

## Reply to comment by Hannington “Are black smokers copper plating the ocean floor?”

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Hannington (2010) challenges the ocean resource prediction made in my paper entitled “What processes at mid-ocean ridges tell us about volcanogenic massive sulfide deposits.” His perspective is based on a 2010 paper of his that assesses the metal accumulation that is observed in the neovolcanic portion of the oceanic crust. Extrapolating this assessment to the entire ocean, Hannington et al. (2010) concluded that the total volcanogenic massive sulfide (VMS) metal resource on top of the volcanic section of the oceanic crust is ~1 Gt (billion tonnes) Cu+Zn, about the same size as the known 0.85-Gt land-based VMS Cu+Zn metal resource (Franklin et al. 2005). This is very different from the 530-Gt ocean Cu+Zn resource I estimate from the ~350°C hydrothermal flux at the ridge axes and the base metal fraction which seems to be removed from this flux at or just below the seafloor. Half of the latter could bring every person in the world up the European standard of Cu consumption and sustain the expected eventual steady-state 10.5 billion person population of the earth for 50 centuries (Cathles 2010), whereas half the former would carry us along this path for less than one century. My estimate may “copper plate the oceans” (although much less so than in VMS districts on land). But Hannington’s estimate seems unduly low. The ocean in many regards is a giant VMS district with three times the area of the continental crust, and it would be strange if the oceans were to host a VMS resource only slightly larger than this land area which is only 8.5% exposed volcanic rock (Franklin et al. 2005: Table 3). Rarely have such disparate

estimates of an important parameter been made so independently and published so simultaneously. This disparity challenges us to discover where the methods might be flawed and identify a reasonable consensus range for the ocean VMS metal resource.

My method of estimation takes the mass of ~350°C metal-enriched seawater that is circulated for each square meter of new ocean crust produced by seafloor spreading ( $m_{350}$  in Cathles 2011), which I argue we know quite well, and assumes that on large-scale average, a fixed fraction of the Cu+Zn contained in this flux is accumulated within minable depths everywhere on the seafloor. I selected 3% for the metal accumulation fraction because this value predicts the size and size range of deposits observed at Mattagami from a sill-driven convection model (Carr et al. 2009) with very similar vent fluid Zn loadings to those assumed in Cathles (2011) (40  $\mu\text{M}$  Zn compared to 30  $\mu\text{M}/\text{kg}$  at 350°C in Carr). The 3% accumulation factor also produces an ocean VMS metal surface density about 20% of the average estimated by Sangster (1980) for seven land-based VMS districts (6,800 t Zn+Cu+Pb/ $\text{km}^2$ ). A 3% accumulation factor thus seems conservative and reasonable. For a Cu+Zn low-end concentration in the venting axis fluids of 50  $\mu\text{M}$  Cu+Zn, a hydrothermal throughput  $m_{350}=1.5\times 10^7$  kg/ $\text{m}^2$ , and an accumulation factor of 3%, the large-scale average Cu+Zn surface metal density of the oceans is 1,470 t/ $\text{km}^2$  (22% of Sangster), and the Cu+Zn resource of the  $3.6\times 10^8$ - $\text{km}^2$  ocean is 530 Gt. Of course it is the product of the accumulation factor and the metal in the hydrothermal upwelling that counts. If the upwelling fluid had 100  $\mu\text{M}$  Cu+Zn, the accumulation factor would be 1.5% rather than 3% under the same calibration.

The method of Hannington et al. (2010) estimates the tonnes of massive sulfide material from observations at 62 sites within the 89,000-km-long and 100-km-wide neo-

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Editorial handling: B. Lehmann

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volcanic zone of the ocean. From the sulfide tonnage variations in these 62 locations, a representative tonnage for the sites was determined to be  $0.6 \times 10^6$  tonnes. There are about 1,000 active hydrothermal vents along the present ocean ridge, and this is considered to also be a reasonable maximum for significant seafloor massive sulfide (SMS) occurrences on the seafloor. The total sulfide tonnage for 1,000 SMS occurrences in the neovolcanic zone is thus  $600 \times 10^6$  tonnes. Assuming the average Zn+Cu grade is 5%, the metal tonnage in the neovolcanic zone is  $30 \times 10^6$  tonnes Cu+Zn metal. Since the ocean area of  $3.6 \times 10^8$  km<sup>2</sup> is 40 times the area of the neovolcanic zone, the total ocean resource is estimated at 1.2 Gt Cu+Zn.

In his discussion of my estimate, Hannington's most basic criticism is that we see nothing in the neovolcanic zone that would justify an ocean resource anywhere near as large as I suggested. Since only ~10% of the upwelling hydrothermal flow vents at black smokers, he maintains that "almost all the metal and sulfur mobilized from the oceanic crust by high-temperature hydrothermal fluids [that is not vented into the ocean] ends up in subseafloor alteration [at the base of the sheeted dike layer] or in marine sediment, not in massive sulfide deposits." The amount of Cu+Zn in sediments could be 300 Gt and the amount at the base of the sheeted dikes could be an additional 300 Gt, but this is "no more than a global geochemical anomaly that characterizes the oceanic crust" and "it is unlikely this metal could be part of any future resource."

Well, as Yogi Berra is reputed to have said: "Predictions are difficult, particularly about the future." Because seafloor equipment can be moved very easily and there is, at least near the ridge axes, very little overburden, caution should be exercised regarding what might, or might not, be mined in the distant future. It might well be that mining the 300 Gt of Cu+Zn in the sediments immediately on top of ocean volcanics would be as economically viable as mining massive sulfide material. In some ways, it might be easier. In this sense, Hannington's 300-Gt resource and my 530-Gt resource are not so disparate.

But since the size of the potentially minable ocean resources is an important matter, and since it was a relatively minor, although significant, part of my paper and did not receive much discussion there (my focus was on processes rather than resources), let me make a few more comments. First let me elaborate on what I regard is an important aspect of my method. A feature of the ridge axis hydrothermal system that has long intrigued me, and which I tried to emphasize in Cathles (2011), is the degree to which we know with confidence the amount of ~350°C metal-enriched seawater that is circulated for each square meter of new ocean crust that is produced by seafloor spreading ( $m_{350}$  in Cathles 2011). Generally, we cannot

tightly constrain the amount of hydrothermal circulation that produces an ore deposit because we do not know the dimensions and location of its intrusive heat source. In the case of seafloor spreading, however, we know quite well the thickness of the gabbro layer that crystallizes and cools within a few kilometers of the ridge axis. Equating the heat released from this cooling to the heat needed to warm seawater to 350°C provides a tight estimate of the total ~350°C hydrothermal throughput that occurs at ocean ridges axes and could deposit Cu and Zn. That we can do this is not in dispute here.

Two implications of this agreement are perhaps less clear. One implication is that, *averaged over a suitably large area*, each square meter of ocean crust receives the same throughput of ~350°C hydrothermal fluid and thus has the same potential metal endowment. The key caveat is "averaged over a suitably large area." Each kilogram of new gabbro layer will cause 1 kg of 350°C hydrothermal upwelling, but that hydrothermal upwelling need not pass equally through every square meter of new ocean crust. In an episodically spreading portion of the ridge, for example, the arrival of seawater heated by a pulse of spreading may be delayed by the need to heat a path to the seafloor. This delay means that the hydrothermal fluids will discharge through the middle of a band of new surface volcanics, an extra large amount of fluid will discharge there, and the metal deposition there will be larger. After the fact, the mineralization will appear to have been swept into ridge-parallel bands of deposits, whereas at continuously spreading ridge segments, the hydrothermal upflow and mineralization will be more uniformly distributed. Episodic spreading at an oceanic plate boundary may also induce sill intrusions, as happens in arc and back arc settings, and sills could produce a pattern of hydrothermal circulation and metal accumulation that is different from that at continuously spreading portions of a ridge. We know the total throughput of 350°C fluid per square meter of new ocean plate, but the pattern of hydrothermal upwelling that the ocean crust experiences may be variable from one location to another.

A second implication of the hydrothermal upwelling is that it is fast enough that it cools in a significant fashion (and dumps at least a portion of its metals) very near the seafloor. This is what we mean by hydrothermal. Hannington (2010) distinguishes the 10% of axial discharge that feeds black smokers from the 90% of the axial discharge that is "diffuse" as if this would reduce the metal resource; the reverse is the case. Metals should precipitate more completely in areas of diffuse venting than in focused black smoker vents. At black smoker vent sites, metal sulfides can be directly discharged into the ocean and carried off by currents in the early stages of venting before chimneys form or when chimneys collapse. It does not matter that a portion of the metal load

may be precipitated at the base of the sheeted dike layer. We know from vent observations that metals are present in the black smoker fluids, and we know from the easy triggering of black smokers in areas of diffuse venting, from the very high heat flow in these areas, and from the replacement of zinc by copper sulfides in mined VMS deposits that metals are carried upward despite whatever metals are deposited in the sheeted dike layer. The source fluids may be very much richer in Cu and Zn than the fluids vented (Hardardóttir et al. 2009), but this does not matter. I suspect that we are not forming significant metal accumulations in the sheeted dike layer or we would be commonly mining deposits at this setting, but this does not matter to the discussion here either. For seafloor venting, there are plenty of metals to go around and plenty to mineralize the seafloor and its immediately underlying volcanics.

If the present distribution of hydrothermal discharge at ocean ridges is taken as a guide to the temporal changes that occur, one can predict that mineralization will be continuous in an interval between transform offsets (whose length depends on the rate of spreading), but episodic near the transforms. At slow-spreading ridges, the hydrothermal activity (and seafloor spreading) will be episodic along the whole ridge. Metal accumulation will be concentrated in ridge-parallel lines of deposits where the spreading is episodic and in smaller deposits that are more equally spaced in both the ridge-parallel and ridge-perpendicular directions where the spreading and hydrothermal discharge is continuous. I know of only one ridge segment near a transform that is actively spreading and hydrothermally venting (Clipperton transform on the East Pacific Rise). Assuming this segment is 20 km long, dividing this into the 89,000 km of ridge, taking our observation interval to be 30 years, and assuming large SMS deposits form in this setting, large seafloor massive sulfide deposits form once every 130,000 years or so. This is quite compatible with Hannington's observation that the larger deposits are all at least 100,000 years old.

The critical issue for my method of estimating the ocean resource is the metal accumulation factor. We stand to learn a lot about this factor from observations in the oceans, but at this point, it must be admitted that this parameter is not well defined. A value of 3% is little more than a guess. It can only be said that it is a conservative guess and that any substantially different value would require that the present-day ocean is not behaving as did the hydrothermal systems responsible for mineralization in VMS districts in the past. Sediment cover probably increases metal retention and the accumulation factor. Differences in the accumulation factor between areas with continuous spreading and episodic spreading are to be expected, but I am not sure which direction they should go. Areas of continuous spreading might retain more or less metal than longer lived venting sites where the spreading is episodic. The deposits where

the spreading is continuous will certainly be smaller, and it may be harder to define the surface metal density, but mining these areas might be as easy as, or easier than, mining the larger deposits. There could be changes in the metal accumulation factor with geologic time. Biologic evolution might be expected to cause the accumulation factor to increase with time, reflecting the ability of vent fauna to engineer chimneys that are ever more effective in dissipating the heat and capturing nutrients while precipitating base metals.

Hannington et al. (2010) argue that metal accumulation in ocean systems has decreased dramatically with geologic time, but I do not find their arguments convincing. They cite a decrease in VMS metal surface densities from 81 to 168 t/km<sup>2</sup> in the Archean and Paleozoic to 15 and 3.8 t/km<sup>2</sup> in the Mesozoic and Cenozoic and further to 3.4 t/km<sup>2</sup> on the modern seafloor (from their resource inventory in the neovolcanic zone). The metal surface densities were calculated by dividing the discovered metals in VMS deposits in several age ranges by the area of exposed volcanic rocks in the same time interval. The exposed areas of the volcanic rocks were calculated from a digital map of the world by Franklin (2005: Table 3). There is a lot of variation in the metal surface densities calculated in this fashion. For example, the metal surface density in the Meso- and Neoproterozoic is 13 t/km<sup>2</sup> (Hannington et al. 2010: Table 3). There are many reasons taking this kind of ratio might encounter serious errors (e.g., not all volcanic rocks are appropriate hosts for VMS mineralization). More location-specific data do not show a temporal trend. The surface metal density calculated from Sangster (1980) for the Miocene Kuroko district is larger (8,600 t Zn+Cu+Pb/km<sup>2</sup>) than that for the Archean Noranda district (3,000 t Zn+Cu+Pb/km<sup>2</sup>), the Proterozoic Flin Flon and Snow Lake Districts (7,700 and 1,700 t Zn+Cu+Pb/km<sup>2</sup>), and the Paleozoic Bathurst 2 district (5,000 t Zn+Cu+Pb/km<sup>2</sup>). It is, however, smaller than the metal densities in the Bathurst 1 and the Archean Matagami districts (17,200 and 13,000 t Zn+Cu+Pb/km<sup>2</sup>). Metals appear to be accumulating on the modern seafloor in at least some places as efficiently as they have in the past, as is indicated in Table 1.

An upper bound on the probable metal surface density in the ocean is probably Sangster's average of 6,800 t/km<sup>2</sup>, which would indicate an ocean resource of 2,400 Gt Cu+Zn, but the resource could be larger than this. The lower bound can be addressed by assessing how Hannington's resource estimate might be modified.

Hannington assumes that there are 1,000 locations on the ocean ridge that are generating minable base metal "VMS"-type mineralization at any instant of time and that these today correspond to areas of hydrothermal venting. His resource of 1.2 Gt of Cu+Zn can be logically increased by projecting this mineralization to the areas of the current

ocean plate that are not currently hydrothermally active by taking into consideration that, according to Hannington, all of his inventoried mineralization is located “within 5 to 10 km of the ridge axis” and by allowing that Hannington may not have identified all the sulfide mounds within his areas of mineralization (because they had no morphological expression, were covered by volcanics, or were smaller than the cutoff used). At the present-day average spreading rate of 40 mm/year, the formula of Baker et al. (1996) suggests that 16% of the ridges will be occupied by black smokers. Assuming that sulfides accumulate episodically in the 84% of the ridge length not occupied by smokers today and presumably not inventoried by Hannington et al. (2010), as required by my dictum that the mineralization must be uniform in large area average, their resource can be increased by a factor of 6.25. If the inventoried sulfide material is within 7.5 km of the ridge axis rather than within 50 km, the area of the inventoried neovolcanic zone is decreased by a factor of 6.67, and the resource estimate increased by 6.67. If Hannington et al. (2010) map 30% of the sulfides that are present, the ocean metal resource would increase by an additional factor of 3.3. Together, these changes increase Hannington’s 1.2 Gt Cu+Zn ocean resource by a factor of 140 ( $=6.35 \times 6.67 \times 3.3$ ) to 168 Gt Zn+Cu. I would say, therefore, that based on (1) the likelihood that the physical and chemical processes involved in massive sulfide accumulation in a hydrothermal area do not change with time or setting and (2) seafloor observations as summarized by Hannington, a reasonable range for the ocean VMS-type base metal resource is between the extrapolated observation estimate of 168 Gt and the Sangster seven-land district upper bound of 2,400 Gt Cu+Zn. If Hannington’s 300-Gt metalliferous sediment (similar perhaps to a widely distributed mine horizon mineralization) is added to the extrapolated observation estimate, the resource becomes

468 Gt, which is pretty close to my 530 Gt resource estimate.

After enough seafloor exploration has taken place, we will have a better idea of the ocean VMS metal resource. That exploration is proceeding now, and my impression is that it has been relatively easy for companies such as Neptune and Nautilus to define seafloor VMS prospects. How could we gain more confidence in resource estimates before a substantial amount of exploration has occurred? For my estimate, I would suggest trying to carefully define the surface metal density adjacent to several ridge segments where hydrothermal activity and mineral deposition is continuous. If the surface metal densities at several such locations are similar, a key aspect of my method will have been supported.

Finally, despite its having been some unanticipated work for me, I want to thank Hannington for taking the time to raise the issues he did. We may not agree on the size of the ocean VMS resource, but I am sure we do agree that it is important that the ocean’s VMS resources be estimated carefully with plausible ranges identified. Too high an estimate might promote the waste of investment resources; too low an estimate might encourage undue pessimism and placing the oceans off-limits to exploration. To get the resource estimate right requires discussion and further work. I hope this exchange between Hannington and me will stimulate the needed discussion.

PS:

In preparing my reply, I noticed an error in Table 1 (line 15) of my paper published online:

S 93.8%, Fe 5%, Zn 1.21% (19% Cu) and S 98.8%, Fe 0.85%, Zn 0.36% (29% Cu)

should read:

Fe 93.8%, Zn 5%, Cu 1.21% (19% Cu) and Fe 98.8%, Zn 0.85%, Cu 0.36% (29% Cu)

**Table 1** Comparison of deposit spacing and surface metal densities in VMS and SMS settings

	Length of ore horizon (km)	Spacing between deposits (km)	Deposition area (km <sup>2</sup> )	Zn+Cu metal resource (10 <sup>6</sup> t) from Franklin et al. (2005)	Zn+Cu surface density (t/km <sup>2</sup> )	Reference
Matagami	70	2.5	175	4.45	25,000	
Noranda	90	3	270	7.3	27,000	
Middle Valley		2	3.14	0.39	123,000	Goodfellow (2010) Hannington et al. (2010)
Solawara 1		2	3.14	0.166	53,000	Lipton (2008)

The metal surface densities here are calculated for one-deposit-spacing-wide stripes along exposed portions of the ore horizon or for areas around deposits that have a radius equal to half the deposit spacing. These surface densities are much higher than the district-wide averages discussed in the text but show metal surface densities on the modern seafloor are comparable to or larger than those in the Archean VMS districts of Matagami and Noranda

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