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ISSN 0016-7037
Volume 72, Number 23
December 1, 2008

ELSEVIER

Geochimica et Cosmochimica Acta

JOURNAL OF THE GEOCHEMICAL SOCIETY
AND THE METEORITICAL SOCIETY

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Geochimica et Cosmochimica Acta 72 (2008) 5855–5856
Geochimica et Cosmochimica Acta
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Response

Response to comment by I.C. Bourg on “Modeling sulfur isotope fractionation and differential diffusion during sulfate reduction in sediments of the Cariaco Basin” by M.A. Donahue, J.P. Werne, C. Meile, and T.W. Lyons

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Received 10 July 2008; accepted in revised form 15 September 2008; available online 27 September 2008

We thank Bourg for his insightful comment, which provides a broader context for the role of isotopic mass dependence in solute diffusion in liquid water and the associated uncertainties. As he correctly notes, our square-root model (Donahue et al., 2008) most likely overestimates the mass dependence of solute diffusion coefficients. Our model is best viewed as an end-member, bracketing the upper limit of the impact that diffusion coefficients have on apparent sulfur isotope fractionation in sedimentary pore water systems. Indeed, if we follow Bourg's (2008) suggestion and vary β (from his Equation 3) between 0.5 (our square root model) and 0.05 (closer to the hydrodynamic model), the predicted fractionation due to diffusion ($\Delta\varepsilon$) varies between maximum and minimum values of 9‰ and 0.9‰, respectively.

The approximately linear dependence of ε on β is a consequence of the exponential shape of the concentration versus depth profiles for $^{32}\mathrm{SO}_4^{2-}$ and $^{34}\mathrm{SO}_4^{2-}$ in the Cariaco Basin ($^{i}\mathrm{SO}_4^{2-} = A_i \mathrm{e}^{b_i z}$, where i denotes the isotope [$i = 32, 34$] and the coefficients A_i and b_i describe the sulfate profiles; Figure 3 in Donahue et al. (2008)). By assuming a constant porosity and combining Equations 5 and 6 in Donahue et al. (2008), the profiles for sulfate reduction rate can be expressed as $f(z)_i = -\phi(D_{\mathrm{sed}(^{i}\mathrm{SO}_4^{2-})} b_i^2 - \omega b_i) A_i \mathrm{e}^{b_i z}$, where D_{sed} is the *in situ* diffusion coefficient and ω is the sedimentation rate. The net fractionation ($\varepsilon_{\mathrm{SR}}$) is defined as $\varepsilon_{\mathrm{SR}}(‰) = 1000 \cdot \left(\frac{f_{34}}{f_{32}} \frac{^{32}\mathrm{SO}_4^{2-}}{^{34}\mathrm{SO}_4^{2-}} - 1\right)$, which when ignoring the negligible advection term and making use of Equation 3 in Bourg (2008) results in $\varepsilon_{\mathrm{SR}}(‰) \approx 1000 \cdot \left(\frac{D_{\mathrm{sed}(^{34}SO_4^{2-})}}{D_{\mathrm{sed}(^{32}SO_4^{2-})}} \frac{b_{34}^2}{b_{32}^2} - 1\right) = 1000 \cdot \left(\left(\frac{m(^{34}SO_4^{2-})}{m(^{32}SO_4^{2-})}\right)^{-\beta} \frac{b_{34}^2}{b_{32}^2} - 1\right)$,where $\frac{b_{34}^2}{b_{32}^2}$ is a function of the $^{32}\mathrm{SO}_4^{2-}$ and $^{34}\mathrm{SO}_4^{2-}$ profile shapes and m indicates mass. Thus, any variation in the ratio of the diffusion coefficients will have a linear effect on the computed fractionation. Furthermore, expressing the power function by a series expansion, $\left(\frac{m(^{34}\mathrm{SO}_4^{2-})}{m(^{32}\mathrm{SO}_4^{2-})}\right)^{-\beta} \approx 1 - \ln\left(\frac{m(^{34}\mathrm{SO}_4^{2-})}{m(^{32}\mathrm{SO}_4^{2-})}\right)\beta + O(\beta^2)$, reveals an approximately linear dependence of ε on β. Thus, in the case of sulfate in the Cariaco Basin pore waters, the predicted fractionation arising from the mass difference of the diffusion coefficient of two isotopes ($\Delta\varepsilon$) varies linearly with Bourg's (2008) exponent β, bracketed by the hydrodynamic model ($\beta = 0$) and the inverse square root of the solute isotopic mass estimate ($\beta = 0.5$).

The roles of advective and diffusive transport in governing isotopic pore water signatures have been demonstrated (e.g., Jørgensen, 1979; Bottrell and Raiswell, 2000) and studied in diverse sedimentary systems (Fossing et al., 2000; Böttcher et al., 2004; Jørgensen et al., 2004). Experiments by Piel (1999) demonstrated that the diffusion coefficients of $H_2{}^{32}S$ and $H_2{}^{34}S$ do differ, albeit only slightly in that study, and most previous work (Jørgensen, 1979; Fossing et al., 2000; Jørgensen et al., 2004) did not consider its impact on isotopic fractionation.

In all likelihood, the actual impact of the difference in diffusion coefficients for two isotopes in natural systems is

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0016-7037/$ - see front matter
doi:10.1016/j.gca.2008.09.016

somewhere in between the range reported above. Thus, for the typical sulfur isotope fractionations observed in marine sediments, which are on the order of 0–50‰, even a small potential difference in diffusion coefficients (~1%) can have a significant impact on isotopic data and their interpretation. We maintain that the isotope effects associated with diffusion, and quantified by considering the mass dependence of the diffusion coefficients, can impact the isotopic trends observed for dissolved pore water species such as sulfate and sulfide. Thus, our fundamental conclusion that these factors should be taken into account in future, rigorous investigations of pore water solute isotope systematics remains valid.

Both Bourg's (2008) analysis and our application of modeling to field data (Donahue et al., 2008) demonstrate the need for further laboratory studies. Such studies are necessary to corroborate or disprove our findings, shown to be important for the interpretation of S isotopic signatures in natural systems.

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