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Published

2014

Journal Title

Environmental Chemistry

Version

Accepted Manuscript (AM)

DOI

[10.1071/EN13209](https://doi.org/10.1071/EN13209)

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1 **Hard X-ray synchrotron biogeochemistry: piecing together the increasingly detailed**
2 **puzzle.**

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11 Synchrotron techniques have increasingly been used to explore complex biogeochemical
12 processes over the last two decades ^[1]. In this relatively short period of time the advances in
13 optics, detector systems and ultimately beamline performance and capabilities have been
14 staggering. While a very large number of synchrotron methods are available and are
15 employed in biogeochemistry, this perspective article will mainly explore recent
16 developments and trajectories for ‘hard’ X-ray techniques. State-of-the-art beamlines, such as
17 the nano-imaging and nano-analysis (NINA) end-stations at the European Synchrotron
18 Radiation Facility ^[2], will increasingly provide users with unprecedented analytical
19 capabilities. For instance, the NINA end-stations will provide nanoscale resolution (10-20nm
20 for imaging and 50-100nm for XAS and XRD) together with high photon fluxes, a wide
21 energy range and sophisticated sample environments. It is pertinent to note that the scientific
22 case for the development of this project specifically mentions environmental and earth
23 science as one of the three main drivers ^[3]. To take full advantage of this increase in lateral
24 resolution two further areas also need to simultaneously develop: sample preparation /
25 preservation and detector technologies. The need for fast detection is dictated by both the
26 necessity to representatively explore the heterogeneity of environmental samples and to
27 minimise the risk of beam damage. In the last few years, the advent of a new generation of
28 fast fluorescence detectors has gone a long way toward meeting this need (e.g. ^[4]). Similarly,
29 an increasing number of beamlines are developing cryo-compatible platforms to reduce
30 radiation damage and allow hydrated samples to be investigated in a frozen state.

31 With a number of upgrade programs at synchrotrons throughout the world and new facilities
32 coming online (<http://www.lightsources.org>), biogeochemists will be able to delve more and
33 more deeply into the complexity of small scale processes that drive element cycling.
34 However, we would argue that this will also translate into a substantial increase in

35 responsibility for users. First of all, sample preparation and preservation, which is always a
36 key step in any successful spectroscopic investigation, will become even more critical. Some
37 approaches, such as 2D and 3D tomography approaches (e.g. ^[5, 6]) will benefit from the
38 development of cryo-stages. However, in many cases the advantages in *lateral resolution* will
39 only be realised if sample thickness is reduced to avoid a loss of *spatial resolution*, in the
40 third dimension, caused by the penetrating nature of X-rays. This will require for instance the
41 capability to prepare and transfer frozen thin sections of environmental samples into
42 appropriate analysis platforms.

43

44 Furthermore, at the end of a technically successful data acquisition, beamtime users will be
45 faced with the exciting but often daunting task of extracting the relevant information from
46 ever larger multidimensional datasets. It is interesting to note here that, in our experience,
47 while we have enjoyed in the last few years an astonishing increase in data acquisition rate,
48 largely driven in our case by the use of the MAIA massively parallel detector array ^[7] at the
49 Australian Synchrotron, the beamtime allocation per experiment has not substantially
50 changed. This is justified by the fact that new data intensive techniques are available (see
51 below) and that experimental designs have grown more complex and exhaustive (e.g. ^[8]).
52 However, this has also translated into a flood of data. In fact, while just a few years ago XRF
53 maps were generated using dwell time per pixel of 0.5-1 sec, nowadays the MAIA detector ^[7]
54 and the use of fast electronics (e.g. ^[9]) allows data collection in the order of milliseconds. The
55 combination of high lateral resolution and fast acquisition has opened the door to large
56 megapixel imaging (e.g. ^[10]) and the development of new multidimensional techniques such
57 as XANES imaging ^[11] and even XANES tomography (Dr. Martin de Jonge, Australian
58 Synchrotron, personal communication). Whatever the application and approach used, it is fair
59 to state that datasets collected at leading beamlines today are much larger than in the past. We
60 contend here that while progress in biogeochemistry, and in any other discipline reliant on
61 synchrotron techniques, is still hampered by the issue of beamtime capacity, another issue,
62 related to data analysis and interpretation, is increasingly becoming a significant bottleneck
63 which hinders progress. This bottleneck is caused by both computational capacity limitations
64 and also by the lack of established data analysis methods and ‘user friendly’ software
65 packages to deal with ever more complex applications and larger datasets. For instance, the
66 development of XANES imaging, where XRF maps of many thousands of pixels are
67 collected at about a hundred or so different energies across an absorption edge, generates
68 multidimensional datasets of large size. While procedures for data analysis of similar datasets

69 are already available for transmission techniques such as STXM (e.g. ^[12]) or for (SR-)FTIR
70 (e.g. ^[13, 14]), these still need to be fully developed for XRF techniques. In any case, even when
71 routines for linear combination fitting at each pixel are developed (such as in the case of ^[11])
72 the issue of how to interpret and fully explore these large datasets remains. This is why the
73 development of approaches such as those described by Marcus and Lam ^[15] are a welcome
74 trend, although it should also be noted that these approaches are dependent on beamline
75 reliability and consistency in the post-processing of raw data. Happily, progress is being
76 made in this direction also and diagnostic frameworks similar to those in development for
77 FTIR biospectroscopy may well be applicable to large X-ray datasets (see ^[16] for a recent
78 review). Moving forward, we are of the opinion that quantum leaps in the understanding of
79 biogeochemical processes will only be achieved, and the promise of these new analytical
80 capabilities realised, if geochemists interact and collaborate with statisticians; much in the
81 same way as modern molecular biology has driven the development of bioinformatics. It
82 would indeed be a lost opportunity and a waste of resources if the data richness of
83 synchrotron datasets was not to be comprehensively explored.

84

85 A further development that should be noted here is the integration of synchrotron techniques
86 with molecular biology approaches. These trans-disciplinary approaches have been very
87 successful in the field of plant molecular biology (see ^[17] for a review) and there is no reason
88 not to expect that further developments will also occur in environmental microbiology (e.g.
89 ^[18, 19]). Furthermore, it is becoming apparent that the integration of various experimental
90 approaches and different spectroscopic techniques is not just beneficial but often essential in
91 order to properly interpret complex systems (e.g. ^[20, 21]). These collaborative and multi-
92 technique approaches are *condiciones sine quibus non* in the quest toward a mechanistic
93 understanding of biogeochemical cycles (e.g. ^[22]) and in linking these to macroscopic
94 phenomena (e.g. ^[23]).

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96

97 **Acknowledgements**

98 We would like to acknowledge the Australian Synchrotron and other synchrotrons around the
99 world for beamtime allocations over the years.

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102 **References**

103

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