

Iron isotopes constrain sources and cycling in the global ocean

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1 **Iron isotopes constrain sources and cycling in the global ocean**

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12 **Abstract**

13 Iron regulates marine productivity, nitrogen fixation and carbon export, yet the fluxes
14 and processes controlling its oceanic distribution are difficult to quantify because
15 external supply and internal cycling are tightly coupled. Seawater iron isotopes ($\delta^{56}\text{DFe}$)
16 provide an independent constraint, yet whether they preserve external source signatures
17 or record fractionation during transport remains debated. Here, we reconcile the global
18 distributions of dissolved Fe (DFe) and $\delta^{56}\text{DFe}$ within a unified framework that
19 accounts for their distinct sensitivities to iron-cycle processes and large-scale ocean
20 circulation. Combining machine-learning reconstructions of global dissolved Fe (DFe)
21 and $\delta^{56}\text{DFe}$ with source partitioning and circulation diagnostics, we find DFe is
22 spatially heterogeneous and strongly overprinted by local inputs and internal cycling,
23 whereas $\delta^{56}\text{DFe}$ more closely follows basin-scale water-mass structure. Endmember
24 analysis reveals strong inter-basin variability in apparent $\delta^{56}\text{Fe}$ source signatures, with
25 reductive sedimentary Fe contributing most among resolved external sources,
26 particularly in the North Pacific Ocean. Along the North Atlantic Deep Water pathway,
27 $\delta^{56}\text{DFe}$ evolution cannot be explained by heavy atmospheric inputs alone, but instead
28 records source imprints progressively modified by mixing and internal Fe cycling. Our
29 results demonstrate a unique role for $\delta^{56}\text{Fe}$ as an integrated tracer of Fe sources,
30 transport and recycling in the ocean.

31 Main

32 Iron is an essential micronutrient that regulates marine primary production, nitrogen
33 fixation and carbon export^{1,2,3}. A quantitative understanding of marine Fe
34 biogeochemistry is therefore critical for predicting ocean ecosystem functioning and
35 global carbon cycling under future climate change^{1,2,3}. Over the last several decades,
36 international programmes such as GEOTRACES have greatly expanded the global
37 database of oceanic Fe observations and transformed our view of its distribution and
38 cycling⁴. Nevertheless, the marine Fe cycle is poorly constrained because external
39 supply and internal cycling are tightly coupled, while both source fluxes and the
40 mechanisms controlling Fe removal remain highly uncertain^{3,4,5,6}. Unlike
41 macronutrients such as nitrate and phosphate, dissolved Fe distributions are not
42 governed primarily by water-mass mixing, but are continuously reshaped by the
43 competing effects of regeneration and scavenging⁶. A central challenge is therefore to
44 quantify the relative contributions of external Fe sources. Although atmospheric
45 deposition, sedimentary inputs and hydrothermal systems are widely recognized as
46 important sources, their effective fluxes to the ocean remain poorly quantified^{7,8,9}.
47 These uncertainties propagate directly into estimates of oceanic Fe residence time and
48 the sensitivity of the biological carbon pump to climate forcing^{7,10}.

49 Over the past two decades, measurements of dissolved Fe isotope compositions in
50 seawater have emerged as a valuable complementary approach for investigating marine
51 Fe biogeochemistry^{8,11,12,13}. Seawater $\delta^{56}\text{DFe}$ can provide information on both the
52 provenance of Fe and the biogeochemical processes that modify DFe after it enters the
53 ocean^{4,8,11,14}. Although seawater $\delta^{56}\text{Fe}$ measurements have increased substantially in
54 recent years, the interpretation of $\delta^{56}\text{Fe}$ distributions and their application to constrain
55 the marine Fe cycle still remain challenging. A first challenge is that, although $\delta^{56}\text{DFe}$
56 offers a promising means to distinguish external Fe sources, source-specific isotopic
57 endmembers are often variable, non-unique and partially overlapping^{11,12}. For instances,
58 hydrothermal vent fluids exhibit highly variable $\delta^{56}\text{Fe}$ signatures, ranging from -0.69‰
59 to -0.12‰ in high-temperature systems and approaching basaltic values ($\sim +0.11\text{‰}$) in
60 some low-temperature systems^{11,12}. The $\delta^{56}\text{Fe}$ signature of dust-derived Fe ($\sim +0.1\text{‰}$)
61 falls within the broad range reported for riverine inputs (-1.3‰ to $+1.8\text{‰}$), making
62 these sources difficult to distinguish on the basis of $\delta^{56}\text{Fe}$ alone^{11,15}. A second challenge
63 is that seawater $\delta^{56}\text{DFe}$ cannot be interpreted as a source tracer alone. After Fe enters
64 seawater, its isotopic composition may be altered by redox reactions^{11,15,16}, ligand
65 complexation^{17,18}, biological uptake^{19,20}, scavenging^{21,22}, and remineralization^{23,24}.
66 These processes can fractionate Fe isotopes in different directions and with different

magnitudes, so the observed seawater signal may deviate substantially from the original source composition. A notable example is the widespread presence of positive $\delta^{56}\text{DFe}$ signatures in the North Atlantic interior⁸. The origin of these isotopically heavy values remains unresolved, with competing explanations invoking fractionation during aerosol dissolution, preferential stabilization of heavy Fe by organic ligands and exchange between dissolved and particulate phases. Recent syntheses therefore emphasize that internal cycling must be treated explicitly if $\delta^{56}\text{DFe}$ is to be used quantitatively¹¹, and model studies further indicate that fractionation during biological uptake and organic complexation is required to reproduce observed seawater $\delta^{56}\text{DFe}$ distributions²⁵. Overall, these studies show that the fundamental challenge in iron isotope research is to resolve, in a mechanistic and predictive framework, the coupled effects of source strength, source heterogeneity, and internal cycling.

Here we develop the first paired, observation-constrained three-dimensional reconstruction of global DFe and $\delta^{56}\text{DFe}$ distributions using machine-learning models trained on observations from the GEOTRACES Intermediate Data Product 2025 (IDP2025)²⁶. Using globally mapped hydrographic, biogeochemical, atmospheric and boundary-related predictors, we fill gaps in the sparse observational record and generate the first paired global distributions of DFe and $\delta^{56}\text{DFe}$. We then integrate four complementary approaches to interpret the reconstructed distributions (see Methods). First, source-dominated regions identified from well-characterized GEOTRACES sections are extrapolated globally using supervised classification. Second, basin-specific apparent isotope endmembers are incorporated into a two-endmember mass-balance model to estimate source-specific DFe inventories. Third, optimum multiparameter analysis (OMP) is used to resolve Atlantic water-mass structure, define a coherent NADW pathway and track $\delta^{56}\text{Fe}$ evolution along this overturning branch. Finally, the reconstructed Fe and $\delta^{56}\text{Fe}$ fields are coupled to the Ocean Circulation Inverse Model (OCIM) to generate circulation-consistent tracer distributions and distinguish circulation-related preformed signals from non-conservative modification in the ocean interior. Together, these approaches allow us to assess how external Fe supply, water-mass transport and internal biogeochemical processing jointly structure the global dissolved Fe isotope distribution.

Global distributions of DFe and $\delta^{56}\text{DFe}$

The DFe and $\delta^{56}\text{DFe}$ reconstructions show that concentration and isotope composition capture different aspects of the marine iron cycle. DFe displays pronounced spatial heterogeneity throughout the water column (Fig. 1a), with sharp gradients near

continental margins, ridge systems, high-latitude regions and dust- or boundary-influenced waters (Supplementary Fig. 1). Surface concentrations are generally depleted across the subtropical open ocean, whereas intermediate and deep waters show elevated Fe concentrations with distinct regional patterns in the North Pacific, Indian Ocean and several margin-proximal regions (Supplementary Fig. 1). This patchiness is consistent with the short residence time and high reactivity of dissolved Fe observed previously, which make its concentration distribution sensitive to localized supply, scavenging and regeneration^{2,3,4,5,6}. By contrast, the reconstructed $\delta^{56}\text{Fe}$ distribution is smoother and more organized at basin scales, which may reflect the integrated effects of source composition, water-mass mixing and subsequent biogeochemical modification across larger spatial scales (Fig. 1c). Although light isotope anomalies occur in parts of the North Pacific and high-latitude ocean, much of the intermediate and deep ocean is predicted to exhibit coherent near-zero to positive values that broadly follow water-mass structure (Supplementary Fig. 2).

The differing predictor dependencies of the two reconstructions further highlight the distinct controls on DFe concentration and isotopic composition (Fig. 1b, 1d; Supplementary Fig. 3-6). DFe is most sensitive to variables associated with external supply and non-conservative cycling, including dust deposition, benthic input, biological activity, anthropogenic combustion and mixed-layer dynamics. In contrast, $\delta^{56}\text{DFe}$ is most strongly associated with salinity, with source-related variables contributing more secondarily. This does not mean that $\delta^{56}\text{DFe}$ are strictly conservative, but rather that their large-scale structure is more closely tied to water-mass organization than is the DFe concentration.

Regional variability in $\delta^{56}\text{Fe}$ endmembers

Source classification provides a first-order framework for resolving distinct Fe isotope regimes across the global ocean^{4,8}. We trained supervised classifiers using geochemical, isotopic, hydrographic, atmospheric and boundary-related predictors selected to differentiate background waters from those influenced by hydrothermal inputs, reductive sedimentary release and non-reductive sedimentary sources. Training labels were generated through K-means clustering and subsequently refined through expert-guided evaluation of their geochemical and spatial characteristics (see Methods). The resulting source-domain map therefore retains the geochemical structure of the labelled training data while enabling source regimes identified along well-characterized GEOTRACES sections to be extended across the global ocean.

The inferred isotope endmembers exhibit substantial regional variability (Fig. 2a),

indicating that major dissolved Fe source classes cannot be represented by single, invariant $\delta^{56}\text{Fe}$ values. Reductive sedimentary endmembers are isotopically light across all basins, with median values ranging from -0.15‰ in the Indian Ocean to -0.93‰ in the North Pacific, broadly consistent with near-margin observations of isotopically light DFe released under reducing conditions^{8,11,15,22,27}. A basin-scale regression based on AOU and oxygen reproduced a substantial fraction of the inter-basin variability in these apparent endmembers ($R^2 = 0.70$; Fig. 2b). Although this relationship is consistent with enhanced release of isotopically light Fe under more reducing depositional conditions, the isotope signal may also reflect subsequent transport and water-column processing. By contrast, non-reductive sedimentary endmembers occupy a considerably narrower isotopic range (-0.10 to $+0.17\text{‰}$) and remain generally close to crustal compositions, consistent with lithogenic Fe mobilized from more oxygenated sediments with comparatively limited isotope fractionation^{8,28}.

Hydrothermal endmembers exhibit pronounced regional variability, with median values ranging from -0.28‰ in the North Atlantic to $+0.38\text{‰}$ in the Arctic Ocean (Fig. 2a). These apparent endmembers are generally heavier than the isotopically light compositions commonly observed in high-temperature vent fluids, supporting the interpretation that they represent hydrothermal Fe that has undergone substantial modification during plume evolution rather than pristine vent-fluid signatures. Oxidation, sulfide precipitation, Fe(oxyhydr)oxide formation, particle scavenging and ligand stabilization can all alter the isotope composition of hydrothermal Fe before it is transported away from ridge systems^{11,29,30}. Temperature and oxygen together reproduced much of the basin-scale variability in the inferred hydrothermal endmembers ($R^2 = 0.75$; Fig. 2b), although the fitted relationship does not indicate a simple control by oxygenation alone. Instead, this regional variability likely integrates differences in plume processing, hydrographic setting and the selective retention of dissolved, colloidal or ligand-bound Fe during plume dispersal^{17,18,29,30}.

Positive $\delta^{56}\text{DFe}$ values are widespread in the ocean interior^{8,17,22,23}. Given the ongoing debate over their origin, we operationally define the background-associated endmember as the basin-scale isotopic baseline in regions lacking resolvable sedimentary or hydrothermal influence^{8,11,15}. This background-associated endmember exhibits pronounced inter-basin variability, with values close to zero in the North Pacific, Southern Ocean and Arctic Ocean, but substantially heavier signatures in the South Pacific, Indian and Atlantic oceans, reaching $+0.47\text{‰}$ in the North Atlantic (Fig. 2a). Atmospheric-related predictors, specifically dust and black-carbon aerosol optical depth, jointly reproduced a substantial fraction of this basin-scale variability ($R^2 = 0.68$;

Fig. 2b). This association is consistent with a potential contribution from atmospheric Fe inputs; in particular, relatively heavy $\delta^{56}\text{Fe}$ signatures in North Atlantic subsurface waters have previously been linked to the dissolution of Saharan dust-derived Fe⁸. Nevertheless, these basin-scale relationships do not establish a uniquely atmospheric origin. The background-associated endmember likely integrates atmospheric inputs with water-mass transport and internal Fe cycling, and the processes responsible for its regional isotopic structure therefore remain to be resolved.

Inter-basin variability in Fe sources

Building upon the isotope mass-balance framework of Conway and John⁸, we used basin-specific apparent endmembers to estimate the contributions of different Fe components to the DFe inventory and quantify their variability among ocean basins. Background-associated DFe dominates the global inventory, contributing a median of 86.4% (81.9–90.7%; 5th–95th percentile; Fig. 2c). Among the resolved external sources, reductive sedimentary Fe is the largest contributor at 8.1% (5.6–11.0%), whereas hydrothermal and non-reductive sedimentary Fe each contribute only ~2.6% (0.7–5.2% and 1.2–4.2%, respectively). The predominance of sediment-derived Fe among the resolved external components is broadly consistent with prognostic model results showing that marine sediments exert an important control on oceanic dissolved Fe distributions^{31,32}. These results indicate that, although external inputs sustain the oceanic Fe inventory, most dissolved Fe resides in a background-associated component shaped by biological cycling, scavenging, ligand stabilization, mixing and large-scale ocean circulation. Its inter-basin variability suggests that, despite attenuation of source-specific concentration and isotopic signatures during transport and internal processing, this component retains a regional imprint of Fe supply and cycling.

Sedimentary Fe forms the principal external source to the DFe inventory. Reductive sedimentary Fe contributes most prominently in the North Pacific, where it accounts for ~16.2% of the DFe inventory, followed by the Indian (7.8%), Arctic (7.6%) and South Pacific (6.8%) oceans. Smaller contributions occur in the North Atlantic (3.7%), South Atlantic (2.1%) and Southern Ocean (0.8%). The particularly strong North Pacific contribution is consistent with observations and modelling studies showing substantial benthic Fe supply from continental margins and enhanced Fe release under low-oxygen conditions^{31–33}. More broadly, the basin-scale distribution indicates that reductive sedimentary influence is not restricted to regions immediately adjacent to reducing margins, but can remain detectable within the ocean interior after lateral transport and water-mass redistribution^{27,32,34,35}. Nevertheless, non-reductive sedimentary Fe makes a smaller global contribution, although its relatively large

fraction in the North Atlantic is consistent with the substantial non-reductive sedimentary source previously quantified by Conway and John⁸. Importantly, the influence of sedimentary Fe is not confined to shallow coastal waters. Once released, sediment-derived dissolved and particulate Fe can be entrained into intermediate and deep water and transported far offshore through lateral advection and large-scale circulation^{27,32,34,35}. Organic complexation and reversible exchange with slowly sinking particles may further extend its residence time and sustain its transport into the basin interior, allowing margin-derived Fe signatures to persist over thousands of kilometres^{32,34,35}. Taken together, these sedimentary components show that margin-derived Fe is not merely a local influence, but a persistent contributor to the global dissolved Fe reservoir.

Hydrothermal Fe represents a smaller fraction of the global inventory, but its distribution remains biogeochemically important. The modest global contribution is consistent with strong near-field removal during plume evolution^{35,36}, whereas elevated fractions in the Arctic and South Pacific Ocean indicate that a stabilized hydrothermal signal can persist after vent-derived Fe escapes precipitation and scavenging. This interpretation agrees with evidence that organic complexation and nanoparticle stabilization can facilitate long-distance transport of hydrothermal Fe away from ridge systems^{37,38}. This persistence is particularly important where hydrothermal Fe is incorporated into deep and intermediate circulation pathways, because subsequent transport and upwelling can connect interior Fe reservoirs with Fe-limited surface waters, especially in the Southern Ocean³⁷. Hydrothermal inputs therefore contribute less to the global standing inventory than sedimentary sources, but may exert disproportionate regional effects where ridge systems, overturning pathways and biological Fe demand intersect.

Overall, the source inventory depicts a global Fe cycle in which distinct local inputs are progressively incorporated into a large background-associated reservoir, while sedimentary and hydrothermal signatures remain regionally detectable. As these inputs are transported away from their sources, local DFe concentration anomalies are rapidly diluted and reshaped by mixing and internal cycling, whereas their isotopic signatures may remain coherent over longer transport distances while continuing to evolve along water-mass pathways. This contrast raises the possibility that $\delta^{56}\text{DFe}$ retains a longer-lived record of source imprint than DFe concentration alone. Such persistence could help explain why the isotope field exhibits coherent basin-scale structure despite the strong spatial heterogeneity of DFe concentrations. We therefore examined how these isotopic signatures evolve along major water-mass pathways and whether their

persistence is related to circulation age.

The interplay between external sources and internal cycling

To investigate the processes that may shape background-associated $\delta^{56}\text{Fe}$ variability in the ocean interior, we used OMP analysis to resolve Atlantic water-mass structure and establish coherent transport pathways along which Fe isotope evolution could be examined⁶. The analysis reproduces the expected large-scale distribution of Atlantic water masses, with AABW largely confined to abyssal waters near the Antarctic margin, CDW dominating the deep Southern Ocean, and AAIW, SAIW and CW occupying intermediate and upper-ocean layers^{39,40}. Most importantly, NADW forms a coherent mid-depth pathway between approximately 1000 and 4000 m, extending southward from the high-latitude North Atlantic into the subtropical and South Atlantic (Fig. 3a). Its well-defined transport pathway and progressive ageing provide a natural framework for examining how Fe isotope signatures are modified after water-mass formation.

Along the NADW pathway, $\delta^{56}\text{DFe}$ increases rapidly in the northern Atlantic, approaches a broad plateau, and then declines toward the southern Atlantic (Fig. 3b). This evolution cannot be explained by a single external source or by a simple nutrient-like regeneration model. Progressive addition of isotopically heavy dust-derived Fe could, in principle, elevate $\delta^{56}\text{DFe}$ ⁸, and $\delta^{56}\text{DFe}$ broadly increases with cumulative dust exposure along the pathway. However, reproducing both the rapid enrichment and subsequent plateau would require a large and poorly constrained effective dust contribution (Fig. 3c), which should be accompanied by higher DFe concentrations. By contrast, DFe concentrations fluctuate without a sustained trend and covary only weakly with cumulative dust exposure, underscoring a decoupling between concentration and isotopic evolution along the NADW pathway (Supplementary Fig. 7). Because such an increase in DFe is not observed, conservative addition of dust-derived Fe alone is unlikely to explain the pathway-scale isotope trend, although atmospheric inputs may contribute to the initial NADW isotope signature. Biological uptake and remineralization may also precondition newly ventilated waters, as preferential removal of heavy DFe isotopes by phytoplankton could leave surface DFe relatively light, whereas remineralization of sinking material may return isotopically heavier DFe to depth^{8,19,24}. Yet a simple remineralization-dominated explanation is also insufficient, because it would be expected to produce a more systematic increase in DFe concentrations than is observed along the pathway. A bottom-up sedimentary explanation is also unlikely. Reductive sedimentary or margin-derived Fe sources are generally isotopically light relative to the NADW signal^{8,11,15}, so their progressive addition would tend to lower, rather than raise, $\delta^{56}\text{DFe}$. Although benthic input may

affect local DFe inventories²⁷, it cannot readily explain the observed enrichment, plateau and southward decline along the coherent NADW branch.

Internal Fe cycling is central to the evolution of Fe isotopes during the NADW evolution in time. As NADW ages southward, we expect DFe to be repeatedly exchanged among soluble, colloidal, ligand-bound and particle-reactive pools through complexation, aggregation, scavenging and remineralization^{2,3,5,6}. These processes may buffer DFe concentrations through compensating gains and losses, while still imparting a cumulative isotopic effect^{20,23,24}. Small fractionations during repeated phase exchange could progressively enrich the dissolved pool in heavy Fe isotopes, consistent with the strong relationship between $\delta^{56}\text{DFe}$ and circulation age (Fig. 3d). Similar interpretations have been proposed from basin-scale observations in both the Atlantic and Pacific Oceans, where DFe isotopes appear to evolve during transport despite relatively modest concentration changes^{21,23,24}. We parameterized this trend with an equilibrium isotope-fractionation model, in which NADW $\delta^{56}\text{DFe}$ approaches an apparent equilibrium composition with increasing ideal age. Relative to a fixed continental-material particle endmember, this equilibrium composition defines an apparent dissolved-particle fractionation factor ($\alpha = 1.0009$), summarizing the cumulative isotope effect of repeated internal Fe exchange. Farther south, this ageing-related enrichment is partly overprinted by mixing with CDW- and AABW-influenced waters, producing the decline in $\delta^{56}\text{DFe}$ at the southern end of the pathway. To conclude, the NADW analysis shows that, along a coherent overturning pathway, the predominantly background-associated seawater $\delta^{56}\text{DFe}$ signal integrates its initial source imprint with subsequent modification by internal Fe cycling, water-mass ageing and mixing with southern-sourced waters.

An integrated framework

The OCIM-based diagnostic decomposition separates dissolved Fe into a ventilation-related preformed component and an interior-generated non-preformed component, revealing how Fe concentrations and isotope signatures diverge after water-mass formation^{2,6}. The decomposition reveals a clear global-scale decoupling between dissolved Fe concentration and isotope structure. Preformed DFe explains only a small fraction of total DFe variability ($R^2 = 0.12$; Fig. 4a), indicating that concentrations are extensively modified after water-mass formation by remineralization, scavenging and external inputs^{2,3,5,6} (Supplementary Fig.8). By contrast, total $\delta^{56}\text{DFe}$ remains more closely related to preformed $\delta^{56}\text{DFe}$ ($R^2 = 0.45$; Fig. 4b), suggesting that the isotope distribution preserves a stronger imprint of surface-ocean source mixtures, ventilation and water-mass transport (Supplementary Fig.9).

The contrast in the role played by ocean circulation between DFe and $\delta^{56}\text{DFe}$ can be understood by distinguishing recycled Fe from newly introduced Fe. Recycled Fe generated through remineralization, particle dissolution and desorption of scavenged or aggregated Fe can substantially alter DFe concentrations while exerting limited isotopic influence if it is derived largely from the existing oceanic Fe pool⁴¹. In contrast, newly supplied Fe from sediments, hydrothermal systems, margin exchange or atmospheric deposition can modify $\delta^{56}\text{DFe}$ when its isotopic composition differs from the preformed background. As a result, $\delta^{56}\text{DFe}$ is most sensitive to isotopically distinct external inputs and cumulative fractionation during internal cycling.

Our results demonstrate that DFe concentration and $\delta^{56}\text{DFe}$ record distinct but complementary aspects of the marine Fe cycle. Concentrations primarily reflect the balance among recycling, external supply and scavenging, whereas $\delta^{56}\text{DFe}$ remains more strongly anchored to the preformed signal established at the surface and redistributed by ocean circulation. Together, these results support a framework in which regional Fe isotope signatures are established by source inputs and surface-ocean processing, redistributed by ocean circulation, and progressively modified by internal Fe cycling and mixing (Fig. 5). Consequently, $\delta^{56}\text{DFe}$ complements DFe concentration by integrating information on Fe sources, water-mass transport and subsequent biogeochemical processing. More broadly, these findings establish Fe isotopes as an integrative constraint on how external supply, ocean circulation and internal cycling jointly shape marine Fe biogeochemistry.

Methods

Producing global distributions of dissolved Fe concentrations and Fe isotopes

Machine-learning methods provide a practical way to extrapolate sparse dissolved Fe observations onto the global ocean grid and have been widely used to reconstruct climatologies of multiple trace metals^{42,43,44}. Here we obtained seawater dissolved Fe concentration and $\delta^{56}\text{Fe}$ observations from the GEOTRACES Intermediate Data Product 2025 (IDP2025)²⁶, retaining only data with a quality-control flag of 1. For both Fe concentration and isotope datasets, extreme values were excluded using a three-interquartile-range criterion to limit the influence of anomalous observations and derive representative multi-year climatological fields.

We evaluated three tree-based algorithms—XGBoost, Random Forest and LightGBM—for separate reconstructions of DFe concentration and $\delta^{56}\text{DFe}$. These algorithms were selected because of their strong performance on tabular Earth science datasets^{44,45}. Model evaluation and hyperparameter optimization were performed using nested cross-validation⁴⁵. The outer loop assessed predictive performance on held-out data, whereas the inner loop optimized hyperparameters within each training set. Both loops used ten folds stratified by deciles of the response variable. For each algorithm, 30 hyperparameter combinations were evaluated, including the number of trees, maximum tree depth, minimum samples required for node splitting and, for boosted-tree models, the learning rate. Global predictions were generated by combining the retained outer-fold models from the three algorithms used in the final ensembles. For both DFe and $\delta^{56}\text{DFe}$, the reconstruction comprised 30 models, with ten outer-fold models each from XGBoost, Random Forest and LightGBM. The three algorithms contributed equally to the ensemble. The spread among the 30 ensemble members was used to quantify between-member reconstruction uncertainty. (Supplementary Fig.10–13).

The models used 16 oceanographic, atmospheric and boundary-related predictors: nitrate, phosphate, silicate, dissolved oxygen, apparent oxygen utilization, salinity, potential density anomaly, temperature, mixed layer depth, chlorophyll-a, $\delta^3\text{He}$, dust aerosol optical depth, black carbon aerosol optical depth, height above bottom, distance to coast and sampling depth. Temperature, salinity, density, nutrients, oxygen, apparent oxygen utilization and mixed layer depth were obtained from World Ocean Atlas 2018⁴⁶. Surface chlorophyll-a was taken from the Copernicus Marine Service Global Ocean Biogeochemistry Hindcast product and averaged over January 2005 to December 2017. Dust and black carbon aerosol optical depth were obtained from the CAMS global

reanalysis (ECMWF Atmospheric Composition Reanalysis 4, EAC4) as monthly mean fields over the same period. Dust AOD was included as a proxy for natural atmospheric Fe supply, whereas black carbon AOD was used to represent Fe emissions from industrial and other high-temperature combustion sources^{8,14}. The $\delta^3\text{He}$ from previous OCIM studies was included as a hydrothermal proxy. Height above bottom was calculated from station bottom depth and sample depth, and distance to coast was taken from the NASA OBP/PacIOOS 0.01° ocean product. All gridded predictors were interpolated to observation locations and to the global model grid before prediction.

Classification of source-dominated regions and quantification of source inventories

Fe source-dominated regions were defined using a hybrid data-driven and expert-guided framework. We first identified subsurface GEOTRACES samples deeper than 250 m with paired DFe concentration and $\delta^{56}\text{DFe}$ measurements. Within individual cruises or sections, samples were clustered by K-means in standardized log-transformed DFe– $\delta^{56}\text{DFe}$ space. The resulting geochemical clusters were then interpreted in the context of bathymetry, hydrography, oxygen and redox conditions, $\delta^3\text{He}$ where available, basin geometry, known source settings and published observations. Spatially coherent section segments were then assigned to four dominant source-influence domains: background, hydrothermal, reductive sedimentary and non-reductive sedimentary. A small number of isotope-unconstrained hydrothermal anchor samples were additionally retained where independent hydrothermal evidence was strong and were assigned reduced training weights. This procedure follows previous section-based Fe isotope source-partitioning approaches, in which large-scale DFe and $\delta^{56}\text{DFe}$ distributions are used to identify regions influenced by distinct Fe sources⁸ (Supplementary Fig.14).

The labelled samples were used to train XGBoost, Random Forest and LightGBM source-domain classifiers using DFe, $\delta^{56}\text{DFe}$ and environmental and hydrographic predictors. The trained models were then applied to the global gridded fields to extrapolate source-influence domains beyond the representative GEOTRACES sections (Supplementary Fig.15). Classification probabilities were interpreted as support for domain membership rather than quantitative source fractions. Source-associated DFe inventories were estimated using basin-specific Fe-isotope mass balance. Apparent $\delta^{56}\text{DFe}$ endmembers were empirically derived from selected subsurface grid cells assigned to each source domain and weighted by grid-cell DFe inventory. Background and non-reductive sedimentary endmembers were represented by weighted medians, whereas hydrothermal and reductive sedimentary endmembers

were represented by lower weighted quantiles to reduce background dilution. These data-derived endmembers therefore represent empirical basin-scale source signatures that integrate source characteristics, mixing and subsequent water-column modification, rather than pure geochemical endmembers. Uncertainty in the apparent endmembers was quantified using a Monte Carlo framework. In each realization, DFe and $\delta^{56}\text{DFe}$ ensemble members were sampled and endmember values were recalculated within the fixed endmember cells, incorporating within-domain variability. Endmember estimates are reported as medians with 5th–95th percentile ranges.

For a grid cell i in basin b assigned to a dominant source-influence class k , where k represents hydrothermal, reductive sedimentary, or non-reductive sedimentary influence, the DFe inventory in that cell was treated as a binary mixture between a basin-specific background component and the corresponding apparent source component:

$$\delta^{56}\text{Fe}_i = (1 - f_{i,k})\delta^{56}\text{Fe}_{bg,b} + f_{i,k}\delta^{56}\text{Fe}_{k,b} \quad (1)$$

where $\delta^{56}\text{Fe}_i$ is the DFe isotope composition of grid cell i , $\delta^{56}\text{Fe}_{bg,b}$ is the background apparent endmember in basin b , $\delta^{56}\text{Fe}_{k,b}$ is the apparent endmember for source k in basin b , and $f_{i,k}$ represents the fraction of the DFe inventory in grid cell i associated with source k . Here, $f_{i,k}$ is referred as a DFe inventory fraction. The source fraction was calculated as:

$$f_{i,k} = \frac{\delta^{56}\text{Fe}_i - \delta^{56}\text{Fe}_{bg,b}}{\delta^{56}\text{Fe}_{k,b} - \delta^{56}\text{Fe}_{bg,b}} \quad (2)$$

Values of $f_{i,k}$ were constrained to the range $0 \leq f_{i,k} \leq 1$. Cases in which the source and background endmembers were too similar were treated as poorly resolved and were not used to infer a source fraction.

The source-associated DFe inventory for source k in basin b was calculated over the set of grid cells $\Omega_{b,k}$ classified as source-dominated by k :

$$I_{b,k} = \sum_{i \in \Omega_{b,k}} f_{i,k} [\text{Fe}]_i M_i \quad (3)$$

where $[\text{Fe}]_i$ is the DFe concentration in grid cell i , and M_i is the seawater mass of grid cell i . The background-associated inventory was calculated as the sum of all DFe in background-dominated cells plus the residual background component in non-background source-dominated cells:

$$I_{b,bg} = \sum_{i \in \Omega_{b,bg}} [\text{Fe}]_i M_i + \sum_{k \neq bg} \sum_{i \in \Omega_{b,k}} (1 - f_{i,k}) [\text{Fe}]_i M_i \quad (4)$$

The total DFe inventory in basin b was calculated as:

$$I_{b,total} = \sum_{i \in b} [\text{Fe}]_i M_i \quad (5)$$

The inventory fraction associated with each source class was then calculated as:

$$P_{b,k} = \frac{I_{b,k}}{I_{b,total}} \quad (6)$$

where $P_{b,k}$ is the fraction of the DFe inventory in basin b associated with source k .

Uncertainty in source-associated DFe inventories was propagated using Monte Carlo sampling of the empirical apparent-endmember uncertainties. In each realization, basin-specific apparent endmembers were sampled from their respective uncertainty distributions, source-associated fractions were recalculated through isotope mixing, and the resulting fractions were applied to grid-cell DFe inventories. Reported inventories and inventory fractions are represented by the median of the Monte Carlo ensemble, with uncertainty given by the 5th–95th percentile range.

Optimum Multiparameter Analysis

Optimum multiparameter analysis was used to quantify conservative water-mass mixing and to provide a physical framework for interpreting DFe and $\delta^{56}\text{DFe}$ variability in the Atlantic Ocean. The analysis followed the previously established basin-wide Atlantic OMP framework³⁹, in which each seawater sample is represented as a non-negative linear mixture of prescribed source water types and solved by weighted least squares with a mass-conservation constraint.

We applied optimum multiparameter analysis to Atlantic samples, where large-scale water-mass structure is well characterized and can be represented by a limited set of source water masses⁴⁰. The analysis was implemented using pyompa⁴⁷, in which each sample is solved as a non-negative linear mixture of prescribed source water types subject to a hard mass-conservation constraint. Seven source water types were prescribed: Central Water (CW), Antarctic Intermediate Water (AAIW), Subarctic Intermediate Water (SAIW), upper North Atlantic Deep Water (uNADW), lower North Atlantic Deep Water (lNADW), Circumpolar Deep Water (CDW) and Antarctic Bottom Water (AABW). These endmembers capture the principal upper-, intermediate-, deep- and bottom-water structure of the Atlantic basin. The OMP solution was constrained by conservative temperature, absolute salinity, oxygen, nitrate, phosphate, silicate and mass conservation. Conservative temperature, absolute salinity and mass conservation were assigned weights of 24, oxygen a weight of 7, and nitrate, phosphate and silicate weights of 2. In addition to the conservative thermohaline tracers, oxygen and nutrients were included as semi-conservative biogeochemical constraints to improve separation among water masses with similar temperature–salinity properties but distinct remineralization histories. Rather than explicitly forming classical composite tracers such as PO and NO, remineralization effects were represented in pyompa using fixed Redfield exchange ratios of $O_2 : PO_4 = -170 : 1$ and $NO_3 : PO_4 = 16 : 1$, allowing non-conservative nutrient and oxygen transformations to be incorporated through mathematical equation terms.

For each sample i , the OMP model solved for the fractional contribution f_{ik} of each source water type k . The fractions were constrained to be non-negative and to sum to one:

$$\begin{aligned} f_{ik} &\geq 0 \\ \sum_{k=1}^K f_{ik} &= 1 \end{aligned}$$

where $K = 7$ is the number of prescribed Atlantic source water types. The total NADW fraction was calculated as:

$$f_{i,NADW} = f_{i,uNADW} + f_{i,lNADW}$$

Because upper-ocean OMP solutions were associated with relatively large residuals in conservative temperature and absolute salinity, all subsequent water-mass-based

analyses were limited to samples deeper than 250 m, where the prescribed endmember framework provides more stable water-mass fractions.

OCIM-based diagnostic modelling

The ML predicted isotope ratio was converted to a heavy-isotope tracer as:

$$\text{Fe}_{iso} = \left(\frac{\delta^{56}\text{Fe}}{1000} + 1 \right) [\text{Fe}]$$

This framework allowed DFe concentrations and isotope compositions to be transported and diagnosed consistently within the same OCIM circulation field. To partition total DFe into preformed and non-preformed components, we additionally solved the tracer transport equations with no interior sources or sinks, prescribing DFe concentrations and isotope compositions in the upper two or three model layers from the machine-learning distributions. The simulations were implemented in AIBECS.jl, an open-source Julia framework for applying biogeochemical models to transport-matrix representations of ocean circulation^{43,48,49,50}.

Ideal age measures the time since a water parcel was last in contact with the atmosphere. It is calculated as an inert tracer whose age is restored to zero in the surface layer and increases at a constant rate in the ocean interior. Therefore, ideal age represents the advective–diffusive transport timescale of a water mass. It does not include biogeochemical effects.

Following the standard AIBECS ideal-age formulation, the ideal age tracer is solved as:

$$\left(\frac{\partial}{\partial t} + \mathbf{T} \right) \mathbf{a} = 1 - \chi_{\text{surf}} \frac{\mathbf{a}}{\tau}$$

where $\mathbf{a}$ is the ideal age vector, $\mathbf{T}$ is the OCIM2 transport matrix, and τ is a short restoring timescale. The restoring term forces the surface age to approach zero, while the source term allows age to increase linearly during interior transport^{48,49,50}.

Data availability

The dissolved Fe concentration and $\delta^{56}\text{DFe}$ observations used for the machine-learning reconstructions were obtained from the GEOTRACES Intermediate Data Product 2025 (IDP2025), as described in the Methods. Source data underlying all figures are provided with this paper. The reconstructed global three-dimensional distributions of DFe and

$\delta^{56}\text{DFe}$ and additional derived products, including source-domain classifications, basin-specific apparent isotope endmembers, source-associated DFe inventories and circulation-diagnostic products, together with their associated uncertainties, will be made available to editors and reviewers upon request during peer review and will be publicly archived upon publication.

Code availability

The custom code used for machine-learning reconstruction, source classification and partitioning, optimum multiparameter analysis, OCIM-based diagnostic modelling and subsequent analyses has been submitted as Supplementary Software for peer review and will be publicly archived upon publication.

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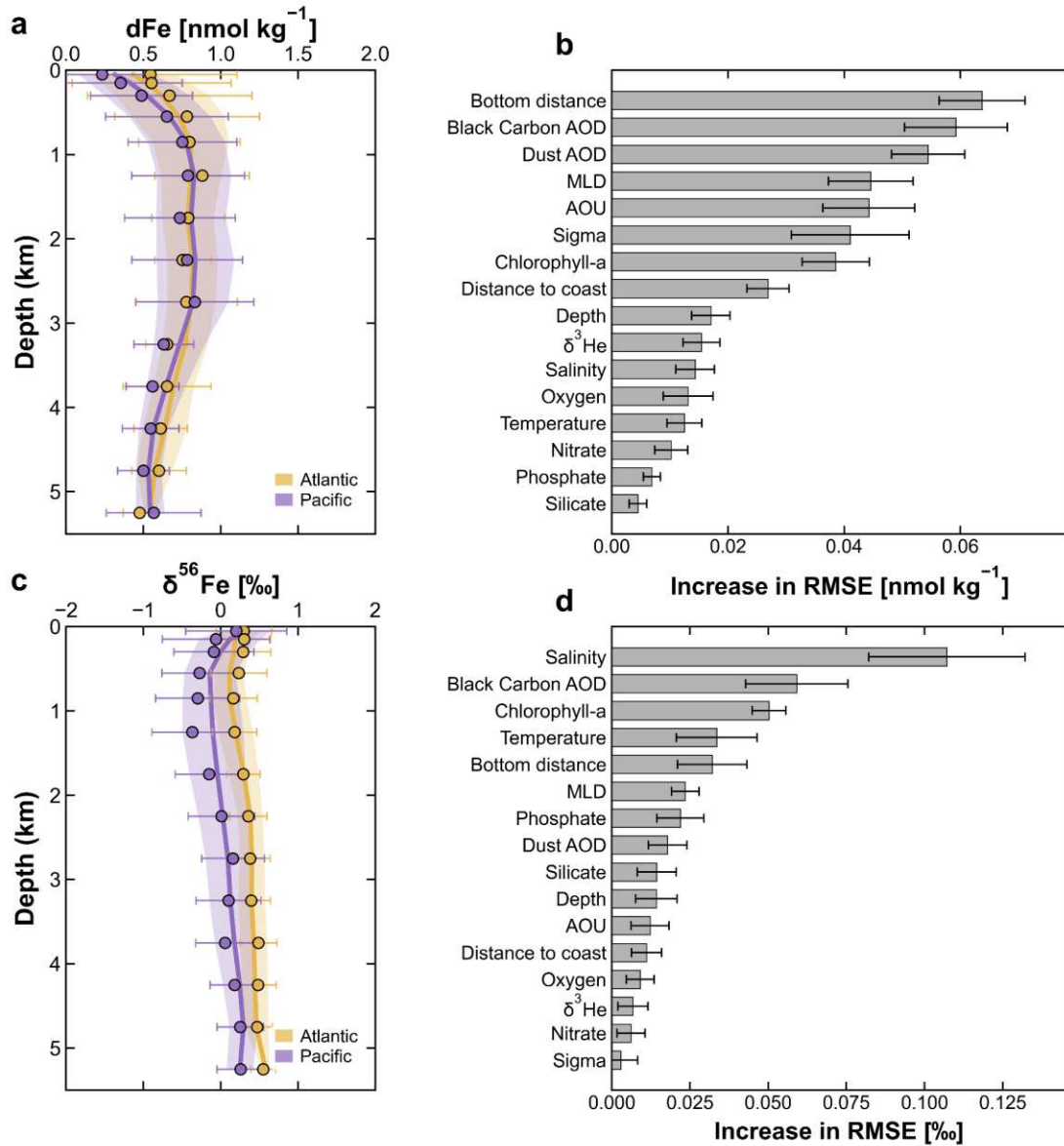
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Author contributions

R.Z. conceptualized and supervised the study. W.K. developed the methodology, performed the analyses and modelling, and prepared the figures with supervision from A.T. and R.Z.. W.K., A.T and R.Z. drafted the manuscript.

Competing interests

The authors declare no competing financial interests.



680

681 **Fig. 1: Depth distributions and predictor importance for dissolved Fe and Fe**
 682 **isotopes. (a)** Depth profiles of dissolved Fe (dFe) in the Atlantic and Pacific oceans.
 683 Observations are shown as dots with horizontal error bars, while model predictions are
 684 shown as lines with shaded areas indicating 1 standard deviation. **(b)** Predictor
 685 importance for dFe, expressed as the increase in RMSE after permutation of each
 686 variable. **(c)** Depth profiles of dissolved δ⁵⁶Fe in the Atlantic and Pacific oceans, shown
 687 as in panel (a). **(d)** Predictor importance for dissolved δ⁵⁶Fe, expressed as the increase
 688 in RMSE after permutation of each variable. In panels (b) and (d), horizontal bars show
 689 mean permutation importance, with error bars indicating uncertainty; larger RMSE
 690 increases denote greater predictive importance.

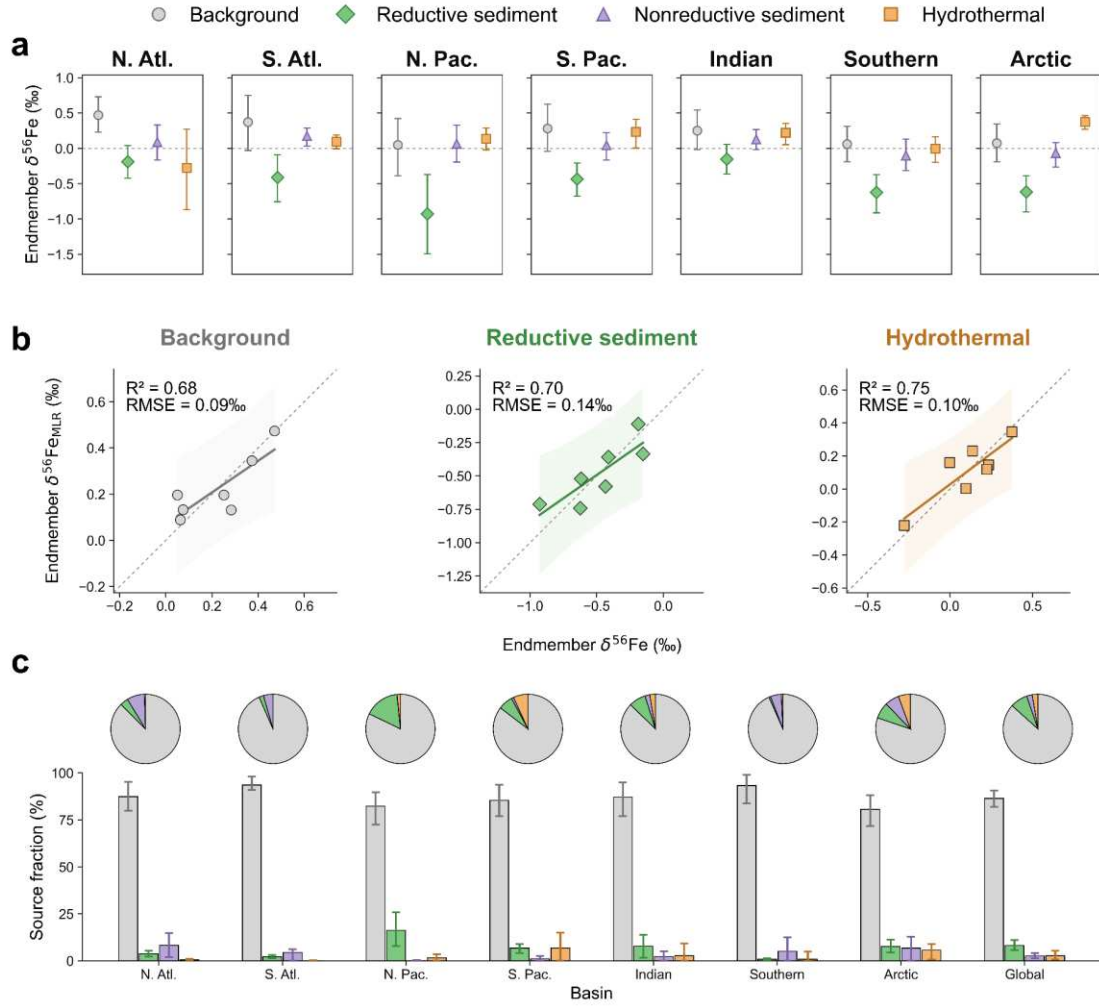
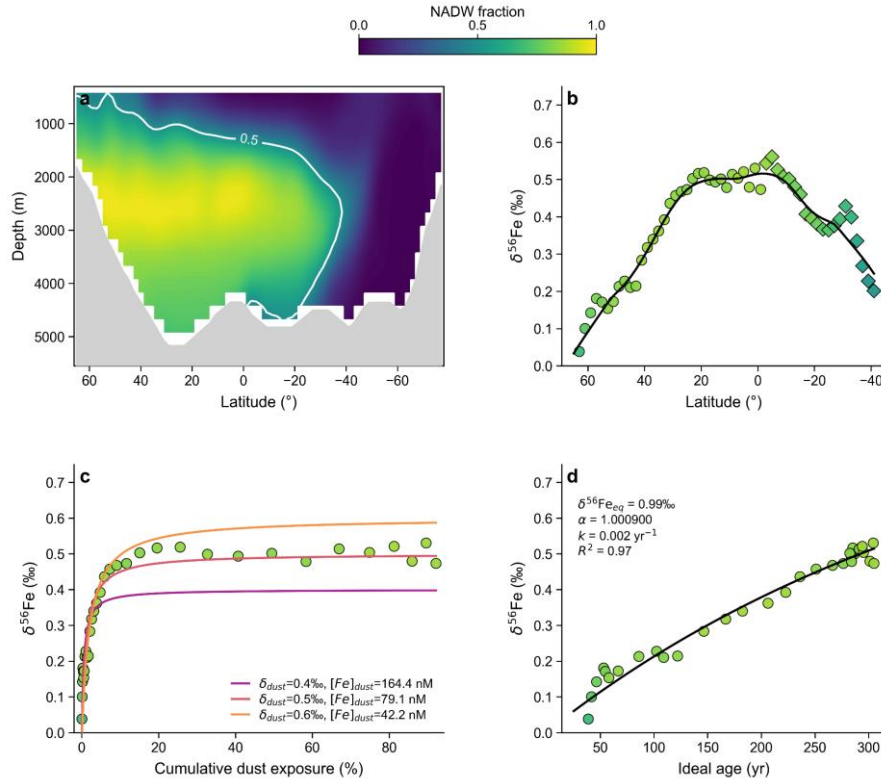


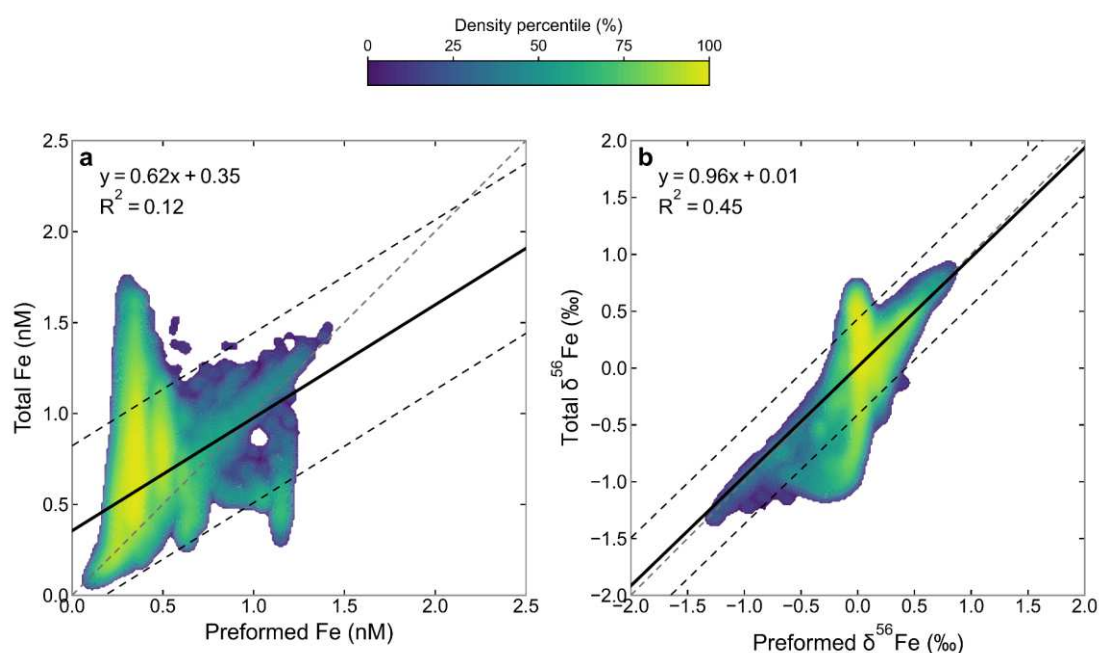
Fig. 2: Basin-scale Fe isotope endmembers, inventory fractions, and relationships with environmental parameters. (a) Basin-specific apparent $\delta^{56}\text{Fe}$ endmembers for background, hydrothermal, reductive sedimentary, and non-reductive sedimentary Fe components. Points show Monte Carlo medians, and error bars indicate the 5th–95th percentile ranges. (b) Comparison between basin-scale Monte Carlo median apparent endmember $\delta^{56}\text{Fe}$ values and those predicted by multiple linear regression for the background, reductive sedimentary, and hydrothermal components. The dashed line denotes the 1:1 relationship, and shaded envelopes indicate prediction uncertainty. For the background endmember, the predicted relationship is $\delta^{56}\text{Fe}_{\text{MLR}} = 0.056 + 3.83 \times \text{Dust AOD} + 25.02 \times \text{Black Carbon AOD}$. For the reductive sedimentary endmember, $\delta^{56}\text{Fe}_{\text{MLR}} = 3.88 - 0.015 \times \text{AOU} - 0.013 \times \text{Oxygen}$. For the hydrothermal endmember, $\delta^{56}\text{Fe}_{\text{MLR}} = 0.970 - 0.208 \times \text{Temperature} - 0.00258 \times \text{Oxygen}$. (c) Relative inventory fractions of the four Fe components for the global ocean and individual basins, expressed as percentages of the total dissolved Fe inventory.



706

707 **Fig. 3: NADW-pathway diagnostics linking water-mass structure, dust exposure,**
708 **circulation age and dissolved Fe isotopic composition. (a)** Meridional section of the
709 OMP-derived North Atlantic Deep Water (NADW) fraction in the Atlantic Ocean. Grey
710 shading indicates bathymetry, and the white contour marks the 0.5 NADW-fraction
711 boundary. **(b)** Binned dissolved $\delta^{56}\text{Fe}$ values along the inferred NADW transport
712 pathway plotted against latitude. Circles represent the rising and plateau segments,
713 whereas diamonds mark the southern declining segment. The black curve shows a
714 LOESS fit to the binned $\delta^{56}\text{Fe}$ values, highlighting a rapid increase from the northern
715 source region, a broad mid-pathway plateau and a decline toward the South Atlantic. **(c)**
716 Isotope mass-balance constraints on the $\delta^{56}\text{Fe}$ –dust exposure relationship, evaluated for
717 conservative mixing between an initial NADW endmember and dust-derived Fe
718 endmembers with prescribed $\delta^{56}\text{Fe}_{\text{dust}}$ values and corresponding $[\text{Fe}]_{\text{dust}}$ concentrations.
719 Cumulative dust exposure was calculated from dust aerosol optical depth accumulated
720 along the north-to-south pathway and scaled to 0–100%. **(d)** Dissolved $\delta^{56}\text{Fe}$ plotted
721 against ideal age for the rising and plateau segments of the NADW pathway. The black
722 curve shows an equilibrium isotope fractionation model of the form $\delta^{56}\text{Fe} = \delta^{56}\text{Fe}_{\text{eq}} -$
723 $(\delta^{56}\text{Fe}_{\text{eq}} - \delta^{56}\text{Fe}_0)e^{-kt}$, where $\delta^{56}\text{Fe}_0$ and $\delta^{56}\text{Fe}_{\text{eq}}$ denote the initial and equilibrium
724 isotopic compositions, respectively, and k is the estimated rate constant. The fitted
725 $\delta^{56}\text{Fe}_{\text{eq}}$ is further expressed relative to a fixed crustal particle endmember, $\delta^{56}\text{Fe}_{\text{particle}} =$
726 $+0.09\text{‰}$ ^{8,15,23}, to estimate the apparent dissolved–particle isotope fractionation factor α .

727



728

729 **Fig. 4: Comparison between total and preformed dissolved Fe concentration and**
 730 **Fe isotope composition in the global ocean.** The total and preformed fields are derived
 731 from the OCIM-based diagnostic decomposition. Joint probability density function
 732 plots of (a) total dissolved Fe concentration versus preformed Fe concentration, and (b)
 733 total $\delta^{56}\text{Fe}$ versus preformed $\delta^{56}\text{Fe}$. Linear regression analyses are applied to show the
 734 relationships between the two datasets, with regression equations and R^2 values
 735 reported in each panel. Solid black lines indicate the fitted regressions, while dashed
 736 lines denote the 1:1 relationship and reference offsets.

737

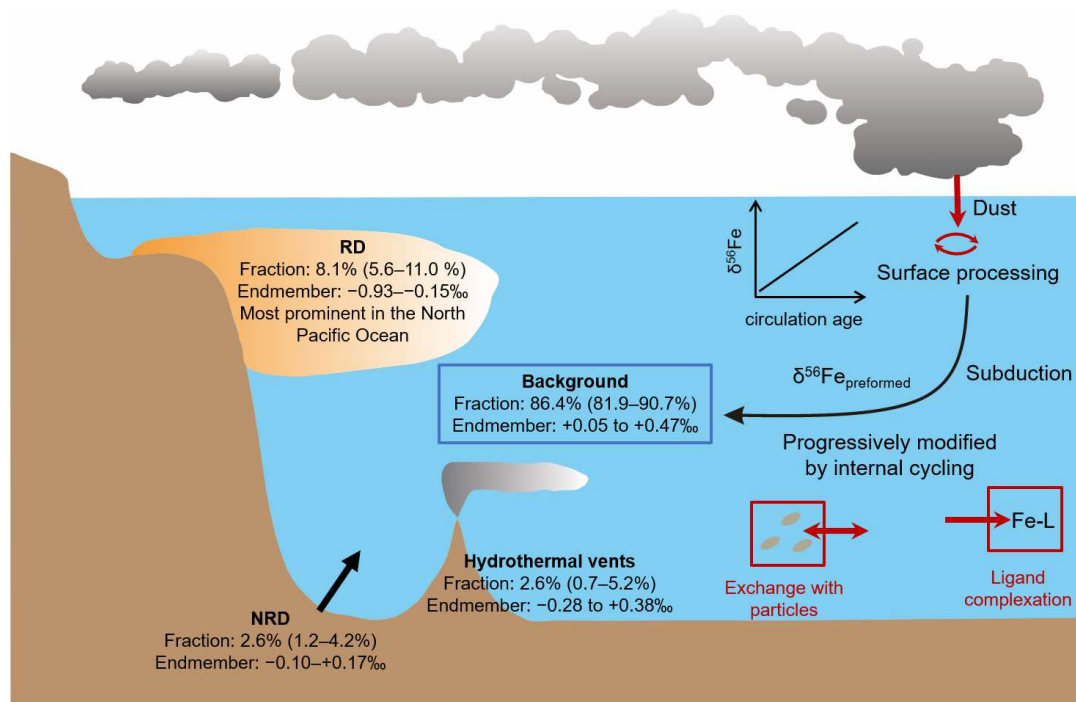


Fig. 5: Conceptual framework linking dissolved Fe sources, preformed isotope signatures and internal modification in the marine Fe cycle. The schematic summarizes the principal dissolved Fe source domains and isotope modification processes resolved in this study. Percentages denote median contributions to the global dissolved Fe inventory, with 5th–95th percentile ranges shown in parentheses, whereas $\delta^{56}\text{Fe}$ ranges represent basin-specific median apparent endmembers. Background-associated Fe dominates the global inventory [86.4% (81.9–90.7%); $\delta^{56}\text{Fe} = +0.05$ to $+0.47$ ‰], followed by reductive sedimentary Fe [RD; 8.1% (5.6–11.0%); -0.93 to -0.15 ‰], hydrothermal Fe [2.6% (0.7–5.2%); -0.28 to $+0.38$ ‰] and non-reductive sedimentary Fe [NRD; 2.6% (1.2–4.2%); -0.10 to $+0.17$ ‰]. Atmospheric and surface-ocean processes establish preformed $\delta^{56}\text{Fe}$ signatures that are transported into the ocean interior and subsequently modified by internal Fe cycling along circulation pathways. The schematic is adapted from the GEOTRACES Science Plan and modified to emphasize the source partitioning and isotope evolution resolved here. **Fe-L**, Fe–ligand complex; **RD**, reductive sedimentary Fe; **NRD**, non-reductive sedimentary Fe; $\delta^{56}\text{Fe}_{\text{preformed}}$, preformed Fe isotope composition.

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