

1 **Iron persistence in a distal hydrothermal plume supported by**
2 **dissolved-particulate exchange**

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35 **First Paragraph**

36 Hydrothermally-sourced dissolved metals have been recorded in all ocean basins. In the oceans'
37 largest known hydrothermal plume, extending westward across the Pacific from the Southern
38 East Pacific Rise, dissolved iron and manganese were shown by the GEOTRACES program to be
39 transported halfway across the Pacific. Here, we report that particulate iron and manganese in
40 the same plume also exceed background concentrations, even 4000 km from the source. Both
41 dissolved and particulate iron deepen by more than 350 m relative to ^3He – a non-reactive
42 tracer of hydrothermal input – crossing isopycnals. Manganese shows no similar descent.
43 Individual plume particle analyses indicate that particulate iron occurs within low-density
44 organic matrices, consistent with its slow sinking rate of 5-10 m year⁻¹. Chemical speciation and
45 isotopic composition analyses reveal that particulate iron consists of Fe(III) oxyhydroxides,
46 while dissolved iron consists of nanoparticulate Fe(III) oxyhydroxides and an organically-
47 complexed iron phase. The descent of plume dissolved iron is best explained by reversible
48 exchange onto slowly sinking particles, likely mediated by organic compounds binding iron. We
49 suggest that in ocean regimes with high particulate iron loadings, dissolved iron fluxes may
50 depend on the balance between stabilization in the dissolved phase and the reversibility of
51 exchange onto sinking particles.

52

53 High temperature vents spanning diverse geologic settings emit fluids enriched in dissolved Fe
54 (dFe) and Mn (dMn), often a million times more concentrated than background deep ocean
55 concentrations¹. In the surface ocean, Fe is an essential², often limiting micronutrient for
56 primary producers. Historically, global-scale studies have focused on atmospheric dust and
57 continental margins as primary Fe sources³, while hydrothermally-sourced Fe was expected to
58 precipitate quantitatively into solid phases that settled onto underlying sediments close to vent
59 sources, as polymetallic sulfides or oxyhydroxides following the rapid oxidation of Fe(II)^{1,4}.
60 Consequently, it was assumed that hydrothermal vents supply negligible dFe to the oceans⁵.

61 More recently, however, distributions of dissolved metals, including measurements
62 from several GEOTRACES studies, have confirmed the long-range transport of hydrothermally-
63 sourced dFe from mid-ocean ridge sources into the interior of the Pacific⁶⁻⁸, Atlantic^{9,10},
64 Indian¹¹, Southern^{12,13}, and Arctic¹⁴ Oceans. Candidate stabilization mechanisms for
65 hydrothermally-sourced dFe include the formation of small inorganic nanoparticles in the
66 colloidal size fraction¹⁵⁻¹⁷ and complexation by organic ligands that protect dFe from
67 precipitation and gravitational settling¹⁸⁻²⁰. For particulate metals, hydrothermal research has
68 emphasized processes proximal to vent sources. Only one study reported pFe along the core of
69 a westward-dispersing ³He plume²¹ overlying a region of metalliferous sediment enrichments
70 near 15°S²², but sampling extended only ~80 km off-axis. Thus, the transformations and lateral
71 extent of particulate metals in distal hydrothermal plumes have been comparatively
72 overlooked.

73 A major goal of the U.S. GEOTRACES GP16 East Pacific Zonal Transect was to determine
74 the long-range fate of trace elements released by venting along the 15°S EPR plume trajectory.

75 Eleven full-depth stations were sampled over a ~4300 km transect starting at the SEPR ridge-
76 axis (15°S, 112.75°W) and extending along the core of the largest known hydrothermal ^3He
77 plume globally²³. Because it is chemically inert, $^3\text{He}_{\text{xs}}$ (“xs” is non-atmospheric ^3He ; see
78 Methods) mixes conservatively during transport through the deep ocean, providing an
79 unambiguous tracer of hydrothermal input²³. Recently, a study of dissolved metals along the
80 GP16 section showed that hydrothermally sourced dFe and dMn were transported along the
81 entire plume length and that, despite anticipated scavenging, dFe was apparently conserved
82 over much of the plume’s length⁸.

83 Here, we report complementary particulate Fe and Mn distributions across the same
84 section (Figure 1). We also highlight the previously unreported deepening of dFe relative to
85 isopycnals and ^3He and infer from isotope and synchrotron speciation techniques that this
86 vertical descent of dFe is mediated by reversible exchange with a sinking pFe phase that, we
87 argue, is likely facilitated by Fe associations with organic matter (Figure 2). Manganese, in
88 contrast, does not sink across isopycnals, due to the association of pMn with low-density
89 microbial capsules as well as the lack of organic and colloidal speciation for dMn, which we
90 argue inhibits exchange with sinking particle phases. This decoupling of Fe and Mn has
91 important implications for the fate of other elements in hydrothermal plumes and the
92 scavenging removal of Fe from the global ocean.

93 ***Particulate hydrothermal plume*** – The hydrothermal plume was detectable across the
94 entire ~4300 km transect from elevated particulate (>0.45 μm) Fe and Mn above ambient deep
95 Pacific concentrations (Figure 1). This is by far the most extensive particulate hydrothermal
96 plume ever documented, complementing the ^3He , dFe, and dMn plume distributions reported

97 previously⁸. Yet, both Fe- and Mn-rich particles must undergo aggregative removal from this
98 plume because they showed exponential loss, from plume depths, that greatly exceeded
99 dilution with particle-poor ambient deep Pacific water (quantified from $^3\text{He}_{\text{xs}}$ dilution; Figure 3).
100 For example, >90% of pFe was lost within the first 200 km off-axis, while $^3\text{He}_{\text{xs}}$ decreased by just
101 2-3 fold across the entire section (Figure 2). Overall, pFe and pMn loss was consistent with first
102 order kinetic removal (Figure S2), suggesting aggregation onto biogenic and/or lithogenic
103 particles settling from above at nearly constant rates²⁴ along the length of the plume. However,
104 near-field (<100 km) particles were removed too rapidly to fit a single exponential function
105 (Figure 2), suggesting that additional self-aggregation at higher particle concentrations in the
106 near-field environment leads to more rapid removal from the proximal plume (Figures 2, S2).

107 Regional advection rates near 15°S at ~2500 m, estimated from circulation models and
108 float observations, are 0.2-0.5 cm/s^{25,26}, yielding plume transport times from the ridge axis (Sta.
109 18) to Sta. 36 of 25-70 years. The anomalously low Fe, Mn, and ^3He concentrations at Sta. 23
110 (Figure 1) reflect an interruption of the continuous plume, perhaps due to anticyclonic
111 recirculation at 112-125°W²⁶; this feature will not be discussed further in this paper.

112 Importantly, the pFe maximum deepened progressively, by ~350 m relative to
113 conservative $^3\text{He}_{\text{xs}}$ over the plume length, crossing isopycnals, (Figures 1, 4a; S3). This implies
114 that persistent hydrothermal pFe sinks slowly at ~5-10 m/yr (0.01-0.03 m/d), consistent with
115 Stokesian settling of ~0.5 μm pure ferrihydrite grains.

116 In contrast, pMn showed no gravitational settling behavior (Figures 1, 4b). Instead, peak
117 pMn concentrations remained close in depth to dMn and $^3\text{He}_{\text{xs}}$ and followed density surfaces,
118 indicative of isopycnal mixing. Thus, while most pMn and pFe are removed exponentially from

119 the plume by aggregation in/onto sinking particles (Figure 3), the vertical positions of the
120 persistent pFe and pMn plumes decouple during transport down-plume (Figures 1, 2),
121 suggesting that Fe- and Mn-bearing particles must differ fundamentally in size, shape, and/or
122 specific gravity.

123 ***Chemical and isotopic composition of Fe-rich particles*** – Scanning Transmission X-ray
124 Microscopy (STXM) and Fe 2p X-ray Absorption Near-Edge Structure (XANES) analyses showed
125 that SEPR pFe is composed predominantly of Fe(III) oxyhydroxides (Figure 5), with little
126 evidence for Fe(II) particles, even directly above the ridge axis. Images obtained from STXM also
127 revealed the morphology of Fe-rich particles in the plume. Within 100 km of the SEPR (Sta. 18-
128 20), the Fe-bearing particles consisted of Fe(III) oxyhydroxides largely co-located with organic
129 matter in ~5-10 μm aggregates (Figure 5, a-c), similar to near-field hydrothermal Fe(II) from 9°N
130 EPR²⁷. Beyond ~100-200 km off-axis at 15°S EPR, however, the physicochemical form of
131 hydrothermal pFe exhibited a marked morphological transition to discrete Fe(III) oxyhydroxide
132 minerals embedded within a matrix of organic carbon (Figure 5, d-f) with much lower optical
133 density. We infer from these results that the high specific gravity of any embedded Fe minerals
134 is offset by the low specific gravity of associated organic matter, resulting in a low overall
135 specific gravity. This allows large Fe-bearing hydrothermal particles to persist within a distinct
136 hydrothermal plume for decades and over thousands of kilometers (Figures 1, 2) instead of
137 settling rapidly at the Stokesian rates that would be predicted for pure ferrihydrite (e.g. ~750
138 m/y for 5 μm spheres in the proximal plume, Fig. 5).

139 Why doesn't pMn also settle across isopycnals in the distal plume? Prior work has
140 shown that Mn uptake into hydrothermal plume particles is dominated by microbially

141 catalyzed^{28,29} dissolved Mn(II) oxidation (otherwise kinetically inhibited³⁰), yielding Mn oxide
142 coatings on bacterial cells. Pure birnessite ($\rho=2.9 \text{ g/cm}^3$) of bacterial-capsule size ($\sim 1 \text{ }\mu\text{m}$) would
143 settle at $\sim 18 \text{ m/y}$, but we hypothesize that the lower specific gravity of such bacterial capsules,
144 even with MnO_2 coatings, prevents the settling of persistent pMn across isopycnals, thus
145 mimicking dMn and $^3\text{He}_{\text{xs}}$ across the section. Future synchrotron investigations of the
146 physicochemical speciation of hydrothermal pMn should test this hypothesis.

147 The isotopic composition of ‘ligand-leachable’ pFe ($\delta^{56}\text{Fe}$) was nearly-constant across
148 the plume ($-0.25 \pm 0.14\text{‰}$, 1σ SD; Figure 6a), even as pFe concentrations decreased ~ 1000 -fold
149 by aggregative removal and dilution. This suggests that hydrothermally-sourced pFe speciation
150 is preserved down-plume, consistent with microprobe Fe XANES results beyond Sta. 21³¹. Most
151 chemical reactions that would alter pFe speciation are associated with isotopic fractionation
152 that ranges from a few tenths up to several ‰ ³². The observed variations in particulate $\delta^{56}\text{Fe}$
153 are smaller than would be predicted even for a reaction with an isotope effect as small as 0.1‰
154 (Figure 6a). This supports our earlier inferences (i) that pFe is removed by non-fractionating,
155 aggregative sinking and (ii) that persistent hydrothermal pFe speciation experiences no further
156 fractionating transformations during plume advection. The slightly heavier particulate $\delta^{56}\text{Fe}$ ($-$
157 $0.13 \pm 0.14\text{‰}$) at the most distal end of our study (Sta. 30-36) indicates the contribution of
158 isotopically heavier, background deep-ocean pFe at significant mixing ratios as hydrothermal
159 pFe concentrations decreased (Figures 1, S1).

160 ***The physicochemical form of hydrothermal dissolved iron*** - A key finding of this study,
161 not discussed previously⁸ but critical to the fate of Fe in the SEPR hydrothermal plume, is that
162 the maximum *dissolved* Fe also deepens by $\sim 350 \text{ m}$ by Sta. 36, mimicking pFe (Figures 1, 4a).

163 We attribute this previously undescribed phenomenon to reversible exchange between dFe and
164 pFe on a rapid timescale relative to pFe sinking. This exchange must occur while apparently
165 conserving total dFe inventories in the plume (Figure 3).

166 To investigate the chemical mechanism of this reversible exchange and resulting dFe
167 descent, we examined the physicochemical speciation of dissolved Fe in the plume.

168 Ultrafiltration (Figure S4) revealed that plume dFe (<0.2 μm , operationally) comprised mostly
169 colloidal species (0.003-0.2 μm ; $63 \pm 10\%$ of dFe), while non-hydrothermal abyssal dFe is $\sim 50\%$
170 colloidal¹⁰. In contrast, dMn was predominantly truly soluble (<0.003 μm ; $98 \pm 2\%$, Figure S4).

171 While the chemical speciation of Fe in hydrothermal colloids is not yet known and may include
172 inorganic compounds or organic complexation^{10,33}, colloids may be important for the
173 stabilization of hydrothermal plume dFe.

174 Our $\delta^{56}\text{Fe}$ measurements showed that hydrothermal plume dFe resides in two chemical
175 forms. In the young, near-field plume (Sta. 18, dFe >5 nM), mean $\delta^{56}\text{Fe}$ was $-0.19 \pm 0.05\%$ (1σ
176 SD, $n=4$; Figure 6b), matching $\delta^{56}\text{Fe}$ values for pFe down-plume ($-0.25 \pm 0.14\%$; Figure 6a).

177 Combined with our ultrafiltration results (Figure S4), this suggests that near-field dFe is
178 dominated by inorganic Fe(III) oxyhydroxides of predominantly colloidal size. However, pure Fe-
179 oxyhydroxide colloids ($\rho=4.25 \text{ g/cm}^3$, $\leq 0.2 \mu\text{m}$) should only sink 30-90 m during the 25-70 year
180 transit down-plume by Stokesian settling, much less than the observed ~ 350 m deepening.

181 Moving westward down-plume, dFe concentrations decreased while dissolved $\delta^{56}\text{Fe}$
182 increased (Figure 6b). This trend was inverse modeled as simple two-component isotope
183 mixing, between a proximal nanoparticulate Fe oxyhydroxide end-member with decreasing
184 concentrations down-plume but fixed $\delta^{56}\text{Fe} = -0.19\%$, and an invariant second end-member

185 modeled from average Sta. 32 values of $[dFe] = 0.77 \text{ nM}$ and $\delta^{56}Fe = +0.66\%$. This model
186 revealed that our dissolved $\delta^{56}Fe$ data are best described by a nanoparticulate Fe oxyhydroxide
187 phase, diminishing down-plume and mixing into a constant, isotopically heavy dFe phase. What
188 is the chemical composition of the distal 0.77 nM , isotopically heavy dFe? It cannot be
189 nanopyrite because precipitated Fe(II) should be isotopically light³⁴. Instead, we infer that this
190 non-oxyhydroxide dFe pool consists of organically-bound Fe(III), which is known to be
191 isotopically heavy relative to unbound Fe(III)^{35,36}. The ligand-bound end-member is higher in
192 dFe concentration and heavier in isotopic composition than estimates of non-hydrothermal
193 background Pacific dFe from throughout the Pacific ($\sim 0.45 \pm 0.5 \text{ nM}^{37}$, -0.10 to -0.22% ^{38,39}),
194 including “upstream” of the SEPR (\sim GP16 Sta. 15: $\sim 0.5 \text{ nM}$, $\delta^{56}Fe \sim +0.4\%$). Thus we conclude
195 that the plume beyond Sta. 32 consists of background deep Pacific Fe ($\sim 0.5 \text{ nM}$) plus an
196 organically-bound dFe fraction of hydrothermal origin ($\sim 0.3 \text{ nM}$, $\delta^{56}Fe > +0.66\%$); dissolved-
197 phase nanoparticulate Fe oxyhydroxides compose $\leq 10\%$ of dFe in the far-field hydrothermal
198 plume (Figure 2).

199 The composition and source of the inferred organic ligands are unknown but could
200 derive from excess unbound Fe ligands that are present throughout the deep ocean⁴⁰, from
201 bacterial release specific to hydrothermal plume environments⁴¹, or through release from near-
202 vent chemoautotrophs and subsequent entrainment into buoyant plumes⁴². Regardless, we
203 propose that the hydrothermally-derived, organically-complexed, and isotopically heavy dFe
204 phase is pervasive throughout the plume but that because of its low concentration ($\sim 0.3 \text{ nM}$), it
205 is not isotopically resolvable in the near-field plume ($dFe > 5 \text{ nM}$).

206 ***Reversible exchange between dissolved and particulate Fe*** - If plume dFe is physically
207 partitioned into soluble and colloidal fractions and chemically partitioned into a near-field
208 nanoparticulate Fe oxyhydroxide phase superimposed on a near-constant background of
209 hydrothermally-derived ligand-bound dFe, how can we explain the along-plume descent of dFe
210 that mimics the sinking of the pFe maximum? Simple disaggregation of pFe into nanoparticulate
211 dFe during pFe settling would require injection of substantial concentrations of dFe with light
212 $\delta^{56}\text{Fe}$ (-0.2‰), but this was not observed: dFe became heavier down-plume (Figure 6b) and
213 total dFe was apparently conserved (Figure 3).

214 Instead we propose that the deepening of peak dFe is caused by active, reversible
215 exchange with a gravitationally sinking particulate phase through rapid adsorption/desorption
216 (or aggregation/disaggregation for the colloidal phase). This reversible scavenging could occur
217 onto material settling through the water column or onto hydrothermal pFe, but the matching
218 descent rates for plume dFe and pFe (~5-10 m/y, or ~0.01-0.03 m/d) are three orders of
219 magnitude slower than typical settling rates for marine aggregates (~17-200 m/d⁴³), suggesting
220 that dFe desorption:sorption rate ratios are high and/or that scavenging onto persistent
221 hydrothermal pFe phases dominates dFe descent (Figure 2). The exchange must involve
222 organically-complexed dFe pools, since dFe descent continues at a nearly constant rate down-
223 plume (Figure 4), even as the concentration of ligand-bound dFe exceeds that of
224 nanoparticulate Fe oxyhydroxides at distances >200 km from the SEPR (Sta. 21+; Figure 2, 6b).
225 We hypothesize, on the basis of the carbon matrix surrounding Fe phases in the plume particles
226 (Figure 5d-f), that this Fe exchange may be mediated by organic compounds binding dFe and
227 pFe, via two potential mechanisms: hydrophobic attraction between pFe organic matrices and

228 organic Fe-ligand complexes, and/or “ligand-exchange” of Fe cations between dissolved ligands
229 and the organic matrices of pFe. The coincidence of reversible dFe scavenging with the organic
230 association of both dFe and pFe suggests a single mechanism for exchange between dissolved
231 and particulate phases, reminiscent of the spontaneously assembling/disassembling marine
232 gels common in the upper ocean and nepheloid layers⁴⁴. Such an exchange-sinking mechanism
233 would not apply to dMn because dMn is minimally complexed by organic matter in natural
234 waters², and negligible Mn was observed in the colloidal fraction (Figure S4).

235 ***Implications for hydrothermal fluxes and scavenging*** - Our results suggest that while
236 nanoparticulate Fe(III) oxyhydroxides dominate hydrothermally-sourced dFe speciation near
237 the SEPR, isotopically heavy organic complexes dominate the hydrothermal dFe phase that
238 persists throughout the distal SEPR plume, influencing the Pacific Ocean dFe inventory. The
239 generality of this conclusion is supported by recent observations of heavy (+0.54±0.14‰)
240 hydrothermally-sourced dissolved $\delta^{56}\text{Fe}$ values found >2000 km east of the SEPR axis at ~25°S in
241 the Peru/Chile Basin⁴⁵. However, our model-derived hydrothermal ligand-bound dFe
242 concentrations (~0.3 nM) are much lower than those currently parameterized in modeling
243 efforts focused on near-field vent geochemistry⁸. New global modeling efforts should seek to
244 capture the vertical migration of dFe plumes to deeper isopycnals as they disperse (Figure 2) to
245 improve estimates of hydrothermal-derived dFe upwelling to the surface ocean, and hence of
246 Fe-fertilized primary production and associated carbon dioxide drawdown⁸.

247 The decoupled speciation and transport pathways of hydrothermal pFe and pMn
248 demonstrated here (Figure 2) have important implications for the oceanic budgets of the many
249 dissolved elements in hydrothermal plumes¹ that sorb to the surfaces of Fe and Mn particles,

250 the “scavengers of the sea”⁴⁶. Particle-reactive elements are numerous, spanning the periodic
251 table⁵, but each has a distinct sorption affinity for Fe versus Mn particles⁴⁷, further complicated
252 by the pFe organic matrix reported here. The decoupled speciation, stabilization, and transport
253 pathways for Fe and Mn particles in hydrothermal plumes revealed by this study must directly
254 govern the fate and oceanic budgets of numerous scavenging-prone elements, in addition to Fe
255 and Mn.

256 More generally, the reversible scavenging model elucidated here represents a paradigm
257 shift for parameterizations of dFe scavenging in ocean models. Current global biogeochemical
258 Fe models invoke irreversible removal to particulate phases as the dominant abiotic dissolved-
259 particulate interaction^{3,48} (with one exception that parameterized reversible scavenging⁴⁹).
260 However, we report an Fe settling rate ~1000 times slower than typical marine aggregate
261 settling⁴³ (Figure 2), suggesting selective dFe scavenging onto the suspended hydrothermal pFe
262 phase and/or a large desorption-sorption rate ratio. Modeling of the Fe distributions presented
263 here (beyond the scope of this paper) will seek to reveal transformation rates that determine
264 the oceanic residence time of hydrothermally-sourced dFe. Future work should investigate
265 whether such reversible scavenging also occurs in other ocean regimes with high particulate Fe
266 loadings, including continental margins, high-dust regions, and benthic nepheloid layers;
267 ultimately, the global oceanic flux of dFe from all of these boundary systems should depend on
268 a balance between stabilization in the dissolved phase and reversible/irreversible scavenging
269 removal onto sinking particles. Perhaps most importantly, our observations of the decoupled
270 composition and settling rates of Fe and Mn suggest that the scavenging chemistry of different
271 elements is unique. Thus, the extent to which the aquatic chemistry of marine species is

272 controlled by organic versus inorganic components will determine how we model ocean
273 processes as thermodynamic systems in the future.

274

275 **Methods**

276 Methods, including statements of data availability, are available in the online version of this
277 paper.

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280 **References**

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410 optimal leach for marine particulate iron isotopes. *Geochimica et Cosmochimica Acta*
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432

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434 J.N.F determined the digested particulate metal concentrations, led data interpretation, and
435 wrote the manuscript. R.M.S., C.R.G., and B.M.T. co-proposed the particulate studies, and
436 R.M.S., S.L.N., and C.R.G. collected samples on the GP16 cruise (C.R.G. as Chief Scientist). S.G.J.
437 and C.M.M. made the Fe isotope measurements, and C.L.H. and B.M.T. made the synchrotron
438 measurements. All authors helped to refine the interpretation and contributed to manuscript
439 revisions.

440

441 **Competing Financial Interest**

442 The authors declare no competing financial interests.

443

444

445 **Figure Captions**

446 **Figure 1: Interpolated concentrations and station map along the U.S. GEOTRACES GP16**

447 **Eastern Pacific Zonal Transect.** (a) Station locations and names in relation to the South

448 American continent and the East Pacific Rise (colors are bathymetry; green hues shallower), (b)

449 excess ^3He concentrations in fmol/kg, (c) dissolved Fe concentrations ($<0.2 \mu\text{m}$, in nM), (d)

450 dissolved Mn concentrations ($<0.2 \mu\text{m}$, in nM), (e) particulate Fe ($>0.45 \mu\text{m}$, in nM), and (f)
451 particulate Mn ($>0.45 \mu\text{m}$, in pM). Note that in each data panel a black line is indicated at 2500
452 m to highlight the deepening of the Fe plumes.

453 **Figure 2: Illustration of Fe, Mn, and $^3\text{He}_{\text{xs}}$ transport and transformation along the SEPR**

454 **hydrothermal plume.** Physical plume bounds are indicated in grey, at representative non-linear
455 distances off-axis (listed at bottom). Concentric circles represent relative peak concentrations
456 of particulate and dissolved metals; circle sizes represent relative concentrations but are not
457 quantitatively accurate between Fe, Mn, and $^3\text{He}_{\text{xs}}$. Pie diagrams show chemical speciation of
458 dissolved Fe. Particulate Fe and Mn are removed through aggregation onto sinking particles
459 from above (white arrows⁴³) and through near-field self-aggregation of hydrothermally-sourced
460 particles. Note that Fe descends relative to Mn and $^3\text{He}_{\text{xs}}$, which mix along slightly deepening
461 isopycnals.

462 **Figure 3: Relationship between excess ^3He and metal inventories in the dissolved and**

463 **particulate phases in the SEPR hydrothermal plume (2200-3000 m).** All stations are included
464 with the exception of Sta. 18 (directly over vent). Sta. 20 is plotted as open circles for Mn
465 because those points fall off of the distal plume trend⁸. Integrating between 2200-3000 m
466 captures the entirety of the sinking Fe plume. Linear relationships between $^3\text{He}_{\text{xs}}$ and dissolved
467 metals suggest that dissolved metal inventories are apparently conserved (controlled by
468 mixing/dilution), while the exponential relationship between particulate metals and $^3\text{He}_{\text{xs}}$
469 indicates aggregative removal of particles to >3000 m depth

470 **Figure 4: Depth of peak concentrations in the SEPR hydrothermal plume.** Vertical bars indicate

471 depths where concentrations were within 2.5% of maximum. The 27.737 line is the potential

472 density layer on which maximum ${}^3\text{He}_{\text{xs}}$ was emplaced at Sta. 20; this is the isopycnal surface on
473 which all dissolved species should have traveled. Notably, Fe species deepened, falling below
474 this isopycnal, while Mn species mixed along it. The label “dFe-Resing” indicates dFe maxima
475 published previously⁸, while “dFe-John” are independent, mass spectrometric dFe
476 measurements reported here; we report both to show that the pattern of dFe descent is
477 reproducible and unrelated to data error.

478 **Figure 5: Scanning transmission X-ray microscopy (STXM) images, elemental maps, and**
479 **spectra for representative plume particles (>0.2 μm).** Transmission images (a) and (d) collected
480 at 290 eV. Distribution of total carbon with optical density of (b) 1.8 and (e) 0.63. Distribution
481 of total iron with optical density of (c) 2.6 and (f) 0.57. Note that (f) does not cover the whole
482 of the area imaged in (d) and (e). (g) Carbon 1s XANES spectra for particulate organic carbon
483 from Sta. 20-21. (h) Iron 2p XANES spectrum for particulate iron(III) from Sta. 20-21, compared
484 to standard ferrihydrite. All scale bars 2 μm .

485 **Figure 6: Dissolved and labile particulate $\delta^{56}\text{Fe}$ results for hydrothermal depths 2200-2800 m.**
486 (a) Constant labile particulate⁵⁰ $\delta^{56}\text{Fe}$ ($-0.25\pm 0.14\text{‰}$) over a wide range of pFe concentrations
487 suggests that pFe loss is controlled by non-fractionating, physical aggregation/disaggregation
488 processes. (b) Dissolved $\delta^{56}\text{Fe}$ increases down-plume, modeled as mixing (black line) between a
489 hydrothermal nanoparticulate Fe(III) oxyhydroxide end-member (-0.19‰) and an isotopically
490 heavier ligand-bound phase ($+0.66\text{‰}$, 0.77 nM; background and hydrothermal FeL complexes).
491 Errors in [Fe] and particulate $\delta^{56}\text{Fe}$ are smaller than data points (5% and 0.02-0.03 ‰ , 2 σ SE,
492 respectively). Errors for some Station 20 dissolved $\delta^{56}\text{Fe}$ were unusually high because of an
493 incorrecion dilution (light gray).

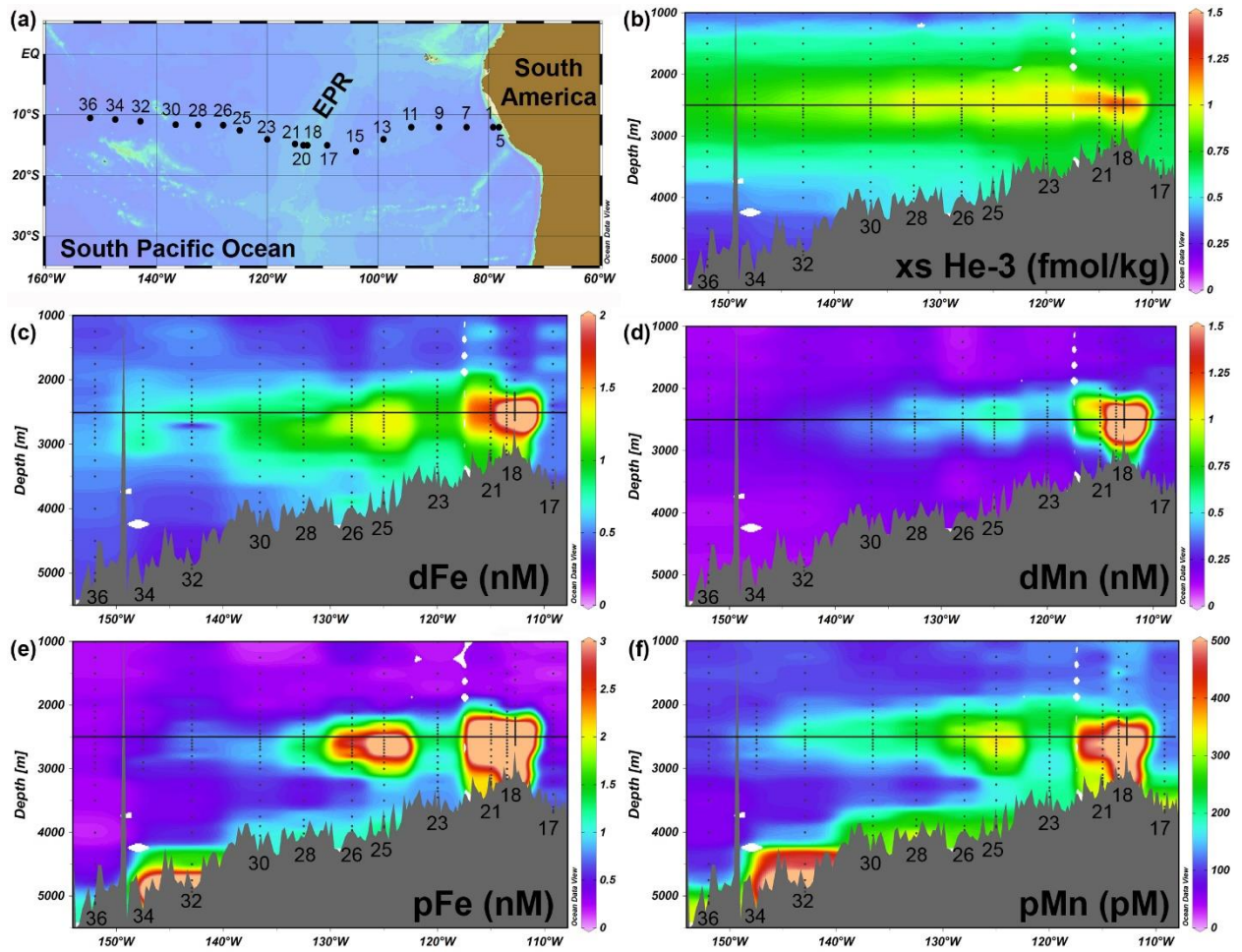


Figure 1

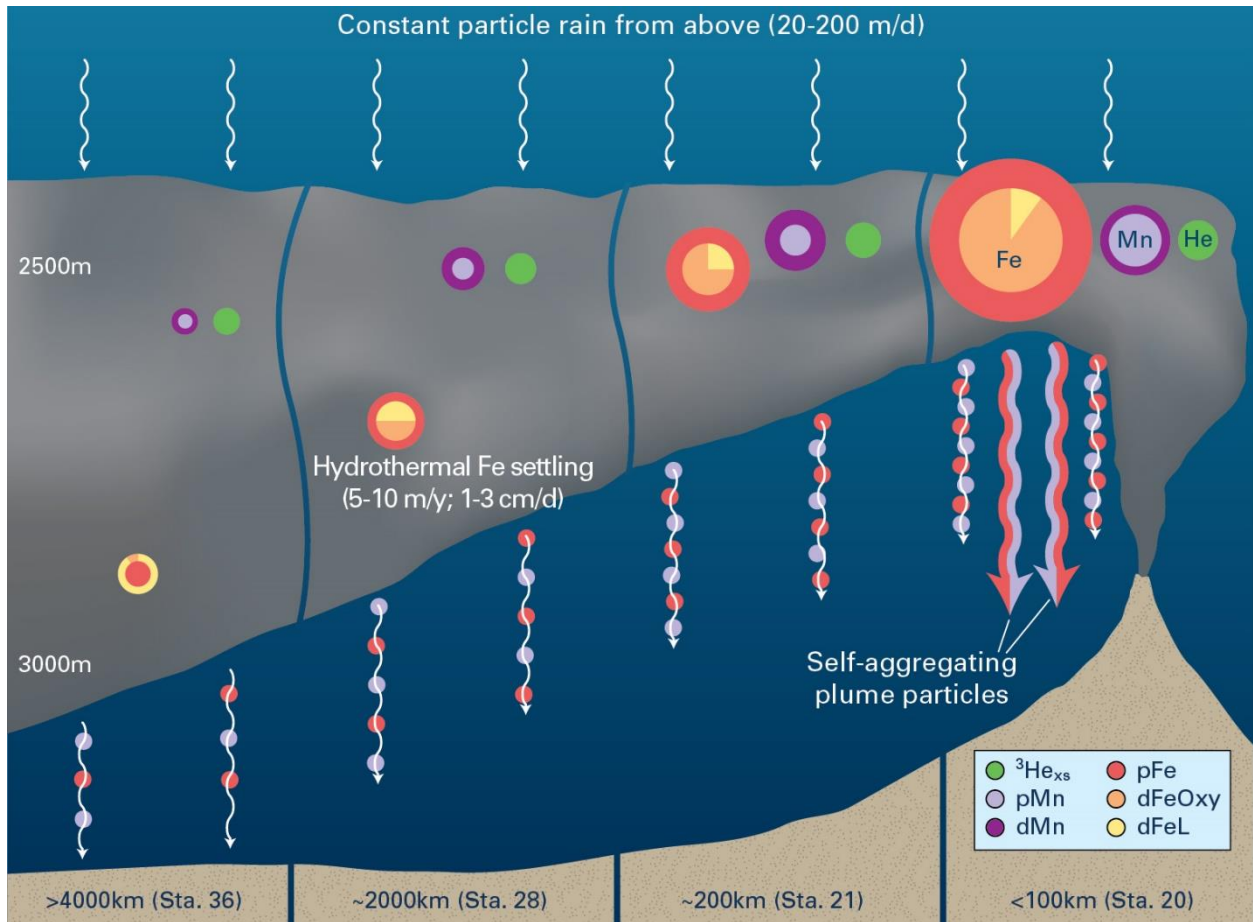


Figure 2 - **Please note that we would like to keep this figure as a 2-column figure, as it has critical components that would not be apparent in a 1-column figure.**

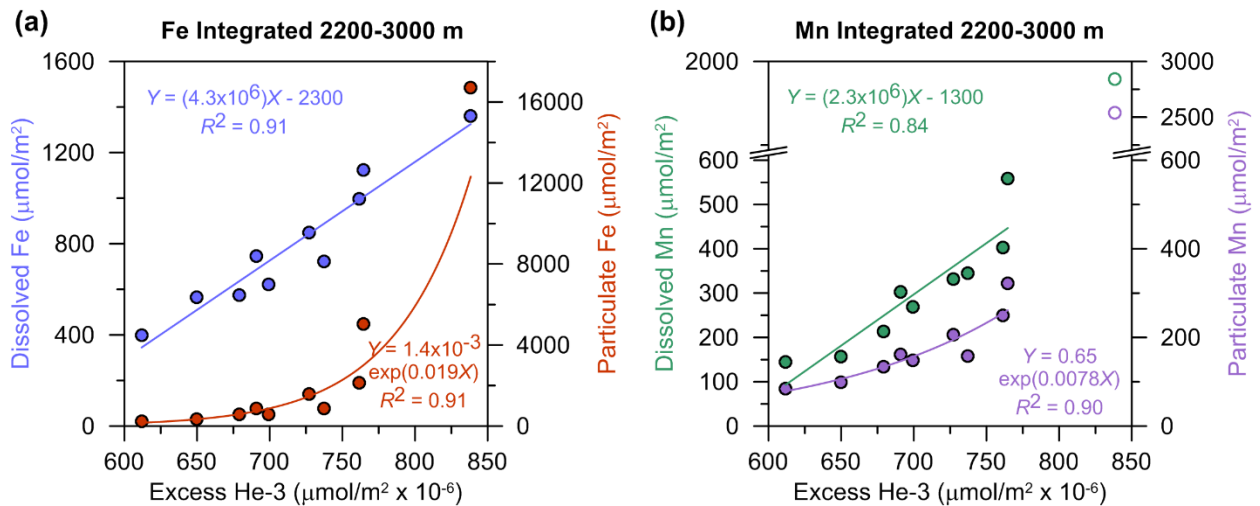


Figure 3

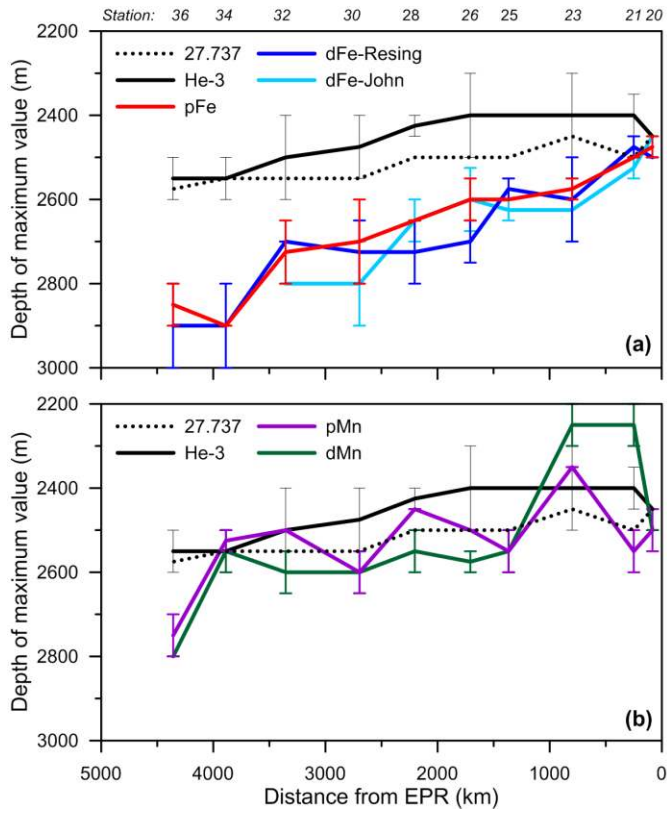


Figure 4

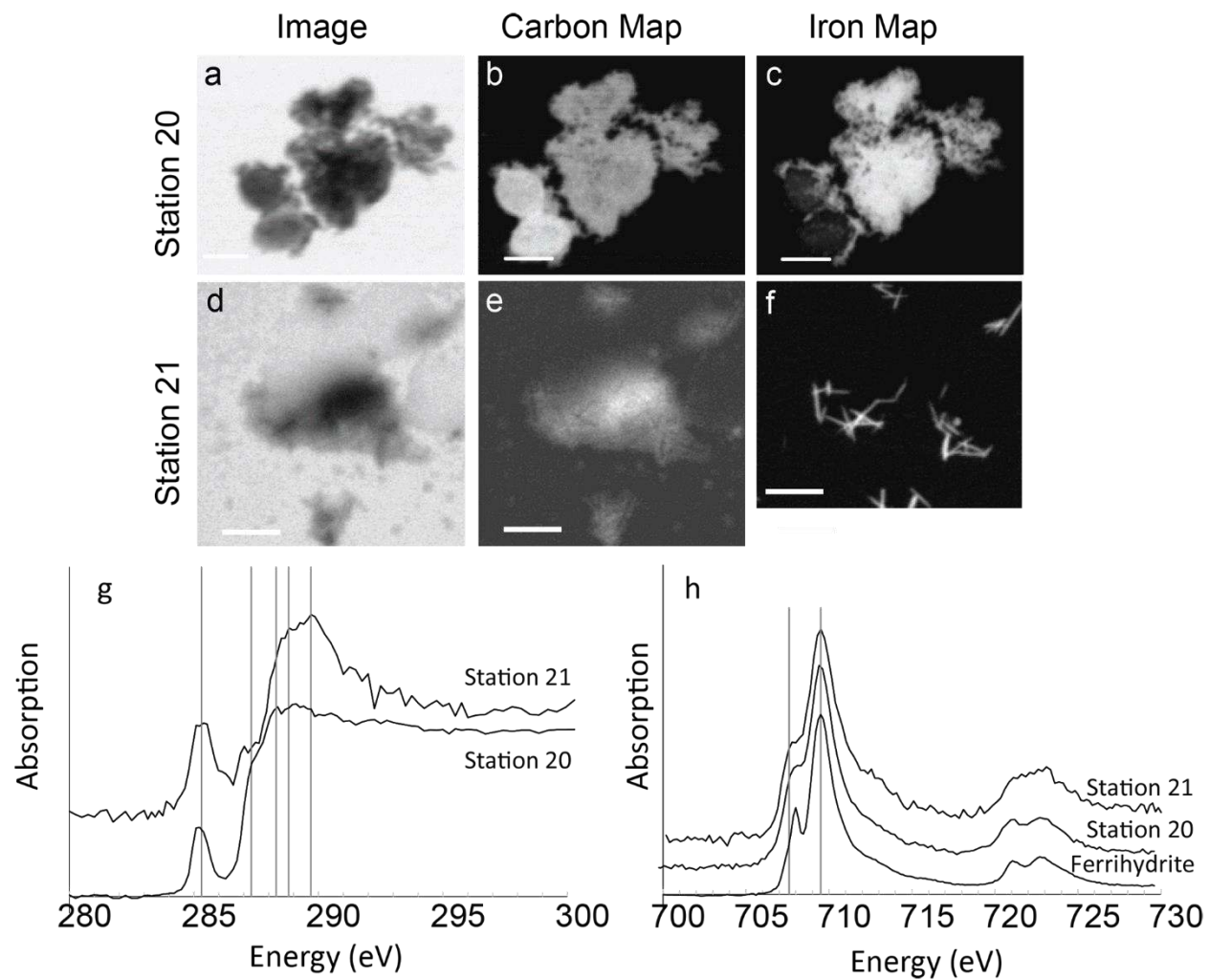


Figure 5

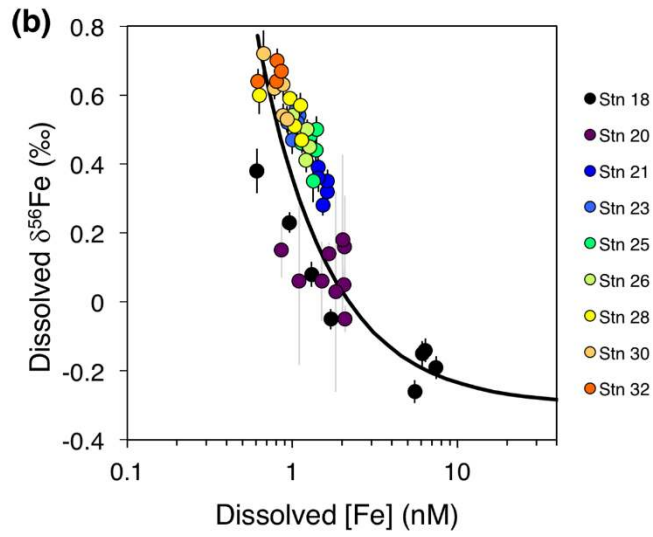
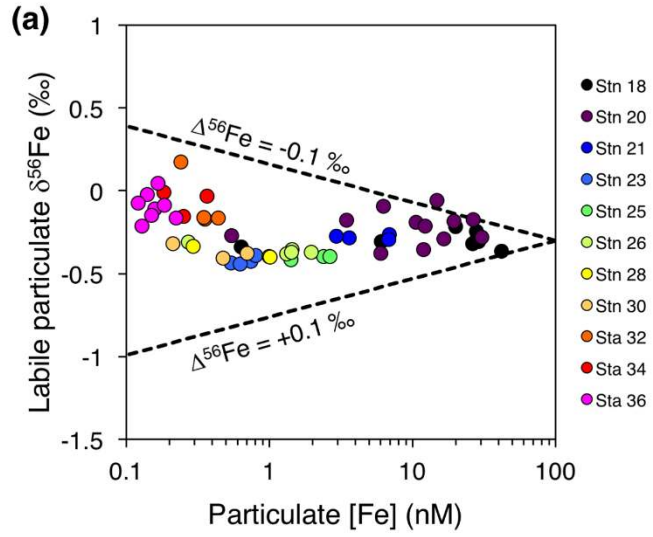


Figure 6

1 **Online-Only Methods for:**

2

3 **Iron persistence in a distal hydrothermal plume supported by**
4 **dissolved-particulate exchange**

5

6 By: Jessica N. Fitzsimmons, Seth G. John, Christopher M. Marsay, Colleen L. Hoffman, Sarah
7 L. Nicholas, Brandy M. Toner, Christopher R. German, and Robert M. Sherrell

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9

10 **Methods**

11 *Sample collection and processing* - Trace metal-clean seawater samples were collected
12 using the U.S. GEOTRACES sampling system consisting of 24 Teflon-coated GO-Flo bottles
13 (General Oceanics) mounted onto an epoxy-coated aluminum frame that was deployed using
14 Kevlar conducting cable¹. GO-Flo bottles were pre-rinsed with a 24+ hour treatment of filtered
15 surface seawater at the beginning of the cruise. At each station, the bottles were deployed open
16 and tripped on ascent at 3 m/min. Upon recovery, the bottles were carried into a shipboard clean
17 laboratory van that was over-pressurized with HEPA-filtered air for sampling under clean
18 conditions. Immediately prior to and following deployments, the bottles were covered on both
19 ends with plastic shower caps to avoid deck contamination.

20 During sub-sampling in the clean van, unfiltered salinity and nutrient samples were first
21 taken from the GO-Flo bottles to create headspace, and then the bottles were inverted slowly
22 three times to re-suspend any large particles that might have settled before sampling. GO-Flo
23 bottles were then pressurized to ~0.7 atm with HEPA-filtered air, and filtration commenced
24 using methods similar to those published previously². Briefly, GO-Flo stopcocks were fitted with
25 an acid-cleaned piece of Bev-a-Line tubing that fed into a polycarbonate elbow that was attached
26 by Luer lock fitting to a 25 mm, polypropylene filter holder (Swinnex, Millipore) containing a 25
27 mm, acid-cleaned 0.45 µm polyethersulfone filter (Supor, Pall Gelman). Immediately prior to
28 sampling, the headspace of the filter holder was flushed with seawater to evacuate any air
29 bubbles in order to prevent air lock or occlusion of the filter surface area by air bubbles during
30 sampling. Filtrate was directed into a plastic bucket, with the filter holders held approximately
31 horizontal such that any residual headspace air bubbles would rise to the top of the filter holder,
32 avoiding occlusion of the filter face. After filtration was complete (filter clogged to <1 drop of
33 filtrate per second) or two hours had passed since the start of filtration, filtration was suspended
34 by closing the stopcock on the GO-Flo bottle. Seawater volume passed through the filter was
35 measured and recorded. The Swinnex filter holders were taken into a HEPA-filtered clean space,

36 and excess seawater was removed by gentle vacuum suction through the filter. The filter holders
37 were then transferred in a sealed plastic bag to the HEPA-filtered “bubble” clean room in the
38 ship’s main lab. Working directly under a vertically flowing HEPA hood, the filter holders were
39 opened, and the filter was removed using Tefzel forceps (held only by the edge of the filter). The
40 non-sampled side of the filter was “blotted” by placing onto an acid-cleaned 47mm Supor filter
41 to remove residual seawater by capillary action. Finally, the visibly dry filter was placed into an
42 acid-cleaned polystyrene Petri Slide (EMD, Millipore) and stored at -20°C until analysis.

43 At the same time, a replicate set of GO-Flo bottles (tripped at the same depths as those
44 sampled for suspended particles) was sampled for dissolved metals through a 0.2 µm Acropak-
45 200 capsule filter (Pall) under the same pressure as described above. An acid-cleaned 1 L low
46 density polyethylene (LDPE) plastic bottle was filled after three 10% volume rinses for Fe
47 concentration and isotope measurements. Additionally, at a subset of depths a 4 L bottle was
48 filled for ultrafiltration separation of soluble and colloidal metals. Ultrafiltration proceeded
49 immediately by cross flow filtration (single-pass mode) across a 10 kDa regenerated cellulose
50 membrane (Pellicon XL PLCGC)³, with initial >200 mL ultrafiltrate discarded as rinse.

51 *Particulate Analytical Methods* – Particulate samples were analyzed in the Sherrell
52 laboratory at Rutgers University. Frozen filters were cut in half using a ceramic rotary blade; a
53 filter-cutting template was illuminated on a light table for guidance during cutting, and filter
54 cutting error performed on blank filters was found to be ≤2% by weight. One filter half was used
55 for sample digestion (reported here), and the other filter half was used for archiving or for acid
56 leaching of “labile” metals (not reported). For digestion, filter halves were placed into the bottom
57 of acid-clean 15 mL PFA vials (Savillex), and 0.4 mL of Milli-Q ultrapure water was added to
58 the top. Once fully wetted, the filter half was pulled up the side of the vial and adhered to the
59 wall, curved edge toward bottom of vial. Then 0.6 mL of a solution containing 16.7% (v/v)
60 hydrofluoric acid (HF, Optima grade, Fisher) and 83.3% (v/v) nitric acid (HNO₃, Optima grade,
61 Fisher) was added by pipet to each vial, aiming at the adhered filter half. The final digestion acid
62 mixture was thus 1.0 mL of a solution containing 10% HF and 60% HNO₃ by volume. The vial
63 was then capped tightly and placed on a Teflon hotplate at least 2 cm from other vials. These
64 “bombs” were refluxed at 135°C for 4 hours. After cooling, solution was gathered to the bottom
65 of the vials, lids were removed, and the digest solution was evaporated until ~5-10 µL of solution
66 remained. At that point, 100 µL of concentrated HNO₃ was added, and the solution was re-
67 evaporated until ~5-10 µL of solution remained. The additional HNO₃ dry-down encourages
68 volatilization removal of HF. Evaporating to dryness was avoided in order to prevent “baking”
69 sample residue onto the Teflon surface, to aid in complete re-dissolution, and to minimize carry-
70 over to subsequent sample digestions upon vial reuse. Finally, the remaining droplet was brought
71 up in 3.0 mL of 5% HNO₃ (v/v) and transferred to a 15mL acid-cleaned polypropylene
72 centrifuge tube for archiving and analysis.

73 Particulate Fe analysis was completed in medium resolution on a Thermo Element 1
74 inductively coupled plasma mass spectrometer (ICP-MS), employing an Apex and ACM
75 sequential desolvation system (ESI) to reduce molecular oxide ion formation. Sample solutions
76 were diluted five times from the archived digest solutions (to reduce chemical matrix) and were

77 quantified using a nine-point standard curve with an identical acid matrix to that of samples and
78 bracketing the concentration range of the samples, run at the beginning and end of each
79 analytical session. Single-point standard additions were also run every ten samples to check for
80 accuracy, and analytical replicates were made every ten samples to monitor analytical precision.
81 Particulate Fe was measured on both ^{56}Fe and ^{57}Fe , and concentration data for each were found
82 to be indistinguishable, raising confidence in the analytical Fe measurement.

83 After correction for dilution and division by equivalent seawater volume filtered through
84 the half-filter, the Fe concentrations in seawater were corrected for process blank. The process
85 blanks consisted of Supor filters through which ~ 2.0 L of $0.2\ \mu\text{m}$ -filtered seawater were passed
86 during sampling at sea. Process blanks were collected from a variety of locations and depths
87 throughout the cruise ($n=18$); no trend in these blanks as a function of particle concentration in
88 the seawater was observed, suggesting that particles smaller than $0.2\ \mu\text{m}$ did not contribute
89 significantly to the elemental composition of the process blank filter. These process blank filters
90 were cut and digested as for normal samples, and the absolute moles of each element were
91 corrected for elemental contributions from residual seasalt using the Na data, assuming that all
92 Na was derived solely from seasalt and using the mean seawater ratio of all measured elements
93 to Na. The median seasalt-corrected process blank for each element was then subtracted from
94 each particle concentration.

95 External accuracy in the particulate Fe measurement was assessed by the digestion of two
96 certified reference materials: BCR-414 (plankton) and PACS-2 (a marine sediment). Recovery of
97 10 mg of these reference materials by the methods described above was $100\pm 8\%$ ($n=14$) for
98 BCR-414 and $89\pm 8\%$ ($n=8$) for PACS-2, indicating excellent analytical accuracy. A complete
99 intercalibration for Fe and the rest of the element suite analyzed in this dataset can be found on
100 BCO-DMO (<http://www.bco-dmo.org/dataset/639847>).

101 *Fe Isotope Analytical Methods* – Fe stable isotope ratios ($\delta^{56}\text{Fe}$) and concentrations were
102 measured using double-spike ICP-MS. Dissolved $\delta^{56}\text{Fe}$ and Fe concentrations were made on 1L
103 seawater samples according to published methods⁴. Briefly, seawater was acidified to pH 1.7 for
104 at least two months before sample processing. Samples were then amended with a double spike
105 containing roughly equal amounts of ^{57}Fe and ^{58}Fe . Fe (as well as Zn and Cd) was extracted from
106 the seawater onto Nobias PA-1 chelating resin (Hitachi) while raising the pH to 6-6.5. Extracted
107 metals were eluted from the Nobias resin with 5% HNO_3 , and purified by anion exchange
108 chromatography. This method is associated with blanks of ~ 0.3 ng Fe and yields analytical errors
109 of ~ 0.03 to $0.05\ \text{‰}$ for deep-ocean seawater samples such as these.

110 Particulate samples for Fe stable isotope analysis were collected using in situ battery-
111 powered pumps (McLane WRT-LV), employing a modified dual-flow configuration and
112 deployed on a trace-metal clean hydrowire^{5,6}. Particulate material was collected by pumping
113 seawater (average volume ~ 400 L) through paired $0.8\ \mu\text{m}$ polyethersulfone (Supor), 142 mm
114 diameter filters loaded behind a $51\ \mu\text{m}$ polyester pre-filter. Subsamples were taken from the 0.8
115 – $51\ \mu\text{m}$ size fraction material by cutting a $1/16^{\text{th}}$ section of the upper $0.8\ \mu\text{m}$ Supor filter, using a
116 ceramic rotary blade.

117 Ligand-leachable (labile) pFe concentrations and $\delta^{56}\text{Fe}$ were determined following
118 application of an oxalate-EDTA leach at pH 8⁷. Each filter section was loosely folded and
119 placed in a 2 mL polyethylene vial, to which 1 mL of oxalate-EDTA reagent was added. The
120 sealed vials were then heated at 90 °C for two hours. Each leachate was then passed through a
121 polypropylene syringe filter (0.45 μm) to remove any loose particles from the solution.
122 Subsamples of leachate were diluted 20-fold using 0.1 M HNO_3 and iron concentrations
123 measured on a Thermo Scientific Element II sector field ICP-MS. Using this measured iron as a
124 guide, an aliquot of each leachate sample was spiked with a ^{57}Fe and ^{58}Fe double spike solution
125 to give a 1:2 ratio of natural to spike iron. Spiked samples were evaporated to dryness, heated at
126 200 °C with concentrated HNO_3 and H_2O_2 to dissolve organic material, then dried down again
127 and reconstituted in 10 M HCl + 0.01% H_2O_2 . Samples were then purified by anion exchange
128 chromatography. Samples were corrected for reagent blank contribution to both concentration
129 and $\delta^{56}\text{Fe}$ as described in Revels et al. ⁷.

130 Observed labile $\delta^{56}\text{Fe}$ was compared to theoretical predictions of particulate $\delta^{56}\text{Fe}$ with
131 different fractionation factors (Fig. 6). We assumed a starting pool of 100 nM pFe with a $\delta^{56}\text{Fe}$ of
132 -0.3 ‰. Particulate $\delta^{56}\text{Fe}$ was then calculated for various Fe concentrations assuming that pFe
133 was lost with an isotope effect ($\Delta^{56}\text{Fe}$) of either +0.1 ‰ or -0.1 ‰, according to Rayleigh
134 distillation, such that

$$135 \quad \delta^{56}\text{Fe}_{\text{particulate}} = -0.3 + \Delta^{56}\text{Fe} \cdot \ln F$$

136 where F is the fraction of the original 100 nM pFe that remains in the particulate phase.

137 The full dissolved $\delta^{56}\text{Fe}$ data set can be found at [http://www.bco-](http://www.bco-dmo.org/dataset/643809)
138 [dmo.org/dataset/643809](http://www.bco-dmo.org/dataset/643809). The full particulate $\delta^{56}\text{Fe}$ data set can be found at [http://www.bco-](http://www.bco-dmo.org/dataset/669178)
139 [dmo.org/dataset/669178](http://www.bco-dmo.org/dataset/669178).

140 *Synchrotron Analytical Methods* – Plume particles for synchrotron-based STXM imaging
141 and C and Fe XANES were collected by in situ filtration using McLane pumps⁵ and a custom-
142 built filter manifold for holding acid-cleaned 0.2 μm polycarbonate filters. Shipboard, the filter
143 holders were opened in a Coy anaerobic chamber set up in a HEPA-filtered “bubble.” All filters
144 were handled under 5% H_2 and 95% N_2 atmosphere. Residual seawater was removed from the
145 filter holders by pulling 2 mL of deoxygenated ultrapure water through the filters using a
146 vacuum pump. The filters were then placed in plastic vials containing ~0.5 mL of deoxygenated
147 ultrapure water for resuspension of particles. The vials were then sealed in Mylar-aluminum
148 laminate bags, removed from the anaerobic chamber, and frozen until analysis.

149 STXM data collection was performed at the Advanced Light Source, Lawrence Berkeley
150 National Laboratory, Berkeley, CA, USA, on beamline 5.3.2.2⁸ for plume depths at Sta. 20 (2550
151 m water depth, GT 8705) and Sta. 21 (combined GT 8885, 8884, 8879, for 2000, 2300, and 3230
152 m water depths, respectively). Using an adapted version of a published method⁹, the plume
153 particles suspension was defrosted and shaken. Then, in an anaerobic chamber, ~1 μL was
154 deposited on a silicon nitride membrane (Silson Ltd.) and dried at room temperature; this
155 preparation resulted in dispersed particles with no sea salt precipitates. Optical density (OD)
156 images were created from X-ray images recorded at energies just below and at the C 1s (280, 290

157 eV) and Fe 2p (700, 710 eV) absorption edges. XANES spectra were collected from image
158 sequences collected at energies spanning the C 1s and Fe 2p absorption edges (280-340 eV for C,
159 685-745 eV for Fe). Theoretical spatial and spectral resolutions were 20 nm and ± 0.1 eV,
160 respectively. All measurements were performed at ambient temperature and < 1 atm He.
161 Calibration at the C 1s edge was accomplished with the 3s (292.74 eV) and 3p (294.96 eV)
162 Rydberg transitions of gaseous CO₂. All data processing was carried out with the IDL *aXis2000*
163 software package (<http://unicorn.mcmaster.ca/aXis2000.html>).

164 *Data usage from the literature* – The dissolved Mn data used in this paper were taken
165 from Resing et al.¹⁰. The ³He data were also updated from the same paper with additional station
166 coverage and improved corrections to attain the non-atmospheric (³He_{xs}) component, as follows:

$$167 \quad {}^3\text{He}_{\text{xs}} = {}^3\text{He}_{\text{meas}} - {}^3\text{He}_{\text{S}} - {}^3\text{He}_{\text{A}}$$

168 where the measured ³He concentration (³He_{meas}) is calculated from the measured isotope ratio
169 anomaly (δHe in %) and measured helium concentration ([He]) as:

$$170 \quad {}^3\text{He}_{\text{meas}} = 1.384 \times 10^{-6} (1 + \delta\text{He}/100) * [\text{He}]$$

171 and is corrected for the solubility abundance of He (³He_S), which is a function of the salinity and
172 temperature of the seawater C_SHe and the temperature-dependent fractionation factor of ³He/⁴He
173 ($\alpha_{\text{S}} = 0.98\text{-}0.99$):

$$174 \quad {}^3\text{He}_{\text{S}} = \alpha_{\text{S}} \times 1.384 \times 10^{-6} \times \text{C}_{\text{S}}\text{He}$$

175 and is also corrected for the amount of ³He injected from the air (³He_A), which is inferred from
176 the super-saturation of neon (Ne) and the atmospheric He/Ne molar ratio (0.28823):

$$177 \quad {}^3\text{He}_{\text{A}} = 1.384 \times 10^{-6} \times 0.28823 \times (\text{Ne} - \text{C}_{\text{S}}\text{Ne}).$$

178 The dissolved Fe data reported in this paper are the high resolution data collected at sea
179 by Dr. Peter Sedwick¹⁰ (PS, Old Dominion University) after corrections for accuracy using the
180 lower resolution but higher accuracy, lab-based data collected on a subset of samples using the
181 aforementioned methods (SGJ). A linear correlation between the data of PS and SGJ at Stations
182 17-36 resulted in an R² of 0.96; the SGJ data set had 188 datapoints over this range, while the PS
183 dataset had 440 points (41% data coverage, distributed nearly every other sample to make the
184 regression).

185 *Data Availability* – The dissolved and particulate concentration and isotope ratio data that
186 support the findings of this study are available on the Biological and Chemical Oceanography
187 Data Management Office (BCO-DMO), <http://www.bco-dmo.org/project/499723>.

188

189 **Supplemental References**

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215

Supplementary Information for:

Iron persistence in a distal hydrothermal plume supported by dissolved-particulate exchange

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Materials:

1. Figure S1: Depth profiles of particulate Fe and Mn concentrations for each station station (log scale).
2. Kinetics of particulate Fe removal from the hydrothermal plume: text discussion
 - a. Figure S2: Kinetic rate order assessment for particulate metal removal from the hydrothermal plume
3. Figure S3: Descent of Fe in the hydrothermal plume: full profile version.
4. Figure S4: Colloidal Fe is a significant component of dissolved Fe in the plume.
5. Figure S5: $\delta^{56}\text{Fe}$ of labile pFe and total digest pFe are the same in plume samples at Station 26.
6. Supplemental References

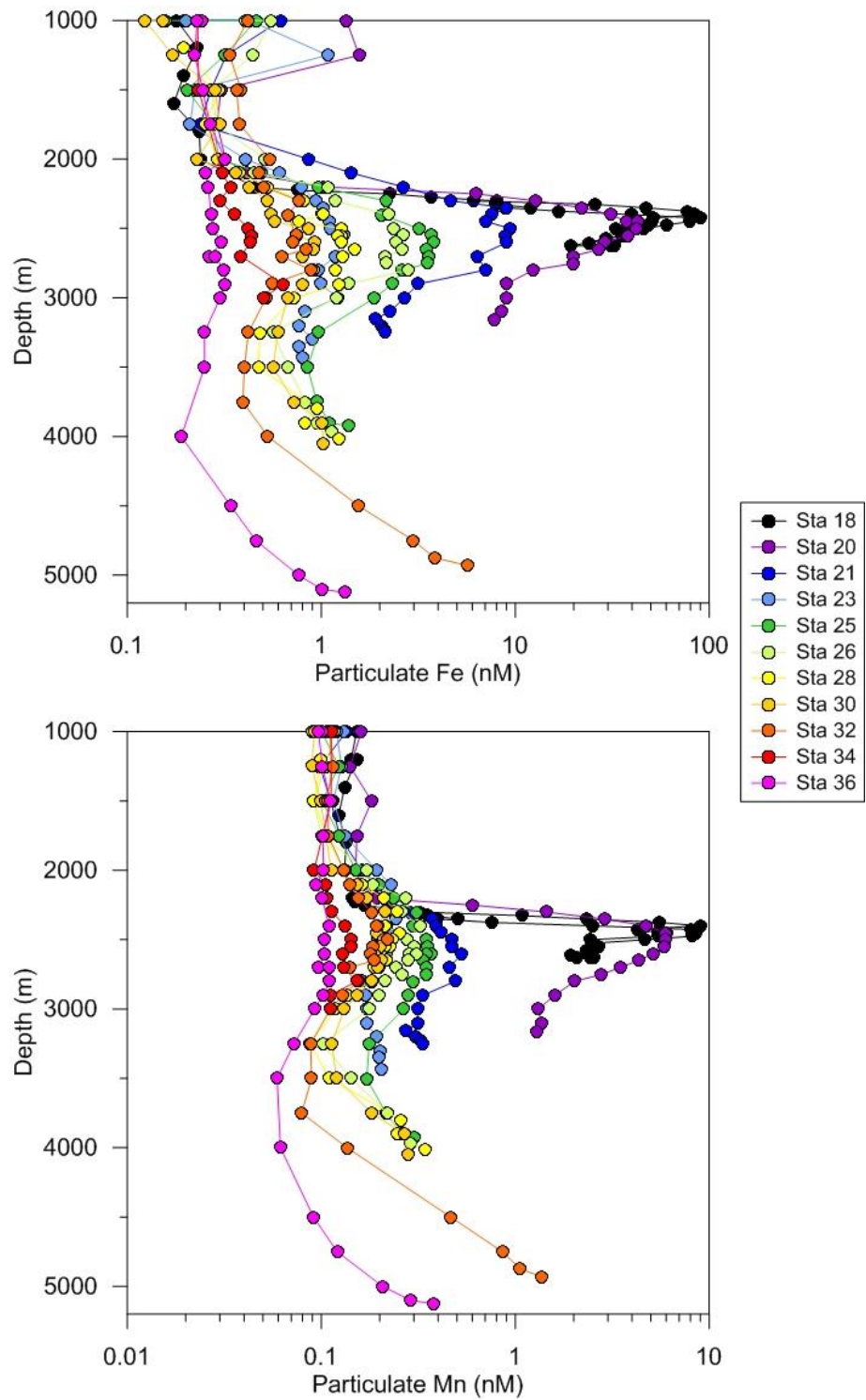


Figure S1. Depth profiles of particulate Fe (top) and Mn (bottom) concentrations on a log scale for each station on GP16 in the hydrothermal plume. Note that the Mn concentration scale is an order of magnitude lower than the Fe concentration scale.

2. Kinetics of particulate Fe removal from the hydrothermal plume

Hydrothermal Fe and Mn particles were non-conservatively removed from the plume, as attested by their non-linear relationships with the conservative hydrothermal tracer $^3\text{He}_{\text{xs}}$ (Figure 3). To attempt to resolve the mechanism of aggregative removal, kinetics testing on the particulate metal data was conducted to determine whether the aggregative removal occurs predominantly by self-collision (second order) or by collision with a sinking particulate phase from shallower in the water column (first order).

Self-aggregation kinetics should occur as a second order function of the hydrothermal particle concentration¹, such that the removal rate is a quadratic function of the particulate metal concentration (two like hydrothermal particles must collide to aggregate):

$$\frac{\partial[C]}{\partial t} = -2k [C]^2$$

where k is the removal rate constant, $[C]$ is the concentration of any element, and t is time. When this removal rate equation is integrated at steady state, a linear relationship between the natural log of the concentration and time can be expected:

$$\frac{1}{[C]} = 2kt + \frac{1}{[C]_0}$$

where $[C]_0$ is the starting concentration of the element in the hydrothermal plume at emplacement. When we evaluated our particulate metal inventories (integrated 2200-3000 m depth) using this technique (Figure S2, top panel), our observations were instead better fit by a first order kinetic model (Figure S2, bottom panel), where the removal rate is a linear function of the particulate metal concentration:

$$\frac{\partial[C]}{\partial t} = -k [C]$$

$$\ln[C] = -kt + \ln[C]_0$$

The first order dependence of particulate Fe and Mn removal is consistent with an aggregative removal mechanism involving collision of hydrothermal particles with sinking aggregates from the surface ocean.

However it is worth noting that the greatest deviation from linearity in the first-order kinetic tests occurred nearest the vents (especially station 20). Thus, nearer to the vents where hydrothermal particulate concentrations are highest, self-collision aggregative mechanisms may dominate. Our sampling resolution did not increase nearer the SEPR axis, and thus we cannot further prove this quantitatively due to lack of data.

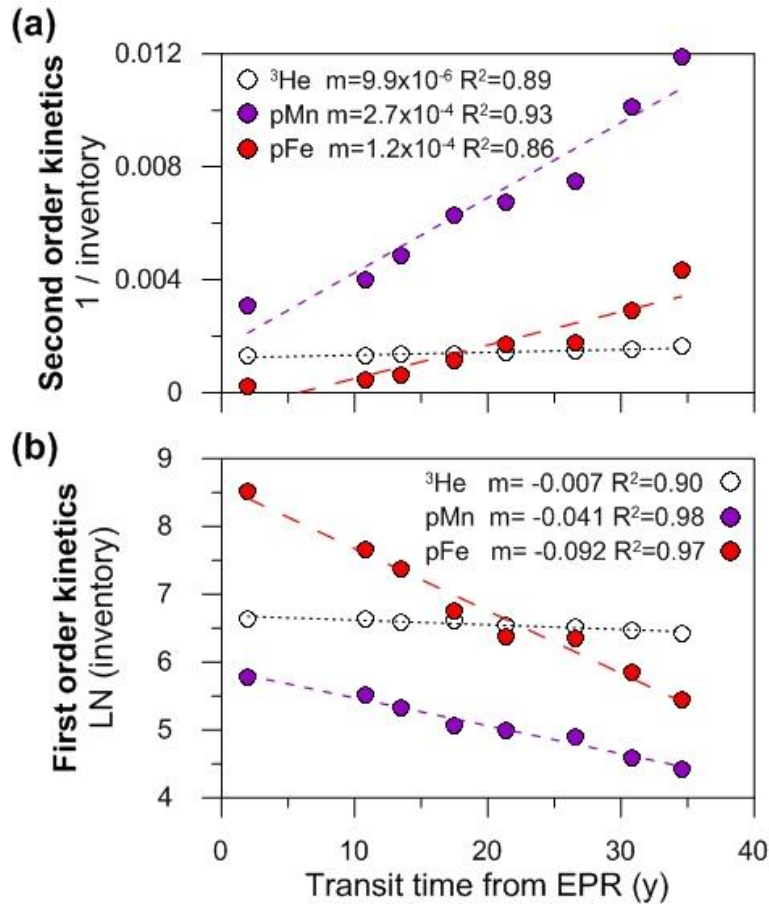


Figure S2: Kinetic rate order assessment for particle metal removal from the distal hydrothermal plume (Stations 21-36). Transit time was calculated using the 0.4 cm/s advection rate calculated using ^{227}Ac inventories² and distance from the 15°S EPR. The negligible slope from the ^3He relationships reveals the second (a) and first (b) order dependence of the conservative mixing/advection terms in the circulation of the hydrothermal plume. (a) Self-aggregative removal of hydrothermal materials are modeled as a second order function of elemental concentration. The slight curvature in the second order kinetic relationships for particulate Fe and Mn suggests that second order kinetics (aggregation by hydrothermal-self aggregation) is not the best model of particulate removal rate for the plume as a whole. (b) Instead first order kinetics (aggregation of hydrothermal particles onto sinking particles from the surface ocean) is an improved model of how hydrothermal particles are removed from the plume. In this model, hydrothermal elements are modeled as a first order function of elemental concentration. Station 23 data are excluded from these kinetics plots because of their anomalous plume behavior.

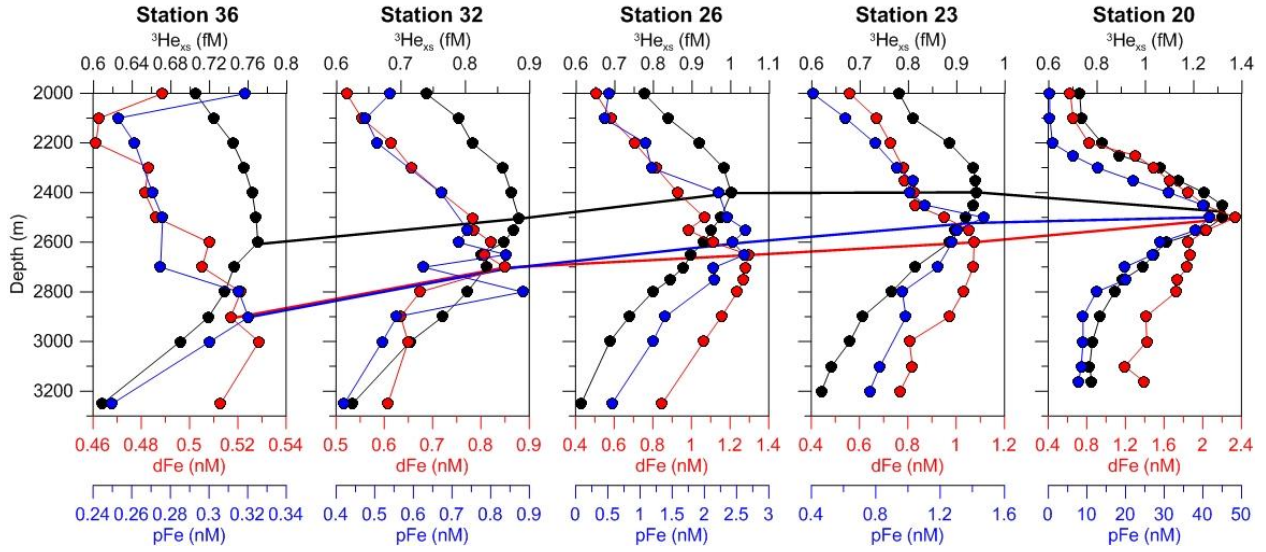


Figure S3: Descent of Fe in the hydrothermal plume from the perspective of the full profiles.

Dissolved Fe is shown in red, particulate Fe in blue, and excess He-3 in black. Note that the concentration scale changes in each panel and often does not go to zero. The bolded lines connect the maximum values for each profile to the maximum values from the flanking profiles. Both Fe phases sink relative to $^3\text{He}_{\text{xs}}$.

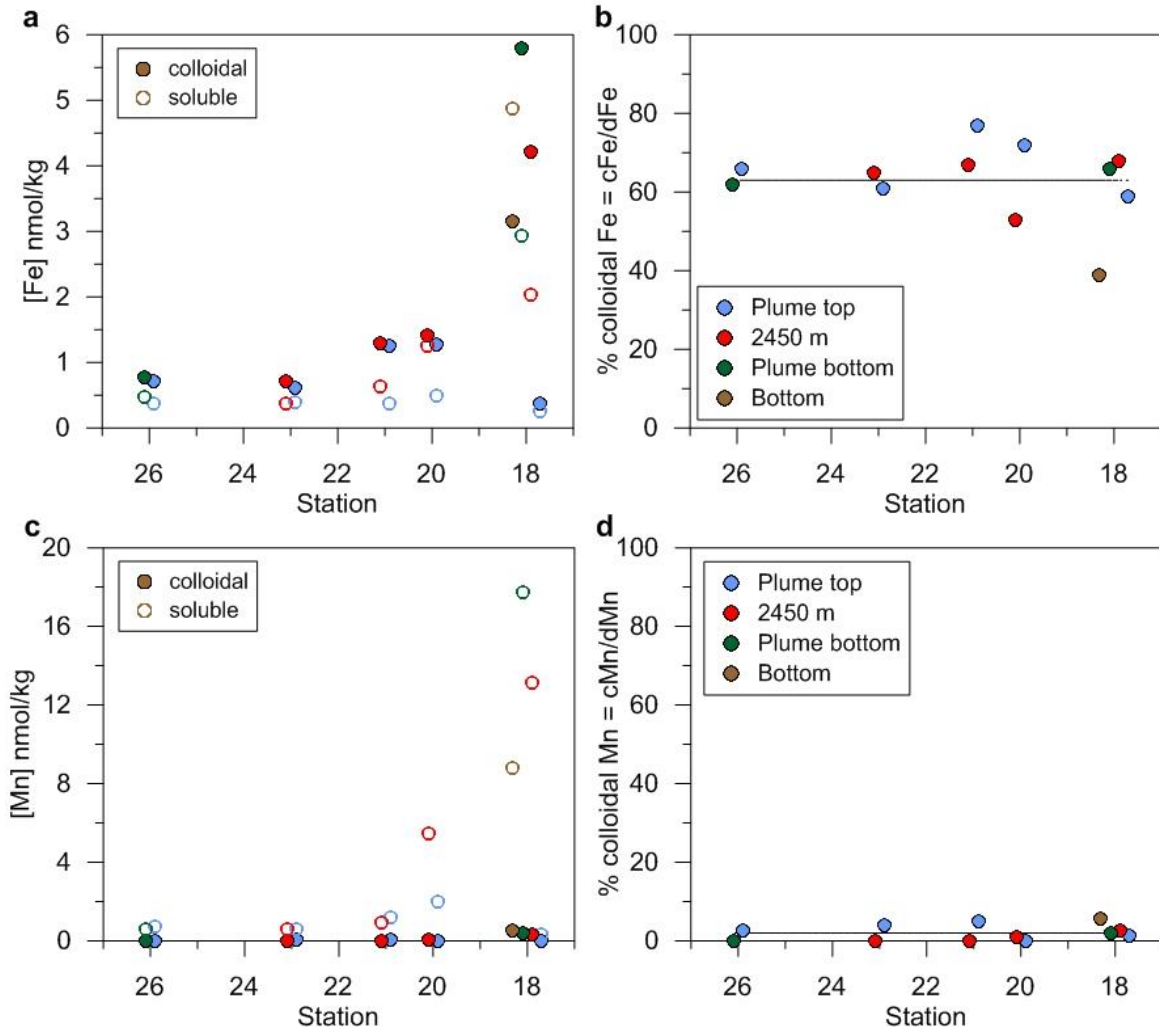


Figure S4: Colloidal Fe is a significant component of dissolved Fe in the plume, while colloidal Mn is an insignificant fraction of total dissolved hydrothermal plume Mn. (a) Measured concentrations of soluble Fe (<10 kDa ~ 0.003 μm ; open symbols) and colloidal Fe (0.003 - 0.2 μm ; closed symbols) are shown as a function of station number. Depths at the top of the plume (≤ 2350 m) are shown in blue, in the plume core (~ 2450 m) are shown in red, at the bottom of the plume (≥ 2500 m) are shown in green, and near-seafloor are shown in brown. (b) The percent contribution to dissolved Fe by colloidal Fe ($c\text{Fe}/d\text{Fe}$) was very constant across all stations and depths at $63 \pm 10\%$ (indicated by the dotted line). Note that physical speciation into soluble vs. colloidal size fractions does not define inorganic vs. organic chemical speciation; marine Fe colloids can be inorganic or organically complexed. (c) Measured concentrations of soluble Mn (<0.003 μm ; open symbols) and colloidal Mn (0.003 - 0.2 μm ; closed symbols) are shown as a function of station number. (d) The contribution to dissolved Mn by colloidal Mn species ($c\text{Mn}/d\text{Mn}$) was very constant across all stations and depths at $2 \pm 2\%$ (indicated by the dotted line); there were negligible Mn colloids.

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