

The geochemistry of basalt-sea-water interactions: evidence from Deception Island, Antarctica, and Reykjanes, Iceland

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SUMMARY. Sea-water from Deception Island was found to contain 0.55–1.48 mg Mn l⁻¹ and 10.2–64.3 mg Si l⁻¹. Reaction of Deception Island basalt and sea-water at 190 °C and 500 bars simulated the measured water composition but leaching experiments suggest that much of the Mn etc. may derive from local volcanic ash. Mn and Mg in thermal waters at Reykjanes have concentrations compatible with equilibrium with components of montmorillonite present as an alteration mineral of average composition Ca_{0.66} Na_{0.33} K_{0.03} (Al_{0.28} Fe_{0.35}^{III} Fe_{0.33}^{II} Mn_{0.01} Mg_{1.28}) [Si_{3.17} Al_{0.83}] O₁₀(OH)₂·2.55 H₂O. However, Fe is controlled by equilibrium with sulphides. Flux calculations based on these and other data place upper limits on hydrothermal Mn input to the oceans of 5–36 × 10¹¹ g yr⁻¹ and Mn accumulation in metalliferous sediments of 2–9 × 10¹¹ g yr⁻¹.

THE concept of chemical mass transfer between sea-water and ocean-floor rocks (e.g. Melson and van Andel, 1966; Hart, 1973; Spooner and Fyfe, 1973) has important implications regarding the geochemical budget of the oceans. This is because several of the hydrothermal reactions assumed to be taking place within the upper layers of ocean crust are capable of providing or consuming elements at rates comparable with their rate of addition to the oceans by rivers. Thus the sub-sea-floor hydrothermal system can, in principle, act to balance the geochemical budgets of elements such as magnesium for which stream supply exceeds sedimentary removal (Drever, 1974) and can provide the source for iron- and manganese-rich sediments found on ocean ridges (Bischoff and Dickson, 1975). There is no direct geochemical evidence of hydrothermally modified sea-water emanating at ocean ridges, and geochemical flux estimates such as those presented by Wolery and Sleep (1976) have been inferred from chemical analyses of metabasalts (e.g. Miyashiro *et al.*, 1971; Muehlenbachs and Clayton, 1972) and from experimental simulations of basalt-sea-water interaction (e.g. Bischoff and Dickson, 1975; Hajash, 1975). However, Wolery and Sleep (1976) quote two field situations where they consider that chemical changes inferred from metasomatism of basalts are approximated: in the Reykjanes geothermal system on Iceland (Bjornsson *et al.*, 1972; Tomasson and Kristmannsdottir, 1972) and on Deception Island, Antarctica (Elderfield, 1972). This paper presents new analyses of Deception Island waters together with experimental evidence for their origin, and analyses of the alteration minerals found in the Reykjanes system, which are used in thermodynamic calculations of chemical exchange. Consideration is given to the viability of applying these data to processes envisaged within the ocean crust and constraints are placed upon estimates of geochemical fluxes that may result from hydrothermal circulation.

Materials and methods

Water samples from Deception Island were collected in acid-cleaned 100 cm³ polyethylene bottles by M. Harvey who visited the island in January 1972. Samples were stored in the collection bottles and transported to the laboratory where they were filtered (< 0.45 μm) and

analysed approximately four weeks after collection. Recent basalt and ash samples from Deception Island were supplied by P. E. Baker. Drill-hole samples from the Reykjanes geothermal area were provided by the National Energy Authority of Iceland, and the $< 2 \mu\text{m}$ fraction was separated by sedimentation.

The Deception Island basalt, ground to < 400 mesh, was used in an experimental simulation of hydrothermal rock-water interaction. Basalt and artificial sea-water were reacted in a PTFE container placed in a stainless-steel pressure vessel in a furnace at 190°C , and 500 bars of argon pressure were transmitted to the reactants via a capillary hole in the PTFE. A water-rock ratio of 14, by weight, was used and a series of consecutive experiments were performed to assess temporal exchange.

Volcanic ash samples from Deception Island were used in simple leaching experiments by shaking 5 g ash in 100 ml of distilled water or $0.5 M$ HCl for 12 hours, and the solution filtered ($< 0.45 \mu\text{m}$) and analysed.

Water samples and products of solubility experiments were analysed for Na and K by emission spectrophotometry, Ca and Mg by atomic absorption spectrophotometry, Cl by titration with silver nitrate, SO_4 gravimetrically as barium sulphate, Si by the method of Strickland and Parsons (1972), and for Mn, Fe, Cu, Ni, Zn, Co, and Cr using atomic absorption spectrophotometry either directly using the method of standard additions or by an unpublished technique employing a graphite furnace. Major elements in basalt and alteration minerals were determined by X-ray spectrometry (Padfield and Gray, 1971).

Structural formulae of Reykjanes alteration minerals were calculated assuming a smectite structure (i.e. a substituted version of either $M_2^{\text{III}}\text{Si}_4\text{O}_{10}(\text{OH})_2$ or $M_3^{\text{II}}\text{Si}_4\text{O}_{10}(\text{OH})_2$), which gives 22 metal equivalents per half-unit cell. The chemical compositions agreed with the mineralogies determined by X-ray diffractometry and attempts to calculate formulae on the basis of 28 equivalents per half-unit cell (the chlorite structure) produced more than 4 Si atoms in tetrahedral sites. Equations involving components identified from these formulae were solved using thermodynamic data (Garrels and Christ, 1965; Robie and Waldbaum, 1968; Helgeson, 1969; Berner, 1971) supplemented by calculating ΔG_f^0 values for the Fe^{III} and Mn components using the method of Tardy and Garrels (1974) and ΔH_f^0 values for Fe^{II} , Fe^{III} , and Mn components using entropies estimated by an additive method with a correction for changes in molar volume.

Deception Island

Water chemistry. Water samples collected from Deception Island during the build-up of fumarolic activity prior to the February 1969 eruption were found to consist of slightly modified sea-water but with high concentrations of Mn (up to 2.4 mg l^{-1}), Si (up to 50.7 mg l^{-1}), and in one case Fe (0.31 mg l^{-1}), especially those samples from crater lakes (Elderfield, 1972). Chemical analyses of the 1972 waters are listed in Table I. Collections were made on 25 Jan. 1972 some 17 months after the 1970 volcanic eruption described by Baker and McReath (1971). These samples (D9–D15) were taken in the same region as the 1969 samples D4–D6 (see map in Elderfield, 1972), which is where both the 1969 and 1972 eruptions occurred. The results show that high concentrations of Mn (0.37 – 2.03 mg l^{-1}) and Si (10.2 – 64.3 mg l^{-1}) had persisted in Deception Island waters. In addition, one sample (D9) was found to contain 5.7 mg Fe l^{-1} and $250 \mu\text{g Cu l}^{-1}$.

Hydrothermal processes. In order to determine whether hydrothermal circulation of sea-water through Deception Island basalt can generate the observed water chemistry an experimental simulation of this process was carried out. Results showed that the composition of sea-water was significantly modified by contact with basalt at 190°C and 500 bars pressure, conditions

TABLE II. Composition of sea-water before and after reaction with Deception Island basalt

Element	St.†	Exp.‡	Nat.*
Na	10 760	—	11 500
K	387	—	500
Ca	413	445	670
Mg	1294	1100	750
Fe	0.001	25.4	5.7
Mn	0.001	11.6	1.81
Cu	0.001	0.90	0.25
Ni	0.001	0.01	—
Zn	0.001	0.50	—
SiO ₂	3	—	110
SO ₄	2712	—	2160
pH	7.9	5.45	7.65

* Sample D8, plus Fe and Cu data for D9; Deception Island water.

† Standard sea water.

‡ Sea water reacted with Deception Island basalt at 190°C, 500 bars.

^{||} mg l⁻¹

TABLE I. Mn, Si, SO₄, and Cl in Deception Island waters

No.*	Comments	Cl‡	SO ₄ ‡	Mn	Si	SO ₄ /Cl
D9†	No evidence of fumaroles; water temp. ca. 10°C	18.35	0.02	0.55	14.0	0.001
D10	Fumarolic activity (steam, bubbles; water ca. 50°C)	19.00	2.82	2.03	42.3	0.148
D11	Bubbles seen in water; temp. ca. 15°C	20.00	2.88	0.93	10.2	0.144
D12	Steam seen but not at time of sampling; temp. ca. 5°C	19.00	2.64	0.74	40.7	0.139
D13	No fumarolic activity; water temp. ca. 5°C	20.40	2.34	0.37	41.0	0.115
D14	Fumarole gassing area; bubble streams in water; temp. ca. 5°C	14.16	1.64	0.89	64.3	0.116
D15	Fumarolic activity; white sublimate on crater walls; water temp. ca. 60°C	16.50	2.06	1.48	51.5	0.125
	Standard sea water	19.36	2.71	0.01	3	0.140

* Samples D1 to D8 described by Elderfield (1972).

† Sample D9 also contained 5.7 mg l⁻¹ Fe and 0.25 mg l⁻¹ Cu; Fe and Cu not detected to D10 to D15.

‡ Parts per thousand.

^{||} mg l⁻¹

Errata: Table II, col. 2, for 0.001 read <0.001 (in 5 places).

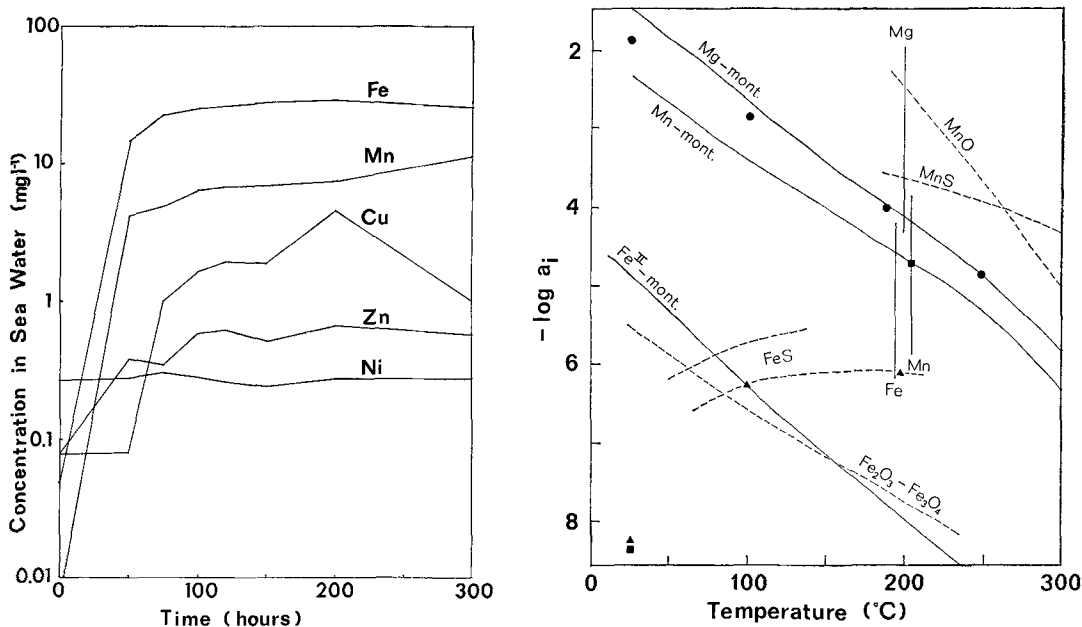
found within the upper layers of oceanic crust (Gass and Smewing, 1973; Spooner and Fyfe, 1973; Bischoff and Dickson, 1975). There was an increase in the concentrations of Mn, Fe, and Cu from leaching of basalt to levels higher than those measured in the water samples (fig. 1, Table I), and the major element composition was modified to approach that of the Deception Island waters by gain of Ca and loss of Mg (Table II). This is a similar result to simulations of the undetected hydrothermal solutions at ocean ridges (Bischoff and Dickson, 1975; Hajash, 1975), which contain more heavy metals, K, Ca, and Si than normal sea-water and less Mg and SO_4 . One criticism of experiments such as these is that they all deal with a closed system and so the hydrothermal fluids they produce may not reflect accurately the composition of submarine hot springs. The comparison made here may be more meaningful in that the Deception Island waters that show very significant enrichment in manganese etc. are those from crater lakes where metal concentrations are able to build up in a restricted environment similar to that reproduced in the laboratory.

Despite the success of these experiments in reproducing the high metal concentrations found in Deception Island waters it is clear that hydrothermal reactions cannot adequately explain their unusual composition. The published experimental studies described above show that sulphate depletion is a consistent characteristic of hydrothermally modified sea-water, yet the range of observed SO_4/Cl ratios (Table I) extends to values higher than as well as lower than normal sea-water. In addition, samples with low SO_4/Cl ratios contain less Mn than samples with high SO_4/Cl ratios and so the process responsible for removal of sulphate cannot be totally responsible for the observed enrichments in manganese. Modifications to chemical composition of sea-water observed in experiments can be used to infer the origin of Deception Island water using, as a criterion for hydrothermal influence, enrichment in Mn, Fe, Si, Ca, and K and depletion in Mg and SO_4 . Only two of the 1969 samples (Table III) fall into this category (unfortunately there is insufficient information to assess the 1972 samples); of these samples D8 (Table II) shows the greatest modification. Thus the possibility exists that hydrothermal reaction of basalt and sea-water does supply manganese etc. to Deception Island water but that the expression of this is partially obscured by an additional process on the island.

Leaching of volcanic ash. The most striking feature associated with the volcanic eruptions is the abundance of pyroclastic deposits. Although part of the activity has been submarine the main events have been fissure eruptions in which vent activity ejected volcanic bombs and ash over large areas. Baker and McReath (1971) show isopachs of ash distribution with a 50-cm thickness on Deception Island. In addition, an outstanding feature of the detrital mineralogy of Antarctic marine sediments is a 'volcanic-glass province' surrounding the S. Shetland Islands where up to 80% of the 62–125 μm size fraction is glass derived from insular volcanism (Edwards and Goodell, 1969). Since large amounts of atmospherically transported volcanic ash fall on Deception Island and in adjacent waters it is possible that ash provides the source for the metal anomalies.

To test this possibility experiments were conducted to compare the concentrations of elements that could be leached from ash that had been in contact with sea-water (material sampled from beaches on the island) with ash that had not been in contact with sea-water. Results showed that more Mn, Si, Cu, SO_4 , Na, and Cl could be leached from samples that had not been in contact with sea-water (Table IV). This contrast is the strongest for sulphate and may explain the variable SO_4/Cl ratios of Deception Island waters (Table I). The beach material used in the experiments may not have been completely leached by sea-water and it is possible that an even greater contrast will be seen in nature. A dilute-acid attack emphasizes the contrast seen in the distilled-water leach between samples for all the elements that were examined (Table IV). Taylor and Stoiber (1973) have examined the soluble material on ash

from Central American volcanos and conclude that this represents elements sorbed on to the ash from volcanic gases during eruption. They suggest that this process would account for all the excess chlorine and sulphur in the oceans. Its importance in supplying elements to Deception Island water is difficult to quantify but the preponderance of volcanic ash on the island and in local marine sediments suggests that it may be very significant. In addition, the water sample



FIGS. 1 and 2: FIG. 1 (left). Concentrations of heavy metals in sea water during reaction with basalt at 190 °C and 500 bars. FIG. 2 (right). Activities of Mn, Fe, and Mg ions as a function of temperature at neutral pH: 7.00 (25 °C), 6.13 (100 °C), 5.82 (150 °C), 5.63 (200 °C), 5.69 (300 °C). The full curves describe equilibrium between an ideal solid solution among the four montmorillonite components (using activities based upon Table V) and an aqueous phase: $-\log a_{\text{Mn}^{2+}} = 2.94 + 2\text{pH} - 4100T^{-1} - \frac{1}{3} \log a_{\text{Mn}}^{\text{montmorillonite}}$; $-\log a_{\text{Fe}^{2+}} = 6.97 + 2\text{pH} - 4704T^{-1} - \frac{1}{3} \log a_{\text{Fe}^{\text{II}}}^{\text{montmorillonite}}$; $-\log a_{\text{Fe}^{3+}} = 11.47 + 3\text{pH} - 2861T^{-1} - \frac{1}{2} \log a_{\text{Fe}^{\text{III}}}^{\text{montmorillonite}}$; and $-\log a_{\text{Mg}^{2+}} = 2.01 + 2\text{pH} - 4376T^{-1} - \frac{1}{3} \log a_{\text{Mg}}^{\text{montmorillonite}}$. The dashed curves describe equilibrium with sulphides and oxides using $M_{\text{S}^{2-}} = 10^{-2.8}$, based on values from Reykjanes (Bjornsson *et al.*, 1972), and $M_{\text{S}^{2-}} = 10^{-1.8}$, which fits the analytical data. Equilibrium with Mn^{II} oxide is shown for $a_{\text{MnO}} = 0.1$. The curve for magnetite-haematite is based on equilibrium constants from Helgeson (1969) and the remainder derive from: $-\log a_{\text{Mn}^{2+}} = 9.37 + 1042T^{-1} + \log M_{\text{S}^{2-}} + \log \gamma_{\text{S}^{2-}}$; $-\log a_{\text{Fe}^{2+}} = 7.23 + 2681T^{-1} + \log M_{\text{S}^{2-}} + \log \gamma_{\text{S}^{2-}}$; and $-\log a_{\text{Mn}^{2+}} = 3.92 + 2\text{pH} - 6473T^{-1} - \log a_{\text{MnO}}$. Values are based on $\gamma_{\text{Fe}^{2+}}$ and $\gamma_{\text{S}^{2-}}$ from Helgeson (1969), $\gamma_{\text{Mg}^{2+}} = 0.26$ (Berner, 1971), and $\gamma_{\text{Mn}^{2+}} = \gamma_{\text{Mg}^{2+}}$. Vertical bars show the range in activities determined from experimental basalt-sea-water reactions (cited in text) and symbols (● = Mg; ▲ = Fe; ■ = Mn) represent compositions of sea-water (25 °C data), Reykjanes spring-water (100 °C), and Reykjanes thermal brines (> 150 °C).

assessed as having been subjected to the greatest hydrothermal influence (Table II) was the only sample taken from the south-west of the island away from the active volcanic sites, which suggests that it has been least influenced by pyroclastic debris. If manganese was leached, according to the acid-leaching result in Table IV, from ash that formed a 50-cm thick layer on the floor of a 50 m-deep crater lake, then the Mn content of the lake-water would be increased by 1.5 mg l⁻¹, which is similar to the largest observed anomaly (Table I and Elderfield, 1972). The corresponding value using the water-leaching result is 30 μm Mn l⁻¹, which is similar to the smallest Mn anomaly.

TABLE III. *Major-element/chlorinity ratios of Deception Island waters*

Samples	Mn ($\times 10^6$)	Fe† ($\times 10^6$)	Si ($\times 10^6$)	Ca ($\times 10^2$)	K ($\times 10^2$)	Mg ($\times 10^2$)	SO ₄ ($\times 10$)
D3,8	3.5–91	10.4	416–2550	3.02–3.36	2.32–2.51	3.77–6.38	0.98–1.08
D1,2,4,5,6,7	1.6–135	17.3	411–2030	1.56–2.88	2.19–3.23	6.40–7.03	1.21–2.77
Standard sea water	<0.01	<0.01	0.16	2.12	2.02	6.67	1.40

*based on data of Elderfield (1972)

† data for D3 and D7 only

TABLE IV. *Soluble material in Deception Island ash*

element ($\mu\text{g g}^{-1}$)	water soluble		soluble in 0.5 m HCl	
	contact with sea water	no contact with sea water	contact with sea water	no contact with sea water
Na	1640	2080	1800	3520
Cl	2340	2780	—	—
SO ₄	800	3040	1040	3520
Si	4.68	6.44	0.44	10.48
Mn	5.6	8.4	16	168
Fe	—	—	340	1140
Cu	0.48	0.65	8.7	25
Zn	<0.5	<0.5	4.6	12.7
Ni	<0.5	<0.5	<0.5	3.9
Co	<0.2	<0.2	<0.2	0.7
Cr	<0.5	<0.5	<0.5	2.1

Reykjanes

Several investigators (Mottl *et al.*, 1974; Bischoff and Dickson, 1975; Hajash, 1975; Wolery and Sleep, 1976) have used the existence and composition of thermal waters at Reykjanes, Iceland, as evidence for the existence of circulating fluids at ocean ridges. The Reykjanes Peninsula lies on the subaerial continuation of the Mid-Atlantic Ridge and the composition of the thermal waters has been successfully reproduced by reacting sea-water and basalt in the manner described earlier. A matter of some importance is to know whether the elements in the thermal waters are in equilibrium with solid phases. If the over-all system is in equilibrium then there is some justification in calculating the composition of unknown (or undetected) hydrothermal solutions from the compositions of known solid phases and in extrapolating from one situation to another as has been done in using Reykjanes as an analogue site of ocean-floor emanations. If, however, the system is not at equilibrium the composition of the hydrothermal fluid on exit may vary considerably from place to place. Also equilibrium concentrations place limits on actual concentrations.

Alteration minerals. Applications of silica- and Na/K-geothermometers to the Reykjanes hydrothermal system (Arnórsson, 1970, 1975) suggest that equilibrium may be approximated for these 3 elements. The thermal waters contain 4–5 mg l⁻¹ manganese and 0.4–4 mg l⁻¹ iron (Björnsson *et al.*, 1972; Mottl *et al.*, 1975) and it has been suggested that these levels are fixed by equilibrium with unknown solid phases, probably hydroxy-oxides or sheet silicates (Bischoff and Dickson, 1975; Wolery and Sleep, 1976). To evaluate this further, analyses have been made of the alteration minerals in Reykjanes drillhole 8. Tomasson and Kristmannsdóttir

(1972) have described the mineralogical zoning for this drillhole. The dominant sheet silicate at temperatures < 200 °C is montmorillonite, which grades into random mixed-layer clays at 200–230 °C and ‘expanding chlorite’ and chlorite at 230–280 °C. Table V lists the structural formulae of the minerals sampled from between 150 m and 850 m (90–180 °C). Particle size analysis showed that clay-sized minerals comprised 70–90% of the samples and X-ray diffractometry revealed no minerals other than montmorillonite in this fraction of the altered rock. Montmorillonite has been identified as an alteration mineral in the experimental work described above. Nothing is known of its stoichiometry but it contains both dioctahedral and

TABLE V. *Formulae of montmorillonites in Reykjanes geothermal system*

152 m.*	Ca _{0.61}	Na _{0.22}	K _{0.05}	(Al _{0.24}	Fe _{0.20} ^{III}	Fe _{0.26} ^{II}	Mn _{0.01}	Mg _{1.73}	[Si _{3.21}	Al _{0.79}]	O ₁₀	(OH) ₂	2.76 H ₂ O
248 m.	Ca _{0.49}	Na _{0.41}	K _{0.05}	(Al _{0.17}	Fe _{0.53} ^{III}	Fe _{0.28} ^{II}	Mn _{0.01}	Mg _{1.34}	[Si _{3.21}	Al _{0.79}]	O ₁₀	(OH) ₂	3.64 H ₂ O
352 m.	Ca _{0.71}	Na _{0.35}	K _{0.02}	(Al _{0.41}	Fe _{0.40} ^{III}	Fe _{0.37} ^{II}	Mn _{0.01}	Mg _{0.86}	[Si _{3.27}	Al _{0.73}]	O ₁₀	(OH) ₂	1.84 H ₂ O
454 m.	Ca _{0.76}	Na _{0.34}	K _{0.01}	(Al _{0.34}	Fe _{0.28} ^{III}	Fe _{0.24} ^{II}	Mn _{0.01}	Mg _{1.29}	[Si _{3.16}	Al _{0.84}]	O ₁₀	(OH) ₂	3.20 H ₂ O
553 m.	Ca _{0.62}	Na _{0.26}	K _{0.02}	(Al _{0.17}	Fe _{0.42} ^{III}	Fe _{0.39} ^{II}	Mn _{0.01}	Mg _{1.37}	[Si _{3.16}	Al _{0.84}]	O ₁₀	(OH) ₂	3.35 H ₂ O
650 m.	Ca _{0.65}	Na _{0.29}	K _{0.02}	(Al _{0.20}	Fe _{0.39} ^{III}	Fe _{0.43} ^{II}	Mn _{0.01}	Mg _{1.34}	[Si _{3.04}	Al _{0.96}]	O ₁₀	(OH) ₂	2.37 H ₂ O
750 m.	Ca _{0.71}	Na _{0.42}	K _{0.02}	(Al _{0.30}	Fe _{0.31} ^{III}	Fe _{0.28} ^{II}	Mn _{0.01}	Mg _{1.17}	[Si _{3.13}	Al _{0.87}]	O ₁₀	(OH) ₂	1.48 H ₂ O
852 m.	Ca _{0.72}	Na _{0.37}	K _{0.01}	(Al _{0.38}	Fe _{0.30} ^{III}	Fe _{0.37} ^{II}	Mn _{0.01}	Mg _{1.13}	[Si _{3.14}	Al _{0.86}]	O ₁₀	(OH) ₂	1.74 H ₂ O

* refers to depths in drillhole at which samples located.

trioctahedral components and is rich in iron (Bischoff and Dickson, 1975; Hajash, 1975) and so appears to be similar to that found at Reykjanes. The compositions given in Table V can be used to describe the concentrations of Fe, Mn, and also Mg in Reykjanes thermal waters. Other controls possible for Mn and Fe are as sulphides, and of Fe by the magnetite-hematite buffer. The possibility of incorporating both Mn and Fe in an alteration mineral as divalent cations was suggested by Bischoff and Dickson (1975). This is achieved by the trioctahedral component of montmorillonite or, alternatively, by Mn²⁺ in solid solution with Fe oxide.

Thermodynamic calculations. The thermodynamics of these hydrothermal reactions have been evaluated and the results are illustrated in fig. 2. Equilibrium with montmorillonite at high temperature reduces the Mg content of sea-water to that observed at Reykjanes. At 200 °C and neutral pH (5.63) the equilibrium concentration of Mg is 7 mg l⁻¹ as compared with nearly 1300 mg l⁻¹ in normal sea-water. In ocean-floor rocks, chlorite appears to be a very abundant alteration product of hydrothermally altered basalts and it is likely that equilibrium with chlorite may control magnesium concentrations at higher temperatures. However, this could not be evaluated in the simple thermodynamic modelling employed here and calculations of structural formulae from deeper drillhole samples containing chlorite was not possible because of the presence of epidote. For iron, equilibrium with montmorillonite produces sea-water enriched in Fe²⁺ ions but the concentrations of iron in the Reykjanes thermal waters are better represented by equilibrium with iron sulphide. A virtual absence of Fe³⁺ ions is predicted since $a_{\text{Fe}^{3+}}$ in equilibrium with Fe^{III}-montmorillonite is $\sim 10^{-15}$. Manganese is significantly enriched in sea-water in high-temperature equilibrium with montmorillonite. At 200 °C and neutral pH the equilibrium concentration is 4.3 mg l⁻¹ as compared with about 0.1 μg l⁻¹ in normal sea-water and this agrees well with the Reykjanes data. MnS cannot control $a_{\text{Mn}^{2+}}$ and $a_{\text{MnO}} \sim 10^{-4}$ is required were Mn^{II} oxide to determine the observed manganese concentrations.

Discussion

The results presented for Deception Island waters and for the equilibrium reactions controlling the composition of Reykjanes thermal waters have in common the characteristics of the rock-water interactions inferred to be taking place on ocean ridges from the observed metasomatic alteration of dredged basalts. However, reservations must be made in applying these results to processes envisaged beneath ridges. For example, the anomalous levels of some elements in Deception Island waters may be explained by leaching of volcanic ash, and the assumption that they derive solely from hydrothermal reactions will place upper limits on the geochemical fluxes pertaining to this process. In addition, hydrothermal fluids on land may be subject to boiling near the surface, which will concentrate the dissolved constituents resulting in an overestimate of fluxes of elements added to solution by rock-water interaction but an underestimate of elements removed from solution. The significance of extrapolating from these land situations to the sub-sea-floor system must be viewed within the context of such uncertainties.

Despite these reservations, the calculation of geochemical fluxes is a useful exercise in that they give some indication of the importance of hydrothermal processes within the context of oceanic budgets. For example, there is a vast literature as to the origin of Mn in metalliferous ocean-ridge sediments and the calculation of a flux for Mn can be used to place an upper limit on the contribution by hydrothermal fluids and so assess whether the Mn in such sediments can be of submarine-volcanic origin. This example will be used to demonstrate the method employed although it is clear that the procedure can be more generally applied.

The assessment involves a simple comparison of the hydrothermal flux with an estimate of the rate of Mn accumulation in metalliferous sediments, but an important requirement is that the fluxes to be compared must be calculated using the same frame of reference. Since the real extent of metalliferous sediment deposition is uncertain, as is the amount of hydrothermally altered basalt, the approach that must be used is to consider the situation that all newly formed crust is altered resulting in Mn-rich hydrothermal solutions, which form metalliferous sediment over the whole of the mid-ocean ridge system. Then if, say, only 5% of basalt is actually altered there is a corresponding decrease in the calculated rate of metalliferous sediment deposition and so the comparison is still valid. It must be stressed that the fluxes calculated in this manner are absolute maxima and the individual values may have little quantitative significance.

Calculation of the hydrothermal flux requires estimates of the rate of production of ridge basalt and the average water-rock ratio in the hydrothermal system. The product of these terms gives the hydrothermal flow rate, which is multiplied by the Mn concentration of the hydrothermal fluid to give the estimated flux. On the basis of an annual intrusion of basalt of 6.6×10^{-5} km³ per km of ridge (Shor *et al.*, 1970), estimates of the length of the mid-ocean ridge system, which vary between 53 700 km and 80 000 km (Bott, 1971; Wright, 1971; Williams and von Herzen, 1974), and a density of layer II of 2.6 g cm⁻³ (Bott, 1971), the rate of basalt generation is $9.2\text{--}13.8 \times 10^{15}$ g yr⁻¹. Alternatively, Williams and von Herzen (1974) estimate that the new area of ocean crust is 2.94 km² yr⁻¹ and, taking a depth of 5 km, this gives a rate of 38.2×10^{15} g yr⁻¹. Spooner (1976) has obtained a rate of 39.4×10^{15} g yr⁻¹ using a method based on half-spreading rates of ocean floor. To calculate the hydrothermal flow rate a water-rock ratio of 20:1 will be assumed, because this ratio has been computed from isotopic data for metamorphic rocks on Cyprus that are thought to have developed in a sub-sea-floor hydrothermal system (Gass and Smewing, 1973; Spooner and Fyfe, 1973; Spooner, 1974; Spooner *et al.*, 1974). In addition, this ratio is of the same order as the ratio used in the experiments described above, which have successfully simulated the compositions

of the fluids found at Reykjanes and of some Deception Island water. On this basis a flow rate of $1.8-7.9 \times 10^{17}$ g yr⁻¹ is obtained. This result is remarkably similar to the range of $1.3-9 \times 10^{17}$ g yr⁻¹ estimated by Wolery and Sleep (1976), who used a thermal balance model. According to Wolery and Sleep (1976) the mean exit temperature of hydrothermal fluids is 150–300 °C. At 200 °C the equilibrium concentration of manganese is ≈ 4 mg l⁻¹ similar to the relevant Reykjanes water composition (fig. 2). This compares with a range of 0.03–2.42 mg l⁻¹ from Deception Island waters (Table I, and Elderfield, 1972) and 11.6 mg l⁻¹ for the reaction of sea-water and Deception Island basalt (Table II). On the basis of the equilibrium manganese concentration, the estimated flux is in the range $5-36 \times 10^{11}$ g yr⁻¹. In comparison the accumulation rate of manganese in metalliferous sediments is $2-9 \times 10^{11}$ g yr⁻¹. This is obtained by multiplying the Mn in metalliferous sediments overlying newly formed ocean crust (21 g cm⁻², Bender *et al.*, in press; or 32 g cm⁻², Lyle, in press) by the length of the mid-ocean ridge system and by its spreading rate ($\approx 2-3$ cm yr⁻¹). This comparison shows that hydrothermal processes can provide the manganese in localized metalliferous sediment. However, the result gives equivocal evidence that hydrothermal manganese contributes to the oceanic excess of $\approx 2 \times 10^{12}$ g yr⁻¹ revealed by Mn budget calculations (Elderfield, 1976). Elderfield (1976) considered that hydrothermal solutions could reasonably provide 10% of this excess. This is feasible from the fluxes presented here but, in view of the method employed in their calculation, it appears to represent an upper limit. The ranges given for each flux reflect the uncertainties in the maximum values calculated and not the ranges in fluxes that are considered feasible. If, for example, only 1% of ocean crust is hydrothermally modified the comparison is between $5-36 \times 10^9$ g yr⁻¹ Mn produced and $2-9 \times 10^9$ g yr⁻¹ Mn forming metalliferous sediment. Since there is conflicting evidence as to the extent of hydrothermal influence (Aumento *et al.*, 1976), the source of excess manganese remains uncertain. Possibilities so far unconsidered are a diagenetic source, not as a consequence of redox reactions but by dissolution of biogenic matter, and the source identified from Table IV, that of leaching of soluble material in volcanic ash, which according to Taylor and Stoiber (1973) can provide a manganese flux of $\approx 10^{11}$ g yr⁻¹.

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