

## ***Interactive comment on “Application of Fourier Transform Infrared Spectroscopy (FTIR) for assessing biogenic silica sample purity in geochemical analyses and palaeoenvironmental research” by G. E. A. Swann and S. V. Patwardhan***

**Anonymous Referee #2**

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General comments:

The paper by Swann & Patwardhan describes a new approach to quantify contamination of biogenic silica samples after purification for geochemical analysis by use of FTIR. Through the definition of pure end-members, contamination of a given sample is determined with a mass-balance model based on the measured FTIR-spectra. The contribution is welcome and valuable for the community, but could further benefit from the presentation of more examples and a more rigorous and in-depth discussion of the limitations of the approach. This would further increase the applicability of the method

C893

and the acceptance by other users. Thus improved, the paper should be accepted for publication

Specific comments:

The analytical reproducibility of replicate FTIR analyses of small sample aliquots is expressed in terms of contamination (p1636, lines 11-13). While this is useful as overall description, it does not show where in the spectra the deviations occur and how strong they really are. Examples from end-members and samples would help to illustrate possible deviations within the analytical limitations.

The definition of end-members is the crucial point of the approach. Two purified diatom standard materials are used as diatom end-members whose degree of contamination was assessed by light microscopy and XRF. In terms of Al<sub>2</sub>O<sub>3</sub> content, contamination of BFCmod is 2.0 wt%, while for PS1772-8 it is given with 0.09% (p1637, line18-19). What is the effect of this contamination of the end-member on the quality of the model? Would it be possible to use a pure diatom opal, e.g. from culture experiments, as the “true end-member” to avoid this source of error. Given the low, but in terms of real samples clear difference in the contamination of the diatom end-members, why does this not lead to larger differences in the estimates of FTIR contamination from these standards (p1637, line 20).

How accurate is the definition of contamination by the Al<sub>2</sub>O<sub>3</sub> content as determined by XRF. I am aware of the problem here, but we know that Al is incorporated into the diatom frustule in amounts that could be of relevance for contamination assessment based on this criterion. Beside inorganic contamination, that is the target of Al<sub>2</sub>O<sub>3</sub> analyses, diatom frustules can contain organic matter encapsulated in their frustules. How would this impact the FTIR spectra? Furthermore, at least lacustrine sediments have others sources of biogenic opal like sponge spicules and phytoliths that are not captured by the end-members used but would have to be seen as contamination. Are there alternative methods to quantify inorganic contamination of diatom samples inde-

C894

pendently to show the accuracy of the definition by Al<sub>2</sub>O<sub>3</sub> content of XRF for selected samples.

Residuals between the best-fit model and the observed FTIR spectra for any end-member model used are between 2.8 % and 19.4 % (p 1738, line 9). This might be an effect not only of the accuracy of the silt end-member definition but also of the contamination of the diatom end-members. What is the effect of high residuals on the determined degree of contamination in the samples and up to what level of deviation can a sound estimate be given. Even low residuals indicate that the end-members can not completely explain the measured sample FTIR spectra and could possibly indicate also contamination.

It is not straightforward for the reader to agree with the statement, that quantitative changes in FTIR contamination closely follow XRF contamination estimates (p1638, lines21-22; figure 5). The picture is dominated by strong peaks in FTIR determined contamination that are obviously related to inadequate end-member model formulation. Beside this, it seems that there are quite considerable deviations between XRF and FTIR estimates for the remaining samples. Differences in contamination amounts of at least about 3 % in the best cases (p1639, line 1) should be explained to assist a wider application of the FTIR method, since this is about the amount of contamination that need to be detected in practice.

Technical comments:

Figures 5 and 7 were difficult to follow for my feeling. Perhaps the information can be presented in a more reader-friendly manner. Y-scales of panels a and b are too large to follow changes in contamination in detail. Discussion on figure 7 results is rather short.

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Interactive comment on Clim. Past Discuss., 6, 1629, 2010.