Phase identification of complex Cu-Fe sulfides using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

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ToF-SIMS is a monolayer-sensitive surface analytical technique that has been extensively used in mineral processing to identify the elemental and molecular composition of a mineral surface. The combination of mass spectrometry and imaging makes ToF-SIMS a sensitive and capable technique for precisely identifying surface chemistry and its distribution across the surface. Traditionally, ToF-SIMS mass spectra have been used to provide the surface chemistry of an ore with little specificity to the local surface chemistry of a particular mineral phase. Some mineral specificity has been achieved by imaging particles using a major element of their composition. However, the identification of mineral phases that contain the same elements in a mixed multi-metal mineral system like chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4) presents a unique challenge for ToF-SIMS. The addition of precipitated, adsorbed, reacted and contaminant species in the outermost molecular layers produce complex mass spectra that are difficult to interpret using conventional methods.

For the effective analysis of such mineral systems, sufficient sensitivity and selectivity are required to detect significant components of the mass spectra. Furthermore the determination of surface chemistry, on a particle by particle basis, requires the selection of a particular mineral phase and statistical analysis of particles with an estimation of the variability of the value. The complex mass spectral data sets were analyzed using an adaption of principle component analysis – artificial neural networks (PCA-ANN). The analysis of ToF-SIMS data, has resulted in the successful classification of bornite, chalcopyrite, chalcocite and pyrite at different flotation stages. A method for phase identification of particles using ToF-SIMS has been used to track the surface chemistry of an individual particle throughout complex processing procedures[1].

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Using isotopic and morphological evidence to determine biogenicity of gypsum precipitates in the Frasassi caves, Italy

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The process of biomineralization can leave unique fingerprints in the chemical and physical properties of a mineral, specifically in its isotopic composition and morphology. In the Frasassi cave system (Italy), gypsum forms at the cave wall-atmosphere interface as a consequence of limestone corrosion by sulphuric acid, which is produced by H_2S oxidation mediated by microbes (i.e., *Acidithiobacillus thiooxidans*). We sampled gypsum, drip water, and $H_2S(g)$ from the Grotto Bella chamber near an active H_2S vent, and measured mineral aspect ratios, particle size, mineral and H_2S $\delta^{34}S_{CDT}$, mineral and limestone $\delta^{44}Ca_{SRM915a}$, and drip water elemental concentrations to find evidence of biomineralization. The gypsum occurs in three distinct morphologies: equant microcrystalline (<50 μm) crystals, wall crust, and needles up to 1 cm in length. The crust is characterized by small needles and aggregates of microcrystalline gypsum held together by biofilm. In Grotta Bella, smaller crystals are generally proximal to the H_2S source, whereas larger needles are found distally. The microcrystalline gypsum and needles are fractionated in $\delta^{34}S$ from the H_2S by -12 and -6‰ ($2\sigma \leq 1$‰) respectively. The $\delta^{44}Ca$ of the microcrystalline and needle deposits are offset from the limestone wall by -0.04 and -0.84‰ ($2\sigma \leq 0.23$‰) respectively. A biogenic origin of the microcrystalline gypsum may be deduced from the unusually low aspect ratios and highly negative $\delta^{34}S$ relative to the H_2S. The microcrystalline morphology may have arisen by crystal nucleation on individual cells embedded in the biofilm. The negative $\delta^{44}Ca$ of the needles may also suggest biogenicity, as the bacteria tend to colonize the larger gypsum needles more than the smaller morphologies.