**"NANO" MORPHOLOGY AND ELEMENT SIGNATURES OF EARLY LIFE ON EARTH: A NEW TOOL FOR ASSESSING BIOGENICITY.** D. Z. Oehler [1], S. Mostefaoui [2], A. Meibom [2], M. Selo [2], D. S. McKay [1], and F. Robert [2]. [1]Astrobiology Group, NASA–JSC, Houston, TX 77058, doehler@ems.jsc.nasa.gov, [2]LEME, CNRS–Museum of Natural History, Paris, France, robert@mnhn.fr.

**Introduction:** The relatively young technology of NanoSIMS is unlocking an exciting new level of information from organic matter in ancient sediments. We are using this technique to characterize Proterozoic organic material that is clearly biogenic as a guide for interpreting controversial organic structures in either terrestrial or extraterrestrial samples.

NanoSIMS is secondary ion mass spectrometry for trace element and isotope analysis at sub-micron resolution. In 2005, Robert *et al*. [1] combined NanoSIMS element maps with optical microscopic imagery in an effort to develop a new method for assessing biogenicity of Precambrian structures. The ability of NanoSIMS to map simultaneously the distribution of 'organic' elements with a 50 nm spatial resolution provides new biologic markers that could help define the timing of life's development on Earth. The current study corroborates the work of Robert *et al*. and builds on their study by using NanoSIMS to map C, N (as CN), S, Si and O of both excellently preserved microfossils and less well preserved, non-descript organics in Proterozoic chert from the ca. 0.8 Ga Bitter Springs Formation of Australia.

**Results:** We used the NanoSIMS 50 of the National Museum of Natural History in Paris to characterize spheroidal and filamentous microfossils (Figs. 1-3) as well as an organic lamina (Fig. 4) that appeared nearly amorphous by both optical and scanning electron microscopy (SEM). Specific results are as follows:

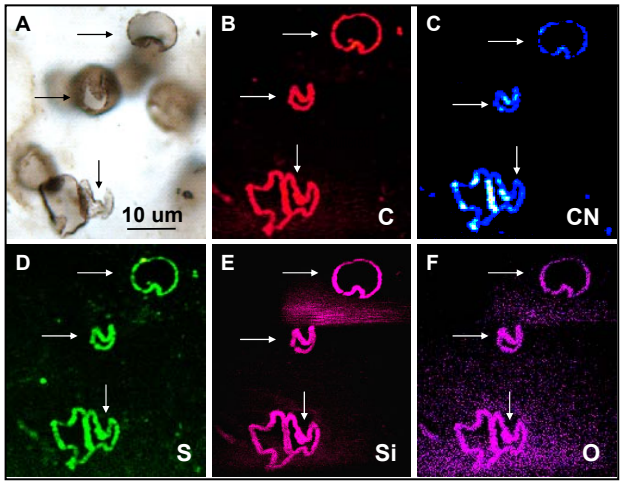


**Fig. 1**. Spheroidal microfossils in polished thin section of Bitter Springs chert. **A**, Optical photomicrograph - transmitted light. **B-F**, NanoSIMS maps of area in **A.** Arrows point to same cells. Scale in **A** applies to all.

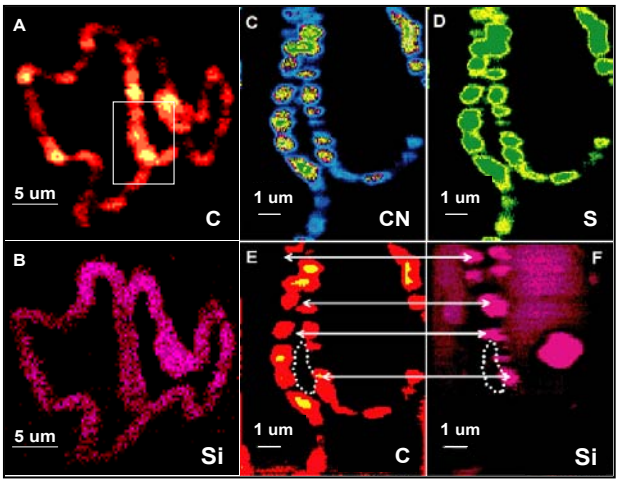


**Fig. 2**. NanoSIMS maps of walls between pair of cells in bottom of Fig. 1. **A-B**, Overview images. **C-F**, High resolution maps of rectangle in **A**; arrows in **E** and **F** tie locations of Si globules in **F** with corresponding locations in **E**; dotted white ovals in **E** and **F** tie identical areas.

- NanoSIMS maps of C, N (as CN), S, Si and O mirror optical microscopic images of spheroidal (Figs. 1-2) and filamentous (Fig. 3) microfossils.
- At high resolution, C, CN and S maps show nearly identical spatial distributions (Figs. 2C-E), whereas Si and O distributions are quite distinct (compare Figs. 2E-F; oxygen not illustrated here).
- The NanoSIMS data reveal internal structures in the lamina previously thought to be amorphous (Fig. 4).
- $^{12}C^{14}N/^{12}C$ ratios are distinctive for filaments, spheroids, and the "amorphous" lamina.

**Discussion:** The Bitter Springs microbiota is exceptionally well preserved and contains a diverse biota of cyanobacteria and algae [2]. Although 3-dimensionally permineralized spheroids and filaments are common in the section analyzed, most of the kerogen is less well preserved, occurring as non-descript organic laminae. However, there is no question that the laminae also are biogenic, as the abundance of microfossils in the formation argues that all the kerogen has had a biological derivation, regardless of its preservational state.

The coincidence between optical images of the microfossils and NanoSIMS maps of C, CN and S (Figs. 1, 3), coupled with the virtually identical spatial distributions of C, CN and S in high resolution (Fig. 2), suggests a biological origin for these elements. C, N, and S are likely

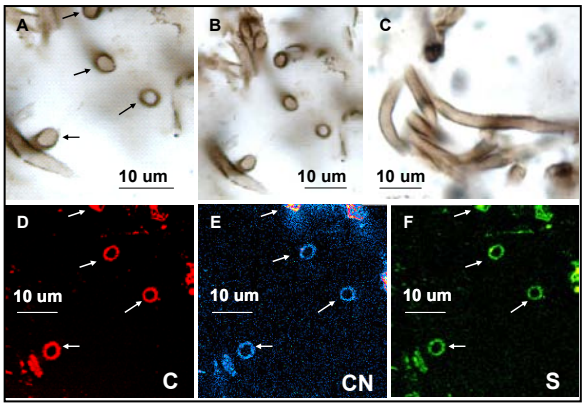


**Fig. 3**. Filamentous microfossils in polished thin section of Bitter Springs chert. **A-C**, Optical photomicrographs - transmitted light; **B-C**, Focal planes below surface illustrating sinuosity of the filaments. **D-F**, NanoSIMS maps of area in **A**. Arrows in **A**, **D-F** point to the same filaments (seen as cross sections).

to derive from remnants of cellular constituents, especially membranes, walls, and sheaths. The S maps may include, additionally, organic sulfur incorporated during degradation of the organic matter by sulfate-reducing bacteria. Si and O also mimic the morphology of the microfossils (Fig. 1), and this most likely has resulted from nucleation of silica-rich phases on organic surfaces during permineralization [3-6]. The spatial alternation of Si and C globules (Figs. 2E-F) may reflect this process. Si in the chert matrix generally has a less intense NanoSIMS response as can be seen in Fig. 2F, to the right and left of the Si globules associated with cell walls. Slight differences between optical and NanoSIMS images are due to the fact that NanoSIMS examines only the very top of a sample, whereas the optical photomicrographs were taken slightly below the topmost focal plane.

Figure 4 demonstrates the potential of NanoSIMS to elucidate structure in an organic lamina that otherwise appears amorphous. Neither optical microscopy nor SEM showed significant structure within this lamina, but NanoSIMS maps reveal morphologies reminiscent of the spheroids and filaments and suggestive of compressed microfossils. This result is particularly important, as the preponderance of organic matter in most Precambrian sediments occurs as similarly "amorphous" kerogen, even in the best preserved deposits. Therefore, it may be that NanoSIMS will provide new insights into a large body of previously uninterpretable organic material.

$^{12}C^{14}N/^{12}C$ ratios are quite distinct for the filaments (0.015 - 0.04) and the spheroids (0.12 - 0.22), possibly reflecting original variations in their chemical make-up (mucilaginous sheath material for the filaments versus cell wall compounds for the spheroids). If such ratios do reflect different biochemical precursors, they may be helpful for interpreting poorly preserved organic fragments in older or even extraterrestrial samples. The organic lamina shows a much greater range of $^{12}C^{14}N/^{12}C$ values (0.12 – 1.0), likely indicating a mixture of microbial constituents (e.g., filaments, spheroids, other algae and bacteria). In fact, a large range of CN/C values may be a characteristic of a natural biological community and could - in itself - be a biosignature useful for discriminating abiotic from biological organics.

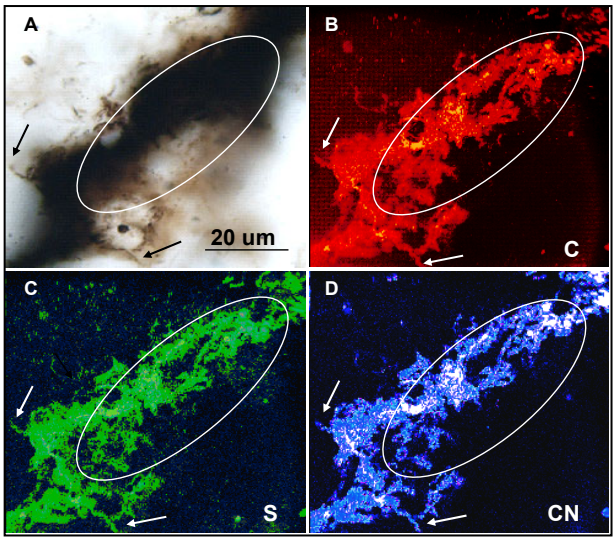


**Fig. 4**. Organic lamina in polished thin section of Bitter Springs chert. **A**, Optical photomicrograph - transmitted light. **B-D**, NanoSIMS maps. Arrows and white ovals are for reference; scale in **A** applies to all.

**Conclusions**: Our understanding of the development of earliest life on Earth continues to be challenged by the problem of distinguishing *bona fide* microfossils from various non-biogenic organic materials [7-11]. Results presented here suggest that "nano" morphology and element chemistry revealed by NanoSIMS may provide new biosignatures that will aid in assessments of poorly preserved and problematic organic materials. This should provide fresh insight into the origin and potential biogenicity of controversial Archean structures and any organic materials that may occur in Martian or other extraterrestrial samples.

**References:** [1] Robert, R., Selo, M., Hillion, F. & Skrzypczak, A. (2005). *LPS XXXVI*, Ab. #1314. [2] Schopf, J.W. (1968*). J. Paleont., 42*, 651-688. [3] Oehler, J.H. & Schopf, J.W. (1971). *Science, 174*, 1229-1231. [4] Oehler, J.H. (1976). *GSA Bull. 87*, 117-129. [5] Benning, L.G., Phoenix, V., Yee, N., Tobin, M.J., Konhauser, K.O. Mountain, B.W. (2002). *Geochemistry of the Earth's Surface 6*, 259-263. [6] Toporski, J.K., Stelle, A., Westall, F., Thomas-Keprta, K.L. & McKay, D.S. (2002). *Astrobiology 2 (1)*, 1-26. [7] Schopf, J.W. (2002). *GSA Prog. Abs*. #67-2. [8] House, C.C., Schopf, J.W., McKeegan, K.D., Coath, C.D., Harrison, T.M. & Stetter, K.O. (2000). *Geology, 28(8),* 707-710. [9] Kudryavtsev, A.B., Schopf, J.W., Agresti, D.G. & Wdowiak, T.J. (2001). *PNAS, 98 (3),* 823-826. [10] Brasier, M.D. *et al.* (2002). *Nature, 416*, 76-81. [11] García-Ruiz, J.M., Hyde, S.T., Carnerup, A.M., Christy, A.G., Van Kranendonk, M.J. & Welham, N.J. (2003). *Science, 302*, 1194-1197.