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Iron controls chemical and mineralogical pathways in organic-rich mudstones: implications for carbon and phosphorus burial and source-rock evolution.

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Early diagenetic pathways in Recent mud and ancient mudstone successions are mediated by microbial respiratory processes. Inevitably, these reactions are dependent upon availability of bioavailable reductants and oxidants. In Recent sediments consortia of micro-organisms exist that efficiently utilise the available reductants and oxidants such that generally very little organic matter leaks out of the biosphere into the lithosphere. In the rock record there are numerous examples where organic matter flux from the biosphere to the lithosphere seems to have been significantly large, resulting in the burial of organic matter rich mudstone successions. These successions, however, display contrasting variability in organic matter composition and diagenetic pathways. This variability is partly the result of the possibility for the organic component to be rendered refractory by early sulfurization (natural vulcanizaton). The chemical pathways that lead to early and rapid sulfurization are poorly known. It is likely however, that they are controlled by the prolonged availability of sulfur in pre-compaction pore waters. This paper seeks to address some of the fundamental mechanisms that might control sulfur-distributions in the pore waters of organic-rich fine-grained sediments.

In order to investigate this problem the diagenetic pathways in two contrasting organic-rich mudstone lithofacies are compared, the Miocene Monterey Formation, California, and the Jurassic Kimmeridge Clay Formation, U.K., to determine the role that initial mineralogy may play in controlling subsequent pore water chemistries and resulting microbially mediated diagenetic pathways. To investigate this problem whole rock geochemical data are compared with high-resolution images of the rocks collected using combined optical and electron-optical methods. These techniques demonstrate that these two mudstones, in spite superficial similarities in their macroscopic appearance are very different. Although both contain significant organic matter and other production-derived components (eg. Coccolithophores), the matrix of the Kimmeridge Clay Formation is dominated by clay minerals, and pyrite, along with carbonate cements. In contrast, the Monterey Formation contains abundant diatoms, only trace pyrite and abundant phosphate cement.

We conclude that the presence of clastic input, specifically the availability of Fe(III) associated with this supply, has a dramatic effect on diagenetic pathways. In iron-rich mudstones, Fe(III) acts as a sink for reduced sulfur species as pyrite is buried, whereas in iron-poor mudstones organic matter acts as a sink for sulfur in the absence of iron, leading to the burial of sulfur-rich organic matter. The varying presence of detrital iron in these settings plays an important role in the subsequent diagenesis of these rocks and is likely one of the fundamental controls on both natural carbon sequestration efficiency and organic matter evolution and maturation during diagenesis.