Diagenetic Features in the Late Cambrian Alum Shale across the SPICE Event, Sweden

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ABSTRACT

Detailed diagenetic studies of the Late Cambrian Alum Shale in southern Sweden were undertaken on an interval in the formation that includes the peak SPICE (Steptoean Positive Carbon Isotope Excursion) Event to evaluate the alteration signature, if any, across this presumed widespread anoxic/euxinic event. This presumed worldwide event has been recorded in both shallow-water carbonates and shelfal black mudstones and demonstrates a positive shift in 0 13C of carbonate carbon paralleled by a positive 034S excursion in pyritic sulfur. The samples used in this investigation, which were originally deposited in the distal, siliciclastic mudstone-rich end of a shelf system and were the focus of a detailed sedimentological study, were collected from the Andrarum-3 core, which was drilled adjacent to the Andrarum quarry in Scania, Sweden. The sample site was also from the same core and intervals that were the subject of a geochemical study.

Sedimentologically, the Alum Shale was deposited through the peak SPICE event, consists largely of siliciclastic mudstones deposited by bed-load processes, and locally a more proximal carbonate facies. Four distinct facies are recognized, including, in decreasing abundance; facies I) clay clast-rich mudstones, facies 2) laminated mudstones with macrofossil debris, facies 3) laminated mudstone, and facies 4) carbonate mudstones/siltstones (not investigated in this study). In facies I mudstones, present day TOC (total organic carbon) values (Leco TOC) range from 6 to 14 wt% (n = 22); the Alum experienced significant thermal maturity insofar as hydrogen indices (HI) from RockEval pyrolysis typically are <10 mg hydrocarbon/gram of TOC. Within facies I mudstones, as with all facies, abundant fecal strings and Planolites burrows provide evidence of biotic colonization.

Diagenesis in the Alum Shale records numerous generations of authigenic mineralization, mechanical compaction, and at least two different types of fracturing, based on preliminary observations of polished thin sections (n = 42) spaced 0.5 m or less throughout about 19 m of Alum Shale. Framboidal pyrite is present in the matrix of samples of all facies types, and the framboids range in size from <5 to >20 O m in diameter. Evidence of mechanical compaction includes grain rearrangement of elongate detrital clay clasts, distortion of bedding around concretions, and distortion of bedding around Planolites burrows. Given that observable porosity is largely absent in these rocks, and that mineralization is dominantly in small concretions, localized in massive pyrite masses, and disseminated in the matrix, compaction is considered a dominant mechanism for porosity reduction. Organic porosity is unlikely to have withstood compaction (ongoing investigations).

Elongate features, which are either continuous along the entire length of individual thin sections (>2 em), or occur as en echelon segments, are parallel or subparallel to bedding. These features are commonly filled with varying amounts of calcite, chalcedony, and pyrite. The calcite occurs as adjacent blocky crystals, and appears to have precipitated perpendicular to the elongation of these features. Chalcedony fills some of these features, and pyrite is locally present at the edges or in more central parts of the features. That the calcite appears to have grown across

them indicates that they were open during mineralization, similar to the appearance of 'beef observed in rocks elsewhere. The presumed 'beef,' considered herein as one of the types of fractures in the Alum Shale, is dominant in facies I mudstones and minimal in other facies. There is also a crude zonation of 'beef infill mineralization with calcite (±pyrite) dominant throughout except in the lower part of the SPICE interval. Chalcedony, however, appears to be the dominant mineralization in 'beef in the lower part of the SPICE interval. Another type of fracture in the Alum is vertical to subvertical, and filled with calcite. These fractures demonstrate relatively straight fracture walls.

Temporally, paragenetic relationships provide useful information concerning the relative timing of the various authigenic minerals discussed above. Framboids in the matrix of Alum sediments (PI) seem to have formed prior to other pyrite generations based on the observation that, locally, framboids are cemented by euhedral pyrite. Anhedral pyrite overgrowths (P5) on large euhedral pyrite (P4) clearly point to a later relative timing of the anhedral masses relative to the euhedra on which they occur. The pyrite (P6) that replaces calcite, including that in 'beef (C4) was paragenetically later than the formation of the reef features.

Concretionary pyrite demonstrates some variability in texture as a function of their location relative to the SPICE interval. Concretions containing framboids (P2) are present in most intervals observed, irrespective of facies, and are, therefore, considered ubiquitous. However, concretions comprised of euhedral pyrite crystals (P3) are generally restricted to samples that are either above or below the SPICE interval but are largely absent within SPICE. Consequently, the SPICE is unique in that only pyrite concretions contain P2 pyrite, whereas both P2 and P3 pyrite occurs away from the SPICE interval. Work continues to consider how the variability in these pyrite textures may relate to a sulfur isotopic variability noted by Gill et al.

The mineralogy and paragenesis together provide a framework for understanding the diagenetic evolution of the Alum Shale. That pyrite framboids in the matrix (PI) are variable in size indicates that they formed diagenetically rather than during deposition in a euxinic water column. Furthermore, deformation of bedding around pyritic concretions of all types (P2-P5) corroborates an early diagenetic timing of their formation, including within organic-rich mudstones of facies I. However, the presence of multiple generations of pyrite (Pl-P5) indicates that neither iron nor sulfur were limiting and the post-depositional waters in the sediments were reducing. The presence of presumed 'beef in the Alum likely is related to overpressuring in the formation; possible mechanisms responsible for overpressuring in the Alum include either petroleum generation or tectonism. Both petroleum generation (through gas generation, based on RockEval data) and tectonism post-dates alterations related to much of the pyrite (Pl-P5) and calcite (CI-C3) mineralization observed in the Alum. 'Beef calcite, as well as subsequent pyrite that replaces it (P6), as well as massive pyrite also are coeval with or post-date overpressuring in the Alum. The vertical fractures in the Alum point to another episode of fracturing and calcite (C4) mineralization, likely post-dating all other alterations described.

Overall, careful sedimentological and diagenetic analysis of the Alum Shale provides important information that assists in unraveling the complex alteration history experienced by it. Diagenesis in the Alum, as revealed from this study, resulted in significant change to the Alum, including the precipitation of multiple generations of cements, compaction, and fracturing. The record left by these diagenetic features corroborates that euxinic conditions were not at all the norm during deposition, but instead were likely dysoxic, including through the SPICE event. Nevertheless, reducing conditions prevailed during diagenesis, which resulted in periodic precipitation of texturally distinct pyrite generations. Also of note is that the presence of 'beef likely records overpressuing in the Alum, either from hydrocarbon generation or tectonism, which provides a glimpse at processes, beyond compaction, that acted to significantly mechanically modify the rocks long after deposition.