Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.7349

S zonation in aragonite and microscale δ^{34}S heterogeneities in barite & pyrite record the geochemical evolution of cold seep environments

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The anaerobic oxidation of methane by sulfate reduction (AOM-SR) produces steep geochemical gradients in active cold seep environments that foster the precipitation of pyrite (FeS_2), barite ($BaSO_4$), and methane-derived authigenic carbonates (MDAC). These minerals preferentially precipitate near the sulfate-methane transition zone (SMTZ) where AOM-SR activity is high and record the δ^{34}S composition of ambient sulfide (pyrite) and sulfate (barite and carbonate-associated sulfate (CAS) in MDAC). In these environments, SMTZ depth and porewater $\delta^{34}S_{\text{sulfate, sulfide}}$ compositions depend on the relative rates of sulfate diffusion and AOM-SR activity, which can also affect mineral saturation state(s). Here, we use a combination of micro X-ray Fluorescence (µ-XRF) mapping, X-ray absorption near edge structure (XANES) spectroscopy, scanning electron microscopy (SEM), and secondary ion mass spectrometry (SIMS) to evaluate the microscale compositional and petrographic variability of MDAC, barite, and pyrite precipitated in active cold seep environments on the continental shelf of northern Norway. Within cm-scale samples, SIMS $\delta^{34}S_{\text{Pyrite}}$ values can range more than 30‰ among framboids, and there appears to be a relationship between framboid diameter, $\delta^{34}S_{\text{Pyrite}}$ composition, and adjacent MDAC mineral phase (aragonite vs. Mg-calcite). Multimodal distributions of $\delta^{34}S_{\text{Pyrite}}$ values within individual samples suggest pyrite precipitated under multiple discrete environmental regimes. The assessed barite are highly enriched in ^{34}S, and the mean $\delta^{34}S_{\text{BaSO4}}$ value from SIMS spot analyses is 70.3‰, but $\delta^{34}S_{\text{BaSO4}}$ values can range more than 40‰ within individual barite aggregates (< 250 µm) and are most variable along growth axes. Similarly, XANES spectra and µ-XRF maps of aragonite reveal systematic fluctuations in CAS concentrations along growth axes and between successive layers, patterns which can be traced over large lateral distances (> 5 mm). We suggest these microscale changes in $\delta^{34}S_{\text{Pyrite, BaSO4}}$ values and CAS concentrations record the geochemical evolution of microenvironments during mineral precipitation and were likely modulated by variable methane flux. These systematic microscale S heterogeneities can provide novel insight into paleo seep conditions.

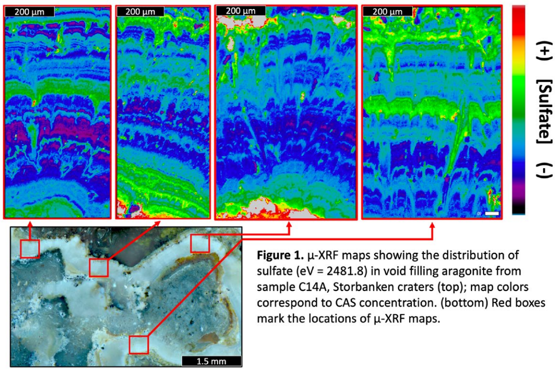

Figure 1. µ-XRF maps showing the distribution of sulfate (eV = 2481.8) in void filling aragonite from sample C14A, Storbanken craters (top); map colors correspond to CAS concentration. (bottom) Red boxes mark the locations of µ-XRF maps.

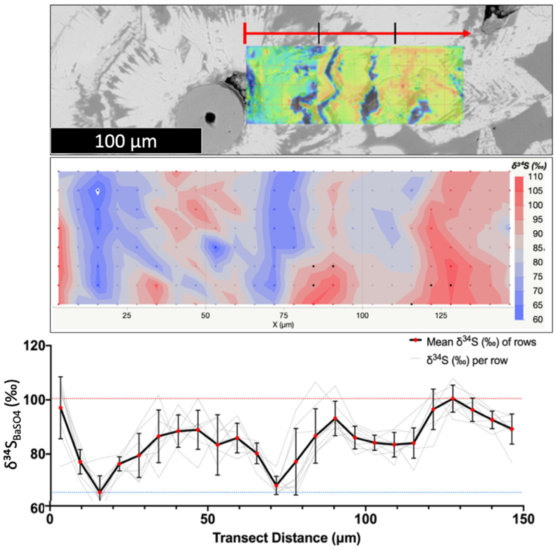

Figure 2. SIMS imaging transects from a layered barite aggregate in sample P-42 from LV continental shelf. (top) BSE image overlain with ion transect; transect colors correspond to ^{32}S count rates. (middle) Heatmap of transect $\delta^{34}S_{\text{BaSO4}}$ values (n = 186); X axis values are parallel to the primary growth axis. (bottom) scatter plot showing mean $\delta^{34}S_{\text{BaSO4}}$ values along the X-axis (red circle) and standard deviation of $\delta^{34}S_{\text{BaSO4}}$ values perpendicular to the primary growth axis.