



The role of black smokers in the Cu mass balance of the oceanic crust



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ABSTRACT

Seafloor hydrothermal systems play an important role in the metal budgets of the oceans via hydrothermal plumes, accumulation of seafloor massive sulfide deposits, and alteration of the oceanic crust. These processes have resulted in large-scale metal anomalies on the Pacific plate, most notably at the Nazca–Pacific plate boundary. This plate-scale variability in metal deposition has important implications for the fluxes of metals to subduction zones and possibly the metal endowment of arc-related mineral deposits. However, the relative contributions to the metal budget from black smokers, deep-sea sediments, Mn nodules and altered crust remain unclear. The Cu contents of more than 10,000 samples of seafloor massive sulfide deposits, subseafloor stockwork mineralization, nodules and sediments reveal that most of the Cu metal originally mobilized by high-temperature hydrothermal convection at the ridges is retained in the crust as subseafloor alteration and mineralization, never reaching the seafloor. This metal accounts for at least 80% of the labile Cu that may be released to subduction fluids driven off a down-going slab. Copper deposited in deep-sea sediments, which account for 17% of the total budget, is derived in part from plume fallout associated with ridge-crest hydrothermal activity but also from pelagic deposition of marine organic matter enriched in Cu metal. Massive sulfide deposits, nodules and manganeseiferous crusts account for only ~3% of the Cu metal of the subducting slab.

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1. Introduction

The global geochemical budgets of many elements in the oceans are determined by a combination of riverine, eolian and hydrothermal fluxes. Because the riverine input is directly observable, most of the uncertainty in element budgets lies in quantifying the hydrothermal flux at oceanic spreading centers (Elderfield and Shultz, 1996; Bruland and Lohan, 2003). Metals, in particular, have a number of different sources, sinks, and transport pathways that include scavenging by hydrothermal plumes, deposition in seafloor massive sulfide deposits, alteration of oceanic crust, hydrogenetic growth of manganese nodules and crusts, and biogeochemical cycling. Many studies have shown that coprecipitation and scavenging within hydrothermal plumes play a significant role in the removal of reactive trace elements from seawater at rates on the same order as the riverine flux (Rudnicki and Elderfield, 1993). Scavenging by Fe-oxyhydroxides in plumes is particularly important for elements such as U, V, As, P, Mo, Th, and REE that are ultimately deposited in deep-sea sediments far from the ridges. In contrast, metals such as Cu are more closely linked to hydrothermal vent sources and are mainly

deposited close to the ridge axis (James et al., 1995; German et al., 1991). Among the most compelling records of hydrothermal deposition of metals at the ridges is the enrichment in surface sediments flanking the East Pacific Rise along the ~3000 km Nazca–Pacific plate boundary (Boström et al., 1969). Long before the discovery of black smokers, Boström et al. (1969) explained the pattern of metal enrichment in the top cores of these sediments in terms of Fe and Mn sourced at hydrothermal vents on the ridge crest. Although mass accumulation rates generally decrease with increasing distance from the ridge, the hydrothermal origin of metals up to 300 km from the ridge axis is confirmed by Pb isotope data (Barrett et al., 1987). Metal enrichment at the basalt–sediment contact (so-called basal metalliferous sediment) also records the intensity of past hydrothermal output at the plate boundary, and the pattern of enrichment in these sediments away from the ridge corresponds well with the plate motions (e.g., Leinen et al., 1986).

Although these processes are reasonably well understood, recent work has shown that the predicted amount of metal discharged by ridge-crest hydrothermal vents is far short of the amount that must have been mobilized by the high-temperature fluids required to cool the crust (Coogan and Dosso, 2012). In order to explain this discrepancy, there must be major, as yet unidentified, sinks for Cu metal in the oceanic crust. This has important implications for understanding metal fluxes to subduction zones and possibly even the metal endowment of arc-related mineral

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deposits (Plank and Langmuir, 1998). This paper examines data on the abundance of Cu in sediments, seafloor massive sulfide deposits, and subseafloor alteration and mineralization at the Nazca–Pacific plate boundary and considers their role in the Cu budget of the Pacific plate.

2. Data

Extensive seafloor research, including ocean drilling, has succeeded in sampling nearly all parts of the oceanic crust from Layer 3 rocks to basal metalliferous sediment on the distal flanks of the ridges. Cu contents of more than 10,000 samples of different types have been compiled for this study and are summarized in Table 1 and Fig. 1. The compilation includes published results from the records of the Deep Sea Drilling Project (DSDP) and its successor, the Ocean Drilling Program (ODP), and a growing database of seafloor massive sulfide deposits (Hannington et al., 2004; Hannington, 2009; Beaulieu, 2010). Analyses of samples of massive sulfide deposits from 20 different sites on the East Pacific Rise (EPR) between 11°N and 38°S ($n=405$) are summarized in Table 2. These data are compared to Cu concentrations in subseafloor stockwork mineralization ($n=42$), seafloor gossans ($n=104$), low-temperature Fe–Mn–Si deposits ($n=490$), samples of black smoke ($n=58$) and near-field plume fallout ($n=97$), as well as the particle load of hydrothermal plumes ($n=384$), basal metalliferous sediment ($n=193$), surface sediments on the flanks of the ridges ($n=335$), and altered oceanic crust ($n=616$). The most complete set of analytical data for these different parts of the oceanic lithosphere is from the fast-spreading East Pacific Rise. Where key data are not available from sites on the EPR, data from different locations on the global mid-ocean ridge (MOR) system

were substituted. The data from these sources are compared to Cu budgets in ferromanganese crusts ($n=3202$) and nodules ($n=2164$) from the extensive Marine Minerals Geochemical Database archived by the National Geophysical Data Center (NGDC) as well as data on north Pacific pelagic sediments ($n=2172$). The full data set is provided as a digital supplement to this paper in Supplementary Table A.1.

3. Fluxes of Cu to the mid-ocean ridges

In order to remove the heat from newly formed crust < 1 m.yr. old, about $3\text{--}6 \times 10^{13}$ kg/yr of seawater must be circulated through the axial zones of the global MOR and heated to a temperature of at least 350 °C (Elderfield and Shultz, 1996; Schultz and Elderfield, 1999). Similar estimates based on the geochemical mass balances of elements in the oceans have ranged as high as 1.5×10^{14} kg/yr to as low as 7×10^{12} kg/yr (see reviews by Baker et al., 1995, 1996; German and Angel 1995; Kadko et al. 1995; Mottl, 2003; Nielsen et al., 2006; Coogan and Dosso, 2012). Using a mass flux of 3×10^{13} kg/yr of 350 °C fluid for the global MOR and measured concentrations of metal in black smoker fluids at 21°N on the East Pacific Rise (e.g., 9.7–44 $\mu\text{mol Cu}$: Von Damm, 1990), the minimum amount of Cu metal mobilized from the lower crust at this temperature is $3\text{--}13 \times 10^8$ mol/yr or $5 \pm 3 \times 10^7$ kg Cu/yr. If every increment of seafloor spreading produces the same amount of metal along the length of the ridge, one can estimate the amount of metal mobilized from each m^2 of new crust. At a global average full-spreading rate of 4 cm/yr, the rate of crustal production at the mid-ocean ridges is 2.56×10^6 m^2/yr ($64,000 \text{ km} \times 4 \text{ cm/yr}$: Hannington et al., 2011), and the flux of Cu metal ($\sim 5 \times 10^7$ kg Cu/yr) would be equivalent to at least 19.5 kg Cu/ m^2 of

Table 1
General statistics for Cu concentrations of MOR hydrothermal precipitates and Pacific plate sediments.

	(n)	25 th Percentile	Median	Mean	75 th Percentile	Std. dev.
Near-field "black smoke"	58	0.67 wt%	4.08	7.40	13.1	8.32
EPR massive sulfides	405	0.34	1.38	6.02	8.47	8.70
Gossans	104	0.26	1.37	7.31	5.28	13.48
High-temperature stockwork	42	0.04	0.20	0.67	0.88	1.21
Near-field metalliferous sediment ^a	97	0.10	0.18	0.73	0.33	1.53
Plume-height smoke	384	530 ppm	887	1372	1628	1326
Basal metalliferous sediment (carb-free)	71	980	1244	1230	1466	311
Basal metalliferous sediment	122	190	346	388	523	286
Low-temperature Fe–Mn–Si	490	36	94	494	295	1272
Pillow-dike transition zone	44	51	115	464	363	923
Altered basalt	572	57	69	68	83	34
Manganese nodules ^b	2164	2100 ppm	6200	6933	10,900	5090
Manganese crusts ^c	3202	463	800	1182	1303	1454
EPR flank sediments (top core, carb-free)	71	710	972	1005	1349	440
EPR flank sediments (top core)	264	316	400	434	510	246
Pacific pelagic sediment (DOMES)	18	435	615	906	1018	914
Pacific pelagic sediment (Central)	117	245	323	435	554	301
Pacific pelagic sediment (Kato et al.) ^d	2037	138	254	310	436	233
Tonga trench sediment (DSDP) ^e	34	181	275	410	468	454
Global average subducting sediment ^e	111	54	89	112	144	80
Northeast Pacific pelagic sediment	14	40	50	54	61	18
North Atlantic pelagic sediment ^f	132	48	71	80	94	71

All sediments are bulk, unless otherwise noted. DOMES=Deep Ocean Mining Experimental Site; DSDP=Deep-sea Drilling Project. See Supplementary Table A.1 for source data.

^a Metalliferous component recalculated on a carbonate-free basis (includes detrital material).

^b USGS Ferromanganese Crust dataset compiled by Manheim and Lane-Bostwick (USGS Open-File Report 89-020).

^c Data from the Marine Minerals Geochemical Database created by NOAA's National Geoscience Data Center, (NGDC, 1983 and 1992) from data source including the Scripps Institution of Oceanography (SIO) manganese, nodule file, the CNEXO ferromanganese nodule file, and data coded at NGDC from the scientific literature.

^d Data from Kato et al. (2011).

^e Data from Plank and Langmuir, (1998).

^f Data from Horwitz and Cronan (1976).

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