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Earth and Planetary Science Letters 211 (2003) 173–187
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Imbalance in the oceanic strontium budget

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Received 15 November 2002; received in revised form 20 March 2003; accepted 28 March 2003

Abstract

Palmer and Edmond [Earth Planet. Sci. Lett. 92 (1989) 11–26] indicated that thermally plausible oceanic hydrothermal inputs of strontium to the oceans are not sufficient to balance the riverine input. It has recently been suggested that off-axis low-temperature hydrothermal circulation may reconcile this discrepancy [e.g. Butterfield et al., Geochim. Cosmochim. Acta 65 (2001) 4141–4153]. Strontium isotope alteration profiles are compiled for sampled in situ ocean and ophiolite crust to calculate a sustainable cumulative hydrothermal flux to the oceanic strontium budget. High-temperature circulation contributes $\sim 1.8 \times 10^9$ mol yr^{-1} of basaltic strontium to the oceans. Enhanced hydrothermal systems in arc-related spreading environments (10% of the crust) may increase this to $\sim 2.3 \times 10^9$ mol yr^{-1}. It is shown that low-temperature flow cannot supply the remaining flux required to reconcile the oceanic strontium budget ($\sim 8.7 \times 10^9$ mol yr^{-1}) because this would require 100% exchange of seawater strontium for basaltic strontium over an 820 m section of MORB-like crust. Currently sampled in situ ocean crust is not altered to this extent. The isotopic alteration intensity of 120 Myr crust sampled in DSDP Holes 417D and 418A indicates that off-axis low-temperature flow may contribute up to $\sim 8 \times 10^8$ mol yr^{-1} of basaltic strontium (9% of that required). The ocean crust can sustain a total basaltic strontium flux of $\sim 3.1 \pm 0.8 \times 10^9$ mol yr^{-1} (^{87}Sr/^{86}Sr ~ 0.7025) to the oceans. This is consistent with hydrothermal flux estimates, but remains less than a third of the flux required to balance the oceanic strontium budget. The ocean crust cannot support a higher hydrothermal contribution unless the average ocean crust is significantly more altered than current observation.

Keywords: strontium isotopes; ocean budget; ocean crust; hydrothermal; ophiolite; ODP

1. Introduction

Hydrothermal circulation at oceanic spreading centers modifies the thermal and igneous structure of the oceanic crust and the geochemical composition of the crust and oceans. Despite its significance to global geochemical cycles fundamental uncertainties remain. In particular, although the magnitude of the high-temperature water flux is reasonably well constrained from a range of thermal modeling and geochemical budget approaches (3–6 $\pm$ 1.5 $\times 10^{13}$ kg yr^{-1} [1]), our knowledge of low-temperature fluxes, geochemical exchange mechanisms, and the structural, temporal and spatial evolution of the systems remains poor.

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doi:10.1016/S0012-821X(03)00191-2

Hydrothermal flux estimates based on geochemical budgets are founded on two alternative approaches: (1) mass balance of geochemical tracers in the oceans against the known river input, and (2) assessing the degree of alteration in oceanic crustal profiles. Mass balance of the oceanic strontium isotope budget should provide one of the more robust estimates of the hydrothermal water flux, because it is free of many of the assumptions inherent in the use of other geochemical tracers (see [1]). Palmer and Edmond [2] used ocean mass balance to calculate that a cumulative high-temperature hydrothermal water flux of $\sim 1.2 \times 10^{14}$ kg yr^{-1} is required to keep the oceanic strontium budget near steady state. This is an order of magnitude greater than other high-temperature flux predictions [1]. They inferred that this is a high-temperature water flux because little significant strontium exchange is expected during low-temperature flow [3]. However, this flux would require a heat supply more than six times greater than the magmatic heat available [4]. Recently Butterfield et al. [5] and Mottl and Wheat [6], amongst others, have suggested that this discrepancy can be reconciled by significant low-temperature exchange in the flank environments.

The extent of alteration observed in ocean and ophiolite crustal profiles provides an important constraint on hydrothermal fluxes. If hydrothermal circulation satisfies the flux required to balance the oceanic strontium budget this will have a discernible impact on the alteration intensity of the crustal profile. In this paper, we compile strontium isotope alteration profiles for five ocean crust areas and two ophiolite complexes to quantify the degree of exchange displayed by the ocean crust from a range of ages and environments. By simple mass balance it is shown that the ocean crust is insufficiently altered by high-temperature fluids to achieve the hydrothermal strontium flux required to balance the oceanic strontium budget. Low-temperature flow cannot reconcile this, because it would require 100% isotopic exchange of basaltic strontium for seawater strontium over an 820 m section of ocean crust or proportionally less exchange over greater depths and such alteration is not observed.

2. Geological setting of selected sites

Strontium isotope data have been compiled for the five best studied areas of oceanic crust (Table 1). The selection of ocean crustal sites was limited to areas where there are sufficient strontium isotope data, and where a significant proportion of the crustal profile can be observed.

Strontium isotope data have also been compiled for the Troodos Ophiolite, Cyprus and the Semail Ophiolite, Oman (Table 1), two of the best studied and most complete ophiolites. However, these ophiolites formed in suprasubduction-related spreading environments and may not be representative of normal oceanic processes.

3. Strontium isotopic alteration profiles through ophiolite and ocean crust

Fig. 1 shows the compilation of published strontium isotope data plotted against approximate stratigraphic depth, for the five ocean crust sites (Fig. 1a,b) and the two ophiolite assemblages (Fig. 1c,d). The amount of isotopic shift from primary basaltic compositions towards the seawater value represents the degree of fluid–rock interaction and exchange in the system. For comparability this is expressed as a percentage exchange of the sampled profile ($^{87}Sr/^{86}Sr_{ROCK}$) relative to unaltered rock ($^{87}Sr/^{86}Sr_{BAS}$) and seawater values ($^{87}Sr/^{86}Sr_{SW}$):

$$\text{percentage exchange} = 100 \times \left(\frac{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{ROCK}} - ^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{BAS}}}{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{SW}} - ^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{BAS}}}\right) \quad (1)$$

3.1. Ocean crust data

ODP Hole 504B penetrates ~ 2 km to near the base of the sheeted dyke complex and is the most complete upper crustal section through intact modern oceanic crust (Fig. 1a). In addition, lava sections have been sampled in several locations (Costa Rica Rift area, Pacific Ocean – ODP Site 896; MARK area, Atlantic Ocean – ODP Sites 332, 335, 395 and 648B; South of Bermuda Rise area, Atlantic Ocean – DSDP Sites 417–418) and sheeted dyke and gabbro sections have been sampled in tectonic windows and regions exhumed by detachment faulting (Hess Deep area, Pacific Ocean – ODP Sites 894; MARK area, Atlantic Ocean – ODP Sites 921–923; Atlantis II Fracture Zone, Indian Ocean – ODP Site 735).

The upper lavas (0–400 m) show the greatest degree of both isotopic exchange (average 5–12%) and scatter. The alteration systematically decreases with depth, until at the base of ODP Hole 504B the lowermost dykes sampled show only minor (2%) elevation in their strontium isotopic composition. The amount of scatter appears to increase with age – the oldest lavas (DSDP

Table 1
Selected ocean crust sites and ophiolite complexes

Site/complex	Location	Age (Ma)	Geology and lithologies sampled (for references see data compilation Fig. 1)	DSDP/ODP holes
Costa Rica Rift area	Pacific	6.9	ODP Site 504B, situated on the southern flank of the Costa Rica Rift, forms the deepest drill hole in the ocean crust penetrating over 2111 m to the base of the sheeted dyke complex. ODP Site 896 is situated ~1 km SE and penetrates ~290 m of the upper volcanic section.	504 and 896
Hess Deep area	Pacific	1	Tectonic dismemberment and escarpment exposure of young EPR eastern flank crust – associated with deep crustal rifting ahead of westward propagation of the Cocos–Nazca Rift. ODP Sites 894 and 895 penetrate gabbros and peridotites within 200 m of the surface.	894
MARK area	Atlantic	< 1–3.5	Tectonic disruption along a major fracture zone displacing ocean crust of varying ages, creating escarpment exposure of the crustal sequence. DSDP/ODP holes penetrate lavas, diabase and gabbro units.	332–335, 395, 648 and 920–924
South of Bermuda Rise area	Atlantic	120	Cretaceous age in situ crust – one of the oldest profiles sampled. DSDP Sites 417 and 418 penetrate 550 m into the basement lava sequence.	417–418
Atlantis II Fracture Zone area	Indian	11–12	Lower crustal gabbros tectonically exhumed by complex transform-related faulting. ODP Site 735 is located on a shallow wave cut platform and penetrates ~1500 m of the lower crustal gabbro sequence.	735
Troodos Ophiolite	Cyprus	93	Fragment of mid-Cretaceous oceanic lithosphere preserved on the island of Cyprus, eastern Mediterranean. Well preserved crustal sequence with minimal tectonic disruption.	
Semail Ophiolite	Oman	95	Fragment of mid-Cretaceous oceanic lithosphere preserved along the Arabian continental margin of Oman. Large and well preserved with minimal tectonic disruption; excellent exposure of the complete crustal sequence and upper mantle.	

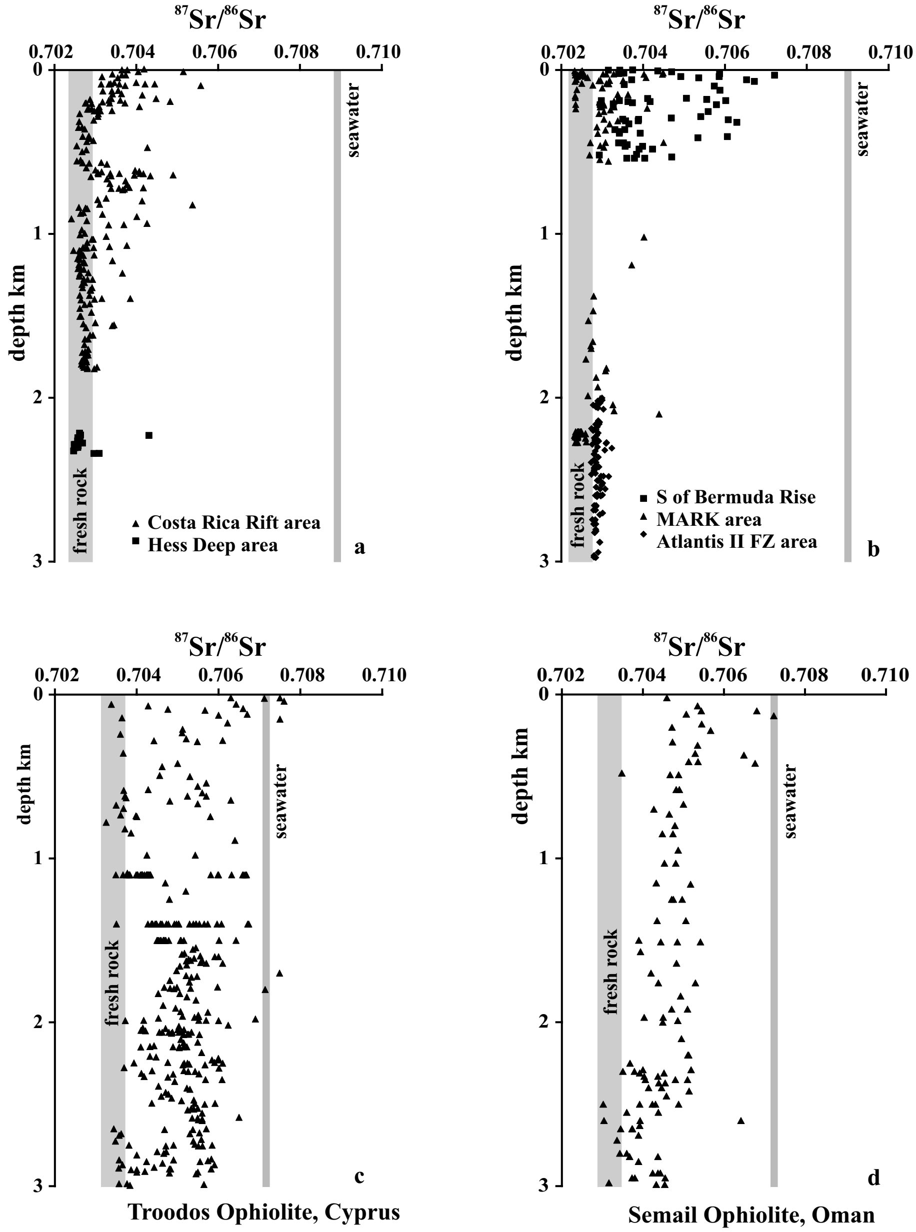


Fig. 1. Composite whole-rock Sr isotope profiles through oceanic crust and ophiolite sections corrected for Rb decay to their magmatic age: (a) the Costa Rica rift area (ODP Holes 504B and 896A [51] and unpublished data); (b) the MARK area [52–63], south of Bermuda Rise area (DSDP Holes 417D and 418A) [7,64–67] and the Atlantis II Fracture Zone [68–71]; (c) the Troodos Ophiolite, Cyprus [8,14,72–75]; and (d) the Semail Ophiolite, Oman [29,76–78].

Holes 417D and 418A at ~120 Ma [7], Fig. 1b) exhibit the greatest scatter with ~19% exchange (to $^{87}Sr/^{86}Sr$ ~0.7041) which is comparable to that shown by ophiolite lava sequences (Fig. 1c,d). Gabbros from Hess Deep and the Atlantis II Fracture Zone show little isotopic exchange and alteration, with mean values similar to igneous compositions. However, the MARK area gabbros show significant exchange (10%) around the sheeted dyke–gabbro transition zone.

3.2. Ophiolite crust

Ophiolitic crust shows more intense alteration and isotopic exchange than any in situ ocean crust sampled to date. The Troodos Ophiolite shows a considerable degree of scatter and exchange, ranging between fresh rock ($^{87}Sr/^{86}Sr$ $\sim$0.7035 [8]) and contemporaneous seawater compositions ($^{87}Sr/^{86}Sr$ $\sim$0.7073 at 90 Ma [9]) throughout the upper lava section (0–1 km). There is an appreciable decrease in scatter below $\sim$1 km with $\sim$50% mean isotopic exchange. The Semail Ophiolite shows significant exchange ($\sim$53%) in the lava sequence. The sheeted dyke complex exhibits a decrease in the degree of alteration and scatter with depth from $\sim$38% to $\sim$22%. The upper gabbro section sampled shows minor elevation ($\sim$13%) above fresh rock values.

4. Discussion

These profiles present a time-integrated record of hydrothermal alteration and indicate that ophiolite crust is significantly more altered than in situ ocean crust. This raises two questions: (1) is the ocean crust sufficiently altered to balance the oceanic strontium budget, and (2) does tectonic environment extend a primary control on the magnitude of hydrothermal fluxes? To address these questions we investigate the hydrothermal basaltic strontium flux required to balance the oceanic strontium budget, and consider the potential contribution of more vigorous hydrothermal regimes associated with arc-related spreading environments.

4.1. Ocean strontium mass balance

To understand the oceanic strontium budget it is necessary to consider the systematics of ocean strontium mass balance and the behavior of basaltic strontium in hydrothermal systems. The strontium isotopic composition of seawater is moderated by the river input ($F\mathrm{Sr}_{\mathrm{RIV}}$), the buffering effect of carbonate diagenesis ($F\mathrm{Sr}_{\mathrm{DIA}}$), and the hydrothermal input ($F\mathrm{Sr}_{\mathrm{HYD}}$) [2]. Variations in seawater strontium isotopic composition with time are given by:

$$\frac{\mathrm{d}(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{SW}}}{\mathrm{d}t} = \left[\frac{F\mathrm{Sr}_{\mathrm{RIV}}(^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{RIV}} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{SW}})}{\mathrm{Sr}_{\mathrm{SW}}}\right] + \left[\frac{F\mathrm{Sr}_{\mathrm{DIA}}(^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{DIA}} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{SW}})}{\mathrm{Sr}_{\mathrm{SW}}}\right] + \left[\frac{F\mathrm{Sr}_{\mathrm{HYD}}(^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{HYD}} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{SW}})}{\mathrm{Sr}_{\mathrm{SW}}}\right] \quad (2)$$

where $F\mathrm{Sr}_i$ is a strontium flux, $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_i$ is isotopic composition and Sr_i is strontium concentration of component i with SW seawater, DIA the diagenetic flux, RIV the river flux and HYD the hydrothermal flux.

Hydrothermal strontium comprises a mixture of a seawater component ($^{87}Sr/^{86}Sr$ $\sim$0.70916) and a basaltic component ($^{87}Sr/^{86}Sr$ $\sim$0.7025). To facilitate discussion of the impact of hydrothermal fluxes on the ocean crust and oceanic budgets, we recalculate the basaltic strontium component ($F\mathrm{Sr}^{\mathrm{bas}}_{\mathrm{HYD}}$) of the hydrothermal strontium flux ($F\mathrm{Sr}_{\mathrm{HYD}}$) where:

$$F\mathrm{Sr}^{\mathrm{bas}}_{\mathrm{HYD}} = F\mathrm{Sr}_{\mathrm{HYD}}\frac{(^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{HYD}} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{SW}})}{(^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{BAS}} - {}^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{SW}})} \quad (3)$$

Eq. 2 can be rearranged to show that hydrothermal circulation must supply a basaltic strontium flux of $\sim 1.1 \times 10^{10}$ mol yr^{-1} to maintain the present seawater strontium isotopic composition allowing for a current increase of $\sim 5.4 \times 10^{-5}$ Myr^{-1} [10], based on the parameters given in Table 2. This estimate is slightly lower than that of Palmer and Edmond [2] because the river input flux used includes revised data for the Ganges and Brahmaputra rivers [11].

4.2. High-temperature vent fluid characteristics and the behavior of basaltic strontium

The hydrothermal basaltic strontium flux may be achieved by transfer of basaltic strontium into

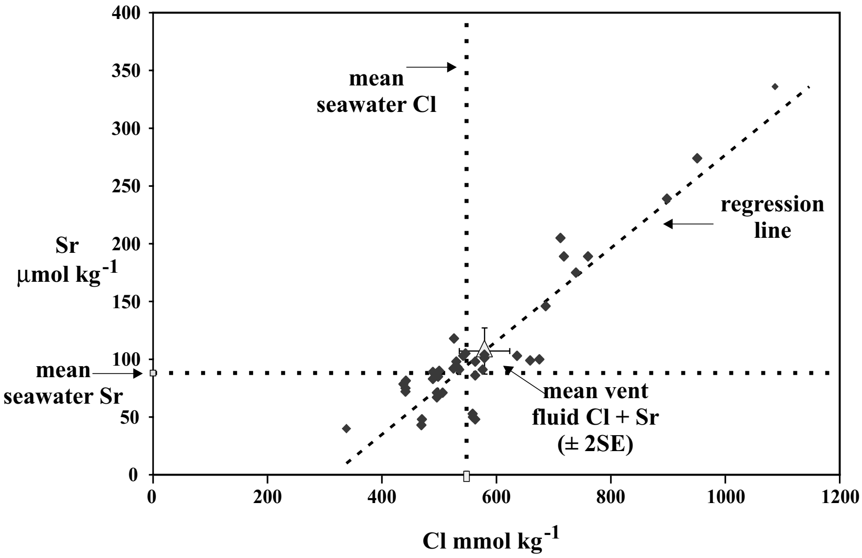


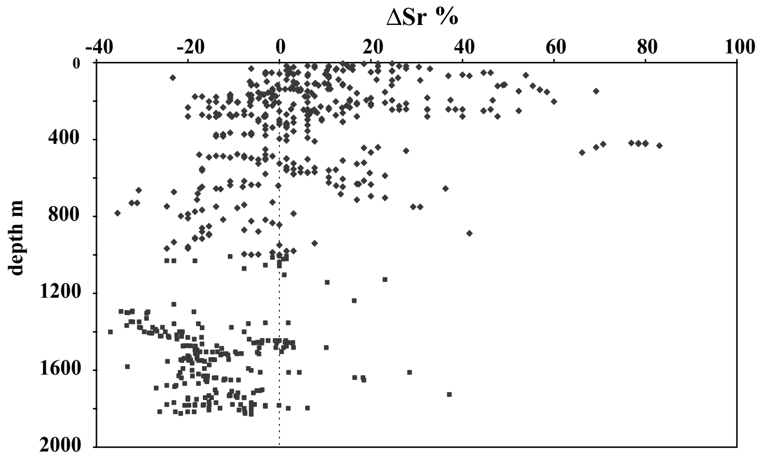
Fig. 2. Sr concentration versus chlorinity of high-temperature end-member hydrothermal fluids, based on data compilation of [47]. Cl and Sr behave conservatively during high-temperature circulation and the mean fluid values plot within 2 standard error of seawater (see text).

the oceans by one or both of two principal mechanisms: (1) loss of basaltic strontium to hydrothermal fluids, reducing the rock strontium concentration but leaving the $^{87}Sr/^{86}Sr$ ratio unchanged, and/or (2) strontium isotopic exchange with hydrothermal fluids, replacing low $^{87}Sr/^{86}Sr$ ratio basaltic strontium with high $^{87}Sr/^{86}Sr$ ratio seawater strontium and leaving the strontium concentration unchanged. High-temperature vent fluid characteristics (strontium concentration and strontium isotope composition) and ocean crust alteration profiles provide the primary constraint on understanding the behavior of basaltic strontium during hydrothermal circulation. High-temperature end-member fluids exhibit a large range in strontium concentration which is correlated with chlorinity [12]. The linear relationship between strontium and chlorine in end-member fluids indicates that both species behave conservatively during high-temperature circulation (Fig. 2). The mean chlorinity of 579 ± 44 mmol kg^{-1} ($2\times$ standard error) and the corresponding seawater-normalized strontium concentration of 95 ± 20 µmol kg^{-1} are within error of seawater values (548 mmol kg^{-1} and 88 µmol kg^{-1} respectively [10,13]). Further, the mean

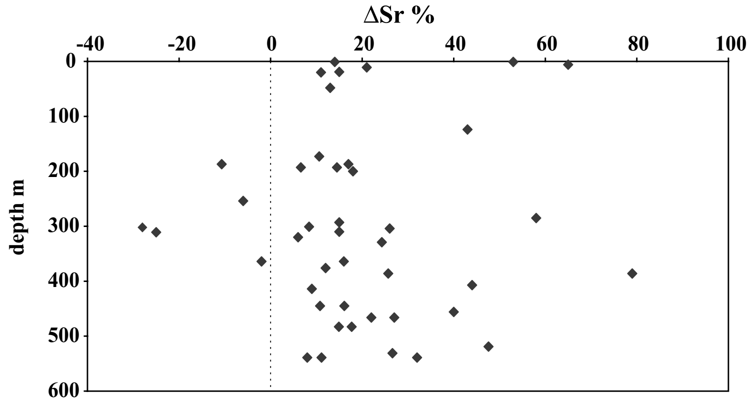
Table 2
Oceanic strontium isotope mass balance parameters

Source	Sr concentration (µmol kg^{-1})	$^{87}Sr/^{86}Sr$	Sr flux (mol yr^{-1})	Inventory (mol)
River input[a]	0.902	0.7116	3.4×10^{10}	–
Benthic flux[b]	–	0.7084	3.4×10^{9}	–
Hydrothermal[c]	95	0.7037	to be calculated	–
Seawater[d]	88	0.70916	–	125×10^{15}

[a] River input calculated from compilation in [2] supplemented with revised and new data of [46] and with revised Ganges–Brahmaputra flux of [11].
[b] Diagenetic flux after [40].
[c] Sr concentration and $^{87}Sr/^{86}Sr$ from data compiled by [47].
[d] Seawater $^{87}Sr/^{86}Sr$ from [10], Sr concentration from [13]



a) whole-rock strontium profile for ODP Holes 504B and 896A



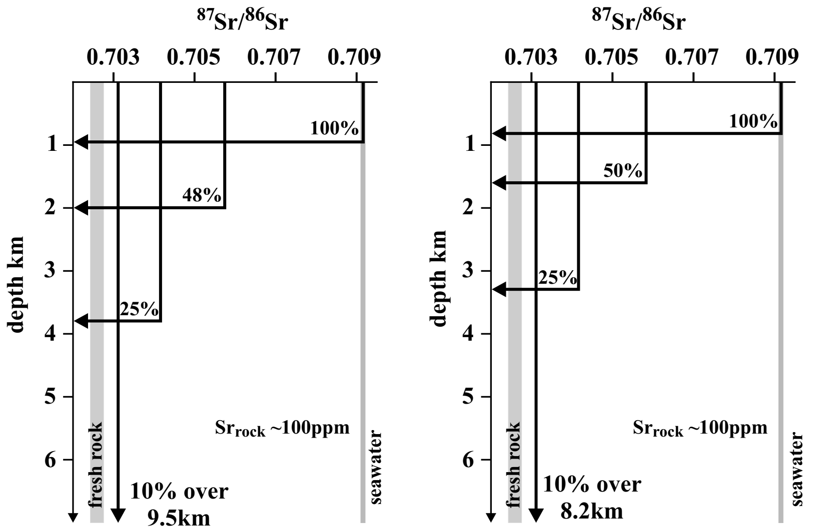
b) whole-rock strontium profile for DSDP Holes 417D and 418A

Fig. 3. Whole-rock Sr concentration profiles for oceanic crust. ΔSr is the percentage difference between measured rock and estimated fresh rock values for: (a) ODP Holes 504B and 896A with an estimated fresh rock value of 65 ppm [79,80], and (b) DSDP Holes 417D and 418A [7,64–66] with an estimated fresh rock value of 100 ppm [65]. Data from same sources as Fig. 1.

(strontium-weighted) end-member fluid isotopic composition ($^{87}Sr/^{86}Sr$ ~0.7037) contains 82% basaltic strontium and records significant interaction with the crustal profile. This indicates that isotopic exchange is the dominant mechanism for the transfer of basaltic strontium into the oceans. This is supported by the strontium isotope and strontium concentration profiles for ODP holes 504B and 896A which show ~12% isotopic exchange, but less than 1% basaltic strontium loss (within error of igneous fractionation) over the sampled profile (Figs. 1a and 3a).

4.3. Ocean crust strontium isotopic alteration profiles

High-temperature circulation cannot satisfy the basaltic strontium flux required to balance the oceanic strontium budget for two reasons. Firstly, the impact on the upper crustal profile of removing $\sim 1.1 \times 10^{10}$ mol yr^{-1}, the basaltic strontium flux required, is inconsistent with the degree of alteration displayed by ocean crustal profiles. Fig. 4a illustrates that to balance the oceanic strontium budget, entirely by high-temperature



a) Prediction: impact on the crustal profile of removing the basaltic Sr flux required to balance the oceanic Sr budget

b) Prediction: low-temperature alteration required to balance the oceanic Sr budget given the predicted high-temperature contribution

Fig. 4. The predicted strontium isotope alteration intensities required for: (a) removing the basaltic strontium flux required to balance the oceanic strontium budget (1.1×10^{10} mol yr^{-1}) from a MORB-like section of ocean crust (fresh rock values of $^{87}Sr/^{86}Sr$ ~0.7025 and Sr ~100 ppm) – this can be achieved by 100% exchange of basaltic strontium for seawater strontium over a 950 m section, 48% exchange over 2 km (the depth of high-temperature flow), 25% exchange over 3.8 km, or 10% over 9.5 km; (b) the low-temperature contribution required to balance the oceanic strontium budget (basaltic flux of ~8.7×10^{9} mol yr^{-1}) given the sustainable high-temperature contribution predicted (with allowance for increased hydrothermal activity associated with arc-related systems) on a profile of MORB-like crust with 8% high-temperature isotopic exchange (to $^{87}Sr/^{86}Sr$ ~0.7030) – this can be achieved, for example, by 100% exchange of basaltic strontium for seawater strontium over a 820 m section, 50% exchange over 1.6 km, 25% exchange over 3.3 km, or 10% over 8.2 km.

flow, would require 100% isotopic exchange of basaltic strontium for seawater strontium over a 950 m section – or lower alteration intensities over greater depths, for example 48% exchange over a 2 km profile (the depth of high-temperature circulation). Ocean crust alteration profiles (Fig. 1a,b) indicate that the ocean crust is not altered to this extent. However, we note that this prediction is comparable with the degree of alteration displayed by the Troodos Ophiolite, Cyprus (Fig. 1c), which is significantly more recrystallized and isotopically enriched than modern ocean crust [14]. This raises important questions regarding the magnitude and contribution of back-arc hydrothermal systems and how increased activity may be thermally maintained. Secondly, the axial heat flux required (~8.1×10^{12} W) to sustain the high-temperature water flux necessary to achieve the basaltic strontium flux predicted is nearly six times greater than that available (~1.3×10^{12} W – see below).

4.4. *Predicting a sustainable high-temperature strontium flux*

A sustainable hydrothermal high-temperature strontium flux estimate must be consistent with: (1) the hydrothermal heat flux available to drive high-temperature circulation, (2) high-temperature vent fluid characteristics, and (3) the observed degree of crustal alteration. The heat flux available and the characteristic temperature to which fluids are heated control the magnitude of hydrothermal water fluxes. For axial high-temperature systems, an upper limit on the heat available is provided from the latent heat of crystallization and cooling the ocean crust from magmatic to hydrothermal temperatures. We assume an axial hydrothermal heat flux of $\sim 1.3\times10^{12}$ W based on 50% hydrothermal efficiency [4,15] and hydrothermal cooling of the upper 2 km to ambient temperatures (0°C) and the rest of the crust (7.1 km thick [16]) to 860°C (see Table 3). This is a maximum estimate because we assume that all of the latent heat is available to heat high-temperature hydrothermal fluids (i.e. in high-level magma chambers). More uncertain is the mean temperature (and range) of high-temperature fluids. The widespread observation of vent fluid temperatures ($\sim$350°C [17]), their phase-separated character (see [18]), and the tendency of high-temperature systems to evolve distributed recharge and concentrated discharge zones [4,15,19,20] suggest that the majority of the circulation in the axial regime is high-temperature. For a global seafloor production rate of 3.45 km^2 yr^{-1} [21,22], we predict a high-temperature hydrothermal water flux of $\sim 2.3\times10^{13}$ kg yr^{-1} (at 400°C and 450 bar – based on [23]). The upper limit on this flux estimate, assuming 100% hydrothermal efficiency, is $\sim 4.6\times10^{13}$ kg yr^{-1}. These estimates are lower than those of Mottl [24] because the estimate of latent heat of crystallization used here (500 J g^{-1} from Paula Smith, personal communication, after [25–27]) is $\sim$26% lower, the specific heat for basalt of appropriate mineralogies after [25] is $\sim$8% lower and the lower crust is assumed cooled to only 860°C rather than 350°C. However, we assume a mean crustal thickness of 7.1 km [16], 9% thicker than that adopted by Mottl. The main difference is that we take the hydrothermal circulation to be $\sim$50% efficient, following [4,15], rather than the 100% efficiency assumed by Mottl [24].

A high-temperature axial system with a water flux of $\sim 2.3\times10^{13}$ kg yr^{-1} and fluid characteristics similar to current observation (mean Sr $\sim$95 μmol kg^{-1} and $^{87}Sr/^{86}Sr$ $\sim$0.7037) will contribute a basaltic strontium flux of $\sim 1.8\times10^{9}$ mol yr^{-1} to the oceanic strontium budget (Table 3). This would require 8% isotopic exchange of a 2 km section of MORB-like crust and no basaltic strontium loss consistent with the degree of alteration displayed by ocean crust alteration profiles. The alteration intensities recorded in Holes 504B and 896A are equivalent to a basaltic strontium

Table 3
Hydrothermal contribution to the oceanic strontium budget

Hydrothermal contribution	Hydrothermal fluid characteristics		Water flux	Basaltic strontium flux	Predicted crustal alteration intensity
	$^{87}Sr/^{86}Sr$	Sr μmol kg^{-1}	10^{13} kg yr^{-1}	10^{9} mol yr^{-1}	$^{87}Sr/^{86}Sr$
High-temperature	0.7037	95	2.3[a]	1.8	$\sim$8% exchange (0.7030) over 2 km[b]
Arc-related	0.7040	77	10	0.7	$\sim$20% exchange (0.7046) over 2 km[c]
Low-temperature[d]	(0.7089)	(91)	*(228)*[e]	8.7	100% exchange (0.70916) over 820 m
Low-temperature[f]	(0.7089)	(91)	*(21)*[g]	0.8	exchange to 20% (0.7038) over 550 m[h]

[a] Assuming 50% of the heat available is removed by high-temperature fluids which cool the upper 2 km of the crust to 0°C and the rest of the crust (7.1 km thick [16]) to 860°C; latent heat of basalt $\sim$500 J g^{-1} (Paula Smith, personal communication; calculated from [25] and consistent with [26,48]); specific heat of basalt and rock $\sim$1.1 J g^{-1} °C^{-1} [25] and melt temperature $\sim$1250°C; specific heat of seawater (integrated from 0 to 400°C at 450 bar) $\sim$4.59 J g^{-1} °C^{-1} based on [49].

[b] Alteration intensity (%) = $100\times(^{87}Sr/^{86}Sr_{ROCK}-^{87}Sr/^{86}Sr_{BAS}/^{87}Sr/^{86}Sr_{SW}-^{87}Sr/^{86}Sr_{BAS})$ – see text.

[c] Arc-related crust with fresh rock values of $^{87}Sr/^{86}Sr$ $\sim$0.7035 and Sr $\sim$150 ppm.

[d] Low-temperature contribution required to reconcile the oceanic strontium budget.

[e] Estimated from the low-temperature basaltic strontium flux required to balance the oceanic strontium budget and the mean strontium concentration and isotopic composition of low-temperature fluids from ODP Holes 1023 and 1024 (Juan de Fuca Ridge [37,50]).

[f] Predicted sustainable low-temperature contribution based on the strontium isotopic alteration profile for DSDP Holes 417D and 418A.

[g] Estimated from the alteration intensity of DSDP Holes 417D and 418A and mean strontium concentration and isotopic composition of low-temperature fluids from ODP Holes 1023 and 1024 (Juan de Fuca Ridge [37,50]).

[h] MORB-like crust with 8% high-temperature isotopic exchange ($^{87}Sr/^{86}Sr$ $\sim$0.7030 and Sr $\sim$100 ppm).

flux of $\sim 1.5\times10^9$ mol yr^{-1}, assuming present-day spreading rates. Therefore, we predict that the ocean crust can sustain a high-temperature basaltic strontium flux of $\sim 1.8\times10^9$ mol yr^{-1}, which contributes ~17% of that required to balance the oceanic strontium budget.

4.5. Arc-related high-temperature contribution

A number of observations indicate that back-arc- and suprasubduction-related hydrothermal systems may have higher hydrothermal water fluxes than mid-ocean ridge hydrothermal systems: (1) crust formed in arc-related settings is more intensely recrystallized with greater strontium isotopic exchange (Fig. 1) than MORB-like crust [14,28]; (2) the strontium isotopic composition of vent fluids inferred for ophiolite complexes [14,29] is significantly more seawater-dominated than non-arc ridge vent fluids; (3) epidosite assemblages, which require high water fluxes and greater fluid channelling, are common in ophiolite complexes [30], but have only been reported from one oceanic locality in an arc-related setting from the Tongan Fore-arc [31,32]; and (4) the magma chamber depth in the Lau Basin is ~1.5 km deeper than other ridges implying proportionally greater hydrothermal heat loss [15]. Further, the high-temperature water flux modeled for the strontium isotopic alteration profile of the Troodos Ophiolite, Cyprus is three times greater than estimates for in situ crust [14]. This raises two questions: (1) does increased hydrothermal activity in arc-related systems make a significant contribution to the cumulative hydrothermal strontium flux to the ocean budget, and 2) how are the higher heat fluxes predicted to support arc-related hydrothermal systems generated and maintained?

Approximately 10% of modern ocean crust is formed in an arc-related environment [21,22]. If these hydrothermal systems have high-temperature water fluxes comparable to that inferred for the Troodos Ophiolite [14] they will contribute a basaltic strontium flux of $\sim 7.0\times10^8$ mol yr^{-1} to the oceans – based on modern arc-related high-temperature vent fluid characteristics (Table 3). This is comparable to the alteration intensity observed in Izu-Bonin fore-arc crust, sampled in ODP Hole 786B; although we note that this hole also displays significant basaltic strontium loss [28].

The higher water fluxes inferred may result from arc-related crust being thicker and thus containing a greater magmatic heat flux. This is supported by observation that the Tongan Fore-arc system is magmatically rich with little tectonic extension [33] although ophiolite sequences seem no thicker than normal oceanic crust.

4.6. The low-temperature hydrothermal contribution

For low-temperature hydrothermal circulation to reconcile the oceanic strontium budget, as suggested by Butterfield et al. [5], flank fluids would have to contribute a basaltic flux of $\sim 8.7\times10^9$ mol yr^{-1} to the oceans (Table 3). This would have a discernible impact on the alteration intensity of the crustal profile. Fig. 4b illustrates that low-temperature alteration cannot supply the necessary basaltic strontium flux because this would require either: (1) 100% isotopic exchange of basaltic strontium for seawater strontium over an 820 m profile of MORB-like crust (with 8% high-temperature isotopic exchange), or (2) lower alteration intensities over greater depths, for example 25% exchange of a 3.3 km profile. No ocean crustal profiles sampled thus far are this altered.

Predicting the behavior of strontium in low-temperature systems and a sustainable low-temperature hydrothermal contribution is problematic, due to poorly constrained low-temperature flank water flux estimates, limited observation of low-temperature fluids, and restricted observation of flank crustal profiles. Cretaceous age crust sampled in DSDP Holes 417D and 418A provides a 120 Myr record of high- and low-temperature alteration and presents the most complete observation of a low-temperature alteration profile. These holes display a greater degree of isotopic exchange and scatter than observed elsewhere in the ocean crust, with ~19% isotopic exchange over the 550 m section sampled. These holes also record a mean gain of ~20% whole-rock strontium (Fig. 3b) which can more than account for the isotopic exchange observed (assuming 20%

gain of seawater strontium with a seawater isotopic signature ($^{87}Sr/^{86}Sr$ ~0.709)). Therefore, it is difficult to determine if significant low-temperature isotopic exchange occurs in flank environments or whether this is due to the ocean crust behaving as a sink for seawater strontium – although it is likely that both are occurring. Data from Hole 417A have not been included in this calculation because this hole is situated on a topographic basement high and exhibits an usually high level of alteration which may not be representative of the global ocean crust.

Currently observed low-temperature fluids indicate that some isotopic exchange occurs, with no basaltic strontium loss, during low-temperature circulation. Off-axis fluids from the Galapagos Mounds and the Equatorial Pacific [34–36] and ODP Sites 1023 and 1024 (on the Juan de Fuca Ridge flank) [37] show isotopic compositions similar to seawater. However, the Juan de Fuca system is anomalous due to high sedimentation rates and early sealing of the hydrothermal system, and flank fluids sampled further off axis are more deeply buried, hotter and more evolved (containing ~25% basaltic strontium in their isotopic signal $^{87}Sr/^{86}Sr$ ~0.7075) [5,37,38]. We note that some of these fluids show strontium concentrations slightly elevated above seawater values, although most fall within the range previously defined for high-temperature fluids. If significant leaching of basaltic strontium occurred during low-temperature flow, as suggested by Wheat and Mottl [39], this would have a discernible impact on the crustal profile yet DSDP Holes 417D and 418A show a net gain in strontium rather than loss. Further, low-temperature fluids sampled in the East Equatorial Pacific [35] contain <1% basaltic strontium in their isotopic signal ($^{87}Sr/^{86}Sr$ ~0.7091) but show a ~11% increase in strontium concentration (98 μmol kg^{-1}) relative to seawater values. The fluid isotopic composition shows that the added strontium is not basaltic and must have a composition similar to seafloor carbonates ($^{87}Sr/^{86}Sr$ ~0.7086) [40]. Therefore, we conclude that limited isotopic exchange occurs with no significant basaltic strontium loss during low-temperature flow. Due to the large fluid fluxes inferred for flank hydrothermal systems [1,41] even a small degree of exchange could make a significant contribution to the oceanic strontium budget. A maximum estimate is provided by the degree of isotopic exchange displayed by the alteration profile for Holes 417D and 418A – indicating that low-temperature exchange isotopically enriches the crust to 20% over the depth of circulation. As the depth of low-temperature circulation is poorly constrained we approximate this to the drill hole depth (550 m). This also assumes that the enrichment observed is derived from isotopic exchange rather than gain of seawater strontium, and is equivalent to a low-temperature basaltic strontium flux of $\sim 7.6 \times 10^8$ mol yr^{-1}, at current seafloor production rates (Table 3). Therefore, based on crustal alteration profiles low-temperature flow cannot balance the oceanic strontium budget and only contributes approximately 9% of the low-temperature basaltic strontium flux that would be required.

5. The oceanic hydrothermal contribution to the oceanic strontium budget

We estimate that the ocean crust can sustain a maximum cumulative hydrothermal basaltic strontium flux of $\sim 3.1 \pm 0.8 \times 10^9$ mol yr^{-1}. This is less than a third of the hydrothermal basaltic strontium budget required to maintain the oceanic strontium budget. The estimate is constrained by: (1) the alteration intensity of sampled oceanic crust, (2) currently observed hydrothermal fluid characteristics, (3) 20% isotopic exchange of the upper 550 m profile by low-temperature fluids, and (4) the maximum plausible flux from arc-related systems. The error estimate includes a 25% uncertainty in the portion of the magmatic heat removed by high-temperature fluids, and 50% uncertainty in the low-temperature and arc-related basaltic strontium flux estimates.

6. How can the oceanic strontium budget be reconciled?

It is possible that the discrepancies in the oceanic strontium budget arise because our present sampling of modern ocean basement is not representative of global in situ crust. For example, ODP Hole 504B forms the oceanic reference section but has recovery rates of less than 20% which may preferentially bias sampling of less altered crust. Ocean crustal profiles exposed by tectonic disruption are by definition atypical and probably more altered than average in situ crust. Also the suite of sampled hydrothermal fluids is limited.

This study does not consider the potential contribution of short-lived highly vigorous hydrothermal systems associated with oceanic (island arc and hot spot) volcanism. Oceanic crustal accretion at spreading centers is by far the dominant oceanic heat source and primary control on hydrothermal fluxes. In comparison, oceanic volcanism is negligible contributing ∼10% of total oceanic magmatism [42]. Therefore, although unquantified due to poor observation, it seems extremely unlikely that this will contribute sufficiently to reconcile the oceanic strontium budget.

An alternative explanation is that the estimate of the riverine strontium flux is unrepresentative. The global water discharge flux is reasonably well established, but the mean strontium concentration and isotopic composition is extrapolated from analysis of only 54% of global rivers. Many rivers have only been sampled once and riverine strontium budgets are likely to be biased by correlations between rainfall, discharge flux, dilution and source controls on strontium concentrations and isotopic compositions [11]. In addition small rivers draining basaltic provinces, and particularly basaltic oceanic islands and island arcs, may contribute preferentially to the unsampled budget [43–45]. However, to balance the oceanic strontium budget, we estimate that the rivers draining basaltic catchments would have to contribute over 50% of the global water discharge flux with near-fresh basalt strontium isotopic compositions (for example $^{87}Sr/^{86}Sr$ ∼0.7049 and Sr ∼0.2 μmol kg^{-1}). This seems unlikely given that basaltic river catchments only contribute ∼9% of the global discharge flux [45], the majority of which are continental basalt provinces with relatively high isotopic signatures, for example $^{87}Sr/^{86}Sr$ ∼0.7097 for the Deccan Province [44]. A further possibility is that current river input measurements are not representative of the average value due to variations in global rainfall between glacial and interglacial events over the last 2 Myr (the residence time of strontium in the oceans [11]). However, to balance the oceanic budget, the mean glacial riverine strontium flux would need to be negligible compared to the present flux which seems unlikely. The hydrothermal flux estimates presented are less susceptible to such errors because they are based on time-integrated records of hydrothermal alteration over 120 Myr.

7. Conclusions

Hydrothermal circulation cannot supply the basaltic strontium flux required to balance the oceanic strontium budget. Crustal alteration profiles and modern hydrothermal fluid characteristics indicate that combined high- and low-temperature strontium isotopic exchange (with allowance for increased hydrothermal activity associated with arc-related systems) may contribute up to a third of the hydrothermal basaltic strontium flux required. The ocean crust is not sufficiently altered to sustain a higher flux, unless the average oceanic crust is substantially more altered than current observations. Uncertainties in the total riverine strontium flux, particularly that from basaltic river catchments and glacial to interglacial variation, may be significant but do not seem large enough to make up the difference. Oceanic mass balance of riverine and hydrothermal inputs is critical to our understanding of geochemical cycles of many elements and the imbalance in strontium raises questions about the validity of all such modeling. More comprehensive sampling of rivers as well as of oceanic crustal profiles is urgently needed to resolve these problems.

Acknowledgements

Chris McLeod introduced A.D. and M.J.B. to the geology of the Oman ophiolite, Laurence Coogan provided helpful comments and Mike Mottl and Claude Allègre are thanked for thoughtful reviews. A.D. acknowledges support from a NERC PhD studentship.*[BW]*

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