Is temperature a good proxy for sulfide in hydrothermal vent habitats?

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Abstract: On the basis of previous studies at 9°N and 13°N East Pacific Rise (EPR) fields, we discuss the general assumption that temperature is a proxy for sulfide in vent fauna habitat. The main conclusion of these works is illustrated here through selected examples. *In situ* measurements were used to assess the variability of chemical parameters as function of temperature at the scale of fauna aggregations. Over a single vent site, aggregations of mussels or *Riftia pachyptila* discretely distributed around diffuse vents exhibit, in first assumption, similar sulfide-temperature correlation. In contrast, sulfide is much higher, for a given temperature, in the habitat of alvinellids than in neighboring habitats of *Riftia pachyptila*. Some consistency in the sulfide-temperature correlation is also found when comparing diffuse vent habitats over distinct sites of the vent field, even when they are not dominated by the same species. In some case, however, this correlation departs substantially from the general trend. The variability in the iron-sulfide ratio in fluids between site is further expected to modulate sulfide biological impact. According to thermodynamic calculation, however, this factor appears to be more relevant when used to discriminate sulfide toxicity in alvinellid habitats than to conclude on the unavailability of sulfide to *Riftia pachyptila* populations at iron-rich sites. When direct *in situ* characterization is not available, these general conclusions should provide a first basis for the extrapolation of chemical features from temperature ranges in EPR habitats.

Keywords: Hydrothermal Vent ● Sulfide ● Temperature ● Mussel beds ● *Riftia pachyptila* ● Alvinellids

Introduction

At vent site scale, animal communities are distributed around vent sources along a gradient of hydrothermal influence. This distribution is expected to reflect the optimum physico-chemical requirements of different species, regarding their physiological tolerance and the availability of chemical energy for their symbionts (Hessler & Kaharl, 1995). Within these limits, biological interactions could predominantly control the temporal succession of species

(Mullineaux et al., 2003). The nature and respective importance of abiotic and biotic drivers of biodiversity and productivity however remain poorly known. Marked transitions in dominant species distribution have been correlated to changes in source fluid composition and subsequent mixing zone chemistry (Shank et al., 1998; Sarrazin et al., 1999; Luther et al., 2001). However, the mechanisms proposed to sustain these transitions remain speculative, partly because of the covariation of chemical, physical and biological factors. For the discrimination of

their relative impact, there is still a need to clarify the relative variation of these factors, and particularly of chemical parameters with temperature.

Sulfide is both an essential nutrient for sulfide-oxidizing symbionts and a potent poison for most organisms. Qualitative comparison of sulfide exposure has often been inferred from temperature ranges, assuming the consistency of the sulfide to temperature correlation between habitats. In order to better define the limits of this hypothesis and to identify the processes that differentiate vent habitats, we have studied the correlation of sulfide with temperature in well-characterized vent fauna habitats of the 9°N and 13°N vent fields of the East Pacific Rise (EPR) (Le Bris et al., 2003; Le Bris et al., 2006). The main conclusions of these studies are reviewed in this paper. The role of iron in the distribution of different forms of sulfide in the medium, and its relevance to the toxicity of the medium or the primary producers requirements as discussed in (Luther et al., 2001), is also considered. Illustrative examples including additional data further supporting these conclusions are provided. Intra-assemblage variability resulting from biological activity itself is not considered here, although it can be of major importance in some habitats (Le Bris et al., 2005; Le Bris et al., 2006).

Methodological requirements

This study was performed through an extensive *in situ* survey of the small scale variability of total sulfide concentration (ΣS) and temperature within animal aggregations at various EPR sites. Material and methods were presented in detail in previous papers. The contribution of different chemical forms to the total sulfide budget was assessed, as described previously, through thermodynamic calculations using combined measurement of the main chemical parameters controlling this speciation, pH and reduced iron concentration.

Within discrete aggregations, such as mussel beds, *Riftia pachyptila* Jones, 1981 bushes or alvinellid colonies, a wide range of environmental conditions is encountered, ranging from the characteristics of the local vent source to that of the surrounding seawater (Johnson et al., 1988, Johnson et al., 1994; Le Bris et al., 2006). To characterize these gradients, submersible flow-analyzers have proven their efficiency (Johnson et al., 1986; Le Bris et al., 2000). Comparison of habitats also requires overcoming the variability of fluid-seawater dilution rate. In the absence of conductive heat exchange, temperature anomaly is proportional to the mixing ratio and can be used as a dilution tracer (Johnson et al., 1988). *In situ* characterization is the only adequate method to assess this correlation of chemical parameters with temperature. Using a fast temperature

sensor tightly attached to the analyzer inlet, combined chemical and temperature data can be acquire at scales relevant to the organism aggregations (Johnson et al., 1988, Le Bris et al., 2006). In comparison, discrete sampling can lead to severe underestimation of the sulfide to temperature relation (Fig. 1). Modifications of sample composition during recovery, and particularly sulfide oxidation by oxygen, are likely to be a main cause of this artifact.
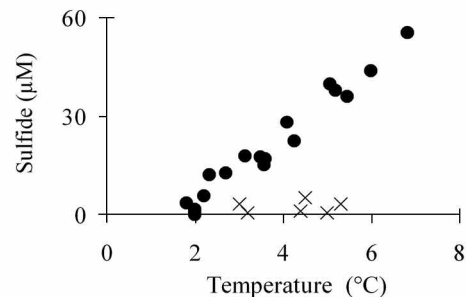

Figure 1. Sulfide-temperature correlation determined for the same *Riftia pachyptila* bush, *in situ* with the flow-analyzer ALCHIMIST (black circles) and from on-board analysis of discrete samples (crosses).

Figure 1. Corrélation entre la concentration en sulfures et la température déterminée sur le même bouquet de *Riftia pachyptila*, *in situ* à l'aide de l'analyseur de flux ALCHIMIST (cercles noirs) et à bord sur des échantillons (croix).

Consistency of the sulfide-temperature correlation within and among sites

Different fauna aggregations of a single vent site

The reproducibility of the sulfide correlation with the fluid-seawater mixing ratio was a main conclusion of the extensive study of fauna habitats at the Rose Garden site on the Galapagos Ridge (Johnson et al., 1988). This also appears to be valid, in first instance, when considering diffuse-flow habitats within a single site of the 9°N EPR vent field (Le Bris et al., 2006). As an example, very similar trends were obtained for distinct mussels-dominated assemblages of the Biovent site, even though the corresponding temperature ranges are different (Fig. 2a). It is interesting to note that the consistency of these trends is conserved when including the data obtained three years before at the same site, possibility indicating a long-term stability of habitat chemistry at this site.

This within-site reproducibility is not confirmed when comparing different types of habitats, like the so-cold 'warm' alvinellid habitats and 'mild' *Riftia* habitats. The
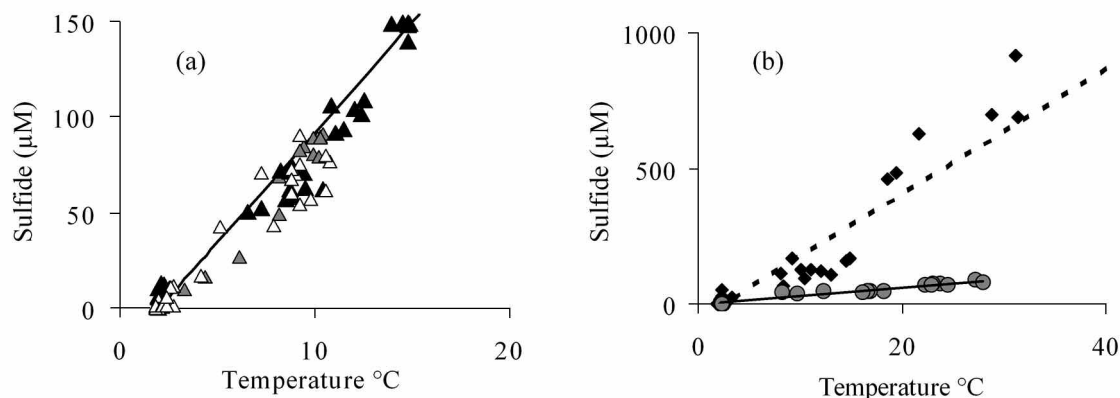
Figure 2. Sulfide-temperature correlation in distinct fauna aggregations within a site: (a) over two mussels-dominated aggregations at Biovent (9°N EPR) in 2002 (black and grey triangles) and a similar assemblage in 1999 (open triangles), (b) above an alvinellid colony (black diamonds) and at the base of *Riftia pachyptila* tubes (grey circles) a few decimeter apart at M-Vent (9°N EPR). Model lines represent the conservative dilution of the local fluid source in seawater.

Figure 2. Corrélation entre la concentration en sulfures et la température au sein de différentes agrégations de faune sur un même site : (a) sur deux assemblages dominés par des moules à Biovent (9°N EPR) en 2002 (triangles noirs et gris) et sur un assemblage semblable en 1999 (triangles blancs), (b) au-dessus d'une colonie d'Alvinellidés (losanges noirs) et à la base d'un bouquet de *Riftia pachyptila* (cercles gris) distants de quelques dizaines de centimètres à M-Vent (9°N EPR). Les droites représentent la dilution théorique (modèle conservatif) du fluide émis par la source dans l'eau de mer.
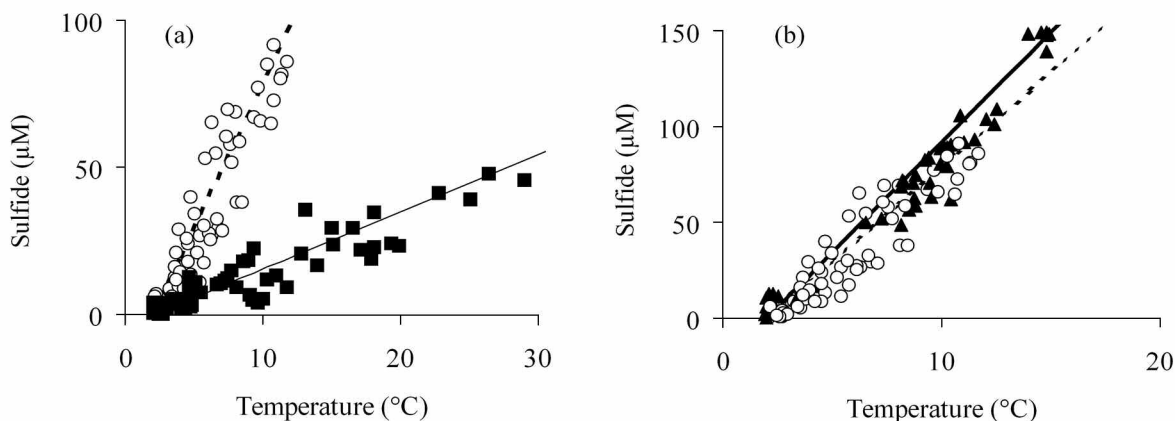

Figure 3. Sulfide-temperature correlation in diffuse flow habitats over different sites: (a) over large *Riftia*-dominated aggregations at Tica (9°N EPR) (open circles) and declining *Riftia*-dominated aggregations at Riftia Field (9°N EPR) (black squares), (b) over *Riftia*-dominated aggregations at Tica (9°N EPR) (open circles) and mussel-dominated aggregations at Biovent (9°N EPR) (black triangles). Model lines represent the conservative dilution of the local fluid source in seawater. Adapted from Le Bris et al. (2006).

Figure 3. Corrélation entre la concentration en sulfures et la température dans des habitats associés à des émissions diffuses de différents sites : (a) sur des assemblages dominés par *Riftia* à Tica (9°N EPR) (cercles blancs) et sur des assemblages en déclin dominés par *Riftia* à Riftia Field (9°N EPR) (carrés noirs), (b) sur des assemblages dominés par *Riftia* à Tica (9°N EPR) (cercles blancs) et sur des assemblages dominés par des moules à Biovent (9°N EPR) (triangles noirs). Les droites représentent la dilution théorique (modèle conservatif) du fluide émis par la source dans l'eau de mer. Adapté de Le Bris et al. (2006).

sulfide concentration above an alvinellid colony was shown to exceed by one order of magnitude the level observed in the same temperature range around *Riftia pachyptila* located only a few decimeters apart (Fig. 3b). These results are in agreement with previous observation at the Genesis site on EPR 13°N, for two aggregations distant of about ten meters (Le Bris et al., 2003). They confirm that the alvinellids-dominated habitats on the EPR do not solely distinguish from *Riftia pachyptila* or mussel-dominated habitats by their larger temperature range but also by much higher sulfide levels even at low temperature. The apparent shift in the sulfide-temperature, below and above 20°C, for the alvinellid colony (Fig. 2b), furthermore, suggests substantial small-scale heterogeneity and might reflect the importance of conductive heat exchange described for this type of habitat (Le Bris et al., 2005).

Fauna aggregations at different vent sites

Over sites located several hundreds of meters apart along the ridge axis, significant discrepancies are observed among diffuse flow habitats. Declining *Riftia pachyptila* communities at Riftia Field (9°N EPR) in 2002 were associated to much lower sulfide-temperature trends than the abundant tubeworm communities at Tica (Fig. 3a). More surprising is the fact that quite similar trends were observed between diffuse flow sites exhibiting very contrasted biological patterns, such as *Riftia*-dominated and mussel-dominated assemblages that were described as characteristic succession stages of fauna colonization of EPR 9°N habitats (Shank et al., 1998). The sulfide-temperature was shown to be similar at Tica and Biovent, although they differ markedly, both in the duration of hydrothermal activity and in the species dominating the aggregations (Fig. 3b). This suggests that, to the exception of the immediate vicinity of fluid sources, there should be only minor differences in the temperature and sulfide conditions experienced within mature mussel and tubeworms aggregations. In contrast, declining *R. pachyptila* aggregations have been associated to a significant reduction of the sulfide-temperature trend.
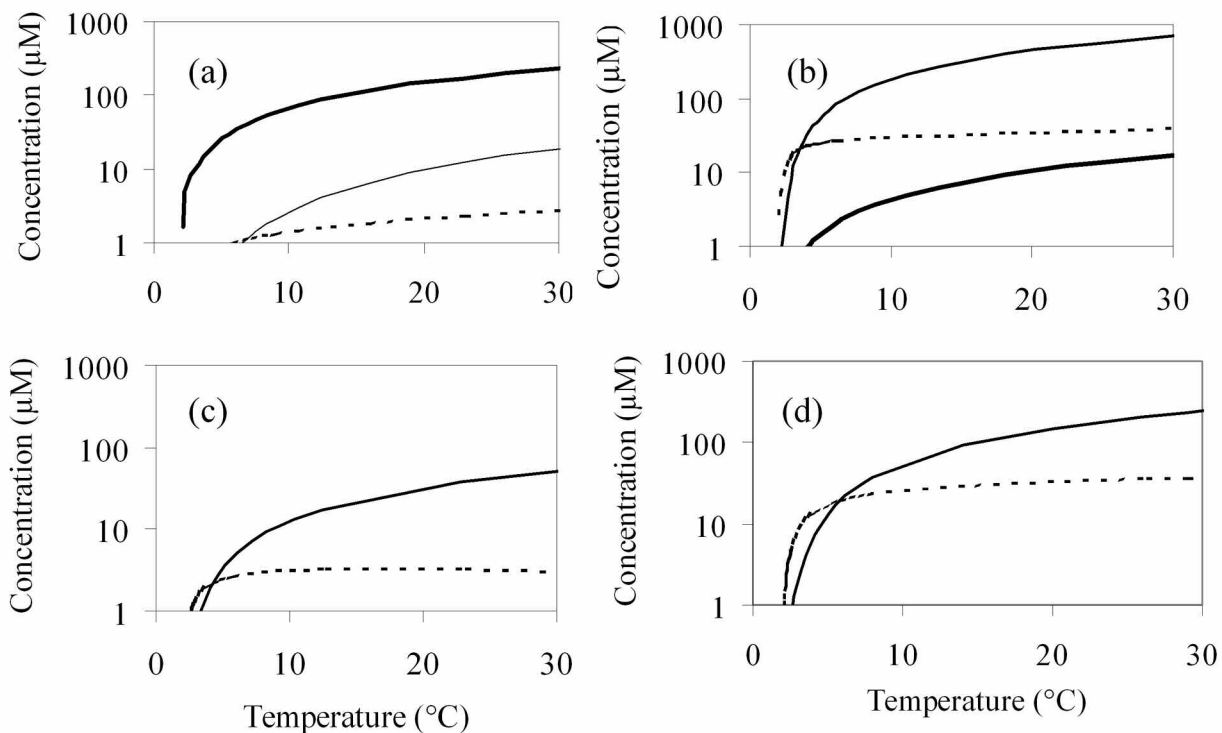

Figure 4. Contribution of H_2S (thin line), HS^- (dotted line) and dissolved or precipitated FeS forms (bold line) as a function of temperature as predicted from the conservative mixing of the local hydrothermal fluid source and seawater. (a) Alvinellid habitat at Elsa (EPR 13°N), (b) Alvinellid habitat at Genesis (EPR 13°N), (c) *Riftia* habitat at Tica (EPR 9°N), (d) *Riftia* habitat at Riftia Field (EPR 9°N).

Figure 4. Contribution de H_2S (ligne fine), HS^- (ligne pointillée) et des formes dissoutes ou précipitées de FeS (ligne épaisse) en fonction de la température selon un mélange conservatif du fluide émis par la source dans l'eau de mer. (a) Habitat des Alvinellidés à Elsa (EPR 13°N), (b) Habitat des Alvinellidés à Genesis (EPR 13°N), (c) Habitat de *Riftia* à Tica (EPR 9°N), (d) Habitat de *Riftia* à Riftia Field (EPR 9°N).

Sulfide speciation as function of temperature

The contribution of different chemical forms of sulfide was shown to vary widely among habitats and was suggested to drive the distribution of communities through the modulation of its biological impact (Luther et al., 2001). Sulfide availability to the symbiotic communities is expected to be restricted to the readily assimilated 'free sulfide' forms, HS- and H_2S (Childress & Fisher, 1992). Among these chemical species, H_2S has the largest capacity to diffuse through respiratory membranes and is considered for this reason as the most toxic (Visman, 1991). By limiting the concentration of these 'free-sulfide' forms, the formation of dissolved, colloid or precipitated metal sulfides in the mixing zone would thus reduce both the availability of this electron donor for symbioses and the toxicity of the medium (Luther et al., 2001).

Figure 4 presents the simulated distribution of these species along the dilution gradient in two alvinellid habitats and two *Riftia* habitats from four distinct sites. There is no general trend in the sulfide speciation pattern arising from these calculations, even when similar habitats are considered. As discussed in Le Bris et al. (2003), the predominance of iron associated forms of sulfide is not confirmed to be a general feature of alvinellid habitats. Like several other sites of the EPR 13°N segment (Le Bris, unpublished data), the Genesis fluids are largely depleted in iron. In these conditions, FeS would only contribute for a few μM to the high millimolar sulfide concentration (Figure 4b), in contrast to the results obtained by Luther et al. (2001) for another EPR site. From this it can be expected that sulfide toxicity in alvinellid habitat is highly variable among sites, depending on the iron to sulfide ratio in the end-member fluids.

The iron content in hydrothermal fluids was also suggested to have a large impact on tubeworm communities (Shank et al., 1998; Von Damm & Lilley, 2004). The decline or complete extinction of these populations was attributed to the depletion of available sulfide through the formation of iron sulfides. Although the Riftia Field site (EPR 9°N) in 2002 exhibited both declining *Riftia* populations and high iron to sulfide ratio (Fe:S ~ 0.7 as compared to Fe:S < 0.1 at Tica where *Riftias* were abundant and healthy), the chemical conditions at this site do not support this hypothesis (Le Bris et al., 2006). According to thermodynamic calculation, neither precipitated nor aqueous FeS species should be stable in this habitat (Figure 4c), as a result of quite low iron and sulfide concentration ranges and low pH (Le Bris et al., 2006). FeS precipitation in subsurface is more likely to occur, as suggested by source fluids relatively more acidic and depleted in sulfide than observed at other sites. Although the exact cause of the tubeworm decline still has to be elucidated, this low pH

could constitute a critical factor for *Riftia pachyptila* population at Riftia Field (Girguis et al., 2002).

Conclusion

The sulfide-temperature relations in different fauna aggregations of a single site do not simply reflect various degree of the end-member fluid dilution. Particularly, focused-flow and diffuse-flow habitats are quite different from each others, resulting of the non-conservative behavior of these parameters along subsurface fluid pathways. Although this cannot be generalized, the sulfide-temperature relation appears much more consistent among diffuse-flow habitats over different sites, even when distinct taxa – mussel or *Riftia pachyptila* - dominate the assemblages. These habitats distinguish mostly from their fluid dilution range, rather than from major differences in source fluids. When source fluids depart from the general trend, large changes in iron to sulfide ratio are observed but its impact on sulfide speciation cannot be generalized. Particularly, iron increase effect on sulfide availability seems rather constrained by subsurface processes, resulting in acidification and sulfide loss prior emission of fluids (Le Bris et al., 2006).

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