Speciation of Fe in modern Mexican lacustrine microbialites

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Microbialites are organo-sedimentary rocks found in abundance throughout the geological record back to 3.7 Ga. They have often been used to reconstruct paleoenvironments but a better characterization of modern analogues is crucial to improve such actualism-based interpretations. Here, we evidenced Fe-rich modern microbialites (up to 2.2 wt.% Fe) in 5 crater lakes in Mexico. The presence of such high Fe concentrations in rocks forming in akaline and oxygenated water was surprising and called for further investigation of the Fe cycle in these environments.

Bulk x-ray diffraction, infrared spectroscopy and x-ray absorption spectroscopy (XANES and EXAFS) analyses were used to characterize the mineralogical composition of these rocks and Fe speciation. We found several Fe-bearing phases: Fe-containing Mg-silicates, Fe-Mg layered double hydroxides (LDH) and Fe-(oxyhydr)oxides. Fe was mostly trivalent. Synchrotron-based x-ray microfluorescence mapping correlated with scanning electron microscopy showed Fe hotspots sometimes arranged as discrete fine laminae, sometimes appearing as patches of ~100 μm width. Using a focused ion beam milling, transmission electron microscopy and scanning transmission x-ray microscopy at the C K-edge and Fe $L_{2,3}$-edges, we showed that LDH was Al-poor and was close to pyroaurite-iowaite composition with Mg^{2+}, Fe^{3+}, Cl^- and CO_3^{2-}. Moreover, pyroaurite was observed in one of the lakes only, sometimes in association with Fe-Mg-silicates. Silicate phases were more abundant in microbialites from the other lakes. We propose that pyroaurite may precipitate where Fe-rich, anoxic groundwater seeps into the Si-poor, alkaline and oxygenated water of the lake. This phase may transform to Fe-rich Mg-silicate over time. Overall, these Fe-rich microbialites covered with biofilms provide interesting modern model systems for studying Fe dynamics at a sharp anoxic-oxic transition.

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