

Deep Anoxic Pyrite Oxidation and Stimulation of Bacterial Activity in Marine Sediments

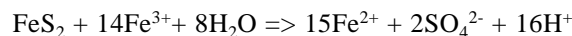
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Bacterial populations have recently been demonstrated in a range of deep sedimentary environments, however the geochemical impact of their presence has yet to be resolved. We have addressed this problem using stable sulphur and oxygen isotopic compositions of pore-water sulphate and rates of sulphate reduction (measured by $^{35}\text{SO}_4^{2-}$ turnover) in sediments from three Ocean Drilling Program sites from the Cascadia Margin accretionary wedge (Sites 888, 890/889 and 891) (see Bottrell et al. 2000 for details). The uppermost 10m of all three sites exhibit decreasing sulphate concentrations with depth and corresponding increases in sulphate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ (generally $\delta^{34}\text{S} > 20\text{‰}$ and $\delta^{18}\text{O} > 10\text{‰}$). These effects are consistent with removal of porewater sulphate of marine origin by bacterial sulphate reduction during burial. At site 891 low concentrations of sulphate persist in the sediment to 165m, there are low rates of sulphate reduction to this depth and both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ remain elevated. At the other two sites sulphate concentration exhibits a minimum at ~ 10m depth and increases again below ~50m. At site 889/890 sulphate in these deep samples is strongly depleted in ^{34}S and ^{18}O relative to shallower depths ($\delta^{34}\text{S} \sim 16\text{‰}$, $\delta^{18}\text{O} \sim 0\text{‰}$) and must reflect a new pool of sulphate formed at depth. Such compositions are consistent with the generation of sulphate by anoxic pyrite oxidation, pyrite formed during early diagenesis providing a ^{34}S -depleted sulphur source for the sulphate. The $\delta^{18}\text{O}$ of the deep sulphate is very light, too light for dissolution of marine carbonate as a sulphate source as this would have the isotopic composition of sea-water sulphate (11‰). If sulphate were produced by anoxic pyrite oxidation, all four oxygen atoms in the sulphate molecules would be derived from the pore-water (which has $\delta^{18}\text{O} \sim 0\text{‰}$ and there is minimal isotopic fractionation during this process; Lloyd 1967). Importantly, these depleted sulphate-oxygen isotopic compositions confirm that the sulphate is not an artefact of atmospheric oxidation of the samples during handling, as this would incorporate isotopically heavy atmospheric O_2 into sulphate. Data from site 888 show similar, though less pronounced, trends toward isotopically light sulphate compositions at depth. There is thus good evidence for deep anoxic pyrite oxidation at two sites which contrasts with the usual assumption that pyrite, once anoxically buried, remains stable. In the absence of dissolved oxygen in these deep sediments, some other agent must be

responsible for the oxidation of pyritic sulphide to sulphate. Aplin and MacQuaker (1993) pointed out that there is abundant Fe^{3+} buried in minerals in sedimentary basins. On a sufficiently protracted timescale, diagenesis could release significant amounts of Fe^{3+} into the pore-water, in which case pyrite oxidation would result via a reaction such as:



Silicate iron reacts on only protracted timescales during diagenesis, with a half-life estimated at $\sim 2 \times 10^6$ years (Canfield et al. 1992) and Fe^{3+} -bearing silicates (and possibly less-reactive iron oxides) will thus persist to the depths at which we observe evidence for anoxic pyrite oxidation. Increased sulphate concentrations stimulate bacterial sulphate reduction at depths of 70-250 m and this locally modifies the porewater sulphate isotopic composition, producing ^{34}S - and ^{18}O -enriched values. Changes in the isotopic composition of pyrite at depth are consistent with the oxidation of early-formed pyrite and the formation of new pyrite associated with deep stimulated sulphate reduction. These changes are less certain, being obscured by original diagenetic variability in pyrite $\delta^{34}\text{S}$, but these mineralogical changes are also reflected in the deep diagenesis of magnetic minerals (Musgrave et al. 1997). The reoxidation processes we describe are important in providing electron acceptors to sustain deep bacterial activity and they should continue with increasing depth, as there is a large solid phase ferric pool, even in ancient deposits. Bacterial processes may thus potentially persist to much greater depths than have previously been considered possible.

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