

Local sulphide oxidation drives carbonate dissolution in modern shallow marine carbonates: Evidence from oxygen and sulphur isotope composition of pore water sulphate

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We have investigated sulphur cycling in modern carbonate sediments from the Florida Platform, U.S.A. Relations among pore water chemistry (SO_4^{2-} , ΣCO_2 , $\text{Ca}^{2+}/\text{Cl}^-$) and oxygen and sulphur stable isotope composition of SO_4^{2-} require a direct coupling between sulphur redox cycling and syndepositional carbonate dissolution. Importantly, despite rapid rates of sulphate reduction, organic-rich carbonate sediment pore waters typically maintain $\text{SO}_4^{2-}/\text{Cl}^-$ ratios within 5% of seawater values, suggesting local reoxidation of H_2S . Shallow shelf carbonates comprise 93% of the entire Phanerozoic carbonate rock record and about 38% of the modern oceanic carbonate accumulation, so quantifying sulphur and carbon coupling during the early marine diagenesis is vital in deciphering biogeochemical cycling (e.g. Ronov, 1980; Milliman, 1993). In low-Fe carbonates, H_2S - O_2 reactions can lower pH values and pore water saturation states promoting carbonate dissolution (e.g. Boudreau, 1991). Given that platform carbonate dissolution fluxes are roughly half of gross biogenic carbonate production, sulphur cycling may greatly affect carbonate preservation and accumulation (Walter and Burton, 1990; Walter *et al.*, 1993).

Pore water sulphate $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values were markedly shifted from the established seawater values of +9.5‰ (SMOW) and +21.0‰ (CDT), respectively. Chemical evolution was least in environments where the sediment-pore water system was relatively 'open' to the overlying seawater. The greatest chemical evolution was observed in bioturbated sediments colonized by *Thalassia* grass. Here, there was a $\delta^{18}\text{O}_{\text{SO}_4}$ shift of 5‰, variable $\delta^{34}\text{S}_{\text{SO}_4}$ values (+17.7 to +23.3‰), and exceptionally high $\text{Ca}^{2+}/\text{Cl}^-$ ratios. These shifts in

pore water sulphate isotopic compositions exist despite the apparent lack of net sulphate reduction (Fig. 1). The natural system isotope trend is in marked contrast to the closed system isotope evolution observed in sediment incubation experiments (Fig. 1).

Importantly, sulphide oxidation is required as an acid source because pore water $\text{Ca}^{2+}/\text{Cl}^-$ and ΣCO_2 values exceed those attributable to the utilization of dissolved oxygen and the small amount of net sulphate reduction. The observed degree of carbonate dissolution (up to 2.3 mM excess Ca^{2+}) and sulphate isotopic values are best explained by a redox cycle where bacterial sulphate reduction is followed by efficient H_2S oxidation resulting in relatively invariant $\text{SO}_4^{2-}/\text{Cl}^-$ ratios. The O_2 required to locally oxidize pore water H_2S may come from oxygenated seawater advection or from marine grass rhizome systems which enhance oxygen supply rates. A mass balance model demonstrates that the observed $\delta^{18}\text{O}_{\text{SO}_4}$ values are consistent with measured sulphate reduction rates and the short pore water residence times.

Pore water geochemistry and sediment incubation experiments confirm that sulphur cycling has a profound effect on the early marine diagenesis of shallow platform carbonates. The important diagenetic processes are oxic respiration, bacterial sulphate reduction, sulphide oxidation, and carbonate dissolution. In most sediments, pore water $\text{SO}_4^{2-}/\text{Cl}^-$ ratios are near overlying ocean values, yet in many cases SO_4^{2-} has been recycled from H_2S .

The regularity of pore water evolution and sediment environment becomes more apparent when the oxygen and sulphur isotope compositions of SO_4^{2-} are examined. Diagenetic effects are most

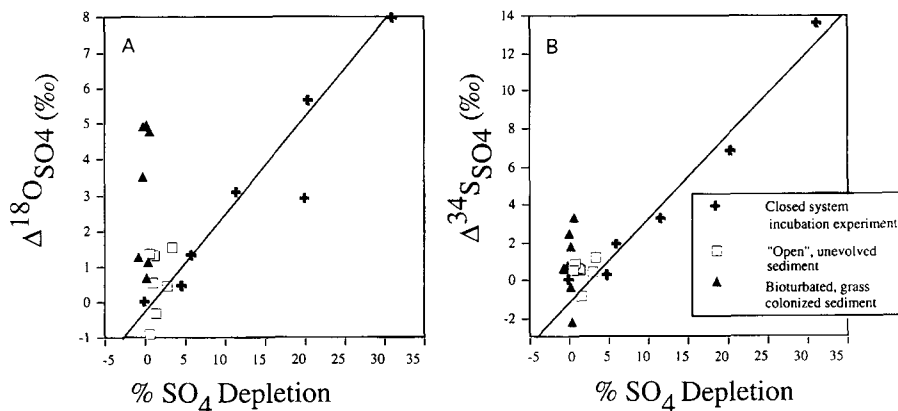


FIG. 1. Comparison of natural sediments and sediment incubation experiments. A) $\Delta^{18}\text{O}(\text{SO}_4)$ vs percent sulphate depletion. B) $\Delta^{34}\text{S}(\text{SO}_4)$ vs percent sulphate depletion. Pore waters are shown in comparison to closed system sulphate reduction experiments. Lines are drawn for closed system sulphate reduction with fractionation factors of 1.022 and 1.036 for $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$, respectively. The SO_4 depletion and Δ values for pore waters are relative to the overlying seawater. The SO_4 depletion and Δ values for sediment incubations are relative to the initial values of the experiment.

modest in sediments where pore water is rapidly exchanged with overlying seawater, and are most pronounced in seagrass populated, intensely bioturbated sediments where rapid sulphur redox reactions promote significant carbonate dissolution.

References

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