l.i.l.e. in the mantle beneath the Azores in comparison to the l.i.l.e.-depleted asthenosphere south of 33° 30′ N or north of 49° N. Enrichment factors of l.i.l.e., F, Cl and Br correlate positively with cationic or anionic size, regardless of relative volatility at very low pressures (Ganapathy & Anders 1974). The strongly volatile and large anions Cl and Br are enriched to the same extent as the mildly volatile Rb and Cs, or highly

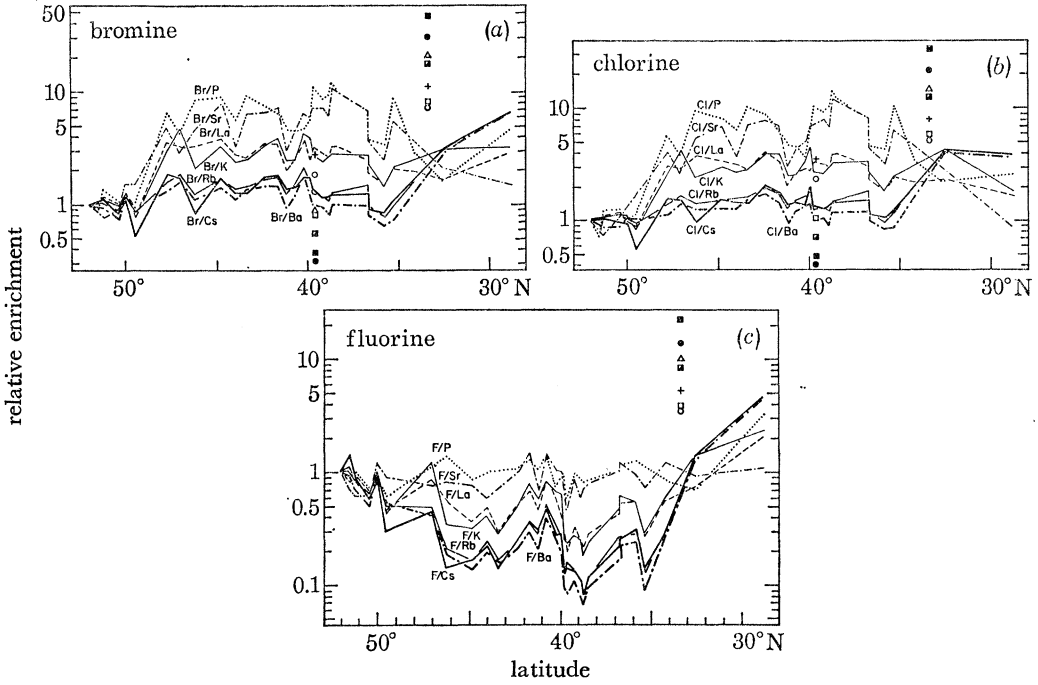

Figure 6. Variation of halogen/l.i.l.e. enrichment ratios along the M.A.R. Definition of enrichment factor is the same as in figure 5. Note the lack of variation for anion/cation ratios of similar size. Stations singled out by symbols are TR139 4D (picrite at *ca.* 33° N) and TR89 22D (metamorphosed basalts at *ca.* 40° N). Symbols stand for ratio of halogen to: Cs (filled squares), Ba (filled circles), La (open triangle), Rb (half-filled squares), P (crosses), K (open squares), and Sr (open circles). Remark given in figure 5 concerning region south of 32° N also applies here.

refractory Ba, all of which are of similar size. The same is true for the smaller ions F (volatile), Sr (refractory) or l.i.l.e. of intermediate size such as K (mildly volatile) and La (highly refractory). These results are not entirely unexpected as the partial pressure of trace volatiles such as the halogens in the mantle is insignificant compared with the load pressure. In other words, volatility loses its meaning for processes occurring well within the mantle (Ringwood 1975). Our results fully support this view, and suggest further that the ion size is not only important in controlling the distribution of incompatible l.i.l.e. in the mantle but also that of the trace halogens, F, Cl and Br, and probably iodine for which we have no data.

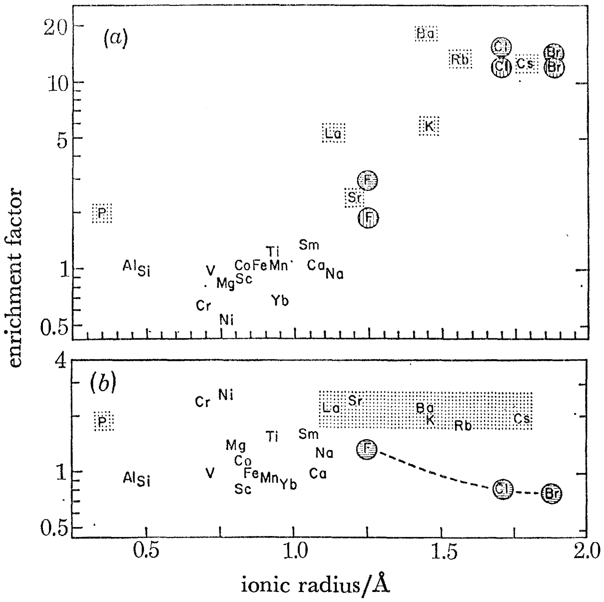

Figure 7. (*a*) Average enrichment factors of concentration ratios for M.A.R. basalts from the Azores transect (37–40° N) relative to M.A.R. basalts from the two normal ridge segments (49–52° N and 28–33° together) against ionic radius. Note the broad positive trend. Dotted squares are for l.i.l.e. and dashed circles for halogens (vertical lines, glasses; horizontal lines, pillow interiors). Data for l.i.l.e. are from White & Schilling (1978) and other elements from Schilling (1975*a*, 1980). (*b*) Average enrichment factors of concentrations for the Azores Island alkali basalts relative to the M.A.R. tholeiitic basalts over the Azores transect (37–40 °N). Note the twofold l.i.l.e. enrichment of the Azores Island alkali basalts independent of ionic size (dotted area), and depletion of F relative to Sr and P, and Cl and Br relative to Rb, Cs and Ba. Average concentrations and standard deviations for these three groups of basalts used to calculate the e.fs are given in table 2.

Finally, also noteworthy are the following points. (1) The ion size – enrichment correlation in figure 7 suggests that the effective ionic size of P is about 1.2 Å, thus indicating that P may occur as a complex in the mantle, rather than as a free ion. The observation confirms early inferences made by Goldschmidt (1937) and by Ringwood (1955). (2) Ti, which is often considered as an l.i.l.e., is only slightly incompatible.

Partitioning of F, Cl and Br in the mantle

Virtually nothing is known about the partitioning of F, Cl and Br between major solid phases and basaltic melts, or solid phases and a fluid phase (CO_2 and/or H_2O rich) in the mantle or during magma ascent and evolution.

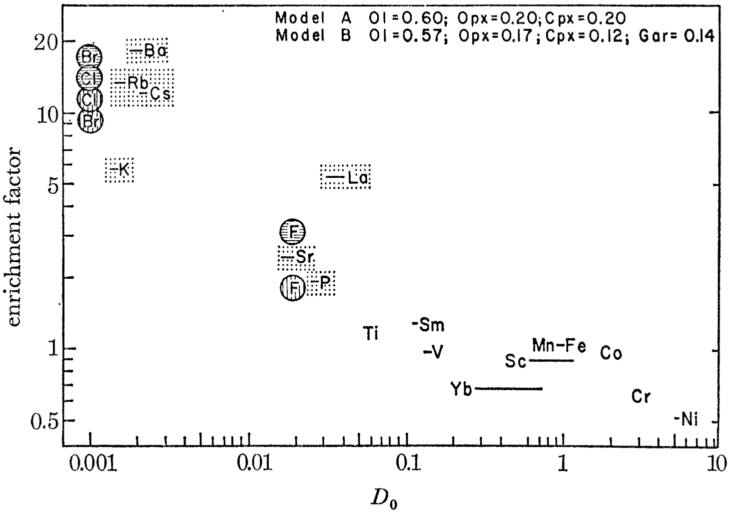

FIGURE 8. Average enrichment factor concentration ratios of M.A.R. basalts from the Azores transect (37–40° N) relative to the two normal ridge segments (49–52° N and 33–28° N) against bulk partition coefficient ($D_0 = \Sigma K_j X_j$), for a lherzolite mineralogical assemblage (model A, shown by chemical symbols), and a garnet lherzolite assemblage (model B, end of horizontal bar). The D_0 for the halogens are estimated from D_0 of l.i.l.e. on the basis of corresponding e.f. values. Note the broad negative correlation between e.f. values and D_0. Shaded areas have the same meaning as given in figure 7.

TABLE 3. CRYSTAL–MELT PARTITION COEFFICIENTS AND OTHER RELEVANT PARAMETERS USED TO CONSTRUCT FIGURE 8

						lherzolite†		garnet lherzolite	
element‡	*K* oliv.	*K* opx.	*K* cpx.	*K* gar.	*K* amph.	D_{II}	P_{II}	D_{II}	P_{II}
Cs	0.0004	0.004	0.008	0.002	0.05	0.0026	0.0053	0.0021	0.0048
Rb	0.0002	0.004	0.005	0.001	0.05	0.0019	0.0036	0.0015	0.0029
K	0.0002	0.0025	0.005	0.002	0.30	0.0016	0.0033	0.0014	0.0034
Ba	0.0001	0.006	0.006	0.001	0.10	0.0025	0.0045	0.0019	0.0035
La	0.0089	0.026	0.18	0.01	0.07	0.0465	0.106	0.032	0.090
Sm	0.0105	0.079	0.571	0.22	0.33	0.1360	0.332	0.12	0.37
Yb	0.023	0.470	0.560	4.0	0.46	0.219	0.408	0.72	2.16
Sr	0.0002	0.013	0.10	0.015	0.20	0.0227	0.058	0.016	0.054
Ni	8.9	3.8	1.4	0.25	1.5	6.38	3.75	5.9	1.16
P	0.043	0.014	0.009	0.15		0.030	0.018	0.049	0.076
Ti	0.007	0.12	0.16	0.13		0.060	0.11	0.062	0.14
V	0.011	0.26	0.5	0.2		0.159	0.33	0.14	0.34
Sc	0.13	0.6	1.6	5.5		0.518	1.03	1.1	3.36
Mn	0.81	0.8	0.43	2.0		0.732	0.60	0.93	1.19
Fe	1.3	0.66	0.28	0.88		0.968	0.61	1.0	0.60
Co	2.5	1.6	0.62	1.0		1.94	1.29	1.91	0.88
Cr	0.17	7.5	8.0	6.0		3.20	5.94	3.17	6.81
lherzolite									
X_j	0.6	0.2	0.2						
P_j	0.25	0.2	0.55						
garnet lherzolite									
X_j	0.57	0.17	0.12	0.14					
P_j	0.03	0.03	0.47	0.47					

† Bulk crystal–melt partition coefficient for trace element i; $D_i = \Sigma X_j K_{ij}$, where X_j is the phase proportion of phase $\alpha, \beta, \gamma \ldots, j$ and K_{ij} is the partition coefficient for element i between crystal $\alpha, \beta, \gamma, \ldots, j$ and the melt. $P_i = \Sigma p_j K_{ij}$, where p_i is the proportion of phase $\alpha, \beta, \gamma, \ldots, j$ entering the melt.

‡ Partition coefficients from Schilling *et al.* (1978) except for Rb, Cs, Sr and Ba evaluated from Hart & Brooks (1974) and Philpotts & Schnetzler (1970).

Some inferences can now be made concerning bulk (or apparently effective) partition coefficients of the halogens by using the apparent relation between ion radii and enrichment factors noted previously for both the halogens and l.i.l.e. (figure 7). Figure 8 shows the Azores Platform relative to 'normal' ridge enrichment factors as a function of reasonably well known bulk crystal–melt partition coefficients (D_0) for l.i.l.e. and other major and trace elements relevant to upper mantle conditions (see table 3 for values and sources). Two upper mantle mineral assemblages in equilibrium with the basaltic melt were considered, namely a lherzolite residual phase assemblage, and a garnet bearing lherzolite residual phase assemblage. A broad negative correlation is apparent between the l.i.l.e. enrichment factor (Azores Platform/normal ridge) and their bulk crystal – melt partition coefficients, for both models considered (figure 8). This is not surprising, as it is now fairly well established that the degree of incompatibility of l.i.l.e. in the mantle is directly related to the ionic size of these trace elements. The corresponding bulk crystal–melt partition coefficients of F, Cl and Br can be predicted on the basis of the close coherence of F with Sr and P, and Cl and Br with Cs, Rb and Ba. The bulk crystal–melt partition coefficients are of the order of 0.02 for F, and 0.002 for Cl and Br for both residual lherzolite and garnet lherzolite mineralogical assemblages considered in figure 8 and table 3. On this basis, the Br, Cl and F contents were estimated to be 0.2, 86 and 109 μg/g for the Azores mantle source, and 0.02, 7.3 and 65 μg/g for the l.i.l.e.-depleted asthenosphere, respectively. We assumed for these calculations a lherzolite mantle residual mineralogy and a 25% degree of melting, in both cases. Initial phase and eutectic proportions were taken from table 3 (lherzolite case), and we used equation (6) in the appendix.

TABLE 4. AVERAGE FRACTIONATION COEFFICIENTS (f) OF UNFRACTIONATED PAIR ELEMENT RATIOS RELATIVE TO CHONDRITES AND BULK EARTH

ratio[1]	Az. Platform[6]	N. Ridge[7]	M.A.R. avg.[8]	C 1 chondrite[2]	bulk Earth[3]	f_c[4]	f_e[4]	R_1/R_2[5]	T_1/T_2[3]
Br/Cl	0.0023	0.0027	0.0025	0.02	0.0054	0.12	0.47	1.09	1.0
Cl/Br	28.7	29.3	29.0	123	43	0.24	0.67	1.10	0.76
Cl/Cs	2280	2200	2240	1497	424	1.50	5.3	0.99	0.76
Cl/Ba	2.1	3.0	2.5	112	4.9	0.023	0.52	1.19	0.52
F/Sr	1.8	2.4	2.1	20	2.9	0.11	0.73	1.03	0.52
F/P	0.38	0.41	0.39	0.169	0.025	2.3	16.0	1.00	0.80
Rb/Cs	79.5	75.0	77.3	12.2	9.83	6.3	7.8	0.88	1.00
Rb/Ba	0.073	0.10	0.087	0.91	0.11	0.096	0.77	1.09	0.68
K/La	348	318	333	1600	354	0.21	0.94	1.29	0.68
Cs/Ba	0.00092	0.0013	0.0011	0.075	0.012	0.015	0.098	1.24	0.68
P/Sr	4.84	5.9	5.38	120	118	0.045	0.045	1.03	0.65
Ti/Sm	2140	2400	2270	2050	3960	1.1	0.57	0.90	0.94
Br/Rb	0.066	0.079	0.072	2.5	0.23	0.029	0.31	1.20	0.76
Br/Cs	5.26	5.9	5.59	30.0	2.3	0.19	2.5	1.09	0.76
Br/Ba	0.0048	0.0080	0.0064	2.2	0.026	0.0029	0.24	1.30	0.52

[1] By mass.

[2] Mason (1971).

[3] T is temperature of condensation from a nebula of solar composition at 10^{-4} atm (ca. 10 Pa) estimated from fig. 1 of Ganapathy & Anders (1974).

[4] Fractionation coefficients: e.g. $f_c = (\mathrm{Br/Cl})_{\mathrm{M.A.R.\ avg.}}/(\mathrm{Br/Cl})_{\mathrm{C1\ chondrites}}$, and $f_e = (\mathrm{Br/Cl})_{\mathrm{M.A.R.\ avg.}}/(\mathrm{Br/Cl})_{\mathrm{bulk\ Earth}}$.

[5] R is ionic radius in sixfold coordination (Whittaker & Muntus 1970).

[6] Average for M.A.R. basalts over the Azores platform transect (37–40° N).

[7] Average for M.A.R. basalts along the two normal ridge segments (49° N and 28–33° N).

[8] Average for M.A.R. basalts from 29° N to 52° N (averaged out from values in columns 2 and 3).

NATURE OF UNFRACTIONATED l.i.l.e. AND HALOGEN PAIR RATIOS

Trace element pair ratios that appear unfractionated along the M.A.R. are of great interest, as their values provide a clue to the composition of a more primitive precursor mantle, before the heterogeneities in the mantle that we have just described occurred. The values of these trace element ratios are listed in table 4. Fractionation coefficients are compared in figures 9 and 10 relative to carbonaceous chondrites and estimates for the bulk Earth made by Ganapathy & Anders (1974) respectively, and as a function of their *relative* ionic radii and estimated temperature of condensation for a solar nebula (Ganapathy & Anders 1974). It can be seen that (1) a broad correlation is observed between fractionation coefficients relative to *chondrites* against both relative ionic radii or condensation temperatures (figure 9); (2) the greater the difference in volatility or ionic radius between each element of these pairs, the greater is the departure from the chondritic value (fractionation coefficient of unity); (3) for comparable ion size the halogens are most depleted relative to chondrites and refractory elements, the alkali elements to a lesser extent, and refractory element pairs have chondritic values; (4) element pair ratios of nearly identical ionic radii and volatility are nearly chondritic whether the element pair is composed of two refractory elements (e.g. Ti/Sm) or of two volatile elements (e.g. Cl/Br) (figure 9). We can further infer that mechanisms of fractionation in the course of the formation of this precursor mantle from a primitive solar composition must have involved, at some undetermined time, both condensation (to satisfy the volatility dependence) and crystal and melts or fluids (to satisfy the ionic radii dependence).

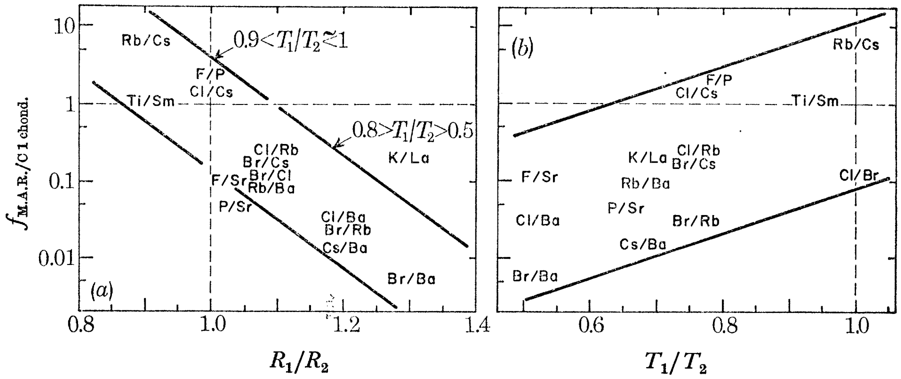

FIGURE 9. Fractionation coefficients, *f*, for average M.A.R. basalts relative to average C 1 chondrites for 'coherent' l.i.l.e. and halogen ratios of similar ionic size (deviating by less than 30%) as a function of (*a*) ratio of ionic size (Whittaker & Muntus 1970) and (*b*) ratio of temperature of condensations (estimated from fig. 1 of Ganapathy & Anders 1974). Note the broad correlation, with $f \rightarrow 1$ as $R_1/R_2 \rightarrow 1$, especially for group with $T_1/T_2 \rightarrow 1$ (particularly for refractory elements such as Ti/Sm). The value of $f = 1$ corresponds to chondritic relative abundance ratio. Coherent l.i.l.e. and halogen ratios are those that remain practically constant along the M.A.R. (see figures 5 and 6).

Finally, comparison of these pair ratios with Ganapathy & Anders's estimate for the composition of the bulk Earth (figure 10) shows the following: (1) the volatility dependence noted previously against chondrites is mostly lost, whereas the ionic size dependency is not entirely cancelled if ratios involving P and Cs are not considered for reasons discussed later; (2) the spread in fractionation is much reduced, and these ratios tend to approach more closely Ganapathy & Anders's estimated values for the bulk Earth (i.e. fractionation coefficient of unity). These results are expected, as it is now well established that the Earth is strongly depleted in halogens and to a lesser extent in alkali metals (Gast 1960; Ganapathy & Anders 1974). It is doubtful that once the Earth accreted and acquired its component of volatiles that relative volatility may have played any significant role in the fractionation of trace elements during subsequent high pressure evolutionary processes in the mantle. Formation of an iron core is not likely to have affected l.i.l.e. and halogen pair ratios of similar ionic radii in the mantle, except for the possible incorporation of phosphorus which now appears notably depleted relative to Sr and F estimates for the bulk Earth, because of its siderophilic affinity (figures 9 and 10). In contrast, subsequent crust formation is likely to have involved crystal and melts or fluids, and ionic size dependent fractionation in the mantle is apparently to be expected, no matter how small the difference in ionic radii between these lithophile element pairs may be.

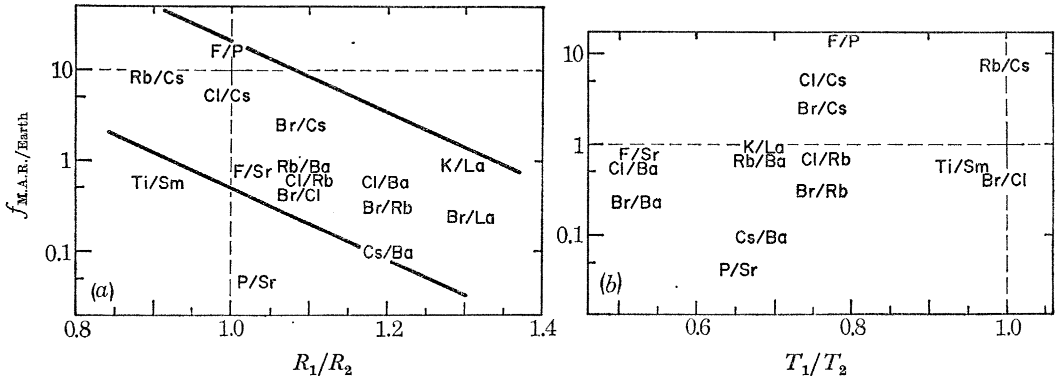

FIGURE 10. Same as figure 10 but fractionation coefficients, *f*, are relative to bulk Earth l.i.l.e. and halogen ratios, as estimated by Ganapathy & Anders (1974). Note that the ratio of these 'coherent' l.i.l.e. and halogens along M.A.R. deviate by less than a factor of 10 relative to bulk Earth estimates but by a factor of 100 relative to C 1 chondrite (figure 10). Ratios involving P and Cs are exceptions (see text).

AZORES ISLANDS COMPARED WITH M.A.R. OVER THE AZORES PLATFORM

The location of historical subaerial volcanic eruption on the Azores islands shows no relation to distance from the M.A.R. ridge axis. It represents intraplate volcanism predominantly alkalic in nature. This is in marked contrast with the ridge transect over the Azores Platform which is uniquely tholeiitic. Our present sampling for the islands includes only basic lavas. Enrichment factors for F, Cl and Br, and l.i.l.e. (taken from White & Schilling 1978) between the Azores island alkali basalts and ridge basalts transecting the Azores Platform are illustrated in figure 7*b* (see also table 2). In marked contrast to the M.A.R., l.i.l.e. and halogen enrichments of the island basalts relative to those on the M.A.R.–Azores transect show no relation to cationic or anionic size. The l.i.l.e. on the islands are all uniformly enriched by a factor two, whereas Cl and Br are distinctly lower than l.i.l.e. of similar size, and thus appear depleted. F is slightly enriched in the island alkali basalts, but yet it is distinctly lower in concentration than its companion Sr ion of similar size. *A priori*, three alternative hypotheses can be invoked to explain this discrepency:

1. As the island lavas were subaerially erupted, the Cl and Br depletion is likely to have been caused by outgassing during ascent of lava above the critical pressure (or depth) of degassing of major volatiles as water and CO_2. The intermediate enrichment in F is consistent

with the fact that it does not have a strong degassing tendency (Rowe & Schilling 1979). Some F loss is, however, suggested by comparing the enrichment with that of Sr.

2. The twofold l.i.l.e. enrichment in the Azores Island alkali basalts relative to the ridge tholeiites over the platform, but similar $^{87}Sr/^{86}Sr$, suggest a factor of one-half for melting beneath the islands, and a similar mantle source composition for both regions, San Miguel excluded (White *et al*. 1979). Because of the lower inferred degree of melting it is also conceivable that the halogens could have been retained in residual mantle phases such as amphibole or phlogopite during the partial melting, or that such minerals were removed as phenocrysts either during the ascent of the lavas or in a magma chamber. The strong partitioning of F for phlogopite relative to an aqueous fluid phase or a melt is experimentally well established (e.g. by Munoz 1969), but to our knowledge no such data seem to exist for Cl or Br for either phlogopite or amphiboles. To our knowledge no F partition factors have been determined between amphiboles and a melt or a fluid phase. However, analyses of phlogopite and amphiboles are usually significantly higher in F than Cl (see, for example, Deer *et al*. 1967).

A greater retention of F relative to Cl by residual phlogopite or amphibole would then be expected (assuming a comparable F and Cl content in the system). But the fact that Cl and Br, and not F, are depleted in the alkali basalts does not support retention of the halogens by residual amphibole or phlogopite in the mantle beneath the islands. Furthermore, any fractional crystallization of these minerals must have been only minor, or non-existent. This alternative model can be further dismissed in the case of phlogopite by considering the partitioning of l.i.l.e. (Philpotts & Schnetzler 1970). Phlogopite–melt partition coefficients suggest that not only F but also Cs, Rb and K should have been preferentially retained in the mantle beneath the islands relative to La or Sr. Yet all of these l.i.l.es appear unfractionated and enriched by a factor of two in the alkali basalts relative to the ridge tholeiites over the Azores Platform (figure 7*b*). The Ti enrichment is also not consistent with such a model. We have dismissed this second hypothesis, and emphasize the preferential degassing of Cl and Br relative to F from the Azores island alkali basalts erupted subaerially or at depths above 500 m (or less than 50 bar). This is further evident from the F, Cl and Br enrichments of submarine glassy basalt TR89 11-GCg which in this case are similar to those of the l.i.l.e. This fresh glassy lava was dredged from a small seamount on the northwest flank of Terceira island at a depth of 2295 m. No degassing would be expected in this case. The relative F, Cl and Br enrichments appear supportive.

3. Involvement of apatite either as a residual phase during partial melting or during factional crystallization can also be dismissed as an important factor in fractionating Cl from the large l.i.l.e., Cs, Rb and Ba; or F from Sr and P. P does not show any sign of depletion, but is also enriched by approximately a factor of two as other l.i.l.es, including Rb and Ba which are known to be effectively rejected by apatite, and Sr which has a strong affinity for apatite relative to silicate melts (see, for example, Deer *et al*. 1967).

Model constraints

Geochemical observations obtained in this study and previous ones constraining *modelling* the origin of the North Atlantic geochemical anomaly are the following:

1. The F, Cl and Br broad *relative* variations along the M.A.R. are similar to those of $^{87}Sr/^{86}Sr$ and l.i.l.e. and cannot be simply the result of processes occurring at shallow depth

such as partial melting, fractional crystallization or preferential degassing by vesiculation. The characteristic 'camel-back' patterns like those of $^{87}Sr/^{86}Sr$, l.i.l.e. and halogens reflect mantle heterogeneities that must have been generated by processes occurring within the mantle.

2. Relative volatility does not seem to have been a significant factor in establishing such mantle *heterogeneities*. This readily rules out the possibility of linking the heterogeneities to relative condensation and accretion early in the Earth's history. A similar conclusion can be reached on the basis of radiogenic Sr and Pb isotope systematics (see, for example, Hutchison 1976). On the other hand, the cationic or anionic size of the l.i.l.e. and halogens seem to have played a preponderant role in controlling their fractionation. This suggests that processes involving crystal–melt or crystal–fluid appear the most likely mechanism(s) responsible for the l.i.l.e. and halogen mantle heterogeneities observed beneath the North Atlantic. However, this is not necessarily so for the segments characterized by large-scale $^{87}Sr/^{86}Sr$ *gradients* which put further constraints on probable dynamical conditions and/or timing of fractionation events in the mantle (White & Schilling 1978).

3. Diffusion cannot account for the several hundred kilometres long *gradients* in l.i.l.e., halogens, and $^{87}Sr/^{86}Sr$ observed along the M.A.R., whether occurring in the solid, or short-circuited through intergranular fluids (Hoffman & Hart 1978). The Earth is too young for such long gradients to develop between heterogeneous mantle domains juxtaposed early in the Earth's history.

4. The possibility of explaining the l.i.l.e. *gradients* by variable partial melting and/or fractional crystallization of melts derived from a single mantle source is rejected as it can explain neither the $^{87}Sr/^{86}Sr$ variations (White *et al.* 1976; White & Schilling 1978), nor the relative volume production rates of lavas along the ridge (Schilling 1973*a*, 1975*a*). A single mantle source model is also rejected from the observed La/Sm variation for the Azores region, and from La and Sm crystal–melt partitioning. It would require acceptance of production of tholeiitic melts in the range of practically 0–100 % (Schilling 1975*b*; Schilling *et al.* 1979). Only a mantle made of eclogite could be reconciled with such evidence.

5. The mantle plume–l.i.l.e. depleted asthenosphere mixing hypothesis previously proposed to circumvent such difficulties has the advantage of readily explaining with a simple dynamic model the geochemical *gradients* observed, whether they are isotopic ratios or ratios of l.i.l.e. (Schilling 1973*a*, 1975*b*; White & Schilling 1978). In this context, our results would suggest that the Azores mantle plume is also richer in halogens and other volatiles such as water, in comparison with the l.i.l.e. depleted asthenosphere. However, the plume model does not specify what kind of process of fractionation in the mantle produced in the first place the heterogeneities between the asthenosphere and the mantle plume masses! We have rejected the possibility that the fractionation may have been inherited early in the history of the Earth during condensation and accretion. This is also evident from the close correlation between Rb/Sr and Sm/Nd radiogenic isotope systematics. It is now clear that if the Earth had originally a chondritic Sm/Nd ratio, neither the mantle source of ridge tholeiites from the Azores Platform nor from 'normal' ridge segments could have evolved as closed systems since primordial time. The $^{87}Sr/^{86}Sr$ of both sources are too low, and the $^{143}Nd/^{144}Nd$ too high, for such a premise (O'Nions *et al.* 1979; Richard *et al.* 1976; DePaolo & Wasserburg 1976*a*, *b*). Both mantle sources must have suffered some depletion of the larger ion in both Rb/Sr and Nd/Sm ratios relative to their bulk Earth value, thus implying fractionation event(s) more recent than 4.55 Ga (4.55×10^9 years), the age of the Earth. A chondritic bulk Earth for the two

refractory elements Sm/Nd ratio equal to 0.308 (atomic) is now well supported from Nd isotope evidence (O'Nions *et al.* 1979; DePaolo & Wasserburg 1976*a*, *b*). Arguments for a bulk Earth originally depleted in the relatively volatile Rb compared with refractory Sr is also well established (Gast 1960; Ganapathy & Anders 1974), and is further confirmed from the ^{87}Sr/^{86}Sr–^{143}Nd/^{133}Nd correlation observed in young oceanic volcanic rocks which suggests a bulk Earth Rb/Sr equal to 0.03 (DePaolo & Wasserburg 1976*a*, *b*; O'Nions *et al.* 1979).

6. The actually measured Rb/Sr and Sm/Nd ratios of 'normal' ridge basalts studied are in full agreement with implications based on ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd and their time-averaged parent/daughter ratios discussed above. There is also no conceptual problem to account for a progressive depletion in l.i.l.e. and halogen contents of the relatively shallow asthenosphere source of normal ridge basalts by successive partial melting and melt removal during geological time (Schilling & Winchester 1967; Gast 1968; Green & Ringwood 1967; Kay *et al.* 1970; Schilling 1973*a*).

7. In contrast, the tholeiitic ridge basalts from the Azores Platform have actually higher Rb/Sr and lower Sm/Nd than the bulk Earth estimate, although arguments based on ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd suggest the converse (DePaolo & Wasserburg 1976*a*, *b*; O'Nions *et al.* 1979). Two alternatives can be invoked to reconcile such inconsistency. (i) The Rb/Sr and Sm/Nd ratios of such basalts are not representative of their mantle source as commonly assumed, which would also imply that ridge basalts from the Azores would have been produced by smaller degrees of melting than generally accepted (and derived from a larger volume of mantle than beneath normal ridge segment to satisfy lava production rates). The validity of this alternative cannot be established from trace element arguments and would have to be decided purely on petrological grounds. So far, degrees of melting greater than 10–20 % are generally accepted for the production of tholeiites. Alternatively, (ii) the Rb/Sr and Sm/Nd ratios of the Azores Platform ridge basalts are representative of their mantle source, in which case we must seek a mechanism of enrichment of the Rb relative to Sr, and Nd relative to Sm in the relatively recent past within the mantle. Such a mechanism of enrichment of large relative to smaller ions in the mantle is not as readily apparent as in the case of depletion of the l.i.l.e. depleted asthenosphere by successive partial melting and melt removal. Metasomatism is one possibility.

It is also impossible to constrain the time of such enrichment unless a model age is calculated for the Azores mantle source, or it is assumed that both the Azores mantle plume and the l.i.l.e.-depleted asthenosphere have been derived from a common mantle source previously isotopically homogeneous. In the later case, the earliest timing of such fractionation event is 230–400 Ma, judging from the ^{87}Sr/^{86}Sr versus ^{87}Rb/^{86}Sr pseudo-isochron correlation of these Mid-Atlantic Ridge basalts (White & Schilling 1978). In the plume model, such correlation was interpreted as reflecting mixing (White & Schilling 1978). Curiously enough, ^{143}Nd/^{144}Nd against ^{147}Sm/^{144}Nd of basalts from Iceland and the Reykjanes Ridge reported by O'Nions *et al.* (1979) also suggest an age of 240 Ma. If such a pseudo-isochron is valid, it would indicate that a major fractionation event occurred beneath the Atlantic before its opening 100–200 Ma ago (Pitman & Talwani 1972). However, we need to establish the mechanism by which these two mantle domains and the intermediate geochemical zoning observed near the Azores would have developed.

8. It is worth exploring whether a CO_2 rich fluid, an H_2O rich fluid, an interstitial melt or a solution of these components is the dominant liquid phase involved in the crystal–liquid fractionation suggested. Comparison of existing experiments on rare earth element (r.e.e.)

partitioning at various pressures and temperatures between crystal–melt and crystal–H_2O or CO_2 rich fluid (see table 3, Shimizu & Kushiro 1975; Mysen 1978*a*, *b*), suggest that the liquid phase, whether it is a silicate melt, an H_2O or a CO_2 fluid phase, plays a relatively passive role in controlling the *relative* r.e.e. partitioning in comparison to the crystals. *Relative* r.e.e. and l.i.l.e. patterns of partition coefficients appear to reflect dominantly (1) the lattice characteristics of the mineral coexisting with the loosely structured silicate melt, and (2) the ionic size of the r.e.e. and l.i.l.e.; whereas absolute partition coefficient values are likely to be dependent on liquid composition. However, this may not be necessarily so for the partitioning of halogens between silicates and fluid phases. Available experiments on the partition of F and Cl between silicate mineral–H_2O fluid at relatively low pressure indicate a contrasting behaviour between the two halogens; namely F prefers the silicate mineral whereas Cl prefers the H_2O fluid phase (Kilinc & Burnham 1972; Burnham 1967). The distinctive behaviour of F and Cl during vesiculation at depths shallower than 500 m on the Reykjanes Ridge is another example of such contrasting behaviour of F and Cl partitioning between silicates and H_2O rich fluids (Unni & Schilling 1978*a*; Rowe & Schilling 1979). An inverse relation would then be expected between F and Cl, provided such experiments remain valid at the higher pressure prevailing in the mantle.

The fact that both Cl and F and other l.i.l.e. of similar size are enriched beneath the Azores relative to 'normal' ridge segments tends to minimize the possibility that an H_2O rich fluid phase is actually the type of liquid involved in the crystal–liquid partitioning in the mantle. However, before dismissing the possibility of the involvement of an H_2O rich fluid phase, it needs to be emphasized that (1) the existing Cl partitioning experiments are for alkali rich silicate systems, and not for mantle-like compositions; (2) the experiments are at relatively low pressure and therefore not readily applicable to the mantle; (3) the extent of Cl degassing during lava vesiculation occurring at depths shallower than 500 m on the Reykjanes Ridge appears to be dependent on the lava composition (Unni & Schilling 1978*a*), thus suggesting a compositional dependence for Cl partitioning between silicate melt–H_2O rich fluid; and (4) the M.A.R. basalts erupted over the Azores Platform and 45° N tend to be significantly higher, not only in halogens, but in H_2O as well.

9. The possibility of distinguishing between involvement of a CO_2 rich fluid phase rather than a silicate melt cannot be established at this time as no experiment exists for the partitioning of silicate mineral – CO_2 rich fluid for the halogens. To our knowledge the only pertinent experiment for l.i.l.es is that of Koster Van Groos (1975) for Sr and indirectly those of Wendlandt & Harrison (1979) for r.e.e. The degree of incompatibility of Sr and r.e.e. for silicate minerals are of similar magnitude whether a CO_2 rich fluid or a silicate melt coexists as the liquid phase at high pressure (*ca.* 20 kbar), thus leaving the question unresolved. However, presence of CO_2 fluid or silicate melts are not ruled out from existing evidence. In fact, CO_2 rich gases in popping glassy lavas have been reported from 36° N near the Azores (Hékinian *et al.* 1973).

MODEL: MANTLE PLUME FORMATION BY FLUID RELEASE AND METASOMATISM

We have indicated that a mechanism of l.i.l.e. enrichment and fractionation other than partial melting and melt removal must have operated within the mantle beneath the Azores. Furthermore, the volatile enrichments making the Azores hotspot also a 'wetspot' need to be explained. The plume model by itself does not explain how it became in the first place fertile in both l.i.l.e. and volatiles. However, the plume–l.i.l.e.-depleted binary mixing model remains a useful model to explain large-scale geochemical gradients, and equally important for explaining abrupt discontinuities in l.i.l.e. contents at fracture zones near hotspots (Schilling *et al.* 1974, 1980). The possibility of phase transformation other than melting during mantle advection deserves some attention. Transformations involving only solid phases are not likely to generate the trace element enrichment and ionic size dependent fractionation needed, as the system during the change of state most probably remains closed to all phases. However, it is conceivable that fluid released and percolating during phase transformations (Fyfe & McBirney 1975; Mysen *et al.* 1978), such as by decarbonation and dehydration reactions (Wyllie 1977*a*, *b*; Fyfe 1970; Akimoto *et al.* 1977) or incipient melting, could transport and concentrate incompatible elements in upper zones of the mantle. Figure 11 depicts a model featuring a deep upwelling region centred beneath the Azores hotspot, with two principal *hypothetical* zones of phase transformation. The deeper phase transition zone involves generation of a fluid phase.

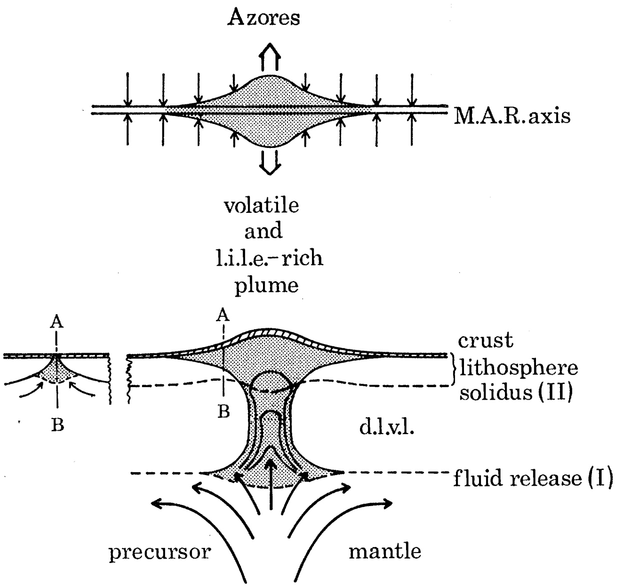

FIGURE 11. Model for development of a mantle plume by fluid release (phase transition I) and metasomatism (shaded zone) during mantle convection (thick arrows); followed by partial melting (phase transition II). D.l.v.l. stands for l.i.l.e.-depleted low velocity layer (assumed of lherzolite mineralogy see table 3 and text); whereas convecting precursor lherzolite mantle (thick arrows) is assumed to bear garnet. The phase transition between these two types of mineral assemblages is not shown for clarity (but could coincide with phase transition I). Phase transition I does not necessarily coincide with the solidus of the precursor mantle mineral assemblage, but could (not shown for clarity). Subaxial ridge magma chambers beneath the crust are not shown for clarity. Thin arrows on top and left-hand bottom diagrams show flow patterns of d.l.v.l. material towards the ridge axis. Shaded area is for more buoyant and less viscous l.i.l.e. and fluid-rich mantle (plume) compared with d.l.v.l. Lines within shaded area illustrate the development of the mantle plume upwelling with time.

Flow lines located near the centre of the upwelling go through the reaction and generate a small flux of interstitial fluids (CO_2, H_2O or interstitial melts, or a solution of these three components), whereas flow further out does not go through the deeper phase transition. A flux gradient of fluids would be generated. During the process, incompatible elements are preferentially partitioned into the fluid phase to an extent depending primarily on their ionic size and the mineralogy of the upwelling mass. Fractionation is particularly effective if garnet is present because of its strong rejection of large incompatible ions when in equilibrium with a fluid or a melt (Shimizu & Kushiro 1975; Mysen 1978*a*, *b*). Therefore the deeper phase transformation (I) in figure 11 is assumed to occur within the field stability of garnet. Owing to higher buoyancy, the l.i.l.e. rich fluid migrates upward faster than the silicate mass, thus metasomatizing the mantle above. Presumably, this in turn could generate an instability owing to the effect of the fluid on the rheological properties of the mantle above (Goetze 1977), causing a mantle diapir enriched in l.i.l.e. and halogens to develop. Zone of transformation (II) in the upper asthenosphere involves partial melting and represents the low velocity layer (figure 11). Upon subsequent continental breakup and drifting the l.i.l.e.-depleted asthenosphere material passively migrates toward the zone of plate divergence and melts further in proportion to the amount of decompression, the existing thermal field and the composition of the mass. So does the 'plume', except that excess 'plume'-derived slush material flows preferentially along the ridge axis and mixes with l.i.l.e.-depleted slush (figure 11). A deeper zone of melting and greater flux of melt (not necessarily greater proportions of melt to crystal per unit volume) is expected beneath the centre of upwelling (Azores platform), primarily because of the higher geothermal gradient and higher content of the major fluid present beneath the region. A third stage, consisting of accumulation of melts in magma chambers at the base of the thin crust beneath the rift, is also expected, but is not shown in figure 11 for clarity. Fractionation in such magma chambers may affect to some extent compatible to less compatible element ratios, obliterating in part ideal interelement correlations expected for binary mixing.

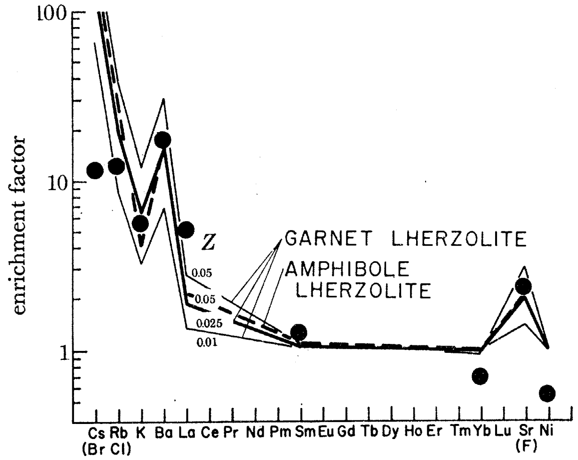

FIGURE 12. Comparison of: (1) predicted patterns of enrichment factor ratio of l.i.l.e. (solid and broken lines) based on the two-stage model described in figure 11, the appendix and text, with (2) actual average enrichments (filled circles) observed in basalts of the M.A.R. transect over the Azores (37–40° N) relative to average normal ridge basalts (49–52° N and 33–28° N combined). $F = 0.005$; $Y = 0.25$. Note the similarity of the predictive and actual pattern observed, except for Cs (see text and appendix). Parameters F, Y and Z are defined in the appendix.

A quantitative description of the trace element fractionation and enrichment during this primarily three-stage process is complex. Various models can be considered depending on assumptions made on physico-chemical conditions of equilibrium during the first phase transformation, subsequent fluid migration and mixing, and how continuous or discontinuous the dynamics of the processes is (e.g. continuous fluid or melt separation against batch separation; whether fluids and melts coexist or not; whether a two stage process rather than a steady state is invoked, etc.).

One possible quantitative formalism describing the trace element behaviour during this multi-stage process is given in the appendix. The choice of equilibrium and dynamic conditions is mostly arbitrary and cannot be defended. However, numerical examples shown in figure 12 indicate that acceptable relative l.i.l.e. enrichments of melts erupted over the Azores relative to normal ridge can be obtained. The model assumes a garnet peridotite mantle for the deep phase transformation releasing fluids, and a lherzolite mantle for the partial melting of both the plume and the l.i.l.e.-depleted asthenosphere. Crystal–melt partition coefficients listed in table 3 were used for both phase transformations, for lack of relevant crystal–fluid data. However, the relative patterns of partition coefficients for the r.e.e. for garnet–H_2O fluid and garnet–melt reported by Mysen (1978*a*, *b*) and Shimizu & Kushiro (1975), respectively, show little deviation from each other. Because of the minerals olivine, orthopyroxene, clinopyroxene and garnet present in the mantle, garnet dominates the r.e.e. fractionation (Schilling 1975*b*); our results may well apply to a crystal–H_2O fluid partitioning situation, but not necessarily to a crystal–CO_2 fluid situation for which there are no direct experimental data. Ganapathy & Anders's bulk Earth composition was used for the deep precursor mantle, whereas White & Schilling's (1978) estimate was used for the l.i.l.e.-depleted asthenosphere present beneath the normal ridge segment. Solutions matching the observations reasonably well can readily be obtained if for every 1 g of mantle material produced by metasomatism, 5–10 g of precursor mantle material is processed through the deep phase transition, and releases 0.25–0.5 % of fluids. These numerical solutions are of course not unique and depend directly on the precursor and l.i.l.e.-depleted asthenosphere compositions assumed. It can also be shown that this particular model is not very sensitive to the type and relative mineral proportions of the mantle assumed. For example, substitution of amphibole for garnet for the deep phase transformation gives equally acceptable solutions (figure 12). Further discussion of the relative importance of the many variables involved seems premature in view of the many uncertainties and lack of adequate crystal–fluid partition coefficient data. However, the point to be made is that both a reasonable mechanism for l.i.l.e. enrichment and fractionation in the mantle plume, and the right order of magnitude of relative enrichments, can readily and quantitatively be obtained. At the same time, we can preserve the usefulness of the mantle plume–l.i.l.e.-depleted binary mixing model for explaining the geochemical gradients and/or discontinuities at fracture zones.

Conclusions

1. The high enrichment of halogens and water in basalts from the Azores ridge transect suggest that the Azores hotspot is indeed also a wetspot.

2. The M.A.R. halogen profile is similar to that of $^{87}Sr/^{86}Sr$, La/Sm and other l.i.l.e. ratios, which suggests a comparable heterogeneity in content of halogens in the mantle source of these basalts.

3. The two large halogen anions Cl and Br behave geochemically similarly to large incompatible elements Ba, Rb and Cs, and the smaller F anion similarly to the less incompatible element Sr and P. Ionic radii play a major role in the fractionation of halogens in the mantle, whereas relative volatility does not. This suggests that crystal–liquid (melt and/or fluid)

processes were involved in the enrichment and fractionation of l.i.l.e. and halogens in the mantle beneath the Azores relative to the l.i.l.e.-depleted asthenosphere source of normal ridge basalts.

4. Coherent l.i.l. and/or halogen element pair ratios of similar size lack variation along the M.A.R. This suggests that both the l.i.l.e.-depleted asthenosphere and the Azores mantle may have been derived from a common, more primitive, precursor mantle remotely in the past. The earliest such separation could have occurred is 240–400 Ma if the pseudo-isochron $^{87}Sr/^{86}Sr$ against Rb/Sr correlation were to be given an age significance (White & Schilling 1978).

5. The value of these unfractionated l.i.l.e. and halogen pair ratios in M.A.R. basalts provide an estimate of the composition of such a precursor mantle. Its relative trace element composition does not resemble that of carbonaceous chondrites, except for pairs of refractory trace elements of practically identical ionic size. The precursor mantle is strongly depleted in halogens and to a lesser extent in large alkali ions Rb and Cs relative to refractory trace elements of similar size such as Ba. These relative depletions tend to approach those estimated for the bulk Earth by Ganapathy & Anders (1974) with the exception of Cs whose abundance in meteorites is also problematic (Laul *et al.* 1973; see also Smith 1977).

6. Fractionation coefficients for these coherent halogen and l.i.l.e. pair ratios relative to corresponding chondritic ratios correlate with either their relative differences in ionic radii or temperature of condensation. This suggests that both processes of condensation and crystal–liquid (melt and/or fluid) must have been involved in the course of formation of the upper mantle from a solar nebula. There is also evidence to suggest that a significant portion of the phosphorus content of the Earth has been removed into the core.

7. With the exception of San Miguel, subaerial alkali olivine basalts from the Azores islands appear to have been derived from the same mantle source as tholeiitic basalts from the ridge transect over the Azores Platform, but by half as much partial melting. There is also evidence that the subaerial Azores basalts have been partially degassed in Cl, Br and F before solidifying. The order of intensity of degassing is Br, Cl, F.

8. Volatiles may have played a key role in the development of the Azores Platform. They might have enhanced convection beneath the Azores by lowering its viscosity. They could also have lowered the melting point of such advecting mantle and increased the amount of melt produced over a deeper region, as well as influencing the composition of such melts. It is now well established that high CO_2/H_2O in the mantle should favour production of silica-deficient melts (Eggler & Holloway 1977; Mysen 1977; Wyllie 1977*a*, *b*). Several ridge basalts from the Azores Platform in fact have lower SiO_2 than commonly found elsewhere along the M.A.R., suggesting that CO_2 may have played a significant role in their genesis. However, the quantitative effect of higher Cl, Br and F content beneath the Azores on melt temperature and composition remains unknown as no experimental data applicable to mantle compositions are yet available. It is also uncertain whether such an effect is of any significance at the halogen concentrations existing beneath the Azores.

9. To judge from (*a*) the limited number of experiments on Cl and F partitioning between crystal–melt and melt–H_2O fluid available (for granitic systems!) which indicate strong preference of Cl for the H_2O fluid but not for F, (*b*) the lack of Cl/F fractionation to the extent that would be expected from such contrasting partitioning behaviour, and (*c*) our previous remarks on SiO_2 content, it is suggested that H_2O may not be the dominant major fluid present

beneath the Azores, but rather CO_2. This inference is also supported from the actual gas composition of popping basaltic glasses near the Azores reported by Hékinian *et al.* (1973), and the composition of gas-filled vesicles of other mid-ocean ridge glassy basalts reported by Moore *et al.* (1977).

10. Experimental evidence by Flynn & Burnham (1978) suggests that high halogen contents may also well have affected the crystal–melt and/or crystal–fluid partitioning of l.i.l.e. beneath the Azores.

11. The importance of the fluid release mantle plume model proposed is not in the details of the dynamics suggested, which are *ad hoc*, but in the emphasis of the need to search for a mechanism by which l.i.l.e. and halogen enrichments and fractionation can be generated within the mantle itself beneath the Azores. As indicated, such a mechanism of enrichment is needed to explain l.i.l.e. and halogen enrichments, and inferences on the nature of the mantle beneath the Azores hotspot based on Rb–Sr and Sm–Nd isotopic systematics. The model is designed to focus in the future on the possible role that fluid release during mantle convection may have on the geochemistry and rheology of the mantle, petrogenesis, and origin of shallow oceanic platform such as the Azores. It is a working model which needs further testing by using radiogenic isotopes, experimental crystal–fluid partitioning at high pressure and temperature, and theoretical and experimental hydro-dynamical and rheological modelling. However, variable mixing at some stage or another is required to account for the large-scale isotopic, halogen and l.i.l.e. gradients observed about the Azores, as diffusion alone is untenable over such large distances given the age of the Earth.

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APPENDIX

(*a*) *Azores ridge transect*

The following three-step processes are considered for generation of ridge basalt beneath the Azores Platform.

1. The trace element composition of the aggregate liquid released during the deep phase transformation I, which upon percolation accumulates above such transformation, is given by

$$\bar{C}_f = \frac{C_I}{F}\left[1-\left(1-\frac{P_I F}{D_{0,I}}\right)^{1/P_I}\right]. \tag{1}$$

This equation is adapted from equation (14) of Shaw (1970), where $\bar{C}_f$ is the trace element concentration in the aggregate fluid; C_I is the trace element concentration in precursor mantle; $D_{0,I} = \Sigma_1^n K_{j,I} X_{j,I}$, the initial bulk crystal–fluid partition coefficient; $K_{j,I}$ is the trace element partition coefficient between residual phase $\alpha_I, \beta_I, \gamma_I, \ldots, j_I$ and the fluid; $X_{j,I}$ is the mass fraction of original phases $\alpha_I, \beta_I, \gamma_I, \ldots, j_I$ in precursor mantle before phase transformation I$(\Sigma X_{j,I} = 1)$; $P_I = \Sigma_1^n P_{j,I} K_{j,I}$; $P_{j,I}$ is the mass fraction of phase $\alpha_I, \beta_I, \gamma_I, \ldots, j_I$ entering the fluid; and F is the mass fraction of aggregate fluid.

2. A fraction Z of the aggregate metasomatic fluid mixes with the l.i.l.e.-depleted asthenosphere above phase transition I, to produce a mantle–fluid phase mixture (metasomatized mantle) of bulk trace element composition C_{m} given by

$$C_{\mathrm{m}} = \bar{C}_{\mathrm{f}} Z + C_{\mathrm{s}}(1-Z). \tag{2}$$

Introducing (1) into (2),

$$C_{\mathrm{m}} = \frac{C_{\mathrm{I}}}{F}\left[1-\left(1-\frac{P_{\mathrm{I}}F}{D_{0,\,\mathrm{I}}}\right)^{1/P_{\mathrm{I}}}\right] Z + C_{\mathrm{s}}(1-Z), \tag{3}$$

where C_{s} is the trace element concentration of the l.i.l.e.-depleted asthenosphere.

3. Batch partial melting of the l.i.l.e.-enriched mantle plume – fluid phase mixture (metasomatized mantle) of bulk trace element composition C_{m}, generating beneath the Azores a basaltic melt of composition $C_{\mathrm{L,\,A}}$:

$$C_{\mathrm{L,\,A}} = C_{\mathrm{m}}/[D_{0,\,\mathrm{II}}(1-Z)+Y_{\mathrm{A}}+P_{\mathrm{II}}(Z-Y_{\mathrm{A}})]. \tag{4}$$

This equation is adapted from equation 9 of Hertogen & Gijbels (1976), where $D_{0,\,\mathrm{II}} = \Sigma K_{j,\,\mathrm{II}} X_{j,\,\mathrm{II}}$, the initial bulk crystal/melt partition coefficient; $K_{j,\,\mathrm{II}}$ is the trace element partition coefficient between residual phase $\alpha_{\mathrm{II}}, \beta_{\mathrm{II}}, \gamma_{\mathrm{II}}, \ldots, j_{\mathrm{I}}{}^{\mathrm{I}}$ and the melt; $X_{j,\,\mathrm{II}}$ is the mass fraction or original phases $\alpha_{\mathrm{II}}, \beta_{\mathrm{II}}, \gamma_{\mathrm{II}}, \ldots, j_{\mathrm{II}}$; $P_{\mathrm{II}} = \Sigma P_{j,\,\mathrm{II}} K_{j,\,\mathrm{II}}$; $P_{j,\,\mathrm{II}}$ is the mass fraction of phase $\alpha_{\mathrm{II}}, \beta_{\mathrm{II}}, \gamma_{\mathrm{II}}, \ldots, j_{\mathrm{II}}$ being molten and entering the fluid phase of the metasomatized mantle (crystal–fluid mixture) to generate a melt of trace element composition $C_{\mathrm{L,\,A}}$; and Y_{A} is the mass fraction of basaltic melt (including fraction Z of fluid in solution) generated beneath the Azores.

Introducing (3) into (4):

$$C_{\mathrm{L,\,A}} = \frac{C_0}{F}\left[1-\left(1-\frac{P_{\mathrm{I}}F}{D_{0,\,\mathrm{I}}}\right)^{1/P_{\mathrm{I}}}\right] Z + C_{\mathrm{s}}(1-Z)\Big/ D_{0,\,\mathrm{II}}(1-Z)+Y_{\mathrm{A}}+P_{\mathrm{II}}(Z-Y). \tag{5}$$

(b) *Normal ridge*

Only one step is considered which involves batch partial melting of the l.i.l.e.-depleted asthenosphere of trace element concentration C_{s}, and generates by a degree of melting Y_{N} the normal ridge basalt of trace element concentration $C_{\mathrm{L,\,N}}$ given by:

$$C_{\mathrm{L,\,N}} = C_{\mathrm{s}}/[Y_{\mathrm{N}}(1-P_{\mathrm{II}})+D_{0,\,\mathrm{II}}]. \tag{6}$$

(c) *Transitional ridge segment*

Trace element concentration gradients along such segments can be generated (1) by batch melting of mixtures of metasomatized l.i.l.e.-enriched plume and l.i.l.e.-depleted asthenosphere materials; (2) subsequently by mixing melts derived from these two distinct sources; or (3) at some intermediate stage between cases (1) and (2). In any of these three cases, the mixing proportions would have to vary with distance along the ridge and range from unity beneath the Azores to zero beneath the normal ridge segment. Further formalism of these three possible conditions will not be considered here.

Conditions for constructing figure 12 are as follows. The fractionation coefficient $f = C_{\mathrm{L,\,A}}/C_{\mathrm{L,\,N}}$ was calculated by using (5) and (6). Since crystal–fluid partition coefficients are scarce or not available, we have considered that the fluid released at phase transformation I is actually a small fraction of melt. The mineral assemblage of the precursor mantle I is assumed to be composed of either a garnet or amphibole lherzolite, whereas melting of both the metasomatized mantle and l.i.l.e.-depleted asthenosphere are assumed to occur in the field stability of a simple peridotite assemblage composed of olivine, ortho and clinopyroxenes. The partition coefficient values are given in table 3. Other parametric values used are shown in table A 1.

Table A 1

Mantle mineralogy and eutectic proportions

		olivine	opx	cpx	garnet	amphibole
		garnet lherzolite				
$F = 0.005$	$X_{j,\,\mathrm{I}}$	0.52	0.14	0.09	0.25	—
	$P_{j,\,\mathrm{I}}$	0.03	0.03	0.47	0.47	—
		amphibole lherzolite				
$F = 0.005$	$X_{j,\,\mathrm{I}}$	0.57	0.23	0.15	—	0.05
	$P_{j,\,\mathrm{I}}$	0.18	0.22	0.50	—	0.10
		peridotite				
$Y_{\mathrm{A}} = Y_{\mathrm{N}} = 0.25$	$X_{j,\,\mathrm{II}}$	0.6	0.2	0.2		
	$P_{j,\,\mathrm{II}}$	0.25	0.2	0.55		

Mantle trace element compositions (micrograms per gram)

	Cs	Rb	K	Ba	La	Sm	Yb	Sr	Ni	reference
C_{I}	0.059	0.58	170	5.1	0.48	0.26	0.29	18.2	1800	Ganapathy & Anders (1974)
C_{s}	0.0017	0.15	152	1.63	0.46	0.62	0.87	25.1	765	White & Schilling (1978)

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Discussion

J. V. Smith, F.R.S. (*Department of the Geophysical Sciences, University of Chicago, U.S.A.*). First, I should like to make a comment about the use of the term 'volatility'. Historically, geochemists have used the term volatility in the classical tradition of V. M. Goldschmidt, but the term must now be qualified to fit one of several possible senses. In the simplest sense, the term could be related to the vapour pressure of an element or a frequently encountered compound. For the cosmochemist, a theoretical condensation sequence in the solar nebular leads to a sequential scale of 'volatility', which perhaps should be described by the inverse sequence of 'condensibility'. Most theoretical calculations are based on a solar nebula with atomic abundances determined from the solar photosphere and C1 carbonaceous meteorites. The resulting sequence for equilibrium condensation (summarized by L. Grossman & J. W. Larimer, *Rev. Geophys. Space Phys.* **12**, 71–101 (1974)) deals with an oxidized nebula with atomic C:O less than unity. The possibility of a reduced nebula with C:O greater than unity gives a different sequence of condensation (J. W. Larimer, *Geochim. cosmochim. Acta* **39**, 389–393 (1975)). A new heterogeneous accretion model (J. V. Smith, *Mineralog. Mag.* **43**, 1–89 (1979)) involves early accretion of reduced condensates and later accretion of oxidized condensates. Depending on the degree of subsequent melting and convection, the effective volatility or condensability of an element in the Earth may vary between the two theoretical extremes for solar condensation. Furthermore, the migration of an element in the Earth may depend greatly on its partition between minerals and either liquid or gaseous species rich in H_2O, CO_2, SO_2 and other molecules. Would Professor Schilling comment on his use of the term 'volatile'?

Secondly, would Professor Schilling comment on the original mineral hosts of the volatile elements, for which he has given so much important information? Can the regularities in his data be related to mica, apatite and amphibole? (The following papers will provide relevant microprobe analyses: 'K, Rb and Ba in micas from kimberlite and peridotitic xenoliths, and implications for origin of basaltic rocks', J. V. Smith, R. L. Hervig, D. Ackermand & J. B. Dawson, in *Proc. Second Int. Kimberlite Conf.*; 'F and Cl in micas from kimberlite and peridotitic xenoliths', J. S. Delaney, J. V. Smith & J. B. Dawson, in preparation.)

J.-G. Schilling.

1. The scale of relative volatility that we used is based on the sequence of 'condensibility' given by Ganapathy & Anders (1974). I agree with Professor Smith that caution must be exercised in concluding on the basis of this particular sequence or any other. The difficulty that we have encountered with Cs may indeed be a reflexion of our particular choice.

2. This is a difficult question to answer on the basis of trace element abundances in lavas only. First, any inference would have to assume, *a priori*, that such minerals were retained as residual phases during partial melting. Secondly, another problem is that more abundant residual phases such as olivine, pyroxenes and garnet tend to mask the possible effect of minor residual phases on trace element abundances in magmas, unless the melts are produced by very small extent of melting. In the case of tholeiitic magma generated below the ridge, my prejudices are that there is little hope of resolving the question, as the degree of melting is probably too large. However, in the case of alkali basalts from the Azores Islands, which we estimate to have been produced by half as much extent of melting as the ridge tholeiites, these

two prerequisites may be more acceptable. The inferences that we have made in this instance are briefly discussed in the text, but are not based on the additional references given by Professor Smith, as they were not available to us at the time. These new data could certainly be used to test further our conclusions indicating a probable lack of *residual* mica, apatite and amphibole in the mantle beneath the Azores Islands during partial melting.