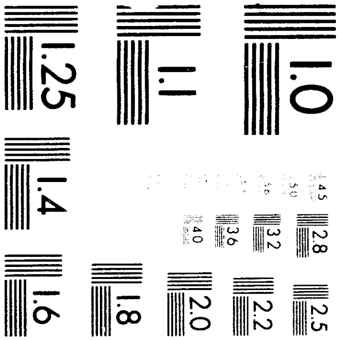
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# HYPERFILTRATION-INDUCED FRACTIONATION OF LITHIUM ISOTOPES IN GEOLOGIC SYSTEMS

Progress Report

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MASTER

## Results

In this run 1.28 grams of freeze-dried, LiCl-saturated bentonite are sedimented onto a chemically inert filter paper fitted to a porous plexiglass plug. The opposing side of the plexiglass cylinder is connected to a syringe pump (ISCO Model LC-5000) capable of delivering solution at a precisely controlled flow rate (Fig. 1). A microtransducer is placed within the cell so that hydraulic pressure can be monitored continuously as a response of pumpage.

Initially, de-ionized water is forced through the membrane so that its hydraulic conductivity coefficient, K, can be measured.

$$J_v = K\cdot(dH/dL) = Q/A \qquad (1)$$

Here, $J_v$ is the solution flux in cm·sec$^{-1}$, Q the flow rate, A the membrane area, and (dH/dL) the hydraulic gradient. For the run discussed here, Q is set at 1.00 cm$^3$·hour$^{-1}$, or a $J_v$ of $1.37 \times 10^{-5}$ cm·sec$^{-1}$ for a membrane whose surface area is 20.29 cm$^2$. A K of $6.79 \times 10^{-11}$ cm·sec$^{-1}$ was obtained after flow of deionized water yielded a steady-state $\Delta P$ of 19.8 bars through the 0.12-cm thick clay. When the deionized water in the syringe pump is exchanged for a 9.411 m$\underline{N}$ LiCl solution, and that solution is hydraulically forced through the cell at the same flow rate as that for the deionized water, the steady-state hydraulic pressure of 20.5 bars is greater than the value recorded for the flux of deionized water because the membrane restricts passage of the solute so that the concentration at the high-pressure interface exceeds that at the low-pressure interface. In other words, an osmotic back-pressure ($\Delta\Pi$) is created that reflects the attempt of the solvent (water) to flow back into the filtration cell where the activity of water is lower.

As solution is advected toward the membrane, solute builds up at the membrane's high-pressure interface so that the concentration change with time is a function of the advective flux ($J_v$), the diffusion coefficient of the solute (D), and the position of interest (x) within the filtration cell relative to the membrane's high-pressure interface where x=0. This is expressed by Fritz and Marine (1983) as:

$$(\partial C/\partial t) = -J_v \cdot (\partial C/\partial x) - D \cdot (\partial^2 C/\partial x^2). \qquad (2)$$

Fritz and Whitworth (in press) gave the transient-state solution of (2) as

$$C_{(x,t)}=[(C_{o(t)}-C_i)/2] \cdot \{\mathbf{exp}(-J_v \cdot x/D) - \mathbf{exp}(-J_v \cdot x_i/D)\} \cdot \{\mathbf{erfc}[(x-J_v \cdot t)/(2\sqrt{D \cdot t})] + \mathbf{erfc}[(x+J_v \cdot t)/(2\sqrt{D \cdot t})]\} + C_i \quad (3)$$

where $C_{o(t)}$ is the time-dependent concentration at the high-pressure interface and $C_i$ is the concentration of the input stock solution. If x=0, then $C_{(x,t)} = C_{o(t)}$ because $\mathbf{erfc}[(x-J_v \cdot t)/(2\sqrt{D \cdot t})] + \mathbf{erfc}[(x+J_v \cdot t)/(2\sqrt{D \cdot t})]\}$ sum to 2, and, in an infinitely long reservoir represented by the length $x_i$, $\mathbf{exp}(-J_v \cdot x_i/D) = 0$. If x>0 and t is large, then $C_{(x,t)}$ reduces to the following steady state solution (given by Fritz and Marine, 1983) because $\mathbf{erfc}[(x+J_v \cdot t)/(2\sqrt{D \cdot t})] \rightarrow 0$ and $\mathbf{erfc}[(x-J_v \cdot t)/(2\sqrt{D \cdot t})] \rightarrow 2$ when $t \rightarrow \infty$.

$$C_x = (C_o - C_i) \cdot [\mathbf{exp}(-J_v \cdot x/D) - \mathbf{exp}(-J_v \cdot x_i/D)] + C_i. \qquad (4)$$

The steady-state profile for the solute is depicted in Figure 2f.

The $x_i$ term in equation 4 is a constant representing the distance out into the filtration cell where the solute concentration equals that of the input concentration--*viz.*, $C_x = C_i$ when $x = x_i$. That segment of the filtration cell between the membrane ($x_o$) and $x_i$ is the Concentration Polarization Layer (CPL). Theoretically, the value of $x_i$ must be infinity in order to satisfy the boundary condition of equation 4 that $C_x=C_o$ when $x=x_o=0$. However, in experimental studies, the $\mathbf{exp}(-J_v \cdot x_i/D)$ term in equation 4 can be ignored if the length of the experimental test cell is large relative to the ratio of $D/J_v$. In that case,

$$C_x = (C_o - C_i) \cdot [\mathbf{exp}(-J_v \cdot x/D)] + C_i \quad \text{when } x_i \geq 10 \cdot D/J_v. \qquad (5)$$

The validity of employing this threshold is demonstrated by examining the product of integrating equation 4 between the limits of $x_o$ and $x_i$.

$$\int_{x_o}^{x_i} C_x\,dx = \bar{C}_x = (C_o - C_i)\cdot Z + C_i\cdot x_i, \text{ where} \qquad (6)$$

$$Z = \{(D/J_v)\cdot[1 - \exp(-J_v\cdot x_i/D)]\} - [x_i\cdot \exp(-J_v\cdot x_i/D)]. \qquad (7)$$

As $x_i$ increases, the value of $D/J_v$ approaches Z.; *e.g.*, if $x_i = 10\cdot D/J_v$, then $D/J_v = 0.9995\cdot Z \cong Z$.

The top portion of Figures 2a-2f portrays the changing geometry of the CPL during the transient state where each curve represents a particular time of effluent collection (Table 1). For example, at t=32,000 seconds the pre-weighed collection flask was removed from the effluent drain pipe and another pre-weighed flask was quickly valved into the system. The net weight of the removed flask (5.73 grams) corresponds to the effluent passed through the membrane since the previous collection at t=9,480 seconds. The concentration of LiCl in the flask is determined by a temperature-compensated conductivity probe which records microSiemens to 4 significant figures. Due to the membrane effect, the concentration of this effluent (3.840 mN) is less than the input concentration of 9.411 mN. (Only at steady state are the concentration of the stock and effluent equal). Because the dimensions of the cell, the flow rate, and the input concentration of the stock solution are precisely known, then careful gravimetric and conductivity measurements permit calculation of the average LiCl concentration in the cell at the time of the collection. This calculated average is $\bar{C}_{x,t}/x_i$, where

$$(1/x_i)\cdot\int_{x_o}^{x_i} C_{x,t}\,dx = (\bar{C}_{x,t})/x_i = \frac{A\cdot x_i\cdot C_i + \left\{J_v\cdot A\cdot C_i\cdot t - \sum(C_k\cdot V_k)\right\}}{(A\cdot x_i)}, \qquad (8)$$

where $\bar{C}_{x,t}$ = average cell concentration per unit area of membrane (moles$\cdot$cm$^{-2}$),
$A$ = membrane area (20.29 cm$^{2}$.),
$x_i$ = length of the cell (12.69 cm),
$C_i$ = input concentration ($9.411 \times 10^{-6}$ moles$\cdot$cm$^{-3}$),
$J_v$ = solution flux ($1.370 \times 10^{-5}$ cm$\cdot$sec$^{-1}$),
t = seconds elapsed since start of experiment,
$C_k$ = concentration (moles$\cdot$cm$^{-3}$) of the kth effluent collection, and
$V_k$ = volume (cm$^{-3}$) of the kth effluent collection.

Using the data in Table 1, we compute that $(\bar{C}_{x,t})/x_i$ at t=32,000sec is 9.666 m$\underline{N}$.

In order to calculate $C_{x,t}$ of equation 3, the value of $C_{o(t)}$ must be known. This is a problem because $C_{o(t)}$ varies continuously with time. For purposes of calculation, the value of $C_{o(t)}$ is assumed constant between collection intervals. In that case

$$C_{o(t)} = [\bar{C}_{x,t} - C_i \cdot x_i]/Q \text{ where} \tag{9}$$

$$Q = 1/2\int_{x_o}^{x_i} \{ \exp(-J_v \cdot x/D) - \exp(-J_v \cdot x_i/D)\} \cdot \{\mathrm{erfc}[(x-J_v \cdot t)/(2\sqrt{D \cdot t})] + \mathrm{erfc}[(x+J_v \cdot t)/(2\sqrt{D \cdot t})]\}\, dx. \tag{10}$$

Q is evaluated numerically for t corresponding to time of effluent collection. Note that as t gets very large, the value of Q approaches $Z \cong D/J_v$ of equation 7. At t=32,000 sec, $C_{o(t)} = 16.21 \times 10^{-6}$ moles·cm$^{-3}$. This value is used to calculate the concentration profile at this time via equation 3.

Li isotope analyses were performed at the Analytical Chemistry Laboratory of Argonne National Laboratory. Their reported 2σ precision of a single measurement of an unknown is ±0.00026 (Fritz, 1992). Their accuracy and precision relative to analysis of SVEC (Flesch *et al.*, 1973) compare favorably with that reported by Chan and Edmond (1988) for the same standard. Since the $^7$Li/$^6$Li ratio is known for both the input solution as well as the effluents (Table 1), then the concentration profile for $^6$Li and $^7$Li can be computed in a manner directly analogous to that for the solute. $\Delta^7$Li is defined on the basis of the $^7$Li/$^6$Li ratio for the input solution. Thus

$$\Delta^7\text{Li} = \delta^7\text{Li}_{\text{Effluent}} - \delta^7\text{Li}_{\text{Stock}}, \text{ where} \tag{11}$$

$\delta^7\text{Li}_{\text{Stock}}$ = 21.48 per mil relative to a $LiCO_3$ standard whose $^7$Li/$^6$Li ratio is reported as 12.02 (Flesch *et al.*, 1973).

## DISCLAIMER

# PROJECTED ACTIVITIES FOR THE UPCOMING YEAR

The results of this grant (running from 4-1-90 to 3-31-93) have shown that hyperfiltration is an efficient mechanism to fractionate lithium isotopes. The grant's second year was spent in honing a technique by which the ratio of aqueous diffusion coefficients for a solute's isotopic components could easily and accurately be performed by osmometry. This technique was published in *Geochimica et Cosmochimica Acta* (v. 56, pp. 3781-3789). The data and explanations within the body of this progress report will constitute a manuscript to be submitted to *Water Resources Research*.

I am submitting a renewal application concurrent with this last yearly progress report. The focus for the requested 3-year renewal is osmotically-induced hydraulic pressure in the subsurface. Hyperfiltration is known commercially as "Reverse Osmosis," or 'RO' for short. A spin-off from these hyperfiltration measurements in this grant are data from which to calculate the 3 phenomenological coefficients ($L_p$, $\sigma$, and $\omega$) dictating the magnitude and kinetic response of osmotically-induced hydraulic pressures in the subsurface. As a subsurface phenomenon, osmosis has been invoked as a mechanism to: 1) facilitate thrust faults; 2) breach clay liners of repositories; and 3) cause anomalous hydraulic heads. $L_p$ is essentially a hydraulic permeability and is easy to measure. The value of $\sigma$ controls the magnitude of osmotically-induced hydraulic pressure, while the value of $\omega$ dictates the rate at which this pressure dissipates. A data base arising from these experiments will lay the foundation for evaluating the magnitude of membrane-induced hydraulic pressures in the subsurface as well as in placement of types of clays surrounding future waste repositories.

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# TABLE 1

| ----------Effluent | Measurements--------- | | | | -----Calculated | Values------ | |
|---|---|---|---|---|---|---|---|
| Effluent | $\Sigma$seconds | grams withdrawn | m$\underline{N}$ LiCl | $^7$Li/$^6$Li | $\Delta^7$Li of Effluent | $\Delta^7$Li of Cell | $\Delta^7$Li at $x_o$ |
| **ST** | | | **9.41** | **12.283** | 0 | | |
| **1** | **9,480** | **3.19** | **0.48** | **12.338** | 4.43 | 0.02 | 0.84 |
| **2** | **32,000** | **5.73** | **3.84** | **12.503** | 17.61 | -0.18 | -0.51 |
| **3** | **74,800** | **10.33** | 6.91 | **12.471** | 15.06 | -0.61 | -4.20 |
| **4** | **161,000** | **21.02** | **8.54** | **12.416** | 10.70 | -1.31 | -8.19 |
| **5** | **333,300** | **44.39** | **8.85** | **12.413** | 10.50 | -2.81 | -16.41 |
| **6** | **512,500** | **48.09** | 8.87 | **12.315** | 2.55 | -3.27 | -14.66 |
| **7** | **681,700** | **6.06** | **8.97** | **12.308** | 2.03 | -3.39 | -12.83 |
| **8** | **1,026,900** | **94.03** | **9.11** | **12.309** | 2.10 | -3.73 | -11.10 |
| **9** | **1,673,500** | **178.83** | **9.35** | **12.293** | 0.84 | -4.20 | -9.53 |
| **CL** | | | **11.28** | **12.215** | | **-5.59** | |

This is a table of the raw data used to calculate concentration and fractionation profiles in Figure 2. ST represents the input Stock solution, and CL is the sampled solution in the cell at the termination of the run. Numbers in **bold** print denote actual measurements, while numbers calculated from data are in plain type. The 'grams withdrawn' and 'm$\underline{N}$ LiCl' correspond (respectively) to $V_k$ and $C_k$ of equation 8.

In this run, a 9.411 m$\underline{N}$ LiCl solution was hyperfiltrated through a 20.29 cm$^2$-area smectite membrane at a flux of $1.37 \times 10^{-5}$ cm·sec$^{-1}$. The length of the cell is 12.69 cm. These constants of $C_i$, A, $J_v$, and $x_i$ are combined with $V_k$ and $C_k$ for each effluent to calculate the average LiCl concentration within the cell via equation 8. Average concentrations for $^6$Li and $^7$Li in the cell are calculated with the measured $^7$Li/$^6$Li ratio and the LiCl concentration data. This allows computation of the $\Delta^7$Li in the cell for any effluent.

The aqueous diffusion coefficients for $^6$LiCl and $^7$LiCl were evaluated from the data of Fritz (1992). This allows calculation of the Q value for each isotope at a particular time of interest via equation 10. Thereafter the concentration of each isotope at the membrane's high-pressure interface ($x_o$) is calculated via equation 9. The result is the $\Delta^7$Li at $x_o$. Finally, these data are used to calculate the concentration profile for each isotope by equation 3 in order to construct the $\Delta^7$Li profile within the CPL for any time of effluent collection.

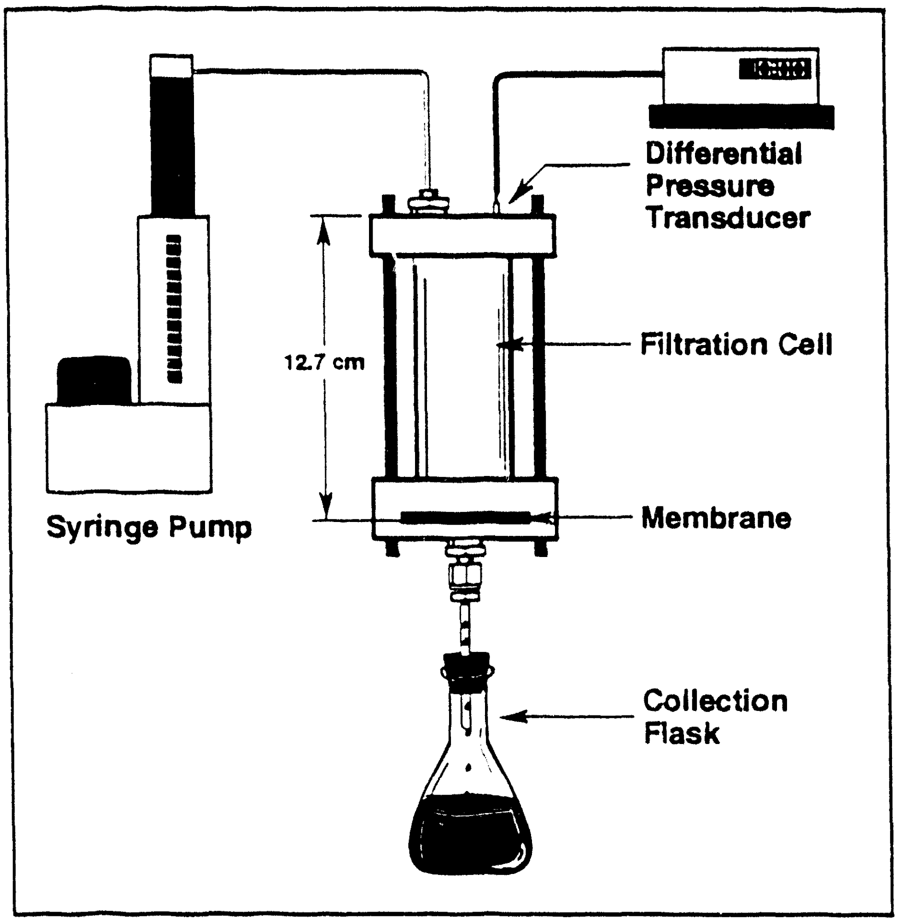

Figure 1. Schematic diagram of the experimental set-up. A syringe pump advects a 9.411 m<u>N</u> LiCl solution through a dialysis sheeting at a flux of $1.37 \times 10^{-5}$ cm·sec$^{-1}$. A microtransducer within the cell monitors $\Delta P$ across the membrane.

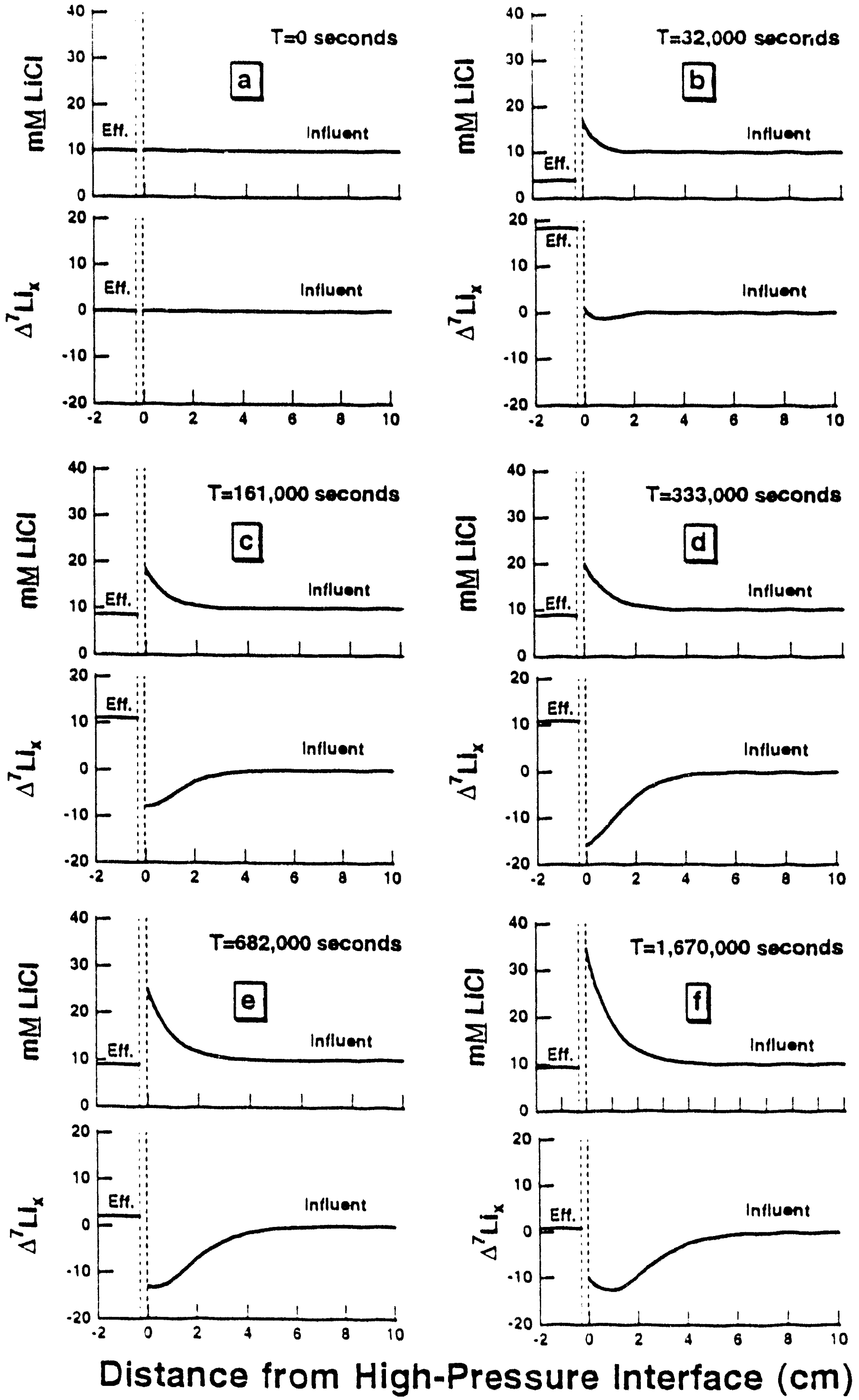

Figure 2. These figures depict the transient-state evolution of the hyperfiltration cell with respect to build-up of solute and fractionation of Li isotopes. The y-axis in all graphs represents the high-pressure interface of the clay membrane. Methodology of calculation is explained in the text and in the caption for Table 1.

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