

Isotopic composition of sedimentary Fe as tracer of Arctic Ocean biogeochemical pathways

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Introduction

Iron is both an **essential micronutrient** for primary production in the ocean and a **key redox element** providing insights on organic matter metabolism at the sea floor.

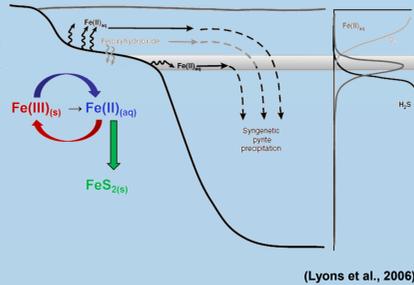
→ Sources and sinks of Fe remain nevertheless poorly documented in the open ocean.

Recent studies highlighted that coastal sediments could be an important source of dissolved Fe in the water column, particularly in oxygen-minimum zones or euxinic basins (Scholz *et al.*, 2014)

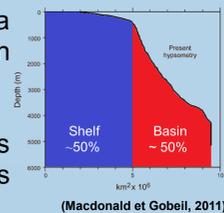
The continental margin in the Arctic Ocean (AO) comprises about 50% of the total area of this ocean. The AO is therefore an exceptional laboratory to investigate shelf-basin interactions and their impacts on biogeochemical cycles.

Here, we have determined the profiles of the concentrations and isotopic compositions of total Fe (**Fe_{Total}**), reactive Fe (**Fe_{Reactive}**) and pyrite Fe (**Fe_{Pyrite}**) in sediment cores collected in AO shelf, slope and basin.

Our objective is to improve understanding of the influence of sediment diagenesis on the AO Fe cycle.

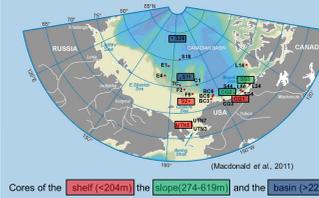


(Lyons et al., 2006)



(Macdonald et Gobeil, 2011)

Sampling sites



(Macdonald et al., 2011)

Figure 1. Seven sediment box-cores from the AO were analyzed for this study. Cores UTN5, S2 and CG1 were collected on the shelf at water depths of 51, 52 and 204 m, respectively, cores SS3 and CG2 on the slope at depths of 274 and 619 m, respectively, and cores S11 and S26 from the AO interior at depths of 2265 m and 3130 m, respectively.

Method

Fe_{Total} was obtained after a complete digestion of the sediment with a mixture of HNO₃, HClO₄ and HF. Fe_{Reactive} was extracted from the sediments with a 1 M HCl solution during 24 h. We assume that a diluted HCl solution removes a very minor portion of Fe from silicate minerals but solubilizes quantitatively Fe oxyhydroxides and Fe monosulfide. Fe_{Pyrite} is operationally defined as the residual Fe left over after having successively extracted the sediments with HCl and HF (Lord, 1982).

Fe concentrations were determined with an ICP-AES, while isotopic measurements were achieved with an HR-MC-ICP-MS following purification through a standard anion exchange protocol (Bio Rad AG1 X4; Beard *et al.* (1999)). The average reproducibility of the measurements, determined by triplicate analyses of each sample, was ±0.06‰. δ⁵⁶Fe obtained for BHVO-2 standard (0.14 ± 0.05‰) was in good agreement with the value found in the literature (0.114 ± 0.011‰) (Craddock P.R. and N. Dauphas, 2010).

Results

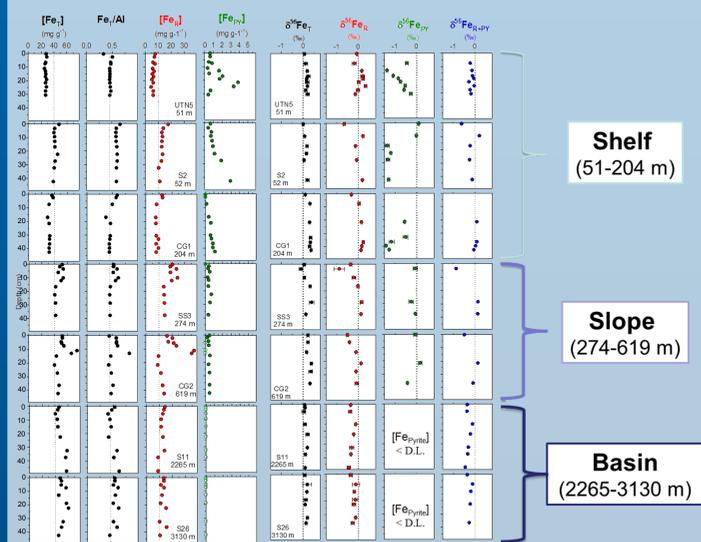


Figure 1. Vertical profiles of the concentrations of Fe_{Total}, Fe_{Reactive} and Fe_{Pyrite} and of the Fe_{Total}/Al ratio in the sediments. Empty symbols represent values below detection limit (~0.1 mg g⁻¹ for Fe_{Pyrite}). Vertical profiles of δ⁵⁶Fe_{Total}, δ⁵⁶Fe_{Reactive} and δ⁵⁶Fe_{Pyrite} in the sediments, where δ⁵⁶Fe = [(⁵⁶Fe/⁵⁴Fe)_{sample} / (⁵⁶Fe/⁵⁴Fe)_{IRMM-14} - 1] × 10³

Key points:

- The profiles of Fe_{Total} and the Fe_{Total}/Al ratios indicate that slope and basin sediments are enriched in Fe relative to shelf sediments.
- The profiles of Fe_{Reactive} suggest that the Fe enrichment in slope and basin sediments is due to the higher presence of Fe oxyhydroxides.
- Fe_{Pyrite} is only abundant in shelf sediments (UTN5, S2 and CG1) where it increases with depth below the sediment-water interface, reflecting an organic carbon metabolism coupled to sulfate reduction.
- δ⁵⁶Fe_{Total} values are always positive (>0‰), while some of the δ⁵⁶Fe_{Reactive} and most of the δ⁵⁶Fe_{Pyrite} are negative.
- In surface sediments of the slope cores, where high concentrations of Fe_{Reactive} were measured, the δ⁵⁶Fe_{Reactive} values are slightly but significantly lower than at depth in the cores.

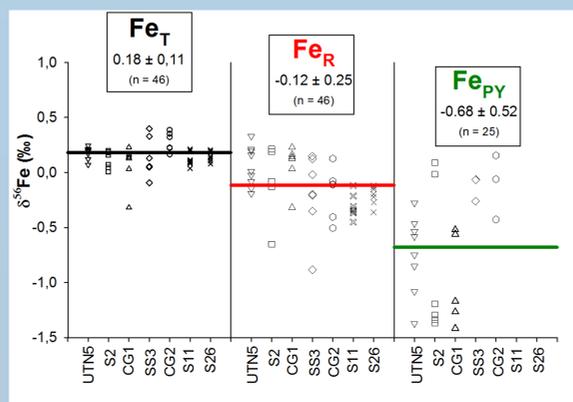


Figure 2. Graphic illustrating differences between δ⁵⁶Fe_{Total}, δ⁵⁶Fe_{Reactive} and δ⁵⁶Fe_{Pyrite}

Key points:

- Fe_{Reactive} is enriched in light isotopes (δ⁵⁶Fe_{Reactive} = -0.12 ± 0.25‰; n=46) compared to Fe_{Total} (δ⁵⁶Fe_{Total} = +0.18 ± 0.11‰; n=49), but depleted in light isotopes relative to Fe_{Pyrite} (δ⁵⁶Fe_{Pyrite} = -0.68 ± 0.52‰; n=25);
- Early diagenetic processes produced Fe authigenic phases (oxyhydroxides, pyrite) that are enriched in ⁵⁴Fe.

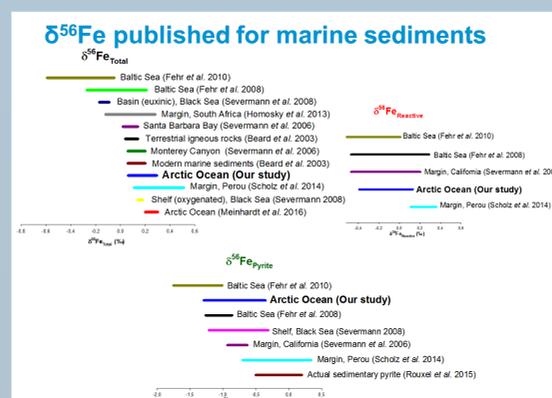


Figure 3. Comparison of the δ⁵⁶Fe values obtained in this project with published values. The results of the present study are in the range of those measured in other continental margin sediments.

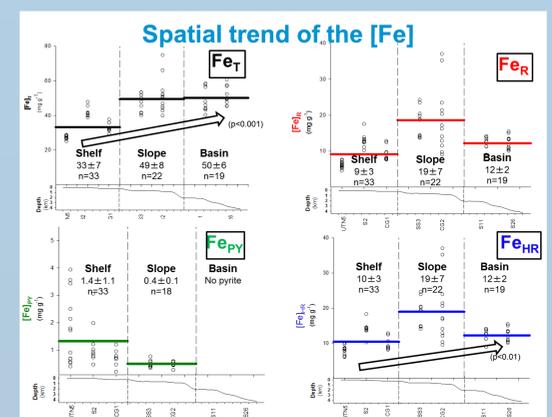


Figure 4. Spatial variations of Fe concentrations between shelf, slope and basin sediments

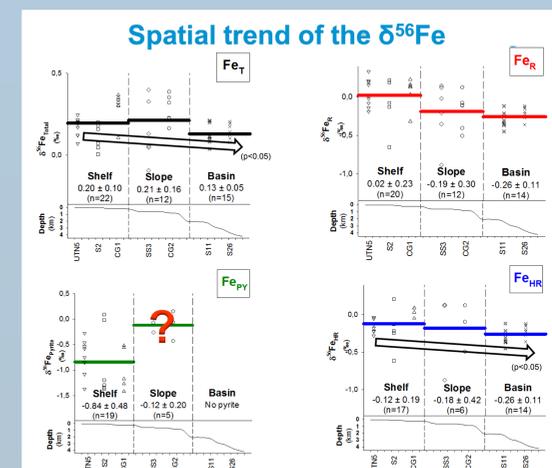


Figure 5. Spatial variations of δ⁵⁶Fe between shelf, slope and basin sediments. Fe_{HR} is defined as Fe_{Reactive} + Fe_{Pyrite}.

Key points:

- The concentrations of Fe_{Total}, Fe_{Reactive} and Fe_{HR} are higher in slope and basin sediments than in shelf sediments.
- Values of δ⁵⁶Fe_{Total}, δ⁵⁶Fe_{Reactive} and δ⁵⁶Fe_{HR} in basin sediments are significantly lower than in shelf and slope sediments.

Concluding remarks

- Elevated concentrations of Fe_{Reactive} and Fe_{HR} in basin sediments and their light isotopic composition compared to those of shelf sediments are consistent with the notion that Fe recycled through early diagenesis in shelf sediments may migrate and be deposited in basin sediments.
- Sedimentary-derived Fe may be transported in the water column as nanoparticles, colloids or organic complexes, as suggested in other studies (Scholz *et al.* 2016).
- Sea-level fluctuations over glacial-interglacial periods may play a critical role on the large-scale cycle of Fe in the AO, as it was proposed for Mn (Macdonald and Gobeil, 2011).

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References

F. Scholz, S. Severmann, J. McManus, A. Noffke, U. Lominiz, C. Hensen, *Chemical Geology*, 389 (2014) 48-59.
B.L. Beard, C.M. Johnson, *Geochimica et Cosmochimica Acta*, 63 (1999) 1653-1660.
S. Severmann, C.M. Johnson, B.L. Beard, J. McManus, *Geochimica et Cosmochimica Acta*, 70 (2006) 2006-2022.
M.A. Fehr, P.S. Andersson, U. Hålenius, C.-M. Mörtz, *Geochimica et Cosmochimica Acta*, 72 (2008) 807-826.
W.B. Homoky, S.G. John, T.M. Conway, R.A. Mills, *Nat Commun*, 4 (2013) 2143.
A.K. Meinhardt, C. März, S. Schuth, K.A. Lettmann, B. Schlegel, J.G. Wolff, H.J. Brumsack, *Geochimica et Cosmochimica Acta*, 188 (2016) 125-146.