

## ***Interactive comment on “Climate dependent diatom production is preserved in biogenic Si isotope signatures” by X. Sun et al.***

**Anonymous Referee #1**

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Review of “Climate dependent diatom production is preserved in biogenic Si isotope signatures” by Sun et al.

Sun et al have analyzed the Si isotope composition of diatoms extracted from a sediment core from the Bothnian Bay (Baltic Sea). The diatom Si isotope composition appears to correlate with the BSi content of those sediments and indicates that high BSi fluxes are associated with high Si utilization in the water column. Sun et al then use a Rayleigh fractionation term to calculate the degree of Si utilization for the past ~200 years. They come to the conclusion that episodes of lower Si utilization correspond to times when air temperature was significantly lower than the average, and finally the study proposes that Si isotope records obtained from diatom records could hold direct temperature information.

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This is a very intriguing idea indeed, and although I'm not completely at odds with their interpretation, I'm afraid the authors fail to convince me that their data actually show such a relation. I don't think the manuscript is publishable in its current form, but I'm convinced that a few additional changes will make it worth while.

My biggest concern is related to the temperature model (Eq.3); How are air and sea-surface temperature related? The temperature model (Eq.3) uses air temperature, which appears to be more variant than the surface water temperature. For instance, considering the period between 1961-1990; According to figure 6b, the air temperature during the summer months varied somewhere between values as low as 6degC and as high as 17degC. For the same period the authors state in section 2: “During the periods of 1961-1990, the summer time ... average maximum surface temperature ... varied between 16 and 16.5 degC”. While air temperature varied considerably, the mean sea surface temperature was very constant. If nutrients were not limited due to other processes, or bio-productivity was not impaired by seasonal ice-cover, it is not obvious to me how diatom productivity should related (or respond) to air-temperature, whilst sea surface temperature remains more or less constant. Once would assume that kinetics of Si utilization and accompanied isotopic fractionation by diatoms were a first-order response to the sea water temperature and not the air temperature. This is in my opinion the weakest point of this study and the authors need to drastically improve the train of thought here. It is mentioned somewhere in section 4.4 that colder (air or water?) temperatures might impair stratification of the water column hence dampening bio-productivity - is there any evidence for that?

Figure 6a shows the calculated f values vs. time depending on different river Si isotope compositions. From reading the manuscript it is not quite clear to me how the “measured f” values were derived - please add a brief discussion. The only river data for this area are from the Kalix River (Engstroem et al 2010), and average close to 1.1pmil. The Kalix is unregulated and gives a constraint on the natural Si isotope composition delivered to the Bothnian Bay. In order to match their calculations to observation in fig-

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ure 6a, the authors assume a shift in river Si isotope composition due to anthropogenic impact on watersheds. Although this is possible, we have however no idea what the effects of hydraulic engineering would be. Without having data for these rivers, it is difficult to say what the effect might be. Hence the assumption that the post 1950 river have higher Si isotope compositions is somewhat unjustified and in my opinion not valid. The Si isotope composition of rivers is, albeit some good research, still a very complex system, and we are far from understanding the interactions between different Si-carrying pools. I'm not saying that enhanced diatom productivity due to dammed lakes is impossible, I just don't think that large scale river systems are that easy and straight forward to interpret.

My next concern is related to the data variability; Taking into account the uncertainty of the Si isotope measurements the actual data barely vary at all. The relation between BSi content and Si isotope composition is far from being a linear correlation, and should not be addressed as such. The regression in figure 5 is rather a spurious correlation based on two distinct data point cluster. Adding error bars to figure 5 and one will immediately see that this is actually not a correlation. The authors write that the uncertainty of the calculated  $f$  values takes into account the 2SD errors of the Si isotope data. I assume the propagated uncertainties be very large, and think this should be added to the plots 6a and 7. Furthermore, the calculated temperatures in figure 6b must also have some uncertainty and it would be good to add them to the plot. Is the 5-year-moving average (dashed line) in Figure 6b based on observations from the data monitoring program or actually derived from the relationship in figure 7? Please clarify. It would be certainly very helpful to plot the data from the monitoring program against calculated temperature data derived from the relation in figure 7. As is, it looks like the dashed line is simply the average of the monitoring program data, if so, where is the point in plotting it?

Actually I think the authors could tremendously enhance this manuscript by adding some more modeling. One very interesting model could be a simple Si isotope transient

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model (box-model), for example similar to De La Rocha et al 2005, but only for the Bothnian Bay and obviously not for the whole ocean. Section 2 describes the sampling site and it already contains most data required for such a box-model approach. Such a Si cycle model could then be used to test some forcing of the diatom productivity due to variations of air temperature and the resulting Si isotope fractionation. This would be a very strong way of testing the sensitivity of the Bothnian Bay system to temperature variations, and could in my opinion add a lot of value to this study.

Other comments:

Maybe somethings went wrong with my pdf copy, but line numbers and at least page numbers would be very helpful!

Section1: The Si isotope fractionation by diatoms is stable between 12-22 degC (De La Rocha et al. 1997), but some of the samples analyzed here fall beneath that range. Are there any isotope effects that the reader must be aware of?

Section 2: The decrease of DSi fluxes due to hydraulic engineering is mentioned. Later in the manuscript (section 4.3) the authors say that the BSi content increased since the 1950s, probably due to an anthropogenic enhanced input of nutrients. I assume they mean macro-nutrients, such as P and N? This is a bit contradictory and maybe one additional sentence could be added.

Section 3: What is the uncertainty of the Pb activity data? Should be added.

Section 3.2: I'm aware that MilliQ-e water is supposed to be 18.2m $\Omega$ , but some readers might not know that. MilliQ-e is not an official term for high quality deionized water, and the authors should use something along the line of "deionized water (18.2m $\Omega$ , MilliQ-e, Milli Pore)". Please change!

Section 3.3: Silicon concentration data are given in mg/L, earlier in the manuscript they are given in molar units, please be consistent throughout the text.

Section 3.4: Were any other reference materials analyzed, such as Diatomite, or some

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USGS rock standards? There are now quite a few reference material data published and I think the authors could considerably strengthen their work by presenting standard data. In fact, it is my opinion that data-sets without standard data are not to be published.

Section 4.4: Somewhere in section 4.4 the authors discuss the relation between  $f$  values and cold weather periods: "The largest amount of remaining ... corresponds to a period with very cold summer". Is that so? How can the authors know that? Please add references here!

Section 4.5: "This isotope shift is also consistent with what is expected to occur ...". As I wrote above, is there any evidence for that? This section is in general rather weak and does require considerable improvement.

Closing remarks: In general I think that the scope of this study is actually very intriguing and of hot topic. However, the data set and the modeling is simply not convincing and fails to win me over. It also seems that only samples from one site in the Bay were samples. The implications of this work could be very important and therefore I think it would be mandatory to confirm the observed trends in other locations from within the Bay. For example, De La Rocha et al (1998) present data for a few sites from the Southern Ocean, and so does Brzezinski et al (2002) etc. I understand that sampling sea sediments is logistically quite challenging, but I also assume that sampling the shallow waters of the Bothnian Bay is less of an enterprise than say the deep Southern Ocean.

What about O-isotope data? With the diatoms being already separated, why not taking some splits to get O-isotopes analyzed? This might add weight to this study.

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