

## ***Interactive comment on “First continuous phosphate record from Greenland ice cores” by H. A. Kjær et al.***

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General comments:

When I first picked up this manuscript, I was really excited. This is an important measurement being made for the first time using a state of the art chemical analytical technique. Sadly by the time I got part way through the discussion I realised that the analysts had made a fundamental mistake in their analytical design which rendered the results not useful. It read in fact like a manuscript written part way through the method development. I would certainly encourage the authors to complete that development since I am sure this is really important data but for the moment I cannot recommend publication.

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The fundamental problem with the method as used at present is that the sample is filtered at the end of the analytical flow just before measurement and not at the beginning. Since the phosphate method involves a highly acidic reagent, this means that an unknown fraction of acid labile P is dissolved from particles during the analytical procedure. The system is measuring (partially) acid-labile P and not as is claimed in the text PO<sub>4</sub><sup>3-</sup>, which seems to be defined as a water soluble labile phase. In fact it is very unclear what this phase (PO<sub>4</sub><sup>3-</sup>) actually is from the text. On page 3961 3rd paragraph it seems to be defined as 'the soluble part of total P' which is generally defined water soluble and/or water labile P. That is not what they measured in this study.

Furthermore by putting a filter at the end of the flow system, they are causing a further potential problem. The molybdate-blue final reagent is as they note is not truly dissolved. At higher concentration it is a 'sticky' colloid which can attach to the walls of the glassware. This can obviously also attach to the filter which will remove an unknown and variable amount of the signal.

I would urge the authors to go back to the chemical method and remove the problems in analysis by filtering the sample at the beginning of the analytical flow rather than at the end, and then repeat measurements so that the scientific community can truly gain the valuable insights that will be available once these exciting measurements are made properly.

I have in addition a number of comments about the methods text which might help the authors improve their measurements and eventually their manuscripts.

Specific comments:

Do not express results as ppb. Especially for phosphate that is truly ambiguous. Ppb of what? Is it PO<sub>4</sub><sup>3-</sup>, PO<sub>4</sub>-P, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>? At worst this needs to be defined early in the text but if molar units were used this problem would not exist. Molar units will also allow sensible comparisons with other chemical species like NH<sub>4</sub> and Ca when interpretations are being made.

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P3962 The section of why P is the limited nutrient in the ocean over long time scales is wrong. It has nothing to do with Fe. It is because the amount of N in the ocean is a balance between N<sub>2</sub> fixation and denitrification. This controls the Redfield ratio and sets it in the modern ocean at very slightly below the level at which N<sub>2</sub> fixation is favoured over regular phytoplankton growth. This controls the short term nutrient limitation (i.e. as N). If however you add more P (or remove P) you move the whole equilibrium up or down and increase total global productivity. In any case Fe has nothing to do with denitrification. It is needed as an enzyme for N<sub>2</sub> fixation.

Page 3965:

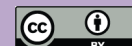
The authors misunderstand the interference of Si on this method. There is no interference caused by rock aluminosilicates which are very insoluble. Hence the mean crustal abundance of silica(te) is irrelevant. If there is a problem is due to dissolved silica (SiO<sub>2</sub>) which is measured by a similar method but is generally not considered to be a problem in aqueous phosphate analysis. I have measured phosphate down to nanomolar levels in surface seawater with silica 1000 time higher concentration with no interference.

A 0.6  $\mu\text{M}$  interference would actually be a serious problem for the authors if It actually occurred but that is highly unlikely.

By contrast there is arsenate interference in this method which nobody has been able to solve and is why we call the analysis SRP (Soluble reactive phosphate) and not PO<sub>4</sub><sup>3-</sup>. The additional reason for calling it SRP is that an unknown fraction of DOP is acid hydrolysed during this method as well but that may not be relevant here.

The authors in paragraph 2 state they have a LoD of 0.1 ppb without defining how they measured that or what it is defined as. Usually it is 2 or 3 times the standard deviation of the blank.

‘A filter was introduced to remove particulates that would otherwise completely obscure

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the LWCC. This is a rather alarming and yet poorly defined statement. Would it be the particles which would block the LWCC or would it be a blue ppt of molybdate which would stick to the walls of the LWCC and 'obscure' the signal? These are not the same thing. If it was the former, then the particles should have been removed before any reagent was added. If it was the later, then the system should have been run at much lower concentrations of phosphate i.e. higher sample dilutions, to stop the sticky colloid forming.

I repeat from the general comments. The procedure as used does not measure conventional labile phosphate i.e. water soluble phosphate. It measures the dissolved phosphate plus an unknown fraction of acid soluble phosphate from the particles. As such the data cannot be used to compare with other results and cannot be interpreted properly.

P3966

Stock solutions are never prepared daily. Stock solutions are stored and used to make up reagents which are used daily.

Last paragraph:

The authors make a rather sweeping statement that 'For the NEEM analyses, variability in the baseline and system sensitivity were observed predominately as a result of the higher impurity content of the samples. 'This reviewer does not understand what is 'an impurity' of a sample nor is this statement actually explained or justified.

P3967

How can increased coating 'cause a lower baseline?' In any case it is bad practice to run system with high coating.

P3968

Not sure what the standard deviation of the data is meant to show. Is it a measure of

range?

The PO<sub>43</sub>- concentration is strongly correlated with dust suggesting similar sources and/or similar transport processes. No correlation curves are shown but anyway this is probably because the methodology used is measuring acid soluble P on the surface of dust particles.

P3969 The reason why there is high phosphate in surface water in winter in the N.Atlantic and Pacific is because there is deep winter mixing combined with no phytoplankton bloom because of low light.

At this point I gave up reading the text however I did look at the figures and tables:

Table 1 states that the authors have calculated 'the uncertainty due introduced by baseline correction' without describing or showing how that correction was made. How was the baseline defined? Was it run with one critical reagent missing such as ascorbic acid? Was it run with no phosphate?

Legend for Figure 3: I have read this several times and I simply do not understand what it is describing

Figure 4 describes the dating used for FIRN core but the dating is from 1783 and 1815 while the core is 1912 to 1994. Is this normal procedure?

These figures are very difficult to read even for me and I think I have very good eyesight.

I would like to review the revised paper which will be an important new paper.

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Interactive comment on Clim. Past Discuss., 7, 3959, 2011.

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