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Climate of the Past Discussions

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 #1

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This paper demonstrates a novel use of FTIR for the rapid and non-destructive assessment of opal purity for the purpose of geochemical analysis, which is a highly desirable goal for palaeoclimate and environmental studies. Although I am not very familiar with the analytical methodology, the approach seems valid and, with the possible addition of further discussion and (if possible) testing, this paper should be accepted for publication.

Specific comments:

As discussed by the authors, one of the key issues surrounding the analysis of biogenic opal is contamination (p1631). Unlike foraminiferal analysis, where tests can be picked individually, the authors correctly say that this is rarely possible for small diatom shells and phytoliths. I would, however, argue that individual picking is possible for sponge spicules (Hendry et al., 2010a), which subsequently suffer from a lower risk of contamination.

Previous methods for assessment of contamination are mentioned by the authors (lines 25-30, p 1631) including spot counts under light microscope/SEM and XRF. However, I would also add into this list dissolution experiments that selectively dissolve smaller particles (presumably contaminants) and surface coatings preferentially (e.g. Ellwood & Hunter, 1999; Hendry & Rickaby, 2008).

A caveat worth mentioning when discussing the use of XRF, or other methods of assessing contamination through Al analysis, is the wide range of Al content observed in diatom opal, especially at the surface-water interface (various papers by Von Bennekom; Dixit; Koning et al., 2007; sediment trap study in Hendry et al., 2010b). Clean, sedimentary diatoms can contain very high Al/Si ratios, ($\sim$0.11, van Beusekom et al,. 1997).

Have other methods of purity assessment been carried out on BFCmod and PS1772-8 (e.g. SEM spot counts, dissolution experiments)? It might be useful to have some further, independent measures of contamination if possible.

When the authors prepare the “silt”, is there any risk of leaching of clays by the NaOH? How concentrated is the NaOH? Perhaps the authors could try leaching in different molarities, and comparing the resulting curves to assess the possibility of lithogenic leaching.

Do the authors have an idea of how the spectrum would compare for phytoliths and sponge spicules (given the range in omega values for diatoms and sponges)? For example, if diatom samples are contaminated with non-diatom opal, which is a partic-

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ular problem for Si isotope analysis, would this be detected in the spectrum? This is touched upon in the conclusion, but it would be interesting to see some examples, if possible.

Is there evidence that a KBR pressed pellet results in material loss? (Line 13-14, p 1634).

Are there other ways the authors could identify the other contaminants? (p 1638). It seems reasonable to assume organic matter could be important – could the authors analyse the organic carbon content?

I think the main point of the paper is summarised well in line 6-8 on p1639: "the FTIR technique nonetheless is able to identify the samples as being contaminated, fulfilling the requirement for the method to determine whether a sample is clean for analysis". Certainly my previous attempts have involved destructive mechanisms, increasing the sample size needed, and have been time consuming, so I welcome the contribution of this manuscript.

Technical comments:

Q3 and Q4 bonds (line 29, p 1632) should be defined, and perhaps it would be useful to mention that the ratio of the two gives an indication of hydration (Leng et al., 2009).

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