Microbial acceleration of sulfuric acid speleogenesis in Kane Cave, WY

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The traditional model of karst and cave formation is that of carbonic acid limestone dissolution, where biologically-produced CO_2 in meteoric water reacts with and dissolves limestone. However, an alternative model has been proposed for several important karst systems where sulfide is abundant; known as sulfuric acid speleogenesis (SAS). Here, acid produced by chemoautotrophic sulfur-oxidizing bacteria (SOB) corrodes limestone while producing dissolved calcium and sulfate. [1]. While it now seems clear that microbes are important in this process, little is known about the rate of limestone dissolution due to SOB activity, or the nature of the microbe-limestone attachment and interaction..

Lower Kane Cave, WY is an active SAS-formed cave where rapid steam H_2S oxidation is associated with microbial mats [1]. Clone libraries have identified the dominant microbial population as *Epsilonproteobacteria* sp., a group that often oxidizes reduced sulfur compounds under microaeophilic conditions [1].

In this study the rate of limestone dissolution due to microbial oxidation of reduced sulfur compounds was investigated using laboratory and field microcosms. Laboratory chemostat chamber experiments were designed to mimic the cave environment with and without SOB. Preliminary results show rapid dissolution in the biotic chambers, even when the bulk chamber solution is supersaturated with respect to calcite. ESEM imaging of the limestone surfaces from the biotic chamber experiments shows extreme pitting, in contrast to the abiotic chamber, particularly where bacteria is visible on mineral surfaces. Parallel experiments where limestone chips were maintained in dialysis tubing show much slower rates in the biotic chamber, and little change in the abiotic. These results suggest that low-pH microenvironments created at the mineral surface by microbial acid generation are primarily responsible for limestone dissolution in microbially mediated SAS caves.

[1] Engel, A.S., Stern, L.A. & Bennett, P.C. (2004) *Geology* **32**, 369-372.

Micro-scale source and diagenesis detection in BIF using femtosecond laser ablation MS of stable Fe and Si isotopes

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We have detected differences between coexisting minerals and also inter-layer differences in Fe and Si isotope ratios in BIF at 30μm resolution using a UV femtosecond laser ablation system connected to a a MC-ICP-MS. In the magnetite-carbonate-chert BIF from the Archean Old Wanderer Iron Formation in the Shurugwi Greenstone belt (Zimbabwe) magnetite δ^{56}Fe values show neither intra- nor interlayer trends giving an overall uniform δ^{56}Fe of ca. +0.9‰. Similarly, bulk iron carbonates are also relatively uniform at near-zero values, but their individual δ^{56}Fe is highly composition-dependent: both siderite and ankerite and mixtures between both are present and δ^{56}Fe endmember values range between +0.4‰ for siderite and -0.7‰ for ankerite. The data suggest either an early diagenetic origin of magnetite and iron carbonates by the reaction of organic matter with ferric (hydr)oxide catalysed by microbes; or an abiotic reaction at low-grade metamorphism. An overall picture emerges in that bulk minerals, especially magnetite, are relatively uniform in composition but bulk layer compositions vary strongly and that these variations appear to be mineralogy-controlled. So are these inter-layer variations preserved from the time of precipitation or are they secondary? We believe the former, because the Si isotope composition of the Old Wanderer BIF also shows significant variations with δ^{30}Si values ranging between -1.0‰ and -2.6‰ for bulk layers. Most importantly, Si and Fe isotope signatures of bulk layers are positively correlated, which can be interpreted as record of fluctuations in the hydrothermal activity in the basin. If that is so, then neither exchange across layering nor back-recycling of diagenetic pore fluids into seawater has taken place and the Fe and Si isotope compositions of bulk layers in the Old Wanderer BIF reflect primary signatures. So with our microanalytical tool we are able to detect both the solute flux history into the sedimentary BIF precursor, and the BIF's diagenetic history from the comparison between co-existing minerals and their predicted fractionation factors.