Answer to comments of RC2 on egusphere-2026-3608

Review #2/B

B1: The paper presents Pb isotope data for 3 marine sediment cores, which are interpreted with support from elemental concentration data. The data exhibit some interesting features, namely variations in Pb isotope composition that co-vary with Si and total organic carbon (TOC) concentrations and inversely with elements diagnostic of lithogenic inputs. The authors interpret this to reflect the alteration of the Pb isotope signature of the sedimentary phases in the water column, related to biological productivity. However, I do not think this conclusion is well supported by the data, finding the arguments towards this conclusion overly complicated and confusing. I therefore recommend major revisions before this paper can be accepted for publication.

We thank the reviewers for their helpful comments. Based on the reviewer's suggestions we have re-written many parts of the manuscript and have now based our approach to decipher the role of primary production on a more robust statistical approach using Al and Ba as proxies for lithogenic and biogenic export of Pb instead of total Si, respectively. Fe and Ca) were further used to identify basaltic tephra layers which showed distinct different Pb isotope signatures. Furthermore, we have tested the role of Fe/Mn oxides in sediments as carriers of authigenic Pb precipitated from the water phase. The new statistical approach shows that biogenic export of Pb appears to be of lesser importance at the sites St9 and St16 compared to lithogenic Pb phases, although both cores indicate high productivity based on Ba concentrations. However, St15 (deepest core) shows a relatively large proportion of biogenic Pb and a clear relationship between Pb isotope ratios and the amount of biogenic Pb in the sediments. This relationship suggests that different Pb pools exist in the water phase -possibly due to selective dissolution and scavenging of isotopically different Ph phases in dust or other / biogenic particles in the water phase. Fe/Mn oxides have been found to be separated and mobilized in our sediments due to high sedimentation rates and the relatively high input of organic matter in this productive area. We assume that redox processes in the sediments such as the dissolution of Fe- and Mn-oxides and the coupled mobilization and dislocation of Pb blurred the statistic relationship between productivity indicators and Pb concentrations and Pb isotope signatures.

In general, our data suggests that Pb isotope ratios and their relation to biogenic and lithogenic phases in deep sea sediments show large variations, which are difficult to decipher due to the manifold processes which alter sinking particles in the water phase and alteration of Pb bearing phases in the sediments. Thus, our data and the used statistical approach shows only a broad brushstroke but display the difficulties in using Pb isotope ratios extracted from deep sea sediments to reconstruct sources or paleo ocean currents.

Major comments-

B2: The concept of reversible scavenging seems confused in its definition in the paper. This refers to the 2-way exchange of Pb between particles and the dissolved phases as they sink through the water column. It is likely dominated by 'authigenic' Pb pools via adsorption-desorption reactions. This is not to be confused with 'detrital' or 'lithogenic' Pb – Pb that is

bound in mineral dust that does not ever get released to the dissolved pool, but simply sinks to be deposited in the sediment. I my view 'scavenging' refers to the transfer of dissolved Pb to particles (i.e. authigenic Pb), so that lithogenic Pb plays no part in 'scavenging' or 'reversible scavenging'. These ideas are confused in the discussion, to create overly complicated interpretations.

B3: -Based on the above logic, the alteration of the isotope composition of sedimentary phases by water column processes is exclusively reserved for the 'authigenic' Pb fraction. Furthermore, for this to occur via reversible scavenging in the water column would require some vertical gradient in dissolved Pb isotope composition – i.e. particles acquire a particular authigenic Pb isotope composition by scavenging dissolved Pb in the surface layer, which is then modified by exchanging with dissolved Pb of a different composition in the deep layer. There is no evidence put forward to suggest that this is the likely scenario to explain the data, hence I do not agree that the interpretation of the data requires the incorporation of reversible scavenging or 'water column alteration'.

We agree with the reviewer that our previous interpretation was overly complicated. However, the available data in the literature is relatively sparse and the given proportions of the different Pb fractions have been often based on operational defined sequential extractions. In addition, we could not find any studies on Pb isotopes in sinking marine particles, which contain the chemical characterization of the particles. Other studies have shown that a considerable proportion of Pb in dust particles can be dissolved in ocean water probably/likely concomitant with isotope fractionation. We agree that only the authigenic and the biogenic fraction can be involved in Pb exchange processes during the descent of particles through the water column. Several studies have assumed that reverse scavenging occurs specifically in productive areas and it is unknown if scavenging is always reverse and how much of the scavenged Pb is exported to the sediment. Moreover, recent studies on water column Pb isotope signatures show strong indications that high particle fluxes in productive areas have significant influence on water phase dissolved Pb isotope signatures as well as Pb export to the sediments, which seems to be mainly related to biogenic particles rather than to Fe-Mn hydroxides. (Chen et al., 2026, Lanning et al., 2023, Olivelli et al., 2024, Griffiths et al., 2026).

In the revised version of the manuscript, we now followed a statistical approach which has been used in other studies before to separate the lithogenic Pb fraction from the biogenic/authigenic fraction. The lithogenic fraction was calculated based on Pb/Al and Pb/Ti ratios and the concentrations of Al or Ti, respectively. The biogenic component was than calculated based on Ba concentrations because TOC and biogenic silica are not stable in the water column.

As suggested by the reviewer we removed most speculations on the dissolution and interaction of mineral particles with organic matter in the water phase. However, as a clear statistical relationship between the biogenic component (TOC, Ba) and changes in the Pb isotope signature was observed, especially at St15, some discussion on this relationship and the underlying Pb pools and processes has been conducted in the revised version.

B4: -The most likely interpretation in my view is that the Pb isotope variations reflect mixing between a lithogenic Pb pool (i.e. Pb in mineral dust that never became solubilized) and an authigenic pool (i.e. Pb that has been scavenged from the dissolved pool). This interpretation does not require any alteration of the authigenic component as claimed, only that it is over

printed by lithogenic contributions to variable degrees in the bulk Pb measurements. This idea is already included in the paper, but it is confusingly linked to ideas regarding scavenging altering isotope compositions.

I would therefore like to see ideas about this data reflecting 'water column alteration' or being evidence of reversible scavenging being removed (change of title, reframing of introduction, and complete re-write of the results and discussion).

In principle, we agree with this statement and the data presentation in the revised version does mainly support this interpretation. However, the interpretation suggested by the reviewer assumes that mixing of the different Pb fractions occurs in the surface water and is than conserved along the water column and into the sediment. This assumes, that the authigenic and the biogenic fractions remain stable. This is unlikely regarding the literature on this topic, but the reviewer is right stating that we cannot infer from our data that water column alteration of Pb pools or reversible scavenging occurs. To our knowledge the existing literature on Pb isotopes in pelagic sediments is quite limited and mostly relies on the assumption that particulate Pb (lithogenic and authigenic) is stable while descending through the water column. However, we did not find any water phase particle measurements in the literature which has investigated or proven this assumption. In contrast, recent studies have at least assumed that reversible scavenging or other particle related processes have changed the dissolved Pb pool in the water column (Chen et al., 2026, Lanning et al., 2023, Olivelli et al., 2024, Griffiths et al., 2026), which hence may alter the original Pb isotope signature of a sinking particle especially those of biogenic origin. Nevertheless, we have now focused and limited the discussion on that aspect explaining the biogenic fraction in our sediment cores. We will also adapt the title accordingly.

B5*:* I would also like to see the elemental data used to constrain more quantitatively the mixing between lithogenic vs detrital Pb sources suing Pb/Al and/or Pb/Ti ratios, with this analysis done early on in the discussion to establish the basic framework within to interpret the isotope data.

As described above, we have now based our interpretation on Pb/Al and/or Pb/Ti ratios as well as Ba concentrations to quantify the lithogenic and biogenic fractions in the sediments.

Minor comments

Section 2.2. Please explain how instrumental mass bias was monitored and corrected. Also what statistic is used for the quoted 'average relative uncertainty'?

Instrumental mass bias: The nine measurements of the isotopic references showed an average relative uncertainty of < 0.0030 % e.g. in case of 206Pb/208Pb. The uncertainty associated with the average of the nine ratios acquired equally spaced during the 5 h sequence duration, was typically the same as the average uncertainty achieved within a single measurement (5 min duration). This indicates that no significant drift of the instrumental isotopic fraction (IIF), commonly referred to as mass bias, occurred during any sequence. Therefore, no drift correction was applied to the data.

Before isotope ratio calculations, isotopic reference measurements were corrected for the acid blank, whereas processed samples were corrected for the procedural blank. Mass bias correction factors were then calculated from the blank-corrected signal intensity ratios of the isotopic reference and its certified isotope ratios, and applied to the blank-corrected sample signal intensity ratios to obtain the final sample isotope ratios.
A full description of all corrections is given in the SI.

Section 2.3. How is the LOQ defined? 10 x SD of the blanks?

Description is provided in the SI.

Section 3.1. The authors claim that the overly water column features natural dissolved Pb distributions, based on the Pb concentration of waters much further north. I don't think this is well supported due to (1) the differences in oceanographic region of the study areas considered, (2) 16.7 pmol/kg is not necessarily the natural baseline. We have no idea what the natural Pb concentration in the ocean is, but it is likely much lower than this in my view.

More importantly, what are the Pb isotope compositions of these waters? Do they conclusively fingerprint natural Pb sources rather than anthropogenic ones?

A more detailed classification of all recorded isotope ratios of the larger area was included in the revised manuscript, mainly showcasing natural Pb sources. Unfortunately, no particle data is available for the region.

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