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## Hydrothermal Impacts on Trace Element and Isotope Ocean Biogeochemistry

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## Hydrothermal Impacts on Trace Element and Isotope Ocean Biogeochemistry

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# Summary

Hydrothermal activity occurs in all ocean basins, releasing high concentrations of key trace elements and isotopes (TEI) into the oceans. Importantly, the calculated rate of entrainment of the entire ocean volume through turbulently mixing buoyant hydrothermal plumes is so vigorous as to be comparable to that of deep-ocean thermohaline circulation. Consequently, biogeochemical processes active within deep ocean hydrothermal plumes have long been known to have the *potential* to impact global scale biogeochemical cycles. More recently, new results from *GEOTRACES* have revealed that plumes rich in dissolved Fe, an important micronutrient that is limiting to productivity in some areas, are widespread above mid-ocean ridges and extend out into the deep ocean interior. While Fe is only one element among the full suite of TEIs of interest to *GEOTRACES*, these preliminary results are important because they illustrate how inputs from seafloor venting might impact the global biogeochemical budgets of many other TEIs. To determine the global impact of seafloor venting, however, requires two key questions to be addressed: (a) What processes are active close to vent-sites that regulate the initial high temperature hydrothermal fluxes for the full suite of TEIs that are dispersed through non-buoyant hydrothermal plumes? (b) How do those processes vary, globally, in response to changing geologic settings at the seafloor and/or the geochemistry of the overlying ocean water? In this paper, we review key findings from recent work in this realm, highlight a series of key hypotheses arising from that research and propose a series of new *GEOTRACES* modelling, section and process studies that could be implemented, nationally and internationally, to address these issues.

# 1. Introduction

Submarine hydrothermal circulation arises when seawater percolates downward through fractured ocean crust – for example, along the globe-encircling ~55,000km volcanic/tectonic mid-ocean ridge system. As it penetrates downward, seawater is first heated and then undergoes progressive chemical modification through reactions with the host rock, reaching maximum temperatures that can exceed 400°C. At those temperatures the fluids become buoyant and rise rapidly back to the seafloor where they are expelled into the overlying water column (see review in [1]). The most spectacular manifestation of seafloor hydrothermal circulation is without doubt the high-temperature ( $\leq 405^\circ\text{C}$ ) vents that expel fluids from the seafloor along all parts of the global mid ocean ridge-crest. In addition to being visually compelling, the fluids emitted from these vents also exhibit important enrichments and depletions in numerous trace elements and isotopes (TEIs) when compared to ambient seawater. Many of the dissolved chemicals released from the Earth's interior during venting precipitate upon mixing with the cold, overlying seawater, generating thick columns of black metal-sulfide and oxide mineral-rich smoke – hence the colloquial name for these vents: “Black Smokers”. Despite their spectacular appearance, however, high-temperature vents may only represent a small fraction of the total hydrothermal heat-flux close to ridge-axes, which may be dominated by much lower-temperature diffuse flow exiting the seafloor at temperatures comparable to those first observed at the Galapagos vent-sites in 1977 [2, 3]. Further, while it is now known that high-temperature venting can occur in all ocean basins and along ridges of all spreading rates [4] there appear to be important differences in the styles of venting that arise in different geologic settings [5, 6].

What is known from studies of ocean budgets for key conservative tracers (e.g.  $^{87}\text{Sr}/^{86}\text{Sr}$  distributions) is that ocean water must be heated to high temperature, deep within the ocean lithosphere, with a residence time for circulation of the entire ocean volume along this pathway that is of the order of 10My [2]. Because end-member vent-fluids then undergo dilution by a factor of ~10,000:1 within turbulently mixing buoyant plumes, immediately upon emission from the seabed [7], it has been estimated that the residence time of the oceans with respect to entrainment into hydrothermal plumes should be much shorter: of the order 1,000-10,000 years. This is directly comparable to the mixing time for the thermohaline conveyor and, consequently, it has long been hypothesized that processes active within deep ocean hydrothermal plumes may influence global-scale TEI ocean biogeochemical cycles (e.g. [1, 8]).

On December 9 & 10, 2015, the authors of this paper formed the membership of a break-out group focused upon *Hydrothermal Fluxes* as part of the larger *Quantifying Fluxes and Processes in Trace-Metal Cycling in the Oceans* scientific meeting hosted by the Royal Society in Chicheley Hall.

After reviewing the key discoveries already made since the start of GEOTRACES (Section 2) the group moved on to identify some key barriers to *quantifying* the impact of hydrothermal inputs to the oceans (Section 3) which, in turn, allowed us to identify a series of high priority future activities, to be implemented at the scale of national and international collaborative programs, to progress this exciting field (Section 4).

## 2. Hydrothermal TEI Fluxes to the Oceans: Novel Insights from GEOTRACES

The first discoveries of seafloor hydrothermal venting were made just as the field-component of the GEOSECS program (predecessor to GEOTRACES), was drawing to a close [9]. Consequently, scientists could only speculate (however presciently) on the importance of hydrothermal inputs to ocean biogeochemistry, at that time [10]. By contrast, the potential importance of submarine hydrothermal venting has been an important point of focus since the inception of the GEOTRACES program [11] where Mid-Ocean Ridges were recognized as one of four locales critical to understanding TEI fluxes to and from the oceans, alongside atmospheric deposition, continental, shelf and margin inputs and the sediment-water boundary [12-14]. In keeping with program priorities and objectives, those ocean sections that have been occupied within the GEOTRACES program to-date [15] have included deep-ocean investigations of TEI distributions wherever ocean sections cross mid-ocean ridge crests. An important first result, arising from that work, is that a number of cruises have now provided independent and objective confirmation that hydrothermal activity is, indeed, active in all ocean basins releasing high concentrations of dissolved Fe into the overlying water column which can be dispersed long distances into the surrounding oceans [16-24]. Importantly, these results include clear evidence for input from hydrothermal sources along ultra-slow and slow spreading ridges in the Arctic and Atlantic Oceans [Fig.1].

Such slow-spreading ridges constitute ~50% of the global mid-ocean ridge axis but, historically, had been considered as unlikely to host significant venting [25]. By contrast, the new results help to confirm a more modern understanding that venting is much more abundant than previously recognized along slow-spreading ridges [4]. Further, these results take on an important socio-economic significance when one considers that such hydrothermal vent-sites along slow and ultra-slow ridges may be particularly prominent, worldwide, in terms of both the size of the seafloor massive sulphide (SMS) deposits that they generate and also the high gold and copper concentrations associated with those SMS deposits [6].

Most recently, the GP-16 section completed by the US GEOTRACES program included, as one focus, an investigation of a deep hydrothermal plume spanning the south Pacific Ocean which was first identified from helium isotope analyses [26] and which, subsequent compilations that included the GEOSECS and WOCE data-sets have confirmed, represents one of the most prominent of such features worldwide [27]. Shipboard analyses from that *GEOTRACES* cruise have now demonstrated that dissolved Fe (dFe) can be dispersed over length scales of thousands of kilometers into the ocean interior [Fig.2]. A particular significance of these results comes from the increasing recognition that the fate of hydrothermally-sourced Fe may be intimately associated with organic carbon [28-35]. This, in turn, has stimulated particular interest in the oceanographic research community: Fe can be more than 1 million fold enriched in vent-fluids, compared to deep ocean waters, and yet it also acts as an essential micro-nutrient that limits photosynthetically driven primary productivity across up to 40% of the world's surface oceans [36]. If hydrothermally sourced Fe can persist long distances through the oceans, then its upwelling into the surface ocean could be responsible for enhancing primary productivity in the iron-limited Southern Ocean [37, 38].

Of course, Fe is not the only TEI impacted by submarine hydrothermal venting. During the US GEOTRACES GA-03 section, sampling of the non-buoyant plume above the TAG hydrothermal site on the Mid-Atlantic Ridge (MAR) revealed enrichment in the plume for several elements including  $^3\text{He}$  [39], Fe and Mn [23], Al [40], and Hg [41]. In contrast,  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  [42] showed reduced concentrations as a result of in-plume scavenging processes. This effect was also seen to reduce the concentrations of Cu [43] and Pb [44] in the plume samples compared to those immediately above or below in the water column. A small lowering of the Si isotope signal was also seen but no Si concentration anomaly was visible [45]. The fact that enriched chemical signals were also observed to the west of the MAR is consistent with the general features of material transport described by Thurnherr *et al* [46], namely inflow from the eastern flank of the Ridge coupled with enhanced diapycnal mixing above the hydrothermal plumes, whose impact is carried westward by beta-plume dynamics [47]. Strikingly, the  $^3\text{He}:\text{Fe}$  ratio at TAG [39] differs substantially from that observed from the faster spreading EPR [24], and is more similar to that observed in the South Atlantic [19]. While the Al:Fe ratio in the TAG plume (0.73-1-15) is similar to the EPR plume (~1) the Mn:Fe ratio is much lower at TAG (0.5-0.54) than in the dispersing EPR plume (1.45). At the EPR both of these values change as the plume is diluted away from the vent site (Al:Fe increases to 1.9 and Mn:Fe drops to 0.26) implying relative scavenging losses of  $\text{Mn} > \text{Fe} > \text{Al}$  in the EPR plume [24]. However, in the case of TAG it is difficult to connect these “far field” signatures to specific vent sites, given the strong meridional flow in the western Atlantic, coupled with robust along rift valley flows and tidal mixing. In addition, it is likely that the off axis anomalies observed at TAG

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result from a significant amount of “integration” from multiple other vent sites that are known to exist, north of the section [6].

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The approach followed to-date is useful because appropriate TEI:<sup>3</sup>He ratios for hydrothermal plumes above sites of venting can be coupled with global-scale hydrothermal <sup>3</sup>He fluxes to drive global biogeochemical models [48] or extrapolate and derive global TEI budgets [24, 49]. That approach takes advantage of the fact that primordial <sup>3</sup>He trapped in the Earth's interior leads to enrichment of <sup>3</sup>He/<sup>4</sup>He ratios in the mantle by a factor of ~8 relative to atmospheric values [50, 51]. These same enrichments are transferred through submarine venting to the oceans where, because He is geochemically inert in the marine environment, enrichments in <sup>3</sup>He can be used as a conservative tracer of hydrothermal plume dilution and dispersion over long distances [26]. By contrast, even those TEIs that may *superficially* mimic dissolved <sup>3</sup>He distributions in hydrothermal plumes (e.g. dFe - Fig.2) do not act as such purely conservative tracers of physical circulation. Instead, what may be operationally defined as “dissolved” Fe in a hydrothermal plume may be more complex in nature. For example, the US GEOTRACES GA-03 section crossing the TAG hydrothermal field on the northern Mid-Atlantic Ridge found that more than 80% of the “dissolved” Fe in that dispersing plume was actually in the form of larger colloids (0.02-0.2µm) and less than 20% was in the form of smaller colloids and soluble Fe (<0.02µm) species [49]. This same topic has also been investigated through a series of more process-oriented studies, conducted close to hydrothermal vents. Results from those studies cannot currently resolve whether the colloidal Fe present is due, primarily, to the formation of organic-Fe complexes [28, 30, 32] or, alternately, to the precipitation of nano-particulate Fe mineral phases [33, 34]. Process studies from Southern Ocean hydrothermal plumes have demonstrated that, there, isotopic fractionation occurs during plume mixing consistent with exchange between different pools of Fe and leading to a net supply of isotopically light dissolved Fe to the oceans [52].

### 3. Hydrothermal TEI Fluxes to the Oceans: Gaps in Current Understanding

To meet the goals of the *GEOTRACES* program [11] we continuously seek to improve our understanding of both the inputs and impacts of hydrothermal venting on TEI ocean biogeochemistry. To identify priorities for future research, it is instructive to consider two recent studies, each of which were extrapolated from limited data-sets to global-scale modelling, revealing critical gaps to our current knowledge.

First, in an attempt to model the contribution of hydrothermal Fe to the global ocean biogeochemical cycle, one approach [48] assumed a known Fe:<sup>3</sup>He ratio for hydrothermal plumes which, when used to drive a global biogeochemical model, could be used to assess what proportion of Southern Ocean primary productivity might be contingent upon a hydrothermally sourced

dissolved Fe supply.  $^3\text{He}$  is known to behave as a purely conservative tracer that can be scaled linearly with heat supply in any given hydrothermal plume, but we do not know whether all global hydrothermal systems exhibit the same  $^3\text{He}$ :heat supply relationship. Moreover, whether  $\text{TEI}:\text{He}$  ratios are the same in all hydrothermal systems needs to be assessed because multiple lines of reasoning suggest such might not be the case. First, a suite of early studies on medium and fast spreading ridges indicated that axial hydrothermal heat flow might be partitioned such that only ~10% of that heat was released through focussed high temperature venting, at temperatures of ~350-400°C, while the remainder of the heat flux would be manifest in the form of dilute fluids that are emitted from the seafloor after sub-surface mixing with ambient seawater [2]. However, while the heat available from cooling of magmatic intrusions at mid-ocean ridge axes may scale with ridge spreading rate [25] what is now recognised is that slow spreading ridges are characterised by a higher proportion of focussed high temperature fluid-flow, per unit of heat-flow, than their fast-spreading counterparts [53]. It is believed that this situation may arise, in part, because of differences in the partitioning of axial heat flux at slow spreading ridges. For example, it has been estimated that the proportions of focussed and diffuse flow at the Mid-Atlantic Ridge may be closer to 50:50 rather than 10:90 [3, 54]. The case for slow and ultra-slow spreading ridges is complicated further by the recognition that not only do slow spreading ridges host more high-temperature hydrothermal vents than previously anticipated [4] but, further, that at least two styles of hydrothermal venting result, each with distinct vent-fluid compositions [5, 55]. An open question, therefore, is:

***Q1: How do the  $\text{TEI}:\text{He}$  ratios introduced into hydrothermal plumes vary as a function of the diverse styles of venting found throughout the world's oceans?***

In a second recent study, SCOR working group 135 sought to use results from process-based investigations in near-vent environments to determine what impacts hydrothermal circulation might have on global biogeochemistry as a whole and, in particular, the global carbon budget [35]. That modelling approach revealed further important gaps in our knowledge of deep ocean hydrothermal processes. First, while it was recognized that no one vent-site on any given ridge-type was likely to be representative of the global whole, insufficient data existed to populate the idealised box-model (which uses Fe as “currency” to calculate organic carbon fluxes [Fig.3]), at any location other than the East Pacific Rise 9°50'N hydrothermal area. Further, even at that site, which had been a particular focus of international research dating from the start of the US Ridge 2000 program, the team lacked sufficient confidence in all the required parameters to run the model in forward (prognostic) mode. Rather, because of uncertainty in the appropriate value for Fe concentrations in

diffuse hydrothermal flow, the model was run in inverse mode instead. Applying global-scale Fe fluxes, [24, 48] this inverse approach was then used to arrive at a *predicted* representative concentration of dissolved Fe in diffuse hydrothermal fluids at the East Pacific Rise. While the calculated concentrations ( $\sim 10\text{--}90\text{ }\mu\text{mol/kg}$ ) are unremarkable, a more surprising result of the same model runs was the prediction that 78–99% of all the dissolved Fe exported from hydrothermal vents to the oceans should originate from diffuse hydrothermal flow. This directly contradicts all previous expectations: because high temperature vent fluids exhibit extremely high Fe (and other TEI) concentrations, and because some trace elements (e.g. Cu) are only mobile in solution at high temperatures in those fluids, it had been assumed that high temperature fluid flow should dominate the TEI flux from hydrothermal venting to the oceans (e.g. [1]). The results of this modelling exercise, therefore, are quite profound. If correct, and widely representative, they may indicate an important role for organic complexation or other “pre-treatment” processes in diffuse flow systems that allow one particular fraction of all hydrothermally sourced Fe (and other TEIs) to be protected against rapid removal into near-field sediments and, instead, exported long distances into the ocean interior. An important second question that remains open at this time, therefore, is:

***Q2: What is the relative importance of diffuse vs focussed fluid flow in the fluxes of TEIs from hydrothermal venting to the oceans?***

Finally, a third issue that arises concerns the fate of Fe and the impact that precipitation of Fe-rich particulates might have on other particle-reactive TEIs, especially given the new realization that hydrothermal venting is distributed more evenly throughout all ocean basins. While, historically, it had been assumed that hydrothermal inputs to the oceans were focussed heavily toward fast spreading ridges which are all located in the Pacific Ocean [25], we now recognize that hydrothermal inputs to the oceans are distributed more evenly in all ocean basins [4] and, hence, all along the entire thermohaline conveyor. This is important because the oxidation rate of dissolved Fe in deep ocean hydrothermal plumes (important in driving the precipitation loss of Fe) is known to also vary systematically along the same trajectory [56, 57]. While changes in the rate of oxidation and precipitation of dissolved Fe will not impact the release of a conservative tracer such as  $^3\text{He}$ , it may - through its impact upon dissolved-particulate Fe interactions - have an impact upon any other TEIs (e.g. REE,  $^{231}\text{Pa}$ ,  $^{230}\text{Th}$ ) that may be scavenged by particulate Fe phases [1]. An important third question that remains open, therefore, distinct from Question 1, which is based on varying water-rock systems, is:

***Q3: How do the TEI:  $^3\text{He}$  signatures in hydrothermal plumes vary, for individual TEIs, as a function of varying water column chemistry along the thermohaline conveyor?***

# 4. Hydrothermal TEI Fluxes to the Oceans: A Road-Map Toward Synthesis

Moving forward, we have now acquired sufficient ocean section data to help identify a path toward synthesis and further targeted sampling that would allow the *GEOTRACES* program to greatly improve our understanding of global scale hydrothermal fluxes of TEIs to the oceans. The approach we outline for future studies continues to be so ambitious in scope that the whole could only be achieved through a level of international collaboration and coordination afforded by the international *GEOTRACES* program. Below, we outline what we consider to be the highest priority activities that should be pursued, in the order: Modelling, Ocean Sections, Process Studies.

## 4.1 Modelling

*a) Improving global  $^3\text{He}$  modelling.* As discussed earlier, we have identified that combining TEI: $^3\text{He}$  ratios with global fluxes of primordial  $^3\text{He}$  offers an extremely powerful tool for investigating the fluxes of hydrothermally-sourced TEIs to the oceans and their spatial extent. While new field programs will be required (see below) to improve our selection of the relevant TEI: $^3\text{He}$  ratios, we also urge a redoubling of efforts to refine the ability of ocean physical models to reproduce the lateral dispersion patterns observed in the historic GEOSECS- and WOCE-era  $^3\text{He}$  data-sets. Schlitzer [27] has already identified an important deficit in the modelled  $^3\text{He}$  input to the SW Pacific Ocean, suggesting that a significant source of venting is currently absent from the model in that region. Consistent with this, the latest update to the InterRidge Vents Data-Base [58] has shown that a large number of new submarine hydrothermal fields have been located throughout this portion of the global mid ocean ridge / back-arc system with almost all of those discoveries having been made since 2000 [Fig.4]. Integrating those new observational data would provide a valuable first effort to further refine global dissolved  $^3\text{He}$  modelling. This will be important because the magnitude of the global  $^3\text{He}$  source is still not fully constrained. Modelling studies currently use global values that range between 450 mol/yr to 1000 mol/yr [27, 59-61]. However, all of those modelling studies are implemented with low horizontal and vertical resolution that, unavoidably, generates shortcomings in their simulated deep circulation. Moreover, the heat forcing from hydrothermal activity can also induce important changes in deep ocean circulation, at both the local and global scale [47, 62] and that, in turn, will affect  $^3\text{He}$  redistribution significantly [63]. We can improve our confidence in the value of the global  $^3\text{He}$  source, in future, through use of higher (vertical and horizontal) resolution

models. Such models would have the capacity to reproduce the smaller scale dynamical processes discussed above which we believe to be of importance to  $^3\text{He}$  dispersion throughout the deep ocean.

*b) Improving biogeochemical modelling.*

The numerous GEOTRACES Ocean Sections that have already intercepted deep ocean hydrothermal plumes (Fig.1; [15]) provide a clear indication that hydrothermal inputs of TEIs are commonplace in Earth's oceans. Where TEIs can persist in solution, upwelling along isopycnal surfaces can lead to outcropping of hydrothermally sourced TEIs in the surface ocean. Preliminary modelling investigations have calculated the impacts that hydrothermal Fe might have on Southern Ocean primary productivity [24, 48]. There are also potential impacts of hydrothermally-sourced TEIs on biological activity in other HNLC regions of the surface ocean [27, 64]. At present, however, we do not have a complete understanding of whether the TEIs injected into dispersing hydrothermal plumes are sustained in solution and disperse, like  $^3\text{He}$ , following isopycnal surfaces. The formation of diverse particulate phases (minerals, microbes, organic floc) that settle out of plumes and sink toward the seafloor is also an important process to consider. Ultimately, modelling of a complex series of soluble-colloidal-particulate interactions within particle-rich hydrothermal plume environments will affect the predicted scavenging of some dissolved TEIs from the oceans and their removal to the underlying sediments. By contrast, current models are only beginning to capture the full complexity of these processes [38]. A first priority for global biogeochemical models, as for the dispersion of hydrothermally sourced  $^3\text{He}$  (see preceding section), would be to increase vertical resolution in the abyssal ocean to resolve the distributions of both laterally dispersing TEIs and those that settle through the water beneath dispersing hydrothermal plumes. In addition, we should also incorporate parameterisations that mechanistically resolve soluble-colloidal-particulate processes that both process studies and ocean section data are already revealing to be important [33, 34, 49] so that their large-scale impact can be assessed quantitatively. For example, more accurately quantifying the stability of dissolved iron organic complexes within hydrothermal plumes may be combined with emerging efforts to represent a continuum of iron binding ligands within current state of the art biogeochemical models [24; 38], perhaps also accounting for pH effects [65]. Finally, while the implementation of hydrothermally sourced Fe into numerical models has greatly increased our understanding of the global Fe biogeochemical cycle [24, 48], it is important to recognize that Fe is only one of the many GEOTRACES TEIs that may be influenced by seafloor hydrothermal inputs. Moving forward, a new ambition should be to assimilate the new hydrothermal data generated from GEOTRACES ocean sections into ever more sophisticated models that incorporate the biogeochemical cycles of other TEIs. Key priorities might be those TEIs that act as co-limiting

micronutrients (Mn, Co, Zn), as water-mass tracers (Nd isotopes), as tracers of particle-scavenging ( $^{231}\text{Pa}/^{230}\text{Th}$ ) or nutrient cycling (N & O isotopes in nitrate) and as toxicants (Hg, Pb, As).

4.2 Ocean Sections

Numerous Ocean Sections have already been occupied within the *GEOTRACES* program that cross mid-ocean ridge axes [15] and one has been targeted to follow down-stream, along the dispersion-trajectory of a basin-spanning hydrothermal plume [24]. A different trajectory that was never previously anticipated, but which we now recommend, is a section that follows along a portion of the mid-ocean ridge axis [11]. Slow spreading ridges are now anticipated to host many more sites of high temperature hydrothermal venting than was previously recognized [18, 66] – so much so that it is now anticipated that there are more vent sites still to be discovered along Earth’s slowest spreading ridges than have yet been discovered worldwide, despite nearly 40 years of exploration [4]. Further, the ~20 vent-sites that have been discovered so far along the Mid-Atlantic Ridge (MAR, each of which emit high concentrations of TEIs into the ocean), appear to fall into two distinctive geologic categories: those set in volcanic terrain and those that are hosted, instead, under tectonic control [Fig.5]. This bi-modal distribution of vent-site settings is of significance to GEOTRACES because it can also give rise to important differences in hydrothermal vent-fluid compositions. On the Mid-Atlantic Ridge, both volcanic and tectonic-hosted systems can give rise to superficially similar “black smokers” emitting fluids at temperatures of 350-400°C [5]. The presence or absence of water-rock interactions with underlying mantle rocks in these systems, however, can lead to dramatic changes in the concentrations of, for example, Fe, Cu, H<sub>2</sub> and CH<sub>4</sub> in the resultant vent-fluids [55]. As a first examination of how constant hydrothermal plume TEI:<sup>3</sup>He ratios might be worldwide, therefore, we recommend that a dedicated ocean section be implemented, to investigate – on a like-for-like basis – how hydrothermal plume geochemistries vary in response to a range of known and geologically diverse vent-sites. Specifically, a single ocean section that followed the length of the Mid Atlantic Ridge, occupying stations directly above multiple known vent-sites between Ascension Island and the Azores would provide immediate and valuable insights into how variable TEI:<sup>3</sup>He ratios might be in hydrothermal plumes worldwide.

4.3 Process Studies

Elsewhere in this volume, Jeandel et al. use the analogy that the result of multiple geochemical or isotopic inputs to the ocean can be envisaged as the mixing of paints of varying colours within the oceans [67]. Extending that analogy to the case of hydrothermal inputs to the oceans, our current model frameworks are rather mono-chromatic. Detailed seafloor investigations have already shown



that hydrothermal circulation hosted in different geologic settings can give rise to different source vent-fluid compositions and, further, that the behaviour of dissolved Fe, one of the TEIs that is present in highest concentrations in hydrothermal vent-fluids, should be expected to behave differently – even in the case of identical source vent-fluids – depending upon where, along the global thermohaline conveyor, those vent-fluids are released into the oceans [1]. Despite our awareness of these issues, current state-of-the-art modelling of global-scale hydrothermal TEI budgets (e.g. [48]) continue to rely upon a single hydrothermal end-member. Whether this affects our large-scale understanding of the importance of hydrothermal fluxes to wider scale ocean biogeochemistry merits careful future investigation. Clearly, understanding the importance of *gross* fluxes exiting the seafloor at vent-sites to broader scale ocean biogeochemistry requires detailed understanding of processes at and close to the seafloor, in addition to complementary ocean sections. A key limitation to past local-scale investigations, however, is that they have not involved a sufficiently broad range of scientists to investigate the full range of TEIs of interest to *GEOTRACES*. Further, even in those study areas that have received most attention, we have found that incomplete sampling has prevented us from constraining either the Fe cycle or any associated organic carbon [35].

*a) Selection of Process Study Sites.* Informed by knowledge gained from the Ridge 2000 program at the East Pacific Rise, 9°50'N hydrothermal field [68] and the value it afforded to the modelling conducted by SCOR Working Group 135 [35] we now recommend that *GEOTRACES* should build upon that modest initial success and conduct/complete a series of detailed process oriented studies, specifically targeting TEI cycling, in a range of “type locality” geologic settings distributed along the global thermohaline conveyor. By conducting multiple studies and connecting them to process modelling, future global modelling efforts will be able to test whether varying the relative inputs from different styles of venting allows a better fit, for different TEIs, between global scale model outputs and direct observations. This would represent an extremely valuable contribution from *GEOTRACES* because it would allow the relative abundances and influences of seafloor venting to be assessed, worldwide, without having to investigate the majority of the global ridge-crest. (For context, 40 years on from when the first seafloor vents were discovered, approximately 80% of the Earth’s 55,000km mid-ocean ridge systems remains to be explored, systematically, for venting). To cover as much as possible of the known diversity of vent-styles within a realistic number of target sites for an international research program, we recommend 5 process study sites for investigation.

i) A hydrothermal field located on a fast spreading ridge and hosted in basaltic rocks is our highest priority. One candidate study site for this work would be at 15°S on the East Pacific Rise where seafloor investigations could be designed to complement a recent *GEOTRACES* ocean section that

has already completed a full suite of TEI investigations in the overlying water column out to a range of ~4,000 km down-plume from the source vent-fields. An alternate approach might be to expand the work already conducted at the better-characterised hydrothermal vents at 9°50'N, East Pacific Rise to include a full suite of measurement types and *GEOTRACES* TEIs. New insights into which of these options might be preferable may come from a forthcoming *GEOTRACES* Pacific Meridional Transect cruise, that is expected to intercept the distal portions of both plumes (those originating at 15°S and 9°50'N on the East Pacific Rise), each of which extend at least as far as 150°W based on  $\delta^3\text{He}$  anomalies.

ii) Our second priority is a hydrothermal field on a slow spreading ridge that is also hosted in basaltic rocks. Our preferred candidate for this study site would be the TAG hydrothermal field at 26°08'N on the Mid-Atlantic Ridge. The TAG field, like EPR 15°S, is a site that has already been visited by a *GEOTRACES* Ocean Section and has already been investigated for a full suite of TEIs in the overlying water column, both directly above and away from the vent-site [69]. Further, there has already been a body of work, internationally, at and around the TAG vent-site including a number of relevant biogeochemical investigations that can provide a strong basis for a more complete study of TEIs [5] using the insights provided by *GEOTRACES* process studies elsewhere. A further consideration is that while much of the end-member vent-fluid chemistry at TAG may be extremely similar to that found at vent-sites on the East Pacific Rise [70] the location of TAG on the northern MAR means that the resultant plume is injected into relatively young and oxidizing North Atlantic Deep Water. Consequently, the half-time for dissolved Fe with respect to oxidation in the TAG hydrothermal plume should be quite distinct from that found at the East Pacific Rise [56]. Thus, inter-comparison of TEI cycling at TAG and an EPR vent-site would also provide new insights into how hydrothermal inputs to the ocean might vary as a function of the varying chemistry of the overlying water column.

iii) Our next priority is to investigate how changing host rock (lithology) might impact hydrothermal TEI inputs to the oceans. For slow spreading ridges, ultra-mafic rocks represent the primary lithology other than basalts that can host hydrothermal venting, so an obvious candidate “type locality” would be the Rainbow hydrothermal field at 36°N on the Mid-Atlantic Ridge [5]. This site, like TAG, has received much prior international attention, up to and including an early European Commission-funded attempt at quantifying export fluxes from the system [54]. Importantly, the site also allows for direct inter-comparison with the TAG hydrothermal field – both of which would ideally be included in any future along-axis MAR ocean section (see Section 4.2, above). Because



both sites are situated at comparable depths and only ~1000km apart along-axis, we would predict that the Fe oxidation rates in hydrothermal plumes at both locations should be very similar. Since end-member vent-fluids also erupt at close to 360°C at both locations [70, 71], therefore, we should expect that any differences in vent-fluid compositions, and in the TEI characteristics of the overlying plumes at these two sites, should be attributable primarily to changes in host rock-type, and not due to changes in the overlying water column's redox poise.

iv) To investigate the role of varying host-rock still further, we also recommend that a detailed hydrothermal process study be initiated at a back-arc setting in the SW Pacific where abundant hydrothermal venting has been discovered in the past decade [58]. While the complex submarine geology of the SW Pacific can lead to a wide array of hydrothermal vent and plume types (e.g. [72]) we specifically recommend, as a candidate location for detailed process studies, the Mariner hydrothermal field at 22°10'S on the Valu Fa ridge [73, 74]. We recommend this particular site because it is here, at the southernmost limit of the Lau Basin system, where host-rocks are most felsic - *i.e.* most distinct from the basaltic EPR. Further, the Mariner site has also already received much international attention in terms of detailed seafloor investigations, providing important underpinning for the proposed work.

v) Finally, while the first four sites discussed above all represent differing forms of deep-water hydrothermal inputs, it is important to recognize that hydrothermal activity can also occur at much shallower depths, for example in association with island arcs and hot-spot volcanoes, and these systems may also provide significant TEI inputs to ocean biogeochemistry [75]. As with back-arc systems, island arcs exhibit a diverse geologic array that is reflected in their overlying plume chemistries (e.g. [76]). At the shallowest extreme, approximately 50 examples of marine hydrothermal vents systems have now been documented at depths of less than 200m, releasing hydrothermal discharge directly into the photic zone [77]. While such shallow vents may have considerable impact on the biologically important coastal ocean, selecting a single "type locality" that might be considered representative of such systems worldwide (hence, allowing us to make a specific recommendation for a future *GEOTRACES* process study) is extremely challenging. Instead, therefore, we (tentatively) suggest that an island arc site suitable for detailed process study might be the NW Rota-1 system in the Southern Mariana arc. A particular attraction of this site is that recent work has documented on-going volcanic as well as hydrothermal activity at this location [78]. Further, that work has also suggested that if NW Rota is representative of all submarine arc eruptions, this type of system may have a significant impact on the global flux of sulphur and aluminium.

b) Selection of Core Measurements for Hydrothermal Process Studies.

To provide realistic constraints upon the impacts of venting on TEI ocean biogeochemistry we propose that future process studies be designed to populate the various boxes of the conceptual model originally designed for an investigation of Fe and organic carbon cycling by SCOR Working Group 135 (Fig.3b). At each site, this would require geochemical characterisation of: high temperature vent fluids, diffuse flow fluids, buoyant hydrothermal plumes rising above the vent-site, non-buoyant plumes directly above the vent-site and settling particulate material sinking back toward the seafloor. In concert, at any one location, such measurements would allow the relative importance of focussed vs diffuse hydrothermal flow to be assessed in terms of their role in the ocean budgets of each TEI. By inter-comparing the results from the various “type localities” outlined above, it would become possible to investigate how the relative importance of these inputs might vary as a function of different geologic settings and also in response to the evolving redox poise of the overlying water column along the thermohaline conveyor (*i.e.* as a function of varying [O<sub>2</sub>], pH and [OH<sup>-</sup>]).

Recognizing that hydrothermal systems have distinct characteristics, beyond those identified within the more “generic” *GEOTRACES* science plan, we recommend that primary parameters that be selected for investigation in each process study would be: He isotopes, Fe (including both physical (e.g. size) and chemical (e.g. redox) speciation), Mn, Al, CH<sub>4</sub>, dissolved organic carbon (bulk DOC and specific ligands such as siderophores), particulate organic carbon (POC) and sulphur (including S speciation). Of course, this is not to suggest that we would not want to measure the complete suite of TEI core parameters throughout the system – rather the suite of tracers here are what we consider essential to provide process based context, capturing the anticipated diversity of hydrothermal systems that we expect might be encountered and which would be required to parameterize future, more sophisticated hydrothermal flux models. It will, for example, continue to be important to study the impact of venting upon classical tracers that have been studied elsewhere within *GEOTRACES* – for example, those that are representative of micronutrients (e.g. Fe), and dissolved-particulate interactions (e.g. <sup>230</sup>Th/<sup>231</sup>Pa). Further, since hydrothermal venting may release variable quantities of key reduced species (H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>) that can be exploited by microorganisms [79] the relative abundances of which may vary according to lithology [80] it will also be important to track N cycling in hydrothermal vents and plumes, for example through isotopic measurements of NO<sub>3</sub><sup>-</sup> [81]. Finally, it will also be important to consider those tracers that may more typically be considered as “toxicants” or tracers of anthropogenic pollution. Mercury is of particular interest, here, because it is illustrative of a suite of *GEOTRACES* TEIs for which there is still a paucity of reliable data

concerning natural hydrothermal inputs to the oceans. In the specific case of Hg, hydrothermal vents are postulated to be the major *natural* source of this element to the oceans [82], but estimated contributions of hydrothermal Hg flux range over several orders of magnitude (20-2000 t.y<sup>-1</sup>). Consequently, quantifying the possible hydrothermal contribution to the global Hg cycle remains elusive [83-87]. To date, Hg concentrations in hydrothermal vent fluids have only been measured on three occasions [86-88] and those results show a strong site specificity, precluding direct estimations for global hydrothermal Hg fluxes. Clearly, more Hg observations of (focussed and diffuse-flow) vent fluids and hydrothermal plumes are needed to better constrain the Hg flux from venting, and its contribution to the global Hg cycle. Without clear understanding of the natural inputs of such TEIs to ocean budgets, constraining the significance of anthropogenic inputs will remain a challenge.

## 5. Concluding Remarks

Since the start of the GEOTRACES program it has become clear that hydrothermal inputs of TEIs are widespread, can occur in all ocean basins, and have the potential to be dispersed widely into the ocean interior. These findings are entirely consistent with hypotheses that had already been posed at the inception of the program and which the design of the ocean sections phase of GEOTRACES was designed to test. Now that these fluxes have been demonstrated to exist in measurable quantities, our next priority is to quantify them and, hence, evaluate their impacts on TEIs' global biogeochemical budgets. Building upon the successes already achieved, this contribution outlines a series of recommendations for future modelling and field programs, to achieve that goal. First, we recommend a more detailed modelling approach that: incorporates the latest data for known and predicted venting, worldwide; introduces greater vertical and lateral resolution throughout the deep ocean, where hydrothermal plumes inject vent-sourced TEIs into the oceans; and introduces a more sophisticated treatment of dissolved-colloidal-particulate interactions into deep-ocean modelling, in recognition that particle formation and scavenging of particle-reactive species in hydrothermal plumes may play an important role in global scale TEI ocean biogeochemical cycles. In parallel, we propose a new body of field programs (one section and a series of process studies) designed specifically to investigate how both the inputs and the fates of TEIs injected into the oceans from submarine hydrothermal venting might vary, both along the thermohaline conveyor (in response to varying hydrographic properties) and at ridges of different spreading rate, which provide diverse geologic settings and, hence, different vent-fluid sources.

# Figure and table captions

Fig.1 The distribution of dissolved Fe in the Atlantic Ocean based on data from the GEOTRACES Intermediate Data Product [15]. Note the presence of Fe-rich plumes centered upon, but dispersing away from the Mid Atlantic Ridge axis.

Fig.2 Cross sections of (top) dissolved Fe and (bottom) excess dissolved 3He in the hydrothermal plume dispersing west from the East Pacific Rise near 15°S (data from [24]).

Fig.3 Illustration (left) and simplified box model (right) of key processes identified by SCOR-InterRidge WG 135 as critical to understanding the impact of hydrothermal venting on the deep ocean Fe and organic carbon cycle (redrawn from [35]).

Fig.4 Map, modified from [58], of known hydrothermal fields along the global ridge crest as inferred from hydrothermal plume signals (circles) or from direct seafloor observations (squares). Sites located prior to 2000 are colour-coded blue while more recent discoveries are coloured red. Note that the majority of discoveries made worldwide in the period 2000-2013 were all located in the SW Pacific Ocean (red and white ellipse) in a region extending from the northern Lau Basin to the North Island of New Zealand.

Fig.5 Map of all active high temperature vent-sites that have been confirmed from direct seafloor observations, to-date, along the slow spreading northern Mid-Atlantic Ridge [6]. Venting extends from the Niebelungen vent-site near Ascension Island, just south of the Equator to the Moytirra vent-site, just north of the the Azores. Colour coding differentiates between high temperature sites of hydrothermal venting that are either in a magmatic setting (red) or a tectonic setting (yellow). Note that vent-sites located in tectonic settings may be either basaltic-hosted (e.g. TAG) or ultramafic-influenced (e.g. Rainbow).

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# Additional Information

Information on the following should be included whenever relevant.

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## Competing Interests

We have no competing interests.

## Authors' Contributions

All authors engaged in the discussions at the Royal Society and contributed to the preparation and revision of this manuscript.

# References

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# Supplementary material

We are not submitting any supplementary material.

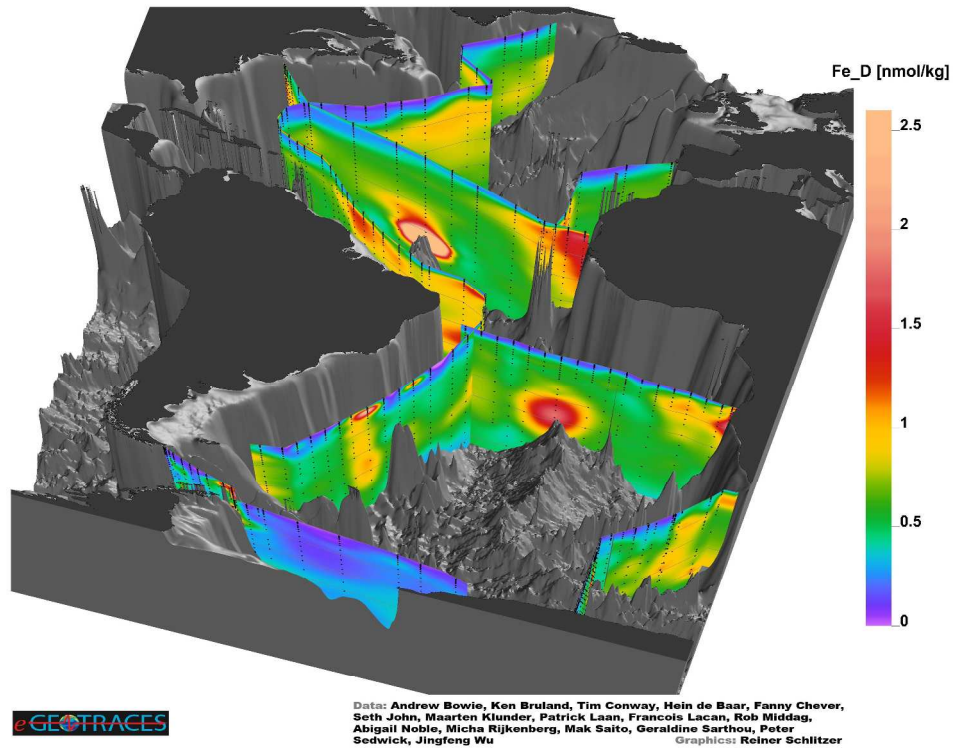


Fig.1 The distribution of dissolved Fe in the Atlantic Ocean based on data from the GEOTRACES Intermediate Data Product [15]. Note the presence of Fe-rich plumes centered upon, but dispersing away from the Mid Atlantic Ridge axis.  
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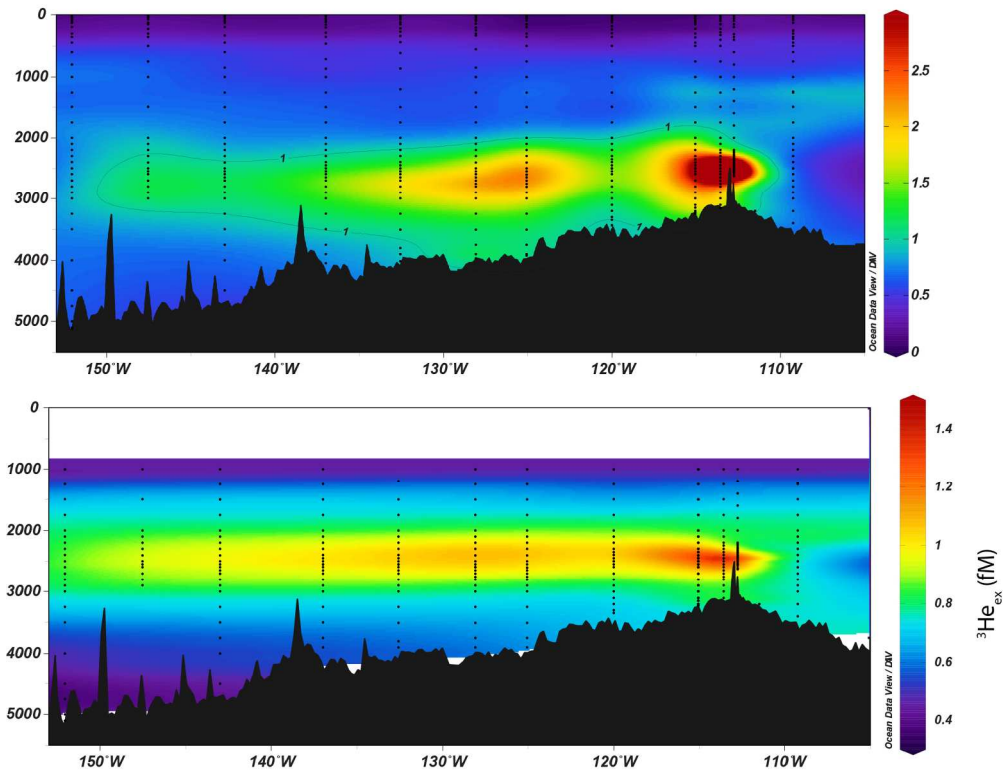


Fig.2 Cross sections of (top) dissolved Fe and (bottom) excess dissolved  $^3\text{He}$  in the hydrothermal plume dispersing west from the East Pacific Rise near 15°S (data from [24]).  
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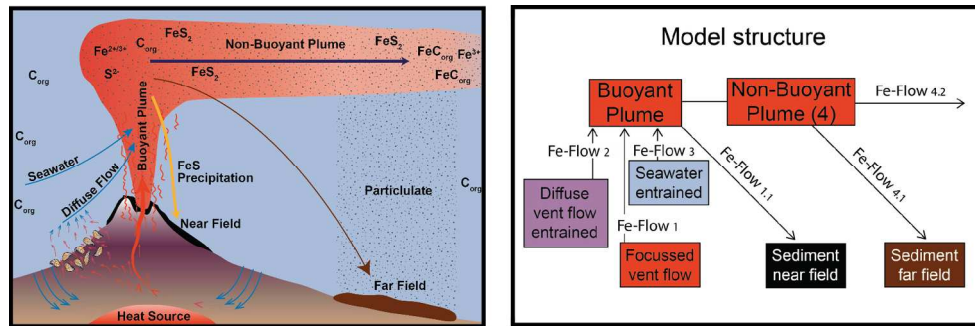


Fig.3 Illustration (left) and simplified box model (right) of key processes identified by SCOR-InterRidge WG 135 as critical to understanding the impact of hydrothermal venting on the deep ocean Fe and organic carbon cycle (redrawn from [35]).  
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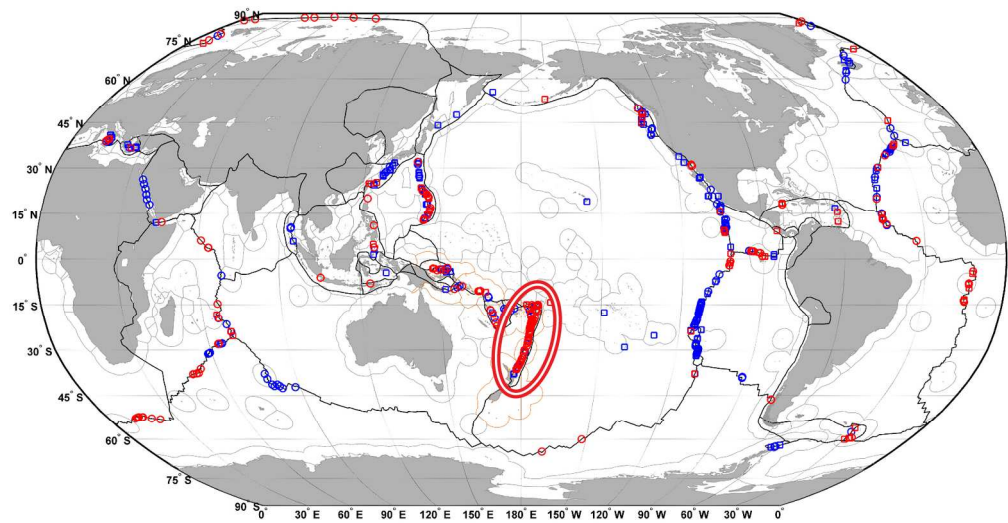


Fig.4 Map, modified from [49], of known hydrothermal fields along the global ridge crest as inferred from hydrothermal plume signals (circles) or from direct seafloor observations (squares). Sites located prior to 2000 are colour-coded blue while more recent discoveries are coloured red. Note that the majority of discoveries made worldwide in the period 2000-2013 were all located in the SW Pacific Ocean (red and white ellipse) in a region extending from the northern Lau Basin to the North Island of New Zealand.

160x84mm (300 x 300 DPI)



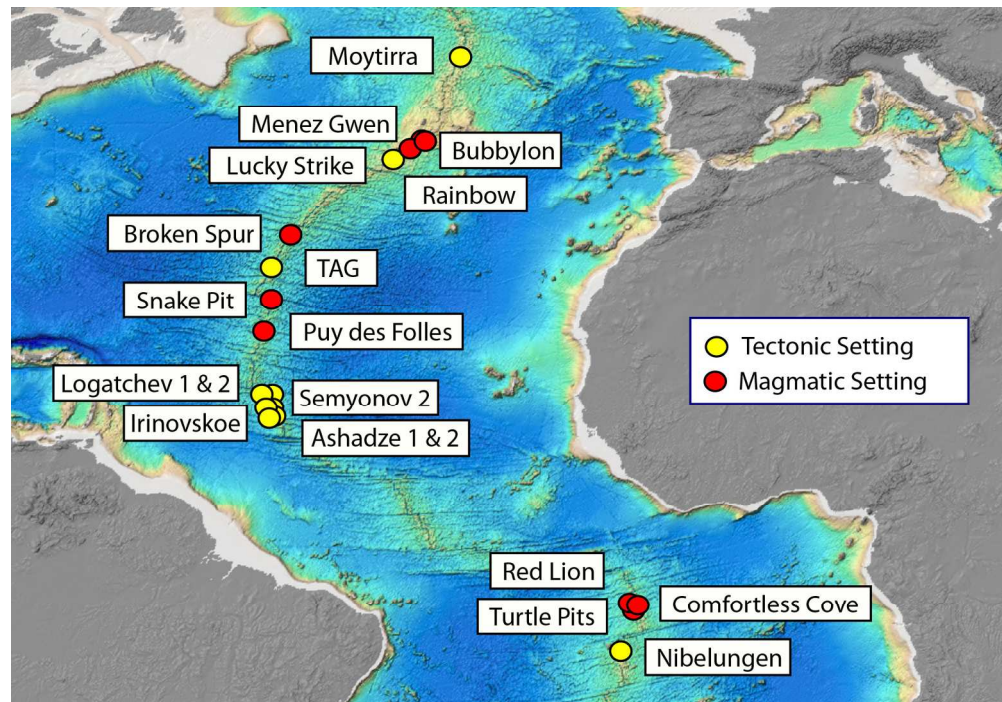


Fig.5 Map of all active high temperature vent-sites that have been confirmed from direct seafloor observations, to-date, along the slow spreading northern Mid-Atlantic Ridge [6]. Venting extends from the Neibelungen vent-site near Ascension Island, just south of the Equator to the Moytirra vent-site, just north of the the Azores. Colour coding differentiates between high temperature sites of hydrothermal venting that are either in a magmatic setting (red) or a tectonic setting (yellow). Note that vent-sites located in tectonic settings may be either basaltic-hosted (e.g. TAG) or ultramafic-influenced (e.g. Rainbow).

165x115mm (300 x 300 DPI)