

Competition between organic matter and iron on reduced S species during the deposition of the Senonian oil shale in Israel

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The Senonian oil shales in Israel were deposited under the upwelling marine high-productivity systems prevailed along the Tethyan margins (Meilijson et al., 2013; Schneider-Mor et al., 2012). The Senonian oil shales sequence from the Aderet borehole in the Shefela Basin represent the thickest, about 350m, oil shale sequence in Israel. It also represents the longest duration of the upwelling marine high-productivity deposition system which spans for ca. 19 Myr (Meilijson et al., 2013). The Senonian oil shales in the Shefela Basin are rich in S in different organic and inorganic phases. Studying the organic and inorganic S distribution and their associated $\delta^{34}\text{S}$ values should be useful for understanding the paleo-environmental history associated with the upwelling system. The present study focuses on the S content and $\delta^{34}\text{S}$ distribution of different S bulk phases extracted from the Senonian oil shales in the Shefela Basin, Israel. Iron content and speciation in organic and inorganic phases were also studied. This study represents the groundwork for a more detailed compound specific S isotope analysis (CSSIA) study that runs in parallel, which is still at work. The CSSIA study of this system will add another dimension for the study and add more controls on this very complex system. We analyzed nine cores that were taken from the Aderet borehole (Israel) that represent the whole Senonian oil shale sequence (depth of ~ 250-600 m below surface). This source rock is organic-rich (up to 20% TOC) and sulfur-rich (up to 3%) and the depth profiles show large variability from a maximum between 341-420 m to a minimum between 420-600 m. The sulfur occurs predominantly as organic sulfur; up to 86 wt. % of the total sulfur. The organic S content as well as TOC show an inverse trend with the pyritic S content (Fig.1-a). This inverse trend suggests either sulphate or iron limited system or their combination. The uniform degree of pyritization (DOP), with an average of 42%, despite the change in highly reducible iron along the section, corroborates the suggestion of iron limited system (Dean & Arthur, 1989) (Fig.1-b). Organic compounds may mask or complex with the iron and thus prevent or delay the pyrite formation. Therefore, small amounts of pyrite could be formed even if there were high concentrations of reactive iron (HRFe) as observed in the studied system (Fig.1-b). The inverse trends between organic iron (Fe-Org) and pyritic iron (Fe-Py) confirms our suggestion that there was a competition between OSCs and pyrite formation (Fig.1-c). The $\delta^{34}\text{S}$ value of the pyrite is affected correspondingly to this competition. As more Fe is trapped by the OM less pyrite formed at the earlier stages and the pyrite $\delta^{34}\text{S}$ became more ^{34}S enriched (Fig.1-d). This ^{34}S enrichment can be the result of the delay in pyrite formation and thus, the Fe react with more ^{34}S enriched reduced S portion according to Rayleigh distillation. The increase in the organic Fe content does not compensate for the decrease in the pyritic Fe content (Fig.1-c). However, the kerogen (>95% of the TOC) iron content, has not been measured yet and might make up the gap between Fe-Org and Fe-Py. The $\delta^{34}\text{S}$ depth profile of the kerogen sulfur (KS) and the pyritic sulfur (PS) show similar trends, both ^{34}S depleted relative to the source sulphate at that period (~17-20‰). However, KS is consistently ^{34}S enriched relative to co-existing pyrite up to about 41‰. This difference is unusual and may point to diverse diagenetic processes that the

CSSIA may explain these processes. A numeric model of the obtained results suggest high S fractionation during the microbial sulphate reduction (MSR) process and that the MSR process is the main source for the ^{34}S depleted reduced S species rather than S disproportionation. High S fractionation ($\sim 60\text{-}70\%$) during the MSR process is needed to explain the observed $\delta^{34}\text{S}$ values for both organic S and pyrite even for the core sample where the $\delta^{34}\text{S}$ of the pyrite is high. The model also supports the iron limited system scenario over sulphate limited system.

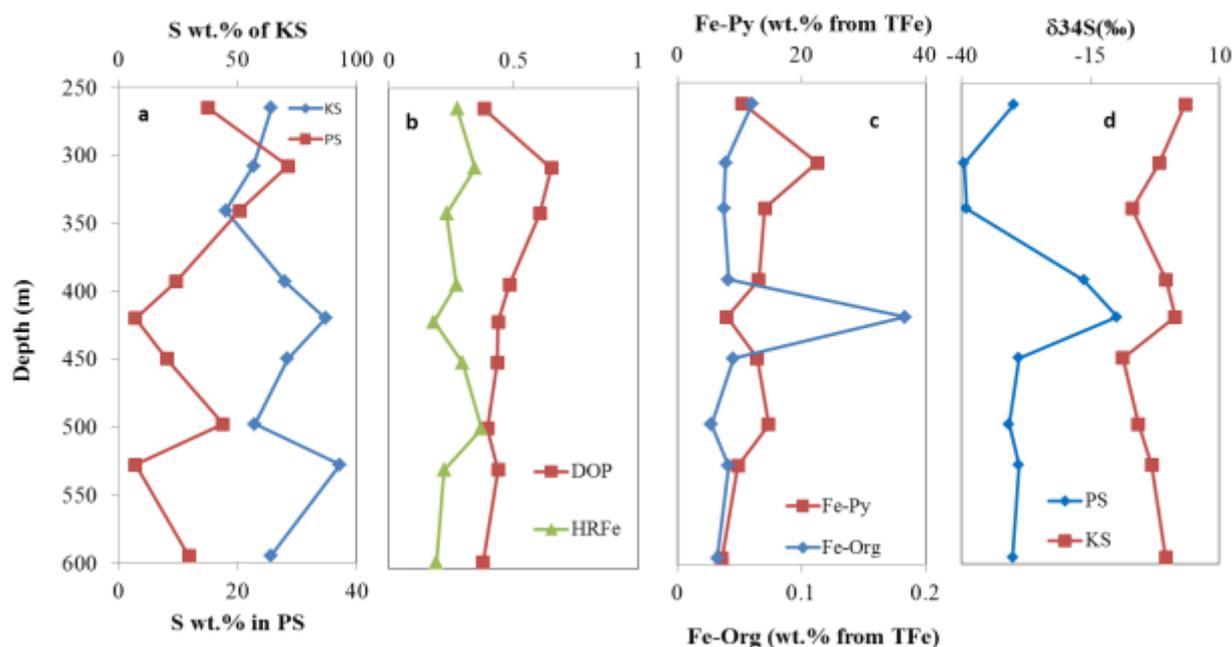


Fig. 1 depth profile of the Aderet borehole of bulk phases, a) S content in pyrite (PS) and kerogen (KS), b) degree of pyritization (DOP) and highly reducible iron of the total iron (HRFe), c) organic iron content (Fe-Org) and pyritic iron (Fe-Py), d) $\delta^{34}\text{S}$ of pyrite (PS) and kerogen (KS)

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