

## NERC Shelf Sea Biogeochemistry Programme

### WP3 THE SUPPLY OF IRON FROM SHELF SEDIMENTS TO THE OCEAN

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**Overview:** Low iron (Fe) concentrations control productivity, phytoplankton community structure and carbon cycling in 25 % of the open ocean. Iron concentrations are tightly coupled to Fe supply, and Fe fluxes from shelf seas to the open ocean are poorly constrained, although estimates indicate they could be 2-10 times higher than atmospheric inputs and thus potentially a major contributor to the oceanic Fe cycle. The goal of this project is to quantify Fe fluxes from NW European shelf seas to the adjacent North Atlantic Ocean. Our goal will be realised during cruises in the Celtic Sea as part of the Shelf Sea Biogeochemistry Research Programme (SSB), which will provide the physical and chemical context for our study. We will utilise trace metal clean sampling techniques, with associated physical diffusion and advection measurements, to determine the supply of dissolved, colloidal and particulate forms of Fe from sediments and their subsequent fate in shelf sea waters and during export to the North Atlantic Ocean. We will use Fe isotopes, physical-chemical Fe species characterisation and geochemical tracers to quantify the Fe supply, attenuation and export processes. To our knowledge this will be the first study to follow the “Fe footprint” from the sediment to the open ocean in such a comprehensive manner.

Shelf edge biogeochemical processes (Fig. 1) that result in Fe export to the ocean are not well understood. It has been suggested that shelf width and contact with reducing sediments are important controls with respect to Fe fluxes<sup>1,2</sup>. Furthermore, concentrations of Fe in offshore plumes are greater than predicted by thermodynamic models indicating that Fe nanoparticles and Fe ligands stabilise dFe and limit scavenging<sup>2,3</sup>. Key questions thus remain about the magnitude and significance of Fe fluxes from the shelf to the open ocean, and specifically the impact of (i) Fe fluxes from the sediment to the benthic boundary layer, (ii) Fe stabilisation by organic ligands and nanoparticles, (iii) rates of Fe scavenging, and (iv) the oceanic water mass transport regime. Thus the 4 main hypotheses to be tested and related approaches to be taken are:

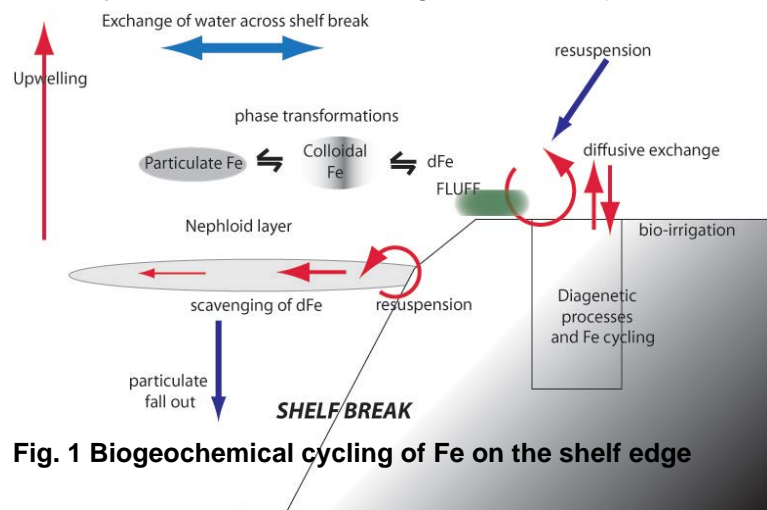


Fig. 1 Biogeochemical cycling of Fe on the shelf edge

**Hypothesis 1. The flux and isotopic signature of iron from shelf sediments is dependent on the physical and chemical characteristics of the sedimentary environment and overlying water column.**

a) *Investigate the redox state and size fractionation of dFe in pore waters and mechanisms of Fe mobilisation in cohesive and non-cohesive sediments.* Sediment cores of both cohesive and non-cohesive sediments will be collected on all cruises, by either box core or megacore techniques<sup>4-6</sup>. Pore waters will be obtained by shipboard rhizon sampling<sup>4-6</sup>. Samples will be divided for Fe redox speciation, Fe isotopes, sFe (truly soluble), dFe (dissolved <0.2µm), and macro-nutrient and sulfur species. Redox conditions will be characterized using an oxygen microsensor and pH microelectrode to yield high resolution sediment profiles<sup>5</sup>.

b) *Determine the relative importance of dissimilatory Fe reduction in cohesive and non-cohesive sediments, and establish the isotope signature of Fe released to pore waters.* Analyses of Fe isotope signatures in sediment pore fluids, and in benthic incubation experiments, will indicate the importance of dissimilatory reduction of solid phase Fe in the North Sea continental shelf setting.

**Hypothesis 2. Interaction with sediment particles and phytodetritus close to the seafloor will significantly modify fluxes of Fe to the overlying water column.**

a) *Determine the fate and different physico-chemical forms of Fe within the SWI-BBL (sea water interface- benthic boundary layer) zone.* Microcosm incubation experiments will be conducted, iron

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isotope tracer experiments (utilising  $^{58}\text{Fe}$ ) will also be used to investigate Fe partitioning during sediment re-suspension experiments, to develop a temporal and mechanistic understanding of (a) partitioning between sFe, dFe and pFe (particulate) phases, and (b) the impact of particle suspensions on the dFe concentration of seawater.

b) *Investigate the impact of phytodetritus on the concentration and form of Fe within the SWI-BBL zone.* Stable isotope labelled phytodetritus (from a crashed lab grown culture that had been spiked with  $^{58}\text{Fe}$ ) will be added to SWI incubations, and the phytodetrital- $^{58}\text{Fe}$  will be tracked between dissolved, colloidal and particulate phases over a period of days, with parallel descriptions of oxygen concentration, Fe speciation and pH.

**Hypothesis 3. Fe export from the shelf to the ocean will be determined by the fate of Fe species within the water column during transport.**

a) *Determine size fractionation and concentrations of dFe (sFe, cFe) and pFe in onshore/ offshore transects over the shelf edge.* At each station, vertical profiles of Fe (II), dFe, sFe, dFe, leachable particulate Fe (LPFe) and pFe will be determined, as well as organic speciation of Fe. Shipboard experiments will follow changes in form of Fe with time.

b) Identify and quantify changes in physical form, speciation and isotopic composition of dFe and pFe during off shelf transport. We will investigate specific physico-chemical characteristics associated with Fe speciation (sFe, Fe colloids and nanoparticles (NPs) and pFe) that influence offshore transport. Work will include determining the concentration of specific Fe-organic complexes (Fe siderophores and hemes) in sFe, dFe and pFe fractions, b) visualising particles and c) size fractionation and obtaining characteristics of Fe colloids and NPs.

**Hypothesis 4. Export of Fe to the open ocean is driven by transport along isopycnals.**

a) *Follow changes in Fe concentration and form along off shelf isopycnals.*

Samples will be collected from nepheloid layers advected along particular isopycnals, identified on CTD downcasts and from glider and autosub long range surveys, rather than depth horizons, in order to directly examine the relationship between density boundaries and offshore Fe transport.

b) *Assess the flux of Fe from the Celtic Sea to the adjacent Atlantic, using measured Fe concentrations and water mass fluxes from Ra measurements and available models.*

Four Ra isotopes with half lives of 3.6 days, 11.4 days, 5.8 years and 1600 years, released together with dFe from sediments, therefore provide an excellent means to quantify near-shore as well as off-shore transport fluxes<sup>7</sup>. Whereas the longer-lived isotopes are used to determine larger-scale off-shore mixing<sup>8,9</sup>, the two shorter-lived isotopes have recently been proven to be powerful tools in the study of dFe fluxes near shore<sup>10</sup>. Large volume samples (~100 L) will be processed through manganese coated fibres. Short-lived isotopes will be counted at sea using a radium delayed coincidence counter, then recounted for the naturally supported isotopes. Models will come from the FASTNet programme, and be used with shipboard measurements for water fluxes.

**Ship Programme.** Work will focus on the Celtic Sea and adjacent shelf break system where detailed physical information on water fluxes and movement will be available, and both main sediment types to be studied are to be found during three seasonal cruises. Work in this area will interface very well with WPs 1 & 2. The work at sea will include both a series of water column profiles extending off shelf, and collection of cohesive and non-cohesive sediments.

**Links to other Shelf Sea studies**

The project links to DEFRA through inclusion of CEFAS work on geochemical profiling of sediment cores to aid interpretation of carbon utilisation in these materials

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