Oceanic phosphorus imbalance: Magnitude of the mid-ocean ridge flank hydrothermal sink

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[1] We present a new estimate for the crustal phosphorous sink that results from reactions among seawater, basalt, and sediment blanketing low temperature mid-ocean ridge flank hydrothermal systems. New estimates for global hydrothermal power output, sediment thickness, and the dissolved phosphate concentrations in basement formation fluids indicate that fluid flow through ridge flanks removes 2.8 $\times$ 10^{10} mol P yr^{-1}. This value is larger (130%) than the riverine dissolved flux of inorganic phosphate and is as much as 35% of the sedimentary P sink. The concordant seawater flux (2.1 $\times$ 10^{16} kg yr^{-1}) is 65% of the riverine fluid flux and circulates a fluid volume equivalent to the entire ocean in about 70,000 yr. Additional sampling of seafloor springs is required to further constrain the range of calculated phosphate fluxes; nevertheless the modern phosphorus budget is clearly unbalanced with total sinks outpacing sources. *INDEX TERMS:* 1045 Geochemistry: Low-temperature geochemistry; 1050 Geochemistry: Marine geochemistry (4835, 4850); 3015 Marine Geology and Geophysics: Heat flow (benthic) and hydrothermal processes; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; *KEYWORDS:* Ridge flank, hydrothermal, phosphate, Ocean Drilling Program, geochemical cycles. **Citation:** Wheat, C. G., J. McManus, M. J. Mottl, and E. Giambalvo, Oceanic phosphorus imbalance: Magnitude of the mid-ocean ridge flank hydrothermal sink, *Geophys. Res. Lett.*, *30*(17), 1895, doi:10.1029/2003GL017318, 2003.

1. Introduction

[2] It has been argued that phosphorus provides the long-term limit on the magnitude of oceanic primary production [*Holland*, 1978; *Broecker and Peng*, 1982]. If true, then successfully modeling changes in ocean fertility and chemistry requires an understanding of the geochemical cycling of this essential nutrient. Despite the substantial body of literature on the cycling of phosphorus in marine systems, the controls on phosphorus removal for the modern ocean are still not well quantified [*Colman and Holland*, 2000]. The sedimentary sink, for example, is estimated to be larger than all the known combined sources [*Ruttenberg*, 1993; *Filippelli*, 1997]. In addition to a large sedimentary P sink, phosphorus is removed from the oceans via hydrothermal processes [*Wheat et al.*, 1996]. Hydrothermal processes include adsorption of seawater phosphate onto Fe-rich plume particles, which then settle to the seafloor, and reactions among seawater, basalt, and the sediment blanketing basalt.

[3] Two approaches have been used to elucidate the effect of hydrothermal systems on global geochemical fluxes. One approach focuses on studies of altered basalt (i. e., secondary minerals and alteration halos) [*Thompson*, 1983] while the other on the composition of formation fluids in basaltic basement [*Mottl and Wheat*, 1994]. Both approaches require simplifying assumptions for the thermal partitioning of the global convective heat loss. Here we improve upon these flux calculations by presenting: (1) additional phosphate data for formation fluids, (2) new constraints for the thermal partitioning of the global convective heat loss, and (3) recent compilations for the global distribution of oceanic sediment thickness. From these data we calculate the distribution of the fluid flux through ridge flanks as a function of crustal age and then multiplied this flux by the observed phosphate to heat anomaly ratio in fluids within basaltic basement. The result is an estimate for the total dissolved phosphate flux to the oceanic crust via low-temperature ridge flank hydrothermal processes.

2. Methods

2.1. Concentration of Phosphate in Formation Fluids

[4] Concentrations of phosphate in formation fluids are estimated from chemical analyses of samples collected using three approaches (Figure 1). The first method (almost 80% of the data) utilizes near-basement sediment pore water data compiled from the Deep Sea Drilling Program and the Ocean Drilling Program [*Wheat et al*, 1996]. Here we present only those data that have phosphate versus depth profiles that penetrate to the sediment-basement interface and have no measurable change in concentration near this interface.

[5] The second method (~20% of the data) includes data from studies that utilized sediment coring and heat flow operations to sample ridge-flank hydrothermal settings. Systematic variations in surficial pore water profiles are modeled to (1) determine the composition of the fluid in basement, (2) provide a measure for the seepage velocity through the sediment, and (3) constrain the general pattern of fluid circulation through the crust [*Wheat and McDuff*, 1995].

[6] The third method, which represents only three of the 74 data points, includes data from direct sampling of

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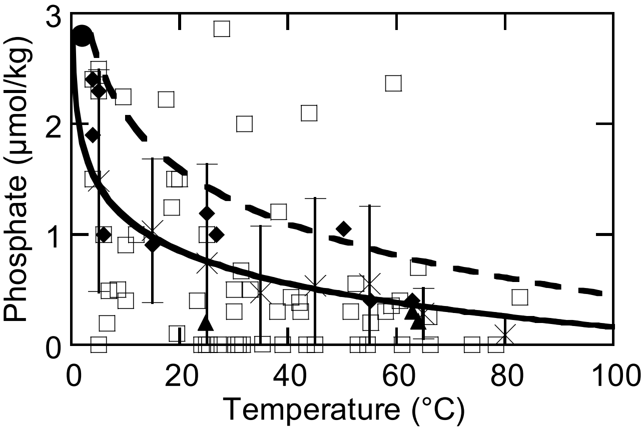

Figure 1. Concentration of phosphate versus temperature in fluids from the upper portion of basaltic basement. Data are from the DSDP and ODP (open squares), surface coring (filled diamonds), springs and boreholes (filled triangles), and bottom seawater (filled circle). Means of 10 Ma bin averages (x) and one standard deviation are shown. Curved lines are the best fit to the data (solid; Phosphate = –0.429 ln (temperature) + 2.14) and to the bin averaged means plus one standard deviation (dashed; Phosphate = –0.708 ln (temperature) + 3.71). Note that the best fit to the data is nearly identical to that from the mean using 10 Ma bins. We have compiled all of the DSDP and ODP data up to and including ODP Leg 198 (Oct. 2002).

formation fluids, either from borehole or directly from seafloor springs [*Wheat and Mottl*, 2000]. Results from each of the three methods agree, in spite of the possibility of sampling artifacts during recovery of pore fluids.

2.2. Distribution of the Convective Heat Loss

[7] The global convective power output is estimated to be 9.9 ± 2 TW [*Sclater et al.*, 1980; *Stein and Stein*, 1994]. This heat is lost along mid-ocean ridge (MOR) axes associated with spectacular black smokers and on ridge flanks in the form of cool springs. The maximum heat available to drive high-temperature MOR hydrothermal systems is 2.8 ± 0.3 TW. This power output would cool the crust to the Moho given the following constraints: (1) 3.3 ± 0.2 km^2/yr of new oceanic crust [*Parsons*, 1981]; (2) an average crustal depth of 6.5 ± 0.8 km (0.7 km for flows, 1.2 km for dikes, and 4.6 km for gabbros, but excluding the 0.7 km of extrusive flows because their heat is exchanged directly with seawater at the seafloor); (3) crustal density of 2.8 g/cm^3; (4) latent heat of basaltic magma of 676 J/g [*Fukuyama*, 1985]; (5) cooling from a magmatic temperature (1175 ± 25°C) to a hydrothermal temperature (350 ± 30°C) [*Von Damm*, 1995]; and (6) heat capacity of basalt of 1.2 ± 0.15 J/g/°C. Cooling the entire crust may be a reasonable assumption for slow spreading centers that have deep crustal faults, but not for intermediate to fast spreading systems where a magma chamber exists in the gabbroic section. For these systems, within which the dikes maintain a temperature of 350°C and the deeper layers maintain a magmatic temperature, the maximum heat loss for MOR systems would be 1.5 ± 0.18 TW. Given the global distribution of spreading rates and hydrothermal systems [*Baker et al.*, 1996], a reasonable value for the power output from MOR axial hydrothermal systems is 1.8 ± 0.3 TW.

[8] The remaining 8.1 ± 2 TW must be associated with low-temperature ridge flank systems. Given the lack of evidence for hydrothermal circulation in young (1.3 Ma) gabbros below 180°C to 250°C [*Gillis et al.*, 1993; *Lecuyer and Reynard*, 1996], we suggest that the deepest gabbroic layers do not cool convectively below 215°C. We updated *Mottl*'s [2003] compilation for heat loss in 1 Ma-old crust to include 2.8 ± 0.4 TW, which cools the entire crust to 350°C, plus 0.15 TW to cool the dikes from 350°C to 2°C and an additional 0.22 TW to cool the gabbros from 350°C to 215°C (Table 1). The remaining heat is lost on older crust (Table 1).

2.3. Sediment Thickness

[9] A global data set for sediment thickness has been compiled by Dr. David Divins at the National Geophysical Data Center (http://www.ngdc.noaa.gov/mgg/sedthick/sedthick.html). The entire compilation is presented as a function of crustal age in Figure 2a [*Muller et al.*, 1997]. This compilation includes continental margins and areas influenced by considerable terrigenous inputs, resulting in a cumulative data set that is skewed towards thicker sediments. From these data we chose a subset to represent typical fast and slow spreading crust that excludes those areas with thick sediment. Representative transects for fast spreading crust center on data from 20°S to 40°S on the East Pacific Rise. Similarly a corridor from 20°S to 40°S in the Atlantic Ocean was chosen to represent typical crust from a slow spreading system.

3. Discussion

3.1. Ridge Flank Fluxes

[10] Several steps are required to calculate a phosphate flux associated with ridge-flank hydrothermal systems. First, the temperature in basaltic basement is determined from a conductive oceanic plate model [*Sclater et al.*, 1980; *Stein and Stein*, 1994]. This model provides a heat flux from which the temperature in upper basaltic basement is calculated assuming an average bulk sediment thermal conductivity of 0.9 W/m°C and a global or basin-wide sediment distribution (e.g., Figure 2a). This calculated basement temperature is then adjusted to account for the partitioning between convective and conductive heat loss [*Stein and Stein*, 1994] (Figure 2b). There is little difference in temperature along transects in the Atlantic or Pacific Oceans. Such a result might be unanticipated as the heat

Table 1. Cumulative Oceanic Convective Heat Loss With Age[a]

Age (Ma)	CHL[b](TW)	Age (Ma)	CHL[b](TW)
0.1[c]	1.8	7	5.1
1	3.2	8	5.4
2	3.4	9	5.6
3	3.8	20	7.5
4	4.1	35	9.0
5	4.5	52	9.8
6	4.8	65	9.9

[a]Modified From *Mottl* [2003] and *Stein and Stein* [1994].
[b]Convective Heat Loss.
[c]Axial contribution from high temperature hydrothermal systems.

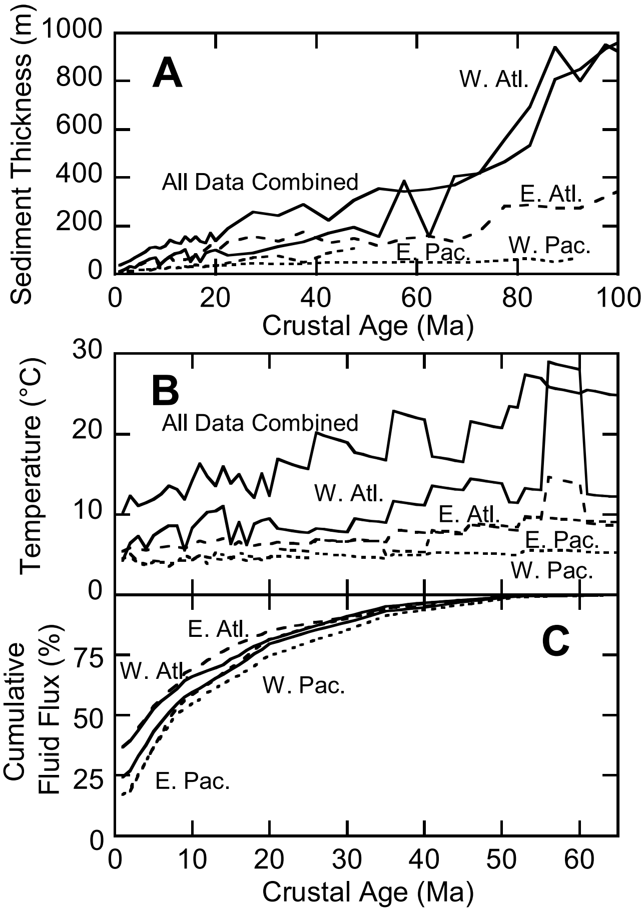

Figure 2. Oceanic sediment thickness, temperature in upper basaltic basement, and cumulative seawater flux versus oceanic crustal age. A. The entire sediment data set (All Data Combined) is shown along with transects east and west of active spreading ridges at 20°S to 40°S on the East Pacific Rise and Mid-Atlantic Ridge. B. Temperatures in basaltic basement are calculated using the sediment thicknesses above, a thermal conductivity of 0.9 W/m°C, a conductive plate model, and an estimate of the global heat loss distribution (Table 2). C. Cumulative seawater flux is calculated for 1 Ma bins and illustrates the importance of young relatively unsedimented crust in fostering hydrothermal circulation.

flux decreases with crustal age; however, the concordant increase in sediment thickness with crustal age acts to insulate the crust and prevents hydrothermal exchange with the oceans. The net result is that crustal temperatures are less than 10°C for much of the oceans.

[11] A seawater (fluid) flux is then calculated for each 1 Ma bin using temperatures calculated above and the power output for each crustal age (Table 1). The 1 Ma bin excludes the 1.8 TW associated with high temperature MOR hydrothermal systems and interpolated values were used for crustal ages greater than 9 Ma. Given the low basement temperatures and the extensive amount of heat that must be removed, the resulting seawater flux based on data for the Pacific is about 70% of the riverine water flux input to the oceans. Because the sediments are thicker in the Atlantic, the warmer crust results in a lower cumulative water flux; yet this water flux extrapolated globally is still about 40% of the riverine input. In both cases almost half of this flow is confined to crust that is less than 7 Ma and most (95%) of this flow occurs in crust less than 43 Ma in the Pacific and 38 Ma in the Atlantic (Figure 2c).

[12] Finally, the combination of temperatures for basaltic basement, the calculated seawater fluxes, a value of 2.8 μmol phosphate/kg for bottom seawater, and a phosphate-temperature relationship allow us to calculate the phosphate flux. We use a logarithmic function to represent the phosphate-temperature relationship (Figure 1). This function provides a nearly identical result to that from bin averaged data using 10-Ma bins. Assuming that 75% of the fluid flow passes through systems dominated by intermediate to fast (Pacific-type) spreading systems and that the balance flows through slow (Atlantic-type) spreading systems [*Baker et al.*, 1996], we calculate a fluid flux of 2.1×10^{16} kg yr^{-1} with a concordant phosphate flux of 2.8×10^{10} mol yr^{-1} (Table 2). These fluxes are 65% of the riverine fluid flux, illustrating that it takes approximately 70 kyr to circulate a volume equivalent to the world's oceans through the oceanic crust on ridge flanks. The concordant phosphate flux is 130% [*Froelich et al.*, 1982] to 220% [*Meybeck*, 1982] of the riverine dissolved inorganic phosphorus flux. Similar to the heat budget, half of the phosphate flux occurs during the first 8 Ma and most (95%) of this flux occurs during the first 40 Ma.

[13] The uncertainty in our calculated flux is difficult to gauge; however, we present the following calculations to highlight different extremes. For example, the entire sediment data set has the thickest sediment, the warmest temperatures in basement, and the smallest fluid flux (Table 2). The calculated flux using these sediment data is 0.95×10^{10} mol P yr^{-1}. In contrast the thinnest sediment section is the Western Pacific with a calculated flux of 3.2×10^{10} mol P yr^{-1} (Table 2). In the previous paragraph we assume a mixture of 75% Pacific-type (fast to intermediate spreading) and 25% Atlantic-type (slow spreading) crust. Using this mixture and either the upper or the lower values for one standard deviation of the sediment thickness results in calculated fluxes that are 2.4×10^{10} mol P yr^{-1} using the thicker values and 7.7×10^{10} mol P yr^{-1} using the thinner values. We can also vary the phosphate-temperature anomaly trend. If we use the mixture of oceanic crust from

Table 2. Calculated Seawater Fluxes Through and Phosphate Fluxes Into the Crust Resulting From Mid-Ocean Ridge Flank Hydrothermal Processes

	Seawater Flux 10^{16} kg/yr	% River Flux[a]	PO_4 Flux 10^{10} mol/yr	% River DIP Flux[b]	Flushing Time 10^4 yr
All Data	0.54	17	0.95	43	26
W.Pacific	2.5	77	3.2	150	5.6
E.Pacific	2.2	69	2.9	130	6.3
W.Atlantic	1.3	40	1.9	85	11
E.Atlantic	1.3	40	1.9	84	11
Mixture[c]	2.1	65	2.8	130	6.7

[a]River flux is 3.2×10^{19}g water yr^{-1} [*Mackenzie*, 1992].

[b]Dissolved river flux of inorganic phosphate is 2.2×10^{10} mol P yr^{-1} [*Berner and Rao*, 1994].

[c]Mixture of 75% of the average fluxes from the Pacific and 25% of the average fluxes from the Atlantic.

above and phosphate anomalies for one standard deviation greater (less altered) than the mean bin average based on the phosphate-temperature trend (dashed line, Figure 1), the calculated flux is 0.42×10^{10} mol P yr^{-1}, which is still 19% of the riverine DIP flux. The concordant flux based on lower concentrations (more altered) of one standard deviation of the phosphate-temperature trend is 4.8×10^{10} mol P yr^{-1}.

3.2. Global Phosphorus Budget

[14] In terms of phosphorus sinks, marine sediments sequester between 8 and 18.5×10^{10} mol P yr^{-1} [*Ruttenberg*, 1993]. In addition, hydrothermal plume particles scavenge from seawater an additional 0.8×10^{10} mol P yr^{-1} [*Wheat et al.*, 1996]. Thus, assuming that ridge flanks sequester 2.8×10^{10} mol P yr^{-1}, the total P sink is between 12 and 22×10^{10} mol P yr^{-1}, with hydrothermal-crustal reactions representing 13 to 23 % of the total removal flux. Admittedly, this estimate of the hydrothermal contribution needs to be further constrained (Table 2), but it is likely that future estimates will not be more than a factor of 2 different. Taken at face value, ridge-flank systems clearly remove phosphorus from the modern ocean. For comparison, the global riverine input of dissolved inorganic P is 2.2×10^{10} mol P yr^{-1}, with an additional combined dissolved organic and reactive components of 5.6×10^{10} mol P yr^{-1} [*Froelich et al.*, 1982; *Berner and Rao*, 1994] totals 7.8×10^{10} mol P yr^{-1}. This value is smaller than, and perhaps considerably smaller (67% to 35%) than, the oceanic removal term.

[15] Notably, our ridge-flank removal estimate is the same as the dissolved inorganic input. Thus, given our current understanding of the modern phosphorus budget, it is clear that total sinks exceed total sources. If true, one consequence is that the phosphorus system may only reach steady state over time scales that exceed its oceanic residence time (<20 kyr) [*Ruttenberg*, 1993]. This situation would require a transient oceanic or terrestrial source term that potentially dominates during glacial periods but not during interglacials.

4. Concluding Remarks

[16] This analysis highlights the potential for low temperature hydrothermal processes to result in a globally significant oceanic phosphate sink. Although this analysis is largely based on sediment pore water distributions, the "spring" samples presented here are consistent with conclusions based on those data. Furthermore, this analysis highlights the need for directly sampling low-temperature (2° to 15°C) hydrothermal springs because much of the oceanic crustal fluid flow occurs at these temperatures. The same analysis illustrated above could be used for calculating fluxes for other elements.

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