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Correspondence/Rebuttal

Correspondence on "Diffusion in Porous Rock Is Anomalous"

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Rajyaguru et al.[1] investigated the diffusion of a tracer in porous rocks. The authors measured molecular diffusion through a series of five chalk and dolomite rock samples over a period of about two months. The authors concluded that the diffusion was anomalous, i.e., non-Fickian. Their results are interesting; however, the conclusion of anomalous diffusion is not reliable.

The experimental setup is shown in Figure 1. Two closed reservoirs of 50 mL were placed at the two ends of a cylindrical

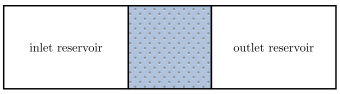

Figure 1. Experimental setup of the authors.

porous rock sample. The inlet reservoir has a initial concentration of C_0. The outlet reservoir is clean initially. When the experiment begins, the gas moves slowly from the inlet reservoir to the outlet reservoir through porous diffusion. The authors measured the inlet and outlet reservoirs. The relative inlet concentration (C/C_0) is 0.95 for desert pink, 0.96 for Edwards Yellow, 0.96 for desert pink, 0.96 for Edwards Yellow, and 0.98 for Silurian dolomite after two months. The relative outlet concentration (C/C_0) is 0.04 for desert pink, 0.07 for Edwards Yellow, 0.03 for desert pink, 0.1 for Edwards Yellow, and 0.02 for Silurian dolomite after two months.

The authors assumed that tracer diffusion was occurring in a semi-infinite space. Based on the Fickian law, the mathematical model is written as follows

$$\frac{\partial C(x,\,t)}{\partial t} = D\frac{\partial^2 C(x,\,t)}{\partial x^2} \tag{1}$$

with the initial condition

$$C(x,\,0) = 0 \tag{2}$$

The authors neglected the variation of concentration in the two reservoirs, assuming

$$C(0,\,t) = C_0 \tag{3}$$

$$C(\infty,\,t) = 0 \tag{4}$$

The solution of eq 1 is

$$C(x,\,t) = C_0\,\mathrm{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) \tag{5}$$

The authors obtained asymptotic (long-time) scaling behavior as

$$1 - \frac{C(x,\,t)}{C_0} = 1 - \mathrm{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) \sim \frac{x}{\sqrt{\pi Dt}} \tag{6}$$

Equation 6 demonstrates $1 - \frac{C(x,t)}{C_0} \propto 1/2$. The experimental data show that $1 - \frac{C(x,t)}{C_0} \propto \beta/2$ with $0 < \beta < 1$. The specific value of β is 0.31 for desert pink, 0.4 for Edwards Yellow, 0.26 for desert pink, 0.49 for Edwards Yellow, and 0.08 for Silurian dolomite, values that are listed in Table 1 of ref 1. Since β is not unity, the authors concluded that the diffusion in porous rocks was anomalous.

When time is infinite, eq 5 yields

$$C(x,\,\infty) = C_0 \tag{7}$$

However, the experimental setup in Figure 1 is a closed system. The total mass of chemical species must be the same all along. When the time is infinite, a uniform distribution of concentrations will be attained between the rock and the two cells. Applying the law of mass conservation for the experimental setup in Figure 1 yields

$$C(x,\,\infty) = C_0\frac{V_0}{2V_0 + \varepsilon V_r} \tag{8}$$

where V_0 is the volume of reservoirs, V_r is the volume of the porous rock, and ε is the porosity of the rock. Equation 7 contradicts eq 8 and violates the law of mass conservation. That is, eqs 1−4 are not applicable for the experimental setup. The conclusion of anomalous diffusion based on eq 5 becomes unreliable.

The authors neglected the variation of concentrations in two cells with time, which led to an incorrect concentration at infinite time. The correct mathematical models should consider the variation of the concentrations in two cells

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{9}$$

$$C\,|_{t=0} = 0 \tag{10}$$

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$$V_0 \frac{dC_{a1}}{dt} = AD\frac{\partial C}{\partial x}, x = 0 \tag{11}$$

$$V_0 \frac{dC_{a2}}{dt} = -AD\frac{\partial C}{\partial x}, x = \delta \tag{12}$$

$$C_{a1}(t = 0) = C_0 \tag{13}$$

$$C_{a2}(t = 0) = 0 \tag{14}$$

$$C_{a1} = C(0, t) \tag{15}$$

$$C_{a2} = C(\delta, t) \tag{16}$$

where C_{a1} is the concentration in the inlet reservoir, C_{a2} is the concentration in the outlet reservoir, A is the effective area of the porous rock in contact with the reservoir, and δ is the length of the porous rock.

The equations presented above can be solved using the Laplace transform technique. The solution in the time domain is

$$\frac{C}{C_0} = \frac{1}{2+R} + 2\sum_{i=1}^{\infty} \frac{R\cos\left[\beta_i\left(1-\frac{x}{\delta}\right)\right] - \beta_i \sin\left[\beta_i\left(1-\frac{x}{\delta}\right)\right]}{\cos\beta_i(R^2+4R-\beta_i^2) + \frac{\sin\beta_i}{\beta_i}(R^2-2R\beta_i^2-3\beta_i^2)} \exp(-D\delta^{-2}\beta_i^2 t) \tag{17}$$

with

$$\tan\beta_i = \frac{2R\beta_i}{\beta_i^2 - R^2} \tag{18}$$

and $R = \frac{\varepsilon V_r}{V_0} = \frac{A\delta}{V_0}$. When time becomes infinite, eq 17 reproduces eq 8.

The relation between $1 - \frac{C}{C_0}$ and t cannot be directly obtained from eq 17 by mathematical manipulation. Numerical calculations can be conducted for specific values of D and R. Numerical results show $1 - \frac{C}{C_0} \sim t^{-\beta/2}$ with $0 < \beta < 1$ for parameters listed in Table 1 of ref 1, which is in qualitative accordance with the experimental result.

In summary, it is important to ensure the validity of the mathematical model for the experimental setup. The above analysis shows that the conclusion of anomalous diffusion in rocks presented by the authors is not reliable due to the use of an incorrect mathematical model.

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Notes

The authors declare no competing financial interest.

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