# *Bona fide* biosignatures: Insights from combined NanoSIMS-SIMS

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*Bona fide* biosignatures are those for which both biogenicity and syngeneity can be established. NanoSIMS, particularly in combination with SIMS, is providing new insights into both these criteria. NanoSIMS yields *in situ*, 50 nm-resolution, element abundance and ratio maps of trace quantities of carbonaceous and mineral materials. In 2006, NanoSIMS was used to characterize C, N, S, Si and O occurrence in undisputed Late Precambrian (~ 0.8 Ga) microfossils excellently preserved in chert [1]. Results provided a baseline for interpreting less well preserved organic remains in older and/or extraterrestrial samples.

More recently, NanoSIMS was used to assess spheroidal and spindle-shaped structures in Early Archean (~ 3 Ga) cherts [2]. Element distributions are similar to those in the ~ 0.8 Ga microfossils but distinct from those of carbonaceous material within a hydrothermal vein. Also, spatial relationships among C, Si and O in the Archean and 0.8 Ga structures may reflect silica nucleation on organic surfaces [1], supporting prior conclusions that the structures are the same age as the enclosing cherts. Initial $\delta^{13}C$ analysis of the individual Archean structures, using SIMS, supports a biogenic interpretation. If further study corroborates this assessment, then the age, size, and complexity of the spindles would suggest that life on Earth was moderately advanced by 3 Ga. Pairing NanoSIMS with other techniques such as SIMS will provide further insights into biogenicity and syngeneity that can be applied to any minute C-bearing residues that might be found in ancient terrestrial or extraterrestrial samples.

[1] Oehler *et al*. (2006) *Astrobiology* **6**(6), 838-850. [2] Oehler *et al*. (2008) *39th LPSC*, Abstract #1303.

# The surface chemistry of multi-oxide silicates

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The surface chemistry of natural wollastonite, diopside, enstatite, forsterite, and albite in aqueous solutions was characterized using both surface titrations in limited residence time batch reactors and electrokinetic techniques [1, 2]. The compositions of all investigated surfaces vary dramatically with pH. Ca and Mg are preferentially released from wollastonite, diopside, enstatite, and forsterite at pH less than ~8.5-10 but preferentially retained at higher pH. As such, the surfaces of these minerals are Si-rich/divalent metal poor except in strongly basic solutions. The preferential removal of divalent cations from these surfaces is coupled to proton consumption. The number of protons consumed for each divalent cation removed varies from 1.5 to 4 depending on the mineral. This suggests the creation of additional 'internal' adsorption sites through the preferential removal of divalent metal cations. Similarly, Na and Al are preferentially removed from the albite surface at all pH; mass balance calculations suggest that three protons are consumed by the preferential removal of each Al atom from this surface. Electrokinetic measurements yield isoelectric points of 2.6, 4.4, 3.0, 4.5, and <1 for wollastonite, diopside, enstatite, forsterite, and albite, respectively, consistent with the predominance of $SiO_2$ in the surface layer of all of these silicates at acidic pH. Taken together these observations suggest fundamental differences between the surface chemistry of simple versus multi-oxide minerals including 1) a dependency of the number and identity of multi-oxide silicate surface sites on the aqueous solution composition, and 2) multi-oxide dissolution rates and surface charge exhibit different pH variations [3, 4].

[1] Pokrovsky & Schott (2000) *GCA* **64,** 3299-3312. [2] Chaïrat *et al.* (2007) *GCA* **71** 5888-5900. [3] Oelkers (2001) *GCA* **65**, 3703-3719, [4] Oelkers & Schott (2001) *GCA*, **65**, 1219-1231.