

Unravelling early diagenesis: New insight from microscale minor sulfur isotopes

MR. VIRGIL PASQUIER, PHD¹, MARIE-NOËLLE DECREAENE², JOHANNA MARIN-CARBONNE², DR. CHRISTOPHE THOMAZO³, DAVID A. FIKE⁴ AND ITAY HALEVY¹

¹Weizmann Institute of Science

²Université de Lausanne

³Laboratoire Biogéosciences, UMR CNRS 6282, Université de Bourgogne Franche-Comté

⁴Washington University in St Louis

Presenting Author: virgil.pasquier@weizmann.ac.il

Marine pyrite preserves the sulfur isotope fingerprint of microbial metabolic activity and physical processes of transport and mineralization. During burial, aqueous sulfide forms primarily by the activity of microbes mediating organoclastic sulfate reduction (OSR) and anaerobic methane oxidation coupled to sulfate reduction (AOM-SR), both of which impart a microbial ³⁴S fractionation (ϵ_{mic}) ranging from -3 to -70 ‰. Distributions of $\delta^{34}\text{S}$ values in individual pyrite grains (measured by SIMS) have recently been shown to distinguish conditions of sulfate drawdown and isotopic (Rayleigh) distillation from conditions of effective diffusive buffering of porewater sulfate $\delta^{34}\text{S}$ values to those of seawater sulfate. Though such approaches have distinct advantages over bulk pyrite isotopic analysis, they cannot constrain the dynamics of sulfide production and consumption during progressive sulfate drawdown and isotopic distillation, which are of interest for understanding diagenetic carbon and sulfur cycling.

Here, we harness microscale minor sulfur isotopic analysis to further constrain sulfur diagenesis. We report measurements from organic poor-sediments, which feature microscale variations in pyrite $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values of up to 134‰ and 0.25‰, respectively, over glacial-interglacial timescales. The data populate a dual array in $\delta^{34}\text{S}$ – $\Delta^{33}\text{S}$ space. Early pyrite tracks the isotopic composition of instantaneous sulfide formed by reduction of sulfate with $^{34}\epsilon_{\text{mic}}$ of ~ -73 ‰ and $^{33}\epsilon_{\text{mic}}$ of ~ -0.515 . From this \sim linear array, it appears that approx. 50% of the porewater sulfate was microbially reduced under near-equilibrium conditions. Later pyrite, which is sometimes inclusion of authigenic carbonate minerals, populates a downward curving array, which markedly departs from the instantaneous sulfide array. A coupled model of microbial fractionation and sediment diagenesis requires accumulation of porewater sulfide to reproduce the curved $\delta^{34}\text{S}$ – $\Delta^{33}\text{S}$ array, with no change to $^{34}\epsilon_{\text{mic}}$ and $^{33}\epsilon_{\text{mic}}$. The morphology of the late pyrite and the authigenic carbonates associated with it suggest that sulfide accumulation may have been related to AOM-SR. We suggest that microscale multiple sulfur isotopic analysis coupled to quantitative diagenetic modelling may allow interpretation of distinct $\delta^{34}\text{S}$ – $\Delta^{33}\text{S}$ arrays to distinguish contributions to sedimentary pyrite from conditions of sulfide accumulation vs.