

Thermodynamics at work - on the limits and potentials of biogeochemical processes

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The preferential use of high potential electron acceptors by microorganisms has led to the classical concept of a redox sequence with a sequential use of O₂ nitrate, Fe(III), sulfate, and finally CO₂ as electron acceptors for respiration (Stumm & Morgan, 1996). Christian Blodau has rigorously applied this concept to constrain the thermodynamical limits at which specific aquatic systems operate. In sediments from acidic mining lakes his analysis revealed that sulfate reducers are not competitive as long as low-crystallinity ferric oxides are available for organic matter decomposition (Blodau et al, 1998). This analysis opened up the possibility to generalize the linkage between the iron and sulphur cycle in such systems and to constrain the biogeochemical limits for remediation (e. g. Peine et al, 2000). In a similar approach, Beer & Blodau (2007) were able to demonstrate that constraints on the removal of products from acetoclastic methanogenesis in deeper peat layers are inhibiting organic matter decomposition and provide a thermodynamic argument for peat accumulation.

In this contribution I will review such ideas and further refine the limits and potentials of biogeochemical reactions in terms of redox-active metastable phases (RAMPS) that are typically mixed-valent carbon-, iron-, and sulfur-containing compounds and which allow for the occurrence of a number of enigmatic reactions, e. g. limited greenhouse gas emission (CH₄) under dynamic redox conditions. It is proposed that redox equivalents are generated, stored and recycled during oxidation and reduction cycles thus suppressing methanogenesis (Blodau, 2002). Such RAMPS will preferentially occur at dynamic interfaces being exposed to frequent redox cycles. The concept of RAMPS will be illustrated along the interaction between ferric (hydr)oxides and dissolved sulphide. Recent studies using modern analytical tools revealed the formation of a number of amorphous products within a short time scale (days) both on the Fe and S side (Peiffer & Wan, 2016; Wan et al, 2014) which will allow for the occurrence of cryptic sulphur cycles, i. e. high turnover of sulphide and sulfate without the appearance of dissolved sulphide species.

References

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