Kinetics of sulfite disproportionation and thiosulfate acid dissociation

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The early biogeochemical sulfur cycle differed markedly from its modern counterpart. Two important differences are that deposition from the early anoxic atmosphere consisted of multiple valence states of sulfur [1], as opposed to only SO_2 and H_2SO_4 today, and that aqueous oxidation of intermediate-valence sulfur species (e.g., sulfite, thiosulfate) was much slower than today [2,3]. Alongside other differences, these may have resulted in the dominance of sulfur species that are minor today in early seawater and in fluxes to the sediment [3]. However, the kinetics of some of the reactions governing the chemistry of sulfur in ancient seawater are poorly constrained under relevant environmental conditions. Two examples, to which biogeochemical model results appear sensitive [3], are disproportionation of sulfite species ($SO_{2(aq)}$, HSO_3^-, SO_3^{2-}) and acid-dissociation of thiosulfate ($S_2O_3^{2-}$). The former has been experimentally investigated at temperatures exceeding ~100°C [4,5], and the latter at pH lower than ~4 [6]. These conditions are likely irrelevant to Earth's early oceans, and lead to uncertainty of several orders of magnitude in reaction rates and, consequently in seawater concentrations of both major and minor sulfur species.

To address the uncertainty in reaction kinetics, we experimentally investigated the rate of sulfite species disproportionation and thiosulfate acid-dissociation under anoxic conditions, and over ranges of temperature and pH relevant to the early oceans. Reaction rates were determined by monitoring the aqueous concentrations of both the reactant and product sulfur species (SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, $S_xO_6^{2-}$) by ion chromatograhy. We included the pH- and temperature-dependent rates of sulfite disproportionation and thiosulfate acid-dissociation in an environmentally-resolved model of the early biogeochemical sulfur cycle [3], and will discuss the effect of the new rates on sulfur chemistry in the early oceans and on the propagation and ultimate preservation of atmospherically-produced mass-independent fractionation of sulfur isotopes.

[1] Pavlov and Kasting (2002) *Astrobiology* **2**, 27–41 [2] Halevy *et al* (2010) *Science* **329**, 204-207 [3] Halevy (2013) *Proc. Natl. Acad. Sci. USA* **110**, 17644–17649 [4] Rempel, *et al* (1974), *Lesotekh. Inst. Sverdlovsk.* [5] Ryabinina and Oshman (1972) *Tr. Ural. Lesotekh. Inst.* **28**, 182-189 [6] Johnston and McAmish (1973) *J. Colloid. Interf. Res.* **42**, 112–119