

# Elements and elemental species in sediment core as proxy of the climate variability and marine biogeochemical processes

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## Abstract

Trace elements and their isotopes (TEI) in marine sediments have a potential to trace sources of sedimentation, paleo-circulation, productivity, depositional redox conditions, diagenesis and climate variations.

Aim of the study was to investigate the possibility to use elemental speciation by sequential fractionation in sediment as a proxy of evaluation of the climate variability and marine biogeochemical processes. The concentration of the extractable forms of elements was analyzed in 2 cm sections of four sediments cores (up to 5 m long) from the Gulf of Gdańsk, Poland and Norway (Oslofjord, Trondheimsfjord and Balsfjord, Tromsø). The samples were analyzed for 62 elements applying the modified BCR sequential extraction procedure and HR-ICP-MS. Further, we examined the element concentrations and their ratios in relation to organic carbon, total nitrogen,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , and pigments analyzed in the same samples. TEI distribution, fractionation and TEI ratios are discussed in view of paleo-environmental conditions that prevailed during their deposition or mobilization in the sediments from Gulf of Gdańsk.

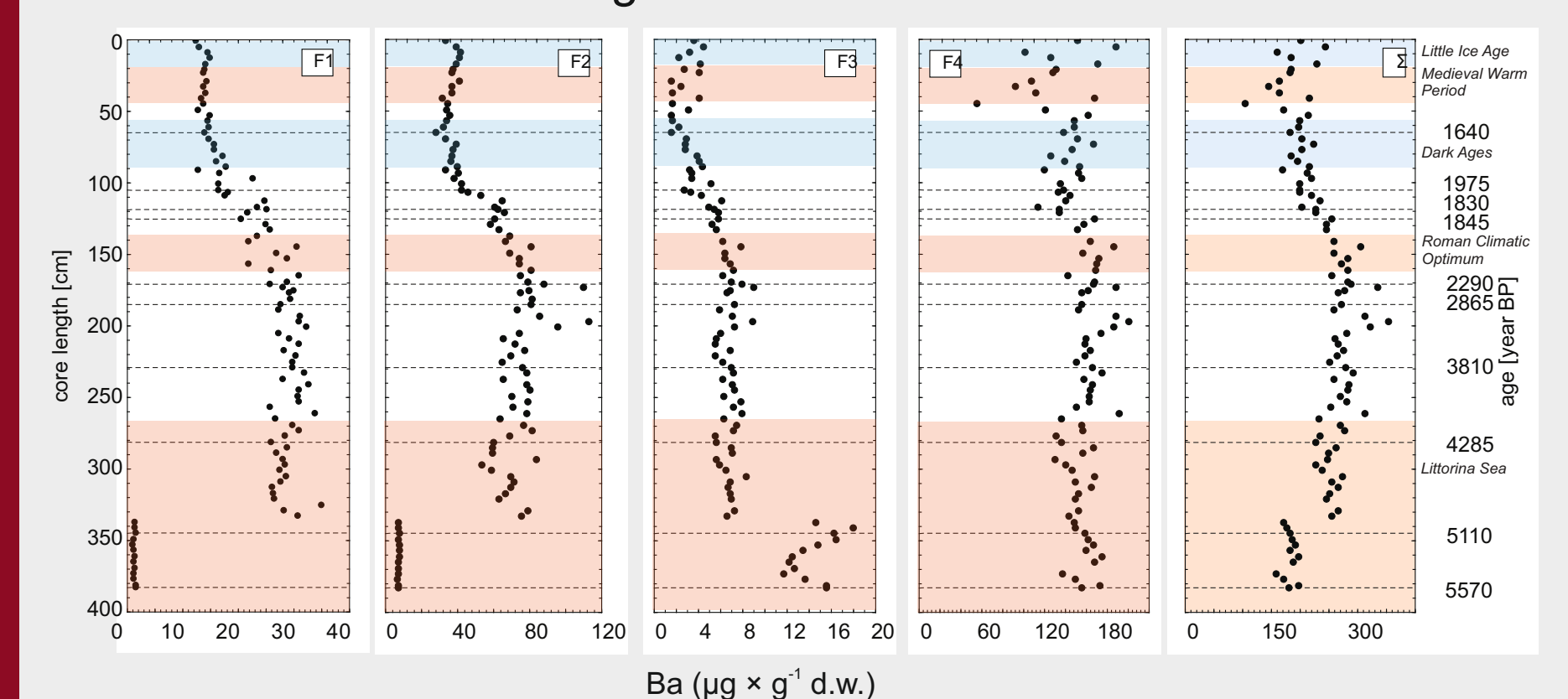
## Qualitative mobility and biological availability of trace elements

Fraction	Metal species and association	Relative availability and mobility
F1	Exchangeable cations, acid-soluble fraction.	<i>High</i> - changes in major cationic composition (e.g. estuarine environment, mono-divalent cations) may cause a release due to ion exchange or pH change.
F2	Metals associated with Fe-Mn hydroxides	<i>Medium</i> - changes in redox conditions may cause a release but some metals precipitate if sulfide mineral present
F3	Metals associated with OM phase Metals associated with sulphide phase	<i>Medium</i> - decomposition of organic matter by favorable conditions. Strongly dependent on environmental conditions. Under oxygen-rich conditions, oxidation of sulfide minerals leads to release of metals
F4	Metals fixed in mineral particles	<i>Low</i> - metals may become available after weathering or decomposition



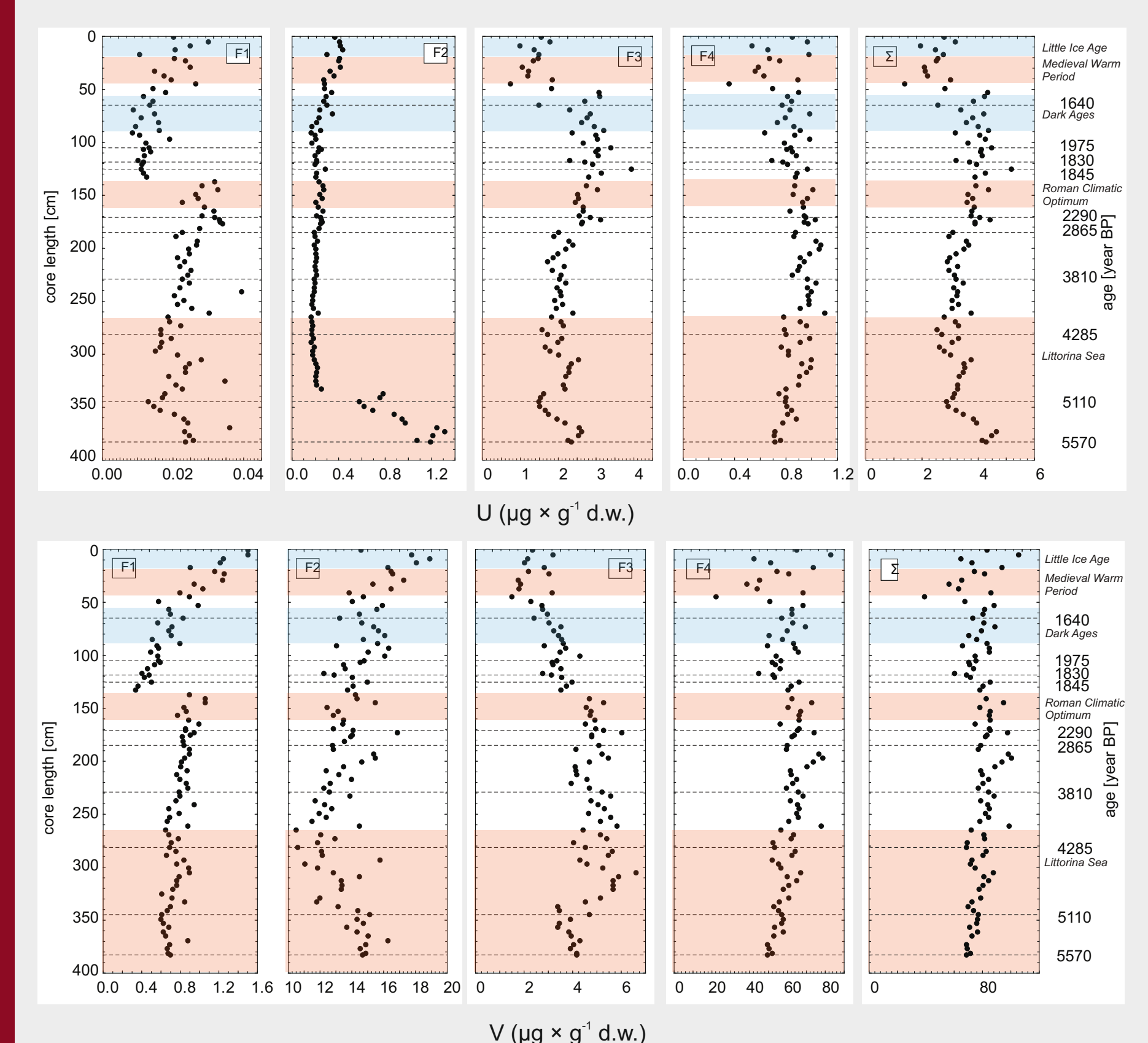
## Paleoproductivity proxy - Ba

Ba enrichment in sediments – formation of mineral barite in the water column: correlation with organic carbon fluxes



## Paleo-redox proxies

With no diagenetic overprinting, increasing conc. of redox. sensitive trace metals (e.g. U, V) generally indicate deposition under reducing conditions.



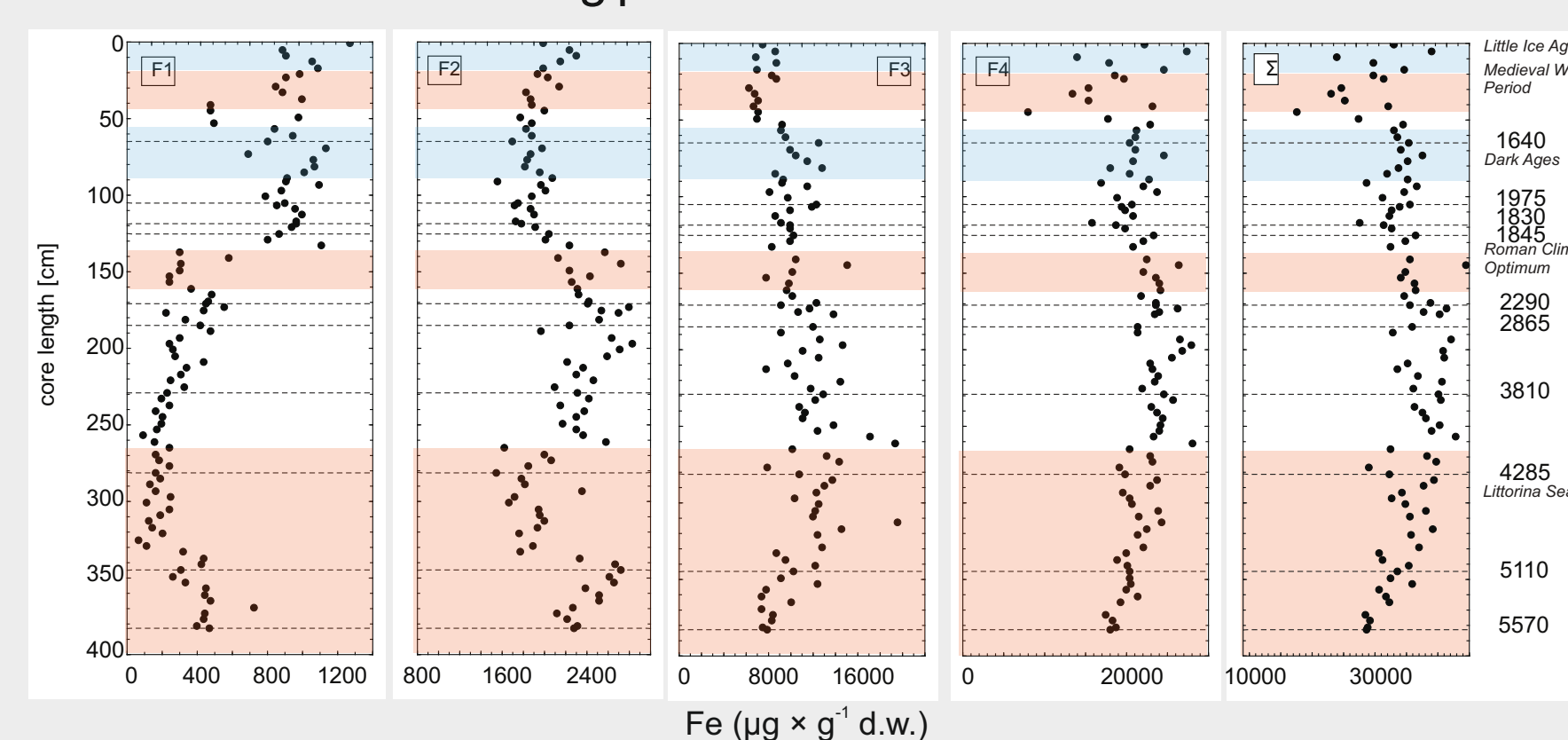
## Steps of modified BCR sequential extraction

Step	Fraction	Reagents
F1	Exchangeable, acid soluble	A - 0.11 M acetic acid
F2	Easy reducible	B - 0.5 M hydroxylamine hydrochloride (pH=1.5)
F3	Oxidizable	C - 8.8 M hydrogen peroxide D - 1.0 M ammonium acetate (pH=2*)
F4	Residual	HNO <sub>3</sub> digestion in high-pressure microwave system

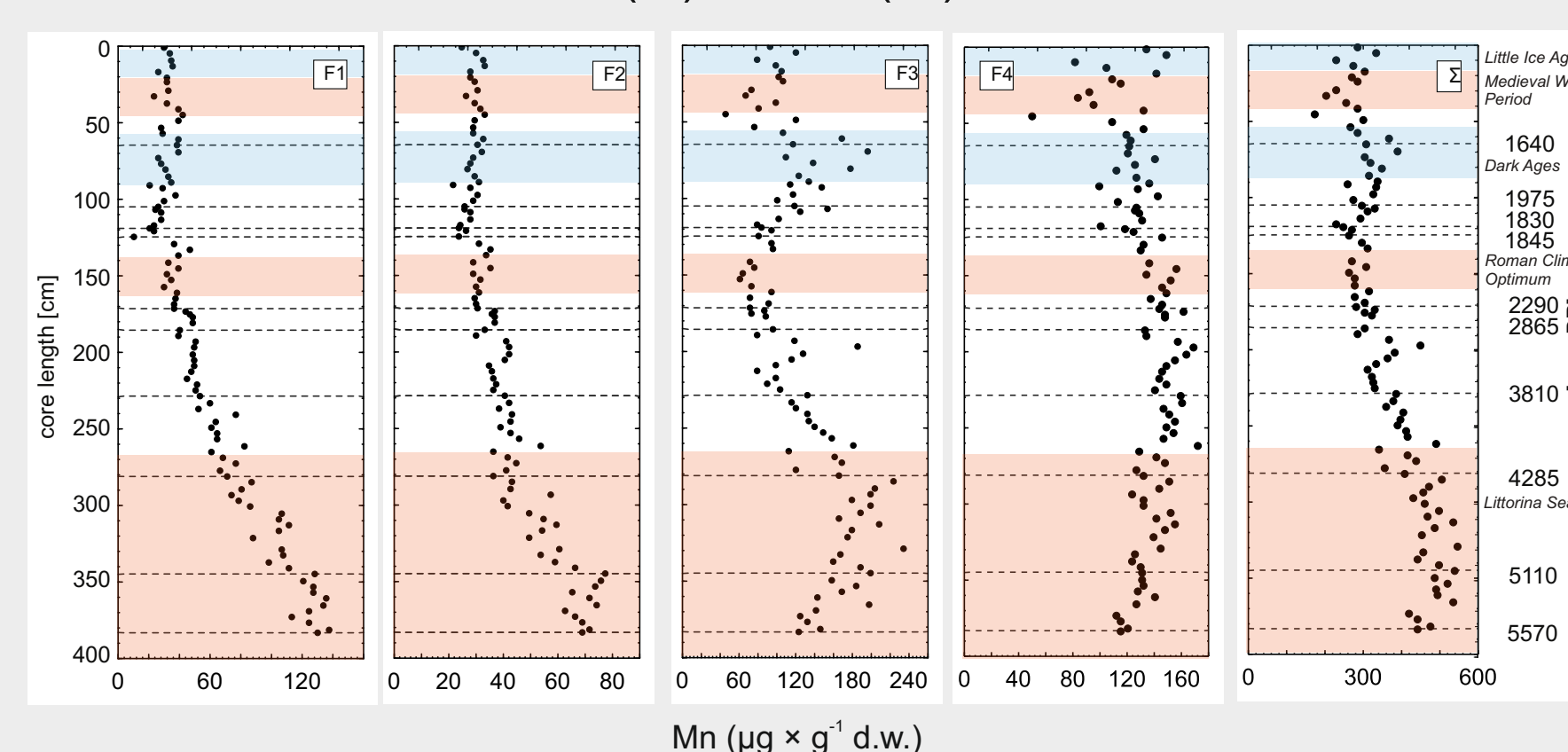
\* pH adjusted with HNO<sub>3</sub>

## Paleo-redox proxies

The mobility and speciation of the metals in the sediments depends on the redox conditions, which influences relative distribution of trace elements due to the different degree in which various metals interact with the sediment binding phases.



In sea water, depending on redox potential: Mn occurs mainly as Mn<sup>2+</sup> and MnCl<sup>+</sup> or insoluble Mn(III) and Mn(IV) oxides.



## Sediment cores



## Conclusions

- ☒ The elemental concentration of the redox sensitive and Ba ratios in the sediment cores was found to dramatically change in different core section which can be explained by dominant biological (primary production) and environmental (redox condition) processes.
- ☒ Moreover, it was observed that the differences can be related to the specific climatic events, such as e.g. Roman Climatic Optimum.
- ☒ The knowledge on how to read and interpret TEI fractions as proxies in the sedimentary records will improve our understanding of environmental changes in the geological past.