Trace element mobility during hydrothermal alteration of oceanic basalts

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Abstract—Trace element analyses have been carried out on hydrothermally altered pillow basalts of greenschist facies dredged from the median valley of the Mid-Atlantic Ridge. Sr is leached from the rock, and its behavior is apparently controlled by the same reactions as Ca. Cu is also leached from the basalt, but often shows local precipitation in veins as sulfides. Fe, B, Li, Ba, Mn, Ni and Co show sufficient variations in concentration and location within the altered basalts to indicate that some mobilisation occurs, but there may be subsequent uptake or precipitation into the secondary mineral assemblages. V, Y, Zr and Cr do not appear to be affected by hydrothermal alteration.

The production of a metal-enriched solution by hydrothermal alteration and subsequent precipitation of metal salts to form metalliferous sediments is indicated, as is precipitation of metal sulfides in the basaltic basement.

INTRODUCTION

THE OCCURRENCE of two types of heavy-metal enriched deposits found in the oceans has been attributed to the migration, and subsequent deposition, of trace elements leached from hydrothermally altered basalts. Rapidly accumulating sediments, which show variable Fe/Mn ratios and enrichment of Ni, Zn, Cu, Co, Pb, Hg, P, Ba and U relative to pelagic sediments, have been recovered from active spreading centers, and are believed to be the result of hydrothermal activity (e.g. BOSTROM et al., 1971; CORLISS, 1971; PIPER, 1973; DYMOND et al., 1973). This origin is supported by the lead isotope ratios in the sediments, which resemble those of mid-ocean ridge basalts (BENDER et al., 1971; DASCH et al., 1971; DYMOND et al., 1973). U apparently originates from both seawater and from a magmatic source (VEEH and BOSTROM, 1971; RYDELL and BONATTI, 1973; RYDELL et al., 1974). However, other sources are suggested for some of the elements. Isotopic and chemical evidence indicates that P (BERNER, 1973) and S in these sediments are primarily derived from seawater by coprecipitation with the principal phases. Deposition of these sediments close to the ridge axes leads to the formation of a metal-enriched basal sediment layer, which has been sampled in several areas away from the spreading centers by the DSDP (e.g. CRONAN et al., 1972; CRONAN, 1973; HOROWITZ and CRONAN, 1976; VON DER BORCH and REX, 1970; VON DER BORCH et al., 1971).

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The other type of heavy-metal enriched deposits found in the oceans and attributed to hydrothermal activity are the Mn-rich and Fe-rich crusts that show high deposition rates compared with hydrogenous Mn crusts. Mn-rich crusts have been found on the Mid-Atlantic Ridge (SCOTT et al., 1974, 1975; THOMPSON et al., 1975) and on the Galapagos Spreading Center (MOORE and VOGT, 1976), and Fe-rich crusts have been reported from the Pacific (BONATTI and JOENSUU, 1966; PIPER et al., 1975).

Metalliferous sediments are also found in ophiolite sequences, which may represent slices of obducted oceanic crust (e.g. MOORES and VINE, 1971; ROBERTSON and HUDSON, 1973). The chemical composition of these sediments, and their stratigraphic position within the ophiolitic unit, are consistent with their formation at mid-ocean ridges. In addition, sulfide ore deposits are widespread within the basaltic unit, both as massive ore bodies and as disseminated mineralisations (SPOONER and FYFE, 1973; BONATTI et al., 1976a; FRYER and HUTCHINSON, 1976). These deposits are believed to be due to leaching of trace metals from basalt by circulating seawater, and the subsequent precipitation of sulfides. Concentrations of metallic sulfides have also been described from high temperature metabasalts in the oceanic crust (ROZANOVA and BATURIN, 1971; HART et al., 1974; SWANSON and SCOTT, 1974; HUMPHRIS and THOMPSON, 1977).

A consequence of these hypotheses for metalliferous sediment and ore formation is that hydrothermally altered basalt should be depleted in Fe, Mn and some trace elements. Fresh basalts show a wide range in trace element compositions (e.g. MELSON et al., 1968; THOMPSON et al., 1972; FREY et al., 1976). These vari-

ations are a function of the basalt source composition, degree of partial melting, and the subsequent fractional crystallisation within the magma before final eruption. For ocean floor basalts, increasing fractional crystallisation gives rise to a depletion in the Cr, Ni and Co contents while the concentrations of elements such as Fe, Zr, Ba, Sr, V and Y will increase (THOMPSON et al., 1972). In this paper, we present trace element analyses of a suite of hydrothermally altered basalts from the Mid-Atlantic Ridge (MAR) at 22°S, 4°S and 22°N latitudes recovered on cruises AII-60, AII-42 and Ch-44 respectively. These samples include pillows having altered rims but fresh interiors, and completely altered samples from dredge hauls in regions of the MAR where the fresh basalts are well documented. The mineralogy and major element chemistry of these samples have been described previously and assessments made of the major element fluxes during hydrothermal alteration (HUMPHRIS and THOMPSON, 1977). The samples are all metabasalts of the greenschist facies, including chlorite-rich greenstones (the dominant type), epidote-rich metabasalts, and quartz-sulfide-containing greenstones. They were all dredged from the median valley of the ridge at the three locations.

METHODS

Analyses of the trace elements, except for Mn, were carried out using direct-reading optical emission spectrometry; details of the methods are given in THOMPSON and BANKSTON (1969). The precision and accuracy of the methods are approximately $\pm 10\%$ of the reported values. The concentrations of Mn were determined by emission plasma spectrophotometry using a d.c. argon plasma. Standards containing varying amounts of Mn were made up in a synthetic basalt matrix. Samples were prepared using the method of INGAMELLS (1970), and Table 1 shows the analyses of four standard rocks, together with the operating conditions used. The accuracy is better than 10%, and the precision is 5–6%.

RESULTS

Trace element analyses are presented in Table 2. The changes in concentrations of iron in these samples, and their relation to mineralogical changes during hydrothermal alteration, were discussed in a previous paper (HUMPHRIS and THOMPSON, 1977), in which modal mineral

Table 1. Analyses of reference rocks determined during Mn analyses by plasma spectrophotometry

	AGV-1	BCR-1	W-1	JB-1
No. of Analyses	15	15	16	16
Mean Value (ppm)	728	1442	1404	1146
Std. Deviation	22	38	40	32
Literature Value: Flanagan (1973)	763	1406	1278	1239[1]

[1] Calculated from reported average values of wt. % MnO.

Operating conditions: instrument—Spectrametrics Spectraspan 2 with d.c. argon plasma jet and echelle diffraction grating; wavelength—2576.1 Å; arc amperage—7.3 A; integration time—10 sec.

and bulk chemical analyses of the same samples were reported.

Boron

B is present in fresh basalts in very low concentrations (2–8 ppm), and so any measurable changes that take place during hydrothermal alteration represent a significant proportion of the amount initially present. B shows a range in concentration in the hydrothermally altered basalts (<2–18 ppm). The core-and-rim analyses indicate that the concentration can increase by up to a factor of two in the altered rim (Fig. 1). Previous studies of B in oceanic basalts (THOMPSON and MELSON, 1970) suggested that low temperature weathering, at ambient bottom water temperatures, resulted in uptake of B, but that hydrothermally altered basalts may be depleted in this element. This latter conclusion was based on the analyses of the cores of some altered basalts from the Ch-44 collection. The data presented here suggest that most of the cores are depleted or similar to fresh basalts in B concentrations, but the outer rims are enriched. However, it should be noted that at the 5 ppm level, the precision of the analyses is only $\pm 50\%$; at the 10 ppm level, it is $\pm 20\%$, so that significant differences are seen only in a few cases.

Other reported data for altered basalts are also somewhat ambiguous because the B concentrations are very close to the detection limit of the standard analytical techniques. Apart from the metamorphosed basalts at 22°N that contain less than 10 ppm of B, BONATTI et al. (1975) and THOMPSON and Melson (1972) have reported greenschist facies metabasalts containing up to 15 ppm B. Low temperature weathering of basalts leads to B concentrations up to 80 ppm (THOMPSON and MELSON, 1970; THOMPSON, 1973) particularly in altered glass rims. We suggest that hydrothermal alteration results in leaching of B from the rocks (seen in altered interiors of samples) but subsequent exposure to seawater at ambient bottom water temperatures may result in further enrichment of B in the margins.

Lithium

The concentration of Li in the fresh rocks and pillow cores is fairly constant at 3–8 ppm (Fig. 2). During hydrothermal alteration, Li is apparently mobilized, and the distribution is very similar to that observed for B, with the cores showing depletion in Li and the rims being enriched (up to 20 ppm). The precision for Li at the 4 ppm level is $\pm 10\%$ so the differences observed are significant. Previous work (MELSON et al., 1968; THOMPSON et al., 1972; THOMPSON, 1973) suggested that, like B, Li is gained during low temperature weathering, but no trends were observed during hydrothermal alteration. Data from MELSON et al. (1968) include two hydrothermally altered samples with Li concentrations of up to 20 and 22 ppm. A metabasalt from 4°S also had a high concentration of Li of 12 ppm (THOMPSON and MELSON, 1972). In addition, mobilization of Li is also indicated in some continental greenschist facies metabasalts. VALLANCE (1974) has observed concentrations of 8–10 ppm, compared with concentrations of about 3 ppm in the fresh precursor, and FLOYD (1976) has reported uptake of Li in highly chloritic zones within greenstones. Thus, like B, enrichment of Li in the outer rims with some depletion in the cores provides evidence for mobilization.

Strontium

The concentration of Sr in fresh basalts generally falls in the range 90–190 ppm (e.g, AUMENTO, 1968; MELSON et al., 1968; THOMPSON et al., 1972). Sr is apparently mobilized during hydrothermal alteration and its concentration has previously been observed to decrease concomitantly with Ca (CANN, 1969; MELSON et al., 1968). However, the relationship appears to be more complex. In the epidote-

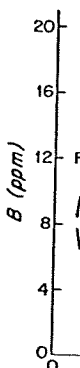rich ass
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Table 2. Results of trace element analyses of fresh and hydrothermally altered basalts (ppm)

Sample I.D.	B	Li	V	Co	Cr	Ni	Cu	Ba	Sr	Y	Zr	Mn
AII-42-												
1-57+	4	5	265	42	530	113	78	4	110	32	64	1305
1-96A	7	9	230	56	290	135	295	5	47	35	105	1060
1-96B	5	9	245	46	310	130	245	5	52	30	80	1068
1-96C	<2	4	260	30	320	130	60	19	160	39	110	1392
1-97A	18	9	245	60	275	155	45	4	65	40	115	1567
1-97B	5	4	260	46	290	130	70	12	120	35	105	1283
1-98+	<5	4	260	46	320	140	26	10	125	37	115	1261
1-99	9	8	220	46	275	150	220	4	30	35	105	1269
1-106	13	10	235	60	295	165	58	4	53	44	130	1695
1-108A	15	14	260	55	370	180	23	10	125	45	135	1623
1-108B	10	3	280	49	300	120	80	15	150	40	125	1201
1-118A	11	10	265	53	330	145	55	25	205	39	125	1231
1-118B	4	3	260	48	290	135	90	18	160	38	115	1288
1-129+	2	4	275	35	320	140	62	12	140	41	120	1268
1-130+	5	5	270	43	345	135	47	4	108	33	105	1277
1-141+	5	3	290	38	365	130	155	1	110	36	112	1274
Ch-44-												
2-1+	5	4	270	37	305	105	63	5	110	34	115	1315
2-2*+	<10	8	245	75	290	150	115	6	110	--	125	--
2-3+	9	6	285	42	320	78	73	5	120	36	115	1264
2-5	6	10	300	32	210	115	12	14	120	49	145	1609
3-2	6	4	230	47	215	100	10	12	250	32	80	1664
3-3*	<10	20	250	45	210	115	80	6	120	--	110	--
3-6*	<10	22	230	35	310	105	70	8	130	--	90	--
3-7*	<10	4	225	70	225	85	290	6	220	--	75	--
3-8	< 2	6	200	45	515	170	23	11	125	30	75	1808
3-12	13	4	295	42	240	115	36	16	215	48	140	1886
3-13	< 2	4	235	38	195	98	12	8	230	29	80	1074
3-17	6	8	285	30	260	110	55	12	105	45	140	1685
3-126	9	11	280	33	220	115	17	12	110	44	140	1250
AII-60-												
2-14	3	4	300	34	280	100	205	4	115	42	140	1481
2-141A	7	14	230	40	310	130	135	2	45	40	130	1552
2-141B	6	5	255	40	300	140	38	2	85	37	120	1508
2-142A	12	19	330	47	405	140	140	5	180	59	145	2548
2-142B	9	7	300	40	230	95	115	2	85	40	135	1837
2-142C	5	3	300	42	230	100	58	4	135	39	130	1375
2-143	2	3	280	37	235	98	21	2	92	37	135	1471

+ Fresh basalt.
A, B, C—zones within a single pillow basalt, from the altered rim (A) towards the interior (B or C).
* Previously reported in MELSON et al. (1968).

rich assemblages from 22°N (Ch-44) (those samples with >15% modal epidote and <15% modal chlorite), uptake of Sr from the circulating fluid is indicated (Fig. 3a). This is in agreement with MELSON et al. (1968) who noted that epidote-rich rocks are marked by higher Sr contents. Compared with the fresh samples, the concentrations increase by a factor of two.

Alteration of the pillow interiors to chlorite-rich assemblages results in very little change in the Sr concentrations compared with the fresh rocks. NICHOLLS and ISLAM (1971) also concluded that, in general, there is no noticeable change in Sr concentration; however, CANN (1969) and MELSON et al. (1968) observed a slight Sr depletion accompanying a decrease in CaO. Our core-and-rim analyses of
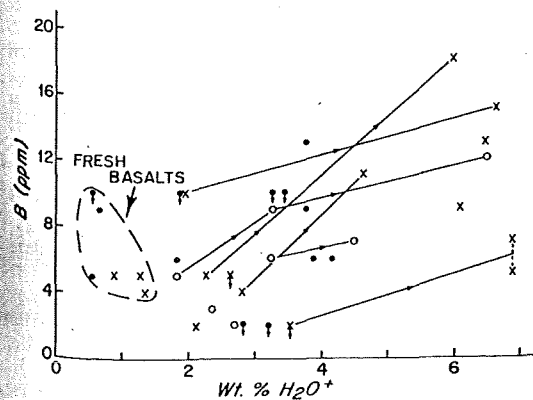

Fig. 1. Boron concentrations (ppm) vs water content (wt.%) for fresh and hydrothermally altered basalts. ×, AII-42 (4°S) samples; ●, Ch-44 (22°N) samples; O, AII-60 (22°S) samples; ×----×, core-and-rim analyses; ↓, analyses recorded as below plotted value.
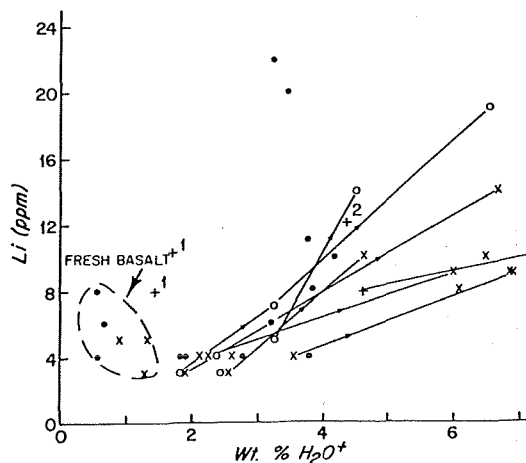

Fig. 2. Lithium concentrations (ppm) vs water content. (Symbols as for Fig. 1.) +[1], data from VALLANCE (1974); +[2], data from THOMPSON and MELSON (1972).
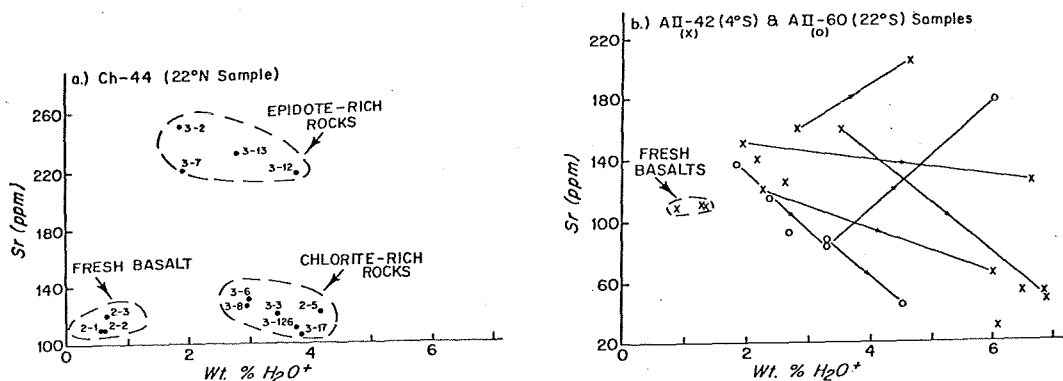
Fig. 3. Strontium concentrations vs water content. (a) Ch-44 (22°N) samples indicating separation between epidote-rich and chlorite-rich samples. (b) AII-42 (4°S) and AII-60 (22°S) samples, showing core-and-rim analyses. (Symbols as for Fig. 1.)

the altered pillows (Fig. 3b) indicate that loss of Sr occurs particularly in the altered rims, which also show marked loss of Ca, although there are two exceptions—AII-42 1-118 and AII-60 2-142.

Figure 4 shows the correlation between Sr and CaO contents for fresh and hydrothermally altered basalts. The epidote-rich rocks fall on a line with a slope (0.08) similar to that for the chlorite-rich assemblages (0.06). The correlation between Sr and CaO ($r = 0.75$) suggests that Sr concentrations are dominantly controlled by the same chemical processes as Ca. We previously indicated that hydro-

thermal alteration of basalts leads to loss of Ca from the rock (HUMPHRIS and THOMPSON, 1977); our trace element data suggest a similar leaching of Sr.

Barium

Ba is present in very low concentrations in the fresh basalts studied (<5 ppm). There appears to be a slight increase in Ba concentration in the altered pillow interiors compared with the fresh rock (Fig. 5a). However, this is not unequivocal since the concentration of Ba in the fresh basalts from a single area can vary by a factor of three
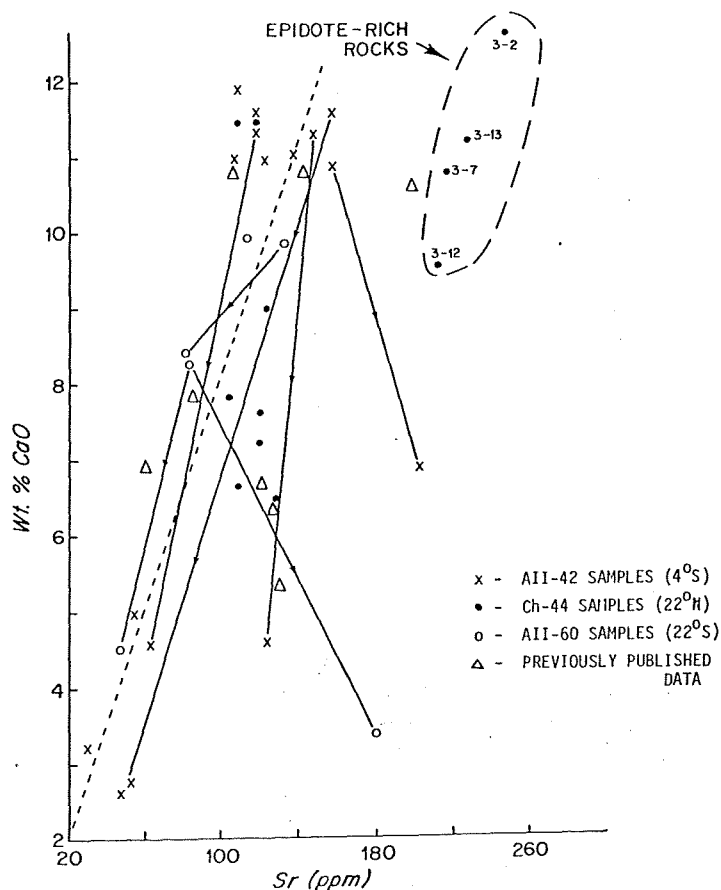
Fig. 4. Correlation between Sr and CaO contents of fresh and hydrothermally altered basalts (symbols as for Fig. 1). △, previously published data mentioned in the text; ————, least squares fit line for data presented here, omitting the epidote-rich rocks and the two core-and-rim analyses discussed in the text.
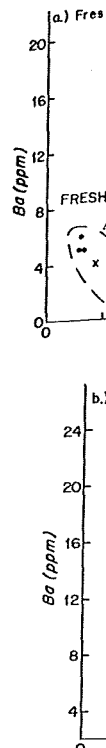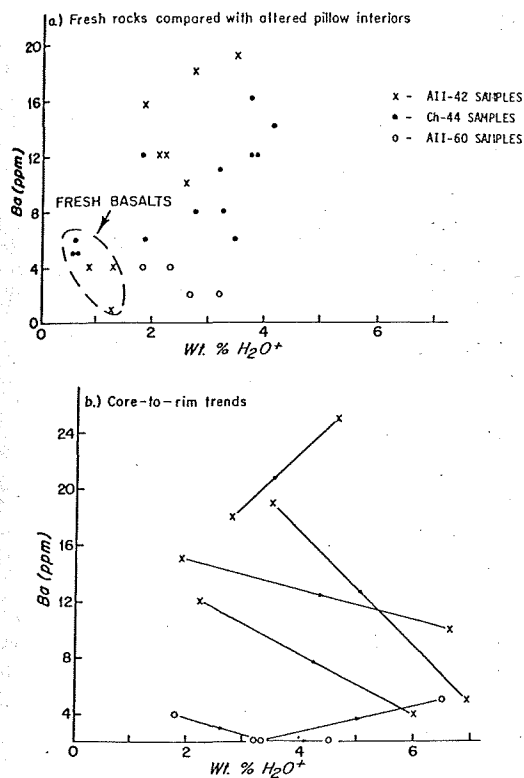
Fig. 5. Barium concentrations (ppm) vs water content. (a) Fresh rocks compared with altered pillow interiors. (b) Core-and-rim analyses. (Symbols as for Fig. 1.)

Fig. 6. Variations in Ni concentration in fresh and altered basalts. (Symbols as for Fig. 1.)

(for example, MELSON et al., 1968). The core-and-rim analyses (Fig. 5b) indicate some mobilization of Ba with the outer rims showing much lower concentrations of Ba than the interiors, except for AII-42 1-118 and AII-60 2-142, the same samples that showed a slight increase in Sr content in the outer margins.

Previously published data are somewhat ambiguous, again because the concentrations are near to the detection limits of the analytical methods. Data from MELSON et al. (1968), NICHOLLS and ISLAM (1971), and THOMPSON and MELSON (1972) show very little variation in Ba concentration in hydrothermally altered basalts compared with fresh basalts. However, CANN (1969) reported a chlorite-rich sample that contained 22 ppm of Ba, but the metabasalts analysed by MEIJER (1976) appear to have lost Ba during alteration. All these results suggest that, in general, Ba concentrations are apparently not greatly affected by hydrothermal alteration, although the different Ba concentrations in the pillow cores and highly altered rims provide evidence of some mobilization, and apparent enrichment of Ba in the interiors of the samples.

Nickel and cobalt

The variations in the concentrations of Co and Ni in fresh oceanic basalts are dominantly controlled by olivine fractionation. For example, the Ni concentrations in the fresh basalts studied vary between 75–140 ppm, and are correlated with the Mg concentration. Alteration of the pillow interiors has no major effect on the concentrations of Ni and Co (Figs. 6 and 7). The core-and-rim analyses for both Co and Ni show higher concentrations in some of the rims, although several of these trends are within the precision of the analytical technique (±10%). Enrichment of Ni and Co in highly chloritic zones within greenstones has been reported previously (FLOYD, 1976). The high concentrations of Ni in the outer margins of AII-42
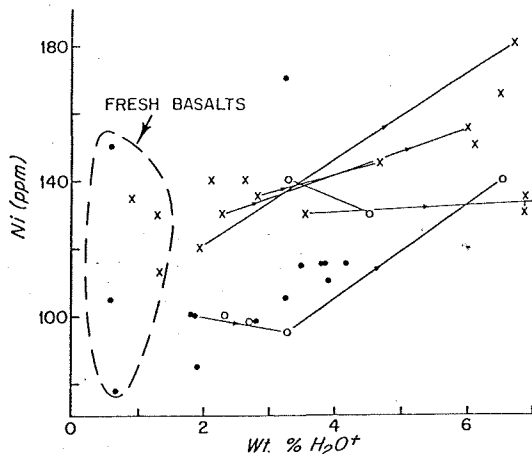
1-108 and AII-60 2-142, are probably due to the occurrence of Ni in vein sulfides, which are abundant in these samples.

Some slight mobilization, particularly in the alteration of glassy basalts, has previously been recognized (AUMENTO and LONCAREVIC, 1969; BONATTI et al., 1975; CANN, 1969; KEAYS and SCOTT, 1976; MELSON et al., 1968; MELSON and THOMPSON, 1971; NICHOLLS and ISLAM, 1971; THOMPSON and MELSON, 1972); however, no definite trends are observed in the alteration of holocrystalline basalts. Overall, hydrothermal alteration shows no major effects on the concentrations of these elements.

Vanadium

The concentrations of V in the fresh basalts analysed are between 245 and 290 ppm. The alteration of the pillow interiors results in no major change in the V content. The core-and-rim analyses also suggest that there is no significant mobilization of V during alteration; all the variations observed are within the precision of the analytical data (±10%). No significant trends in V content between fresh and hydrothermally altered basalts have been reported from other areas, although the previously published data indicate a wide variation in V concentration.

Chromium

The wide variability in the concentration of Cr in the fresh samples (from 280 to 550 ppm) is due to the effects of fractional crystallisation and the degree to which spinel and olivine have crystallised. This wide variation in concentration makes changes due to hydrothermal alteration
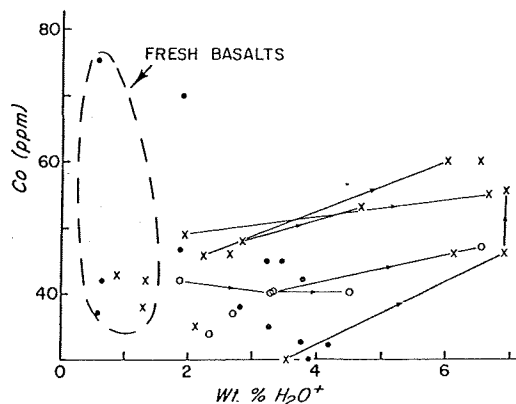

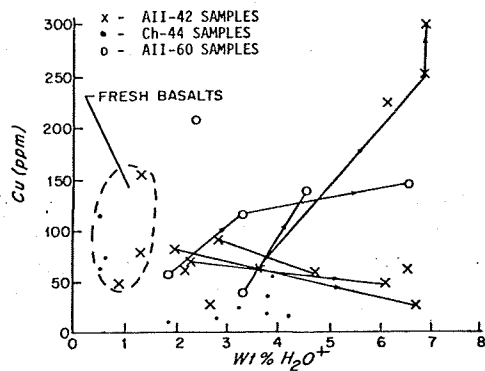Fig. 7. Variations in Co concentration in fresh and altered basalts. (Symbols as for Fig. 1.)

Fig. 8. Cu concentrations vs water content in fresh and hydrothermally altered basalts. (Symbols as for Fig. 1.)

extremely difficult to observe. The-core-and-rim concentrations of Cr show no consistent trends and, apart from AII-42 1-108 and AII-60 2-142 which show marked increases in Cr concentrations in the rims (370 ppm in the rim compared with 300 ppm in the interior, and 405 ppm compared with 230 ppm respectively), the concentration of Cr stays constant within the precision of the analytical method.

Other analyses of Cr in oceanic basalts also indicate wide variability in the Cr contents of both fresh basalts (100–500 ppm) and greenschist facies metabasalts (70–400 ppm) (e.g. AUMENTO and LONCAREVIC, 1969; BONATTI et al., 1975; CANN, 1969; MELSON et al., 1968; MELSON and THOMPSON, 1971; KEAYS and SCOTT, 1976; NICHOLLS and ISLAM, 1971; THOMPSON and MELSON, 1972), but no consistent trends during alteration are observed.

Copper

The concentration of Cu in the fresh samples analyzed is quite variable ranging from 48 to 155 ppm. Alteration of the pillow interiors to both chlorite-rich and epidote-rich assemblages indicates, with only a few exceptions, leaching of the Cu into the circulating fluid, with a resultant decrease in the Cu concentrations of the metabasalts (Fig. 8). Several of the core-and-rim analyses also indicate a lower concentration of Cu in the outer margins; however, others show marked increases in the concentration of Cu in the outer rims. Those samples of Cu-enriched rims or Cu-enriched interiors are those containing vein sulfides, and scanning electron micrographs of the veins clearly indicate the occurrence of Cu and Zn in these secondary deposits. The leaching of Cu from greenstones was also observed by MEIJER (1976) and FLOYD (1976). Hence, enrichment of Cu in the circulating fluid is suggested, with occasional local sulfide precipitation.
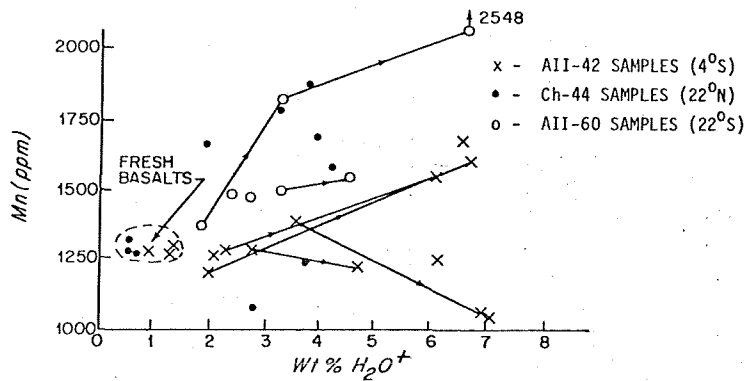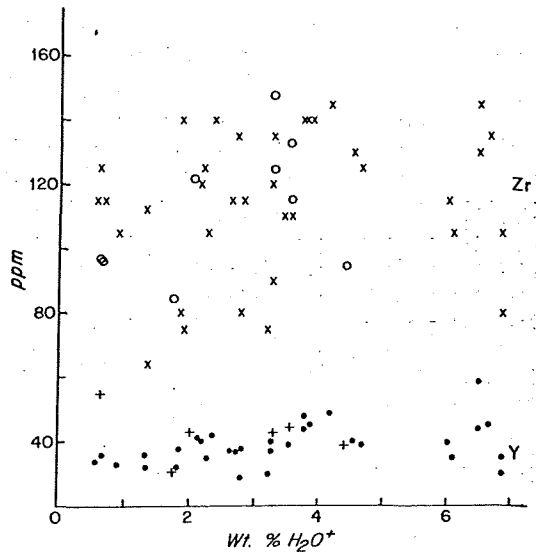

Fig. 10. Concentrations of Y and Zr vs water content in fresh and hydrothermally altered basalts. ×, Zr concentrations (ppm): this study; ●, Y concentrations (ppm): this study; O, Zr concentrations (ppm): +, Y concentrations (ppm): taken from BONATTI et al. (1975); CANN (1969); MELSON et al. (1968); THOMPSON and MELSON (1972).

Manganese

The wide variation in the concentrations of Mn in the altered basalts (Fig. 9) suggest that this element is mobilized during hydrothermal alteration, and migrates in the circulating fluid. No consistent trends can be seen during alteration of either the pillow interiors or the outer margins. KEAYS and SCOTT (1976) observed Mn enrichment in the rims of pillow basalts from the Mid-Atlantic Ridge, and attributed it to loss of Mn from the interiors during hydrothermal alteration. Our data indicate some enrichment of Mn in the altered rims compared with the interiors, although there are exceptions. Some of the rim cores are slightly depleted in Mn compared to the fresh basalts. Variable Mn concentrations, with no consistent trends during alteration, have previously been observed (AUMENTO and LONCAREVIC, 1969; CANN, 1969; BONATTI et al., 1975; CHERNYSEVA, 1971; HEKINIAN and AUMENTO, 1973; MELSON and VAN ANDEL, 1966; MELSON et al., 1968; OZIMA et al., 1976; SHIDO et al., 1974; THOMPSON and MELSON, 1972). Thus we suggest that Mn is mobilized during hydrothermal alteration with some redistribution in the altered basalts.

Fig. 9. Mn concentrations vs water content in fresh and hydrothermally altered basalts. (Symbols as for Fig. 1.)

Yttrium and zirconium

Y and Zr are concentrated in the residual liquid during fractional crystallization; thus, fresh basalts show a range in concentration dependent on the amount of crystallization before eruption. Hydrothermal alteration apparently has little effect on the concentrations of these elements (Fig. 10). If the data are recalculated on a volatile-free basis or to a density of 2.9 g/cm^3, then the variation in concentration is much reduced. This constancy during alteration is of particular interest due to the use of these elements, together with Ti, for the identification of the original tectonic settings of basic volcanic rocks (PEARCE and CANN, 1973; FREY *et al.*, 1976).

DISCUSSION

The data presented here demonstrate that hydrothermal alteration of basalts results in mobilization of some of the trace elements. These exchanges should be reflected in the chemistry of the fluid with which the rocks reacted. It is therefore pertinent to compare these trends with data from the Reykjanes geothermal system and from experimental studies, examples of which are summarized in Table 3. The experimental and the Reykjanes data show similar metal enrichments in the reacted solutions compared with seawater, probably because they both involve low water/rock ratios, and hence are both rock-dominated systems. The directions of the concentration changes in the circulated fluid are mostly consistent with those in the altered basalts we have studied. Fe is generally enriched in the reacted fluid, although the degree of enrichment is highly variable. We have shown that Fe is leached during alteration (HUMPHRIS and THOMPSON, 1977). A correlation between changes in oxidation state and the mineralogy was also noted, with the epidote-rich assemblages becoming more oxidised (i.e. losing FeO and gaining Fe$_2$O$_3$) relative

to the fresh basalts, and the chlorite-rich assemblages maintaining their FeO/Fe$_2$O$_3$ ratio during alteration, except for those containing sulfides where a local increase in FeO was apparent. The concentrations of both Fe and Mn in the experimental solutions are generally low at temperatures less than 300°C; however, MOTTL (1976) has observed a sharp increase in the concentrations between 300° and 400°C.

The changes in concentrations of Fe and Mn are partly controlled by changes in a_{H^+}. BISCHOFF and DICKSON (1975) have suggested that a decrease in pH results from the incorporation of seawater Mg^{2+} and OH$^-$ ions into smectites found in the alteration of basalts in experimental systems. The formation of chlorite observed in the naturally altered basalts could provide such a mechanism of pH lowering and, as the seawater reacts with the rock, f_{O_2} will also decrease, thereby increasing the solubility of the metals, and hence making leaching a more effective process. However, uptake of Fe and Mn into secondary phases will tend to counteract this process. Electron microprobe analyses of alteration products in these metabasalts indicate that chlorites contain 20–23% FeO* (total iron expressed as FeO) and 0.1–0.25% MnO, and amphiboles contain 13–17.5% FeO* and 0.1–0.35% MnO (HUMPHRIS and THOMPSON, 1977). In addition, under conditions of low f_{O_2} and high f_{S_2}, sulfides precipitate within veins and hence some iron will be removed from the circulating fluid. If conditions of increasing f_{O_2} or pH are encountered, Fe and Mn oxides can form, again changing their concentrations in the circulating fluid. Therefore, the concentrations of Fe and Mn observed in the reacted fluid will be dominantly controlled by the balance between the effectiveness of leaching and their subsequent uptake into secondary phases.

Table 3. Trace element composition of fluids from the Reykjanes geothermal system, Iceland, and from experimental systems. (Concentrations in ppm)

	Temp. °C.	B	Li	Ba	Sr	Fe	Mn	Cr	Co	Ni	Cu	V	Zn
LAND GEOTHERMAL SYSTEMS													
Reykjanes Spring[1]	99	12.0	7.4	--	--	0.2	--	<0.001			--	<0.001	<0.002
Reykjanes Drillhole 8[2]	269	7.4	--	10.3	9.1	0.5	2.0	<0.05	<0.1	<0.1	--	<0.1	--
Reykjanes Spring 1918[2]	99	11.9	--	7.1	11.9	0.3	4.5	<0.05	<0.1	<0.1	--	<0.1	--
EXPERIMENTAL SYSTEMS													
Seawater/Basalt; 4752 hrs; 500 bars; Water/Rock- 10:1[3]	200	--	--	--	--	5	5	--	--	0.2	0.2	--	<0.03
Seawater/Basalt; 336 hrs; 500 bars; Water/Rock- 5:1[4]	200	--	--	--	--	0.4	0.26	--	--	--	0.15	--	--
Seawater/Basalt; 14,448 hrs; 500 bars; Water/Rock- 1:1[5]	200	4.6	--	0.9	3.5	12	16	0.08	<0.08	<0.07	<0.05	<0.1	--
Seawater/Basalt; 6432 hrs; 1000 bars; Water/Rock- 1:1[5]	500	9.9	--	3.8	0.2	653	116	0.04	<0.08	<0.07	<0.05	<0.1	--
SEAWATER	25	~5	0.1	~0.2	~7	<0.01	<0.01			<0.002			

[1] BJORNSSON *et al.* (1972) and ARNORSSON *et al.* (1974).
[2] MOTTL *et al.* (1975).
[3] BISCHOFF and DICKSON (1975).
[4] HAJASH (1975).
[5] MOTTL (1976).

Both the experimental data and the Reykjanes drill-hole waters show enrichment in B and Ba, and the Reykjanes water enrichment in Li. These elements are present in oceanic basalts in very low concentrations, so in order to achieve the high concentrations found in both sets of fluid data, interactions must have occurred at relatively low water/rock ratios. Sr shows a loss from some experimental fluids, and is gained by others, while the Reykjanes brines show enrichment compared with seawater. The correlation between Sr and CaO contents was shown earlier, and since the flux of CaO depends, to a large extent, on the modal mineral assemblages, the Sr flux will also be dependent on this factor. The detection limits of the analytical techniques used for the fluids make interpretation of the transition elements ambiguous. However, the experimental work suggests that there may be slight enrichment of some of the transition elements in the circulating fluid, especially copper.

IMPLICATIONS FOR THE FORMATION OF METALLIFEROUS DEPOSITS AT MID-OCEAN RIDGES

The previous discussion of the data suggests that hydrothermal alteration provides a mechanism for the production of a metal-enriched solution which can be debouched on to the sea floor. Trace element analyses of metalliferous deposits are shown in Table 4. The sediments from the DSDP sites in the central North Pacific and those from the crest of the East Pacific Rise are similar in composition, and, in general, sediments from the East Pacific Rise are characterized by quite uniform Fe/Mn ratios. Accumulation rates of Fe and Mn are much higher than normal in the metalliferous sediments from the East Pacific Rise (Bostrom, 1970; Bostrom et al., 1973), the Bauer Deep (Sayles et al., 1975), and in the basal sediment on the Galapagos Rise (Dymond et al., 1976). Mottl (1976) calculated that at 300°C, a minimum concentration of 7.5 ppm would be needed to supply the Fe at an adequate rate to account for the rate of hydrothermal Fe deposition on the East Pacific Rise,

assuming a convective seawater flux sufficient to explain the heat flow anomaly (Wolery and Sleep, 1976). This is much higher than observed in the Reykjanes system (Table 3). However, the water-to-reacted rock ratio in this system is about 1:1 by weight, and Bischoff and Dickson (1975) have shown that solutions in systems with a ratio of 10:1 can have high Fe concentrations at 200-300°C. The FeO* fluxes calculated from analyzed metabasalts (Table 8 of Humphris and Thompson, 1977) are extremely variable, suggesting that there is considerable redistribution of iron within the basalt. Assuming a water/rock ratio of 5-60:1 by volume, then a process of leaching of basalts to give a flux of $-7\,g$ FeO*/100 cm^3 rock, comparable to estimates by Humphris and Thompson (1977), has the capability of producing sufficient iron for the formation of East Pacific Rise sediments.

Our observations clearly indicate that sulfides containing Fe, Cu, Zn, and small quantities of Ni and Co, precipitate in veins within the basaltic pile. However, the sulfide mineralization we have observed is not as massive as that reported by Bonatti et al. (1976b) and Rozanova and Baturin (1971).

CONCLUSIONS

The effects of hydrothermal alteration to greenschist facies on the trace element composition of oceanic basalts can be summarized:

(1) B and Li are mobilized during hydrothermal alteration; higher concentrations are often observed in the chlorite-rich rims of the altered pillows, and pillow interiors are often depleted.

(2) Sr is taken up in the epidote-rich assemblages, stays relatively constant in the alteration of pillow interiors to chlorite-rich assemblages, and is lost in the alteration of the rims. The correlation of Sr with Ca indicates that they are both controlled by the same reactions.

(3) Ba is not greatly affected by hydrothermal alteration, although some slight mobilization is indicated with higher concentrations in the altered pillow interiors than in the margins.

Table 4. Trace element analyses of metalliferous sediments (on a CaCO$_3$-free basis)

	Wt. %				ppm					
	Fe	Mn	Si	Al	Cu	Ni	Zn	Co	Cr	
DSDP Sites (37, 38, 39)	23.6	6.66	7.11	2.39	1070	630	600	86	16	(1)
Crest of EPR (12°- 14°S)	18.0	6.00	6.10	0.5	730	430	380	105	55	(2)
Mid-Atlantic Ridge (26°N)	0.01	39.2	--	--	12	100	--	18	--	(3)
Av. Comp. Pelagic Clay	6.5	0.67	25.0	8.4	250	225	165	74	90	(4)

(1) Dymond et al. (1973).
(2) Bostrom and Peterson (1966).
(3) Scott et al. (1974).
(4) Turekian and Wedepohl (1961).

(4) Co, Cr and Ni show only slight variations in the hydrothermally altered basalts. Enrichment of Co, and particularly Ni, in sulfide-rich samples, and some depletion of Co and Ni in other samples suggest there is some mobilization of these elements.

(5) In general, Cu is leached from the basalt during hydrothermal alteration. Clearly, as for Ni, some Cu is precipitated as sulfides in the basalt. Qualitative analyses of the sulfides indicate that this is also true for Zn.

(6) Y and Zr concentrations show no marked variations in hydrothermally altered basalts and remain as in the precursor.

(7) Mn is mobilized during hydrothermal alteration but the metamorphosed samples show wide variability in the Mn concentrations.

(8) Hydrothermal alteration of basalts is a process of producing a metal-enriched solution. However, its role in the formation of metalliferous sediments cannot be quantitatively assessed at this time because the effects of temperature, pH and water-to-rock ratios are unknown. The precipitation of sulfides in veins within altered basalt has been observed; however, it has not been on a very large scale.

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