

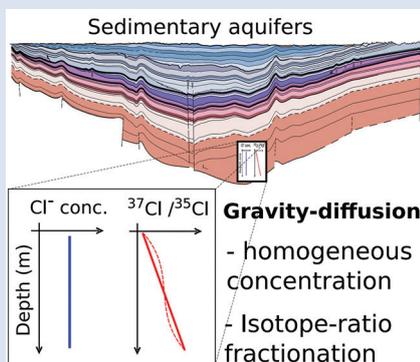
## The *gravitas* of gravitational isotope fractionation revealed in an isolated aquifer

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### Abstract



Despite the ubiquitous effects of gravitation on Earth, its potential influence on relative distribution of isotopic substances has remained elusive – and so far only identified in confined gaseous systems (Craig *et al.*, 1988; Severinghaus *et al.*, 1996, 1998). Yet, in a motionless and chemically homogeneous water column, dissolved isotopic substances must be distributed according to their masses. Here we report the first resolvable isotopic variations resulting from gravitational effects on solutes, identified on dissolved chloride (Cl) and bromide (Br) in a sedimentary aquifer from the Illinois Basin (USA). We show that the correlations between depth and both  $^{37}\text{Cl}/^{35}\text{Cl}$  and  $^{81}\text{Br}/^{79}\text{Br}$  – varying by 1.1 ‰ and 1.6 ‰ respectively – reflect the evolution toward a gravity-diffusion equilibrium of porewater in the sediment column. This observation reveals that these deep groundwaters have been mostly stagnant for at least 20 Myr, possibly up to 300 Myr. As chloride and bromide are often conservative in groundwater systems, we highlight their essential role in unravelling the hydrodynamics and residence

times of isolated aquifers. Furthermore, this study reveals gravitational fractionation as a viable process, potentially affecting other isotopic systems in various geological settings.

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### Letter

With the growing need to sequester anthropogenic material (CO<sub>2</sub> and nuclear waste) in stable geological formations, the characterisation of hydrodynamics and residence time of deep groundwaters is a first order societal challenge. In order to demonstrate the sustainability of sequestration sites on long timescales, it is crucial to justify that fluid movement and/or mixing with other reservoirs are limited. Long residence time groundwaters revealed by the accumulation of radiogenic noble gases suggest that some aquifers in sedimentary basins remained isolated for millions of years (Marty *et al.*, 2003; Clark *et al.*, 2013), or even billions of years in deeper fracture-controlled systems in crystalline bedrock (Holland *et al.*, 2013). However, the accuracy of this technique depends on the estimation of crucial parameters such as the average porosity, the content of radioactive elements (U, Th and K) within host rocks, as well as assuming a closed system (Lippmann *et al.*, 2003). Unfortunately, these parameters are often poorly

constrained. Here we expand upon the largely ignored historic concept of solute gravitational settling within a static water column (Russell *et al.*, 1933) and present the first evidence that isotopic ratios can be affected by this process, providing a new tool to constrain the degree and timing of isolation for sedimentary aquifers.

If fluids within an aquifer are sufficiently isolated to become effectively motionless (*i.e.* no net advective component), the transport of solutes will be dominated by diffusion, but the Earth's gravitational field would prevent complete homogenisation of solute concentrations by tending to concentrate solute species downward. At equilibrium, the vertical distribution of a solute concentration  $C_i$  reaches a Boltzmann distribution such as  $C_i \propto e^{-E_i/RT}$  where  $R$  is the ideal gas constant,  $T$  is the temperature (°K) and  $E_i$  is the gravitational potential energy corrected for buoyancy expressed as  $E_i = (M_i - \rho \bar{V}_i)gz$  (Pytkowicz, 1963), where  $M_i$  is the molar mass (kg mol<sup>-1</sup>),  $\rho$  is the density of the fluid,  $\bar{V}_i$  is the partial molar volume (m<sup>3</sup> mol<sup>-1</sup>),  $g$  is the acceleration of the Earth's

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gravitational field ( $m\ s^{-2}$ ), and  $z$  is the depth (m). The potential effects of gravitation on solute distribution have been previously explored to determine if it could influence seawater salinity distribution (Pytkowicz, 1963) or the salinity enrichment with depth (Mangelsdorf *et al.*, 1970) often observed in sedimentary basins (*e.g.*, Kharaka and Hanor, 2003). However, all these studies concluded that the effect on solute concentrations must be too minor to be detected, with for instance the equilibrium distribution of chloride (Cl) resulting (see Supplementary Information) in a  $\sim 0.5\%$  concentration enrichment *per* 100-metres at  $25\ ^\circ\text{C}$  (*i.e.* within the typical 3–5 % analytical error on the determination of Cl concentrations).

Yet, the same reasoning also predicts that isotope ratios should be fractionated according to their mass. Here, we propose that isotope ratio measurements, for which the sensitivity is much better than that for solute concentrations, should allow identification of a gravitational distribution. Such evidence arises when writing the equilibrium distribution for an isotopic ratio  $R_i = C_H/C_L$ , which also has a Boltzmann distribution  $R_i \propto e^{-\Delta E_i/RT}$ , where  $\Delta E_i$  is the difference of gravitational potential energy between two isotopic substances of masses  $M_H$  (heavy isotope) and  $M_L$  (light isotope). Since the difference in partial molar volume between two isotopes is negligible, the relative per mille enrichment of the isotopic ratio  $\Delta R_i(z)$  as function of depth reads:

$$\Delta R_i(z) = \left( e^{-\frac{M_H - M_L}{RT}gz} - 1 \right) \times 1000 \quad \text{Eq. 1}$$

Accordingly, the ratio between two isotopes of two-neutron mass difference, such as the stable isotopes of chlorine ( $^{37}\text{Cl}/^{35}\text{Cl}$ ) or bromine ( $^{81}\text{Br}/^{79}\text{Br}$ ), should be enriched by  $\sim 0.78\%$  per 100 metres at  $25\ ^\circ\text{C}$ . This is significantly above the analytical uncertainties on  $\delta^{37}\text{Cl}$  or  $\delta^{81}\text{Br}$  measurements, respectively of  $\pm 0.10\%$  (Godon *et al.*, 2004; Giunta *et al.*, 2015) and  $\pm 0.24\%$  (Louvat *et al.*, 2016), for  $2\sigma$ . To identify such fractionation in a sedimentary aquifer therefore requires a high resolution multi-level sampling of the porewater column.

The Cambrian age Mount Simon Sandstone (MSS), a highly saline (TDS > 150 g/L) Na-Ca-Cl type aquifer, was chosen by the Illinois State Geological Survey as the injection reservoir for a large scale  $\text{CO}_2$  sequestration demonstration project. The MSS is dominantly composed of quartz, with three main lithostratigraphic units (Freiburg *et al.*, 2014): the Lower,

Middle, and Upper units. The Middle unit is considered a low permeability (*i.e.* “tight”) zone because of the massive diagenetic quartz cementation that has filled its primary porosity and likely prevents hydrogeological connection between the Upper and the Lower units. Importantly, the MSS is confined between two very low permeability units, the crystalline Precambrian basement (below) and the Eau-Claire Shale (above). Porewaters were sampled through a single, multi-level observation well (Locke *et al.*, 2013) at two and six discrete depths in the Upper and Lower units, respectively (the low permeability of the Middle unit precluded sampling). While the Upper unit has been shown to have experienced minor dilution (Panno *et al.*, 2013; Labotka *et al.*, 2015), both Upper and Lower porewaters were recently interpreted as dominated by modified Cambrian seawater (Labotka *et al.*, 2016), illustrating the long-standing isolation of these brines.

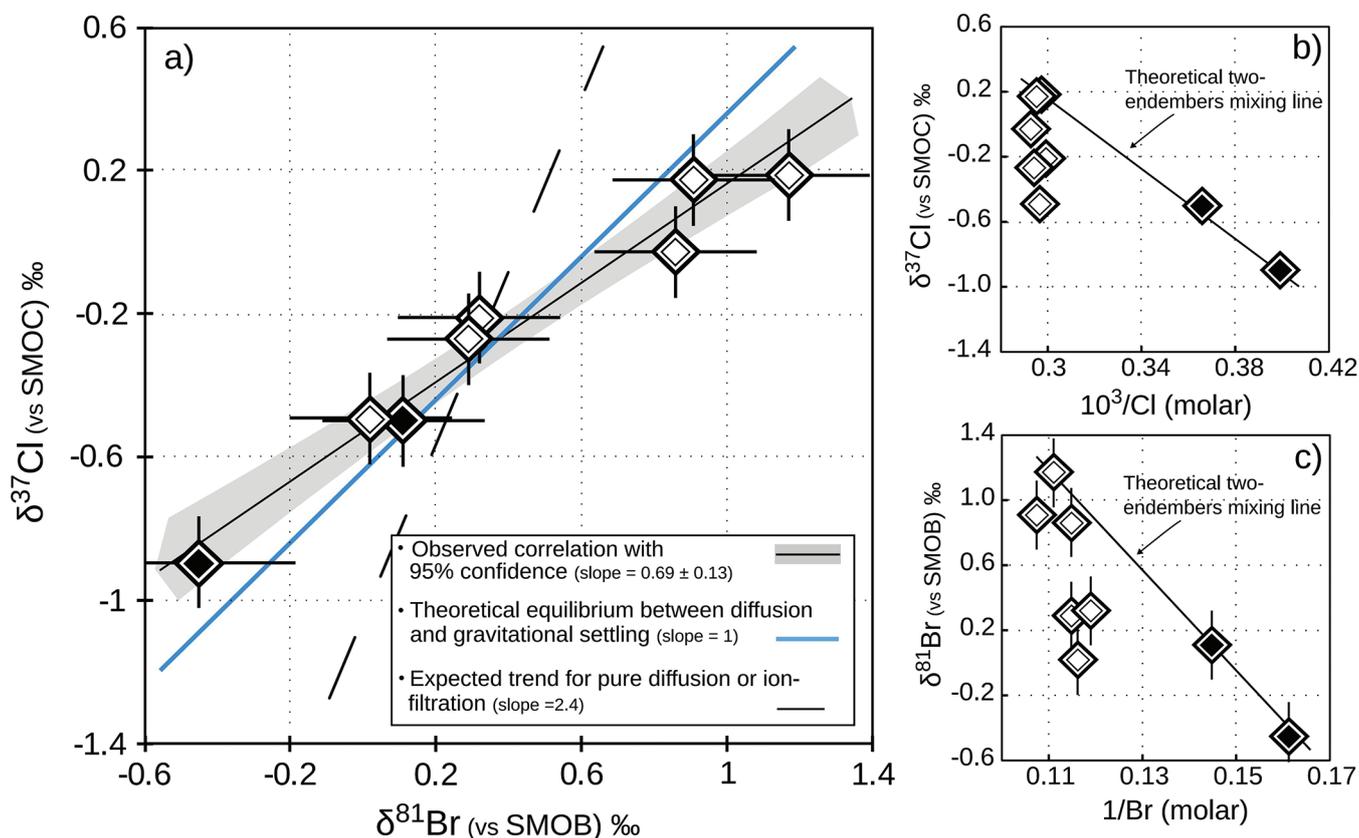
In this set of porewater samples,  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  are strongly correlated (Fig. 1a), and are both consistently increasing with depth, from  $-0.90$  to  $+0.18\%$  and from  $-0.45$  to  $+1.17\%$  (Table 1), respectively. The absence of correlation between concentrations and isotopic compositions for both Cl and Br (Fig. 1b,c) suggests that these vertical profiles do not reflect mixing relationships between the Upper and Lower unit porewaters, and that the observed  $\delta^{37}\text{Cl}$ - $\delta^{81}\text{Br}$  correlation is rather inherited from a process conjointly affecting both isotopic compositions. Because the MSS is free from salt/evaporite deposits, these variations cannot result from salt dissolution. Nor can they result from processes such as pure diffusion (Eggenkamp and Coleman, 2009) or ion filtration (*i.e.* electrolyte flow forced through a negatively charged membrane such as clay; see Phillips and Bentley, 1987) because of (i) the rather homogeneous  $\text{Cl}^-$  and  $\text{Br}^-$  concentration profiles – while both diffusion and ion filtration should conjointly affect isotopes and concentrations; and (ii) the wider variations of  $\delta^{81}\text{Br}$ , expected to be less fractionated than  $\delta^{37}\text{Cl}$  because of the smaller relative mass difference of bromine isotopes.

In contrast, these large isotopic variations are associated with remarkably homogenous concentrations and salinities in each of the considered units (only 3 % variations in the Lower unit). This observation, together with the relatively good agreement between the observed  $\delta^{37}\text{Cl}$ - $\delta^{81}\text{Br}$  regression slope and the theoretical slope predicted for equilibrium between diffusion and gravitation (Fig. 1a), are thus supporting the idea of a long term vertical immobility of the MSS porewaters.

**Table 1** Porewaters sampled at nine discrete depths within the MSS from a single, multi-level observation well. All data except the  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  were measured at the ISGS (Panno *et al.*, 2013; Labotka *et al.*, 2015).  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  were measured at IPGP. Errors are reported in  $2\sigma$ .

Sample	Depth (m)	T ( $^\circ\text{C}$ )	TDS (g/L)	[Cl-] (mmol/L)	[Br-] (mmol/L)	Cl/Br	$\delta^{18}\text{O}$ -SMOW ( $\pm 0.6$ ) ‰	$\delta\text{D}$ -SMOW ( $\pm 4.0$ ) ‰	$\delta^{37}\text{Cl}$ -SMOC ( $\pm 0.10$ ) ‰	$\delta^{81}\text{Br}$ -SMOB ( $\pm 0.24$ ) ‰
<b>Upper Mt. Simon</b>										
VWS 9	-1714	46	150.8	2504	6.2	404	-4.9	-32	-0.90	-0.45
VWS 8	-1770	48	172.9	2732	6.9	396	-5	-34	-0.50	0.11
<b>Lower Mt. Simon</b>										
VWS 7	-1944	50	203.8	3371	8.6	392	-3.8	-25	-0.49	0.02
VWS 6	-2010	51	205.3	3397	8.7	390	-3.6	-25	-0.27	0.29
VWS 5	-2036	48	203	3341	8.4	398	-2.9	-23	-0.21	0.32
VWS 4	-2072	48	205.5	3414	8.7	392	-2.8	-22	-0.03	0.86
VWS 3	-2105	50	207.3	3384	9.3	364	-2.9	-23	0.18	0.91
VWS 2	-2116	50	208.5	3362	9	374	-3	-24	0.18	1.17





**Figure 1** Isotope ratios and concentrations co-variations in the Upper (black diamonds) and in the Lower units (white diamonds).  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  are apparently linearly correlated ( $R^2 = 0.95$ ) throughout the MSS (a). This linear correlation cannot be attributed to mixing between the Upper and Lower porewaters given the absence of inverse correlation with concentrations (b,c). Instead, this correlation is explained by gravitational settling affecting both systems. Errors are  $2\sigma$ .

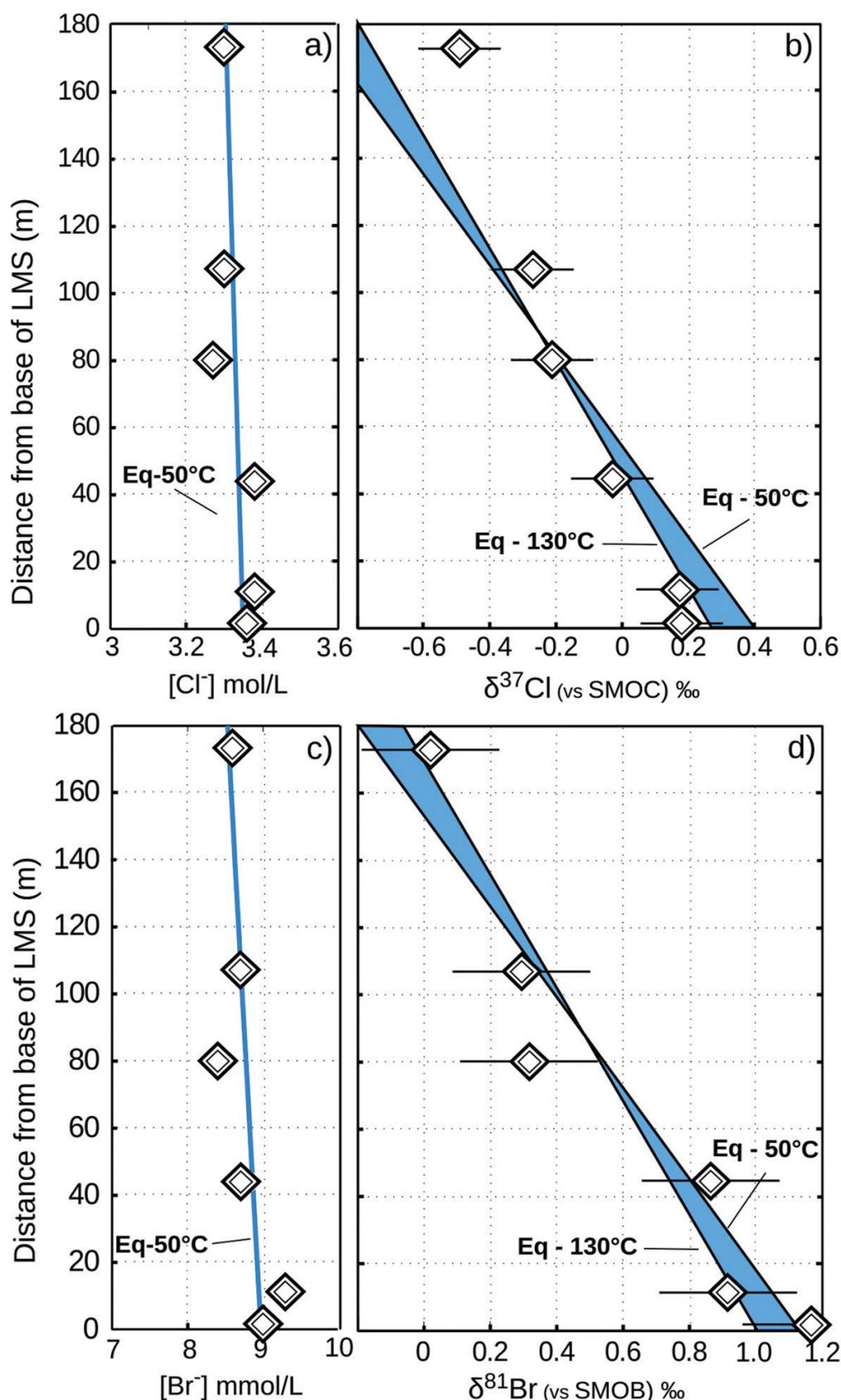
In the Lower unit,  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  are respectively enriched by +0.67 ‰ and +1.15 ‰. Given the thickness of the sediment column (~180 m), these variations are typically within the equilibrium range for temperatures between 50 °C (current temperature of the aquifer) and 130 °C (maximal cementation temperature; Fishman, 1997; Pollington *et al.*, 2011) – see Figure 2. It is unclear yet why the uppermost sample (VWS7) has a  $\delta^{37}\text{Cl}$  (-0.49 ‰) that is not fitting the expected range, but we speculate it could indicate that chloride has not fully reached equilibrium yet. Such equilibrium is established after  $t \approx 5\tau$ , where the characteristic time ( $\tau$ ) is defined analytically as (details in Supplementary Information):

$$\tau = \frac{h^2}{\pi^2 D} \quad \text{Eq. 2}$$

with  $h$  is the height of the water-column and  $D$  is the effective diffusion coefficient (accounting for the effects of ionic composition and of tortuosity – see Supplementary Information). As a first order estimation, using  $h = 180$  m and  $D = 2.5 \times 10^{-11}$   $\text{m}^2 \text{ s}^{-1}$  (effective diffusion coefficient in a sandstone similar to the one in Al *et al.* (2015), corresponding to a low-end tortuosity factor of ~3, see Supplementary Information for details), we calculate a characteristic time of 4.2 Myr. This means that the gravity-diffusion equilibrium should be fully established in the Lower unit after ~20 Myr (*i.e.* about five times the characteristic time). We recognise that the role of a complex electrolyte mixture on equilibrium dynamics is, as yet, poorly understood. For instance, while  $\text{Cl}^-$  and  $\text{Br}^-$  have almost identical self diffusion coefficients in water (Li and Gregory, 1974), because of  $\text{NaCl}$  or  $\text{CaCl}_2$  salt diffusion, they might have distinct diffusion coefficients (see Supplementary Information for additional details), yielding slightly different characteristic times according to Eq. 2.

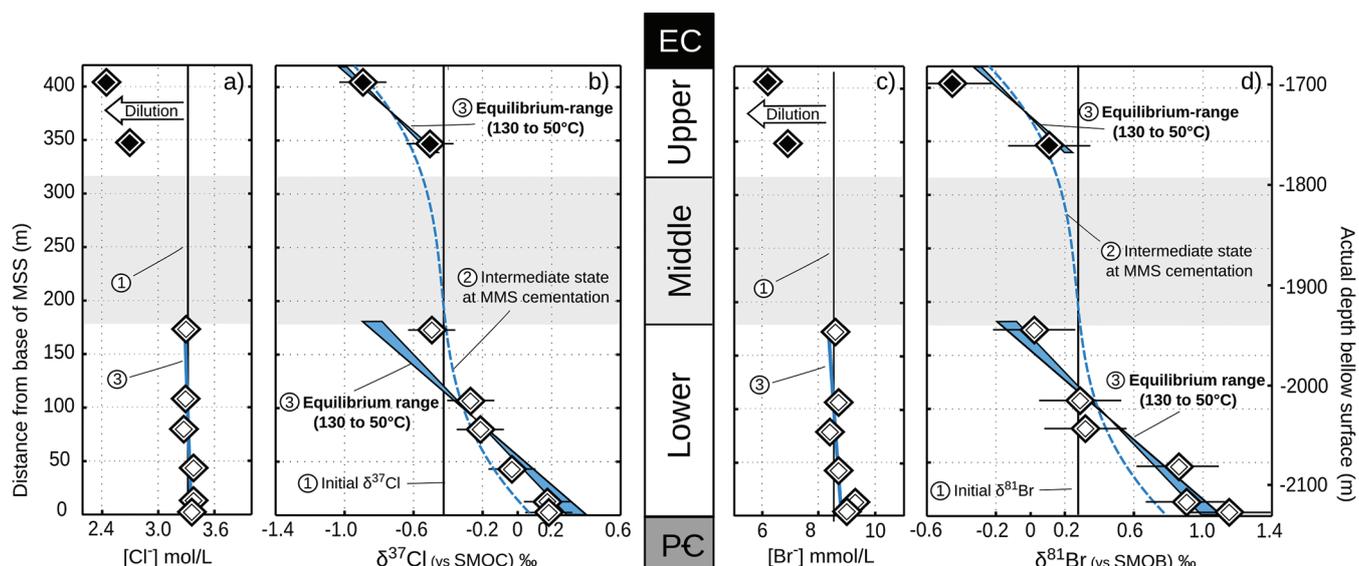
The long term immobility of Lower unit porewaters is reinforced by observations of the Upper unit, where  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  variations are also consistent with equilibrium profiles (see Fig. 3). Interestingly, while Upper and Lower unit porewaters are now separated by the highly cemented Middle unit, they share a similar and homogeneous Cl/Br ratio ( $388 \pm 13$ ), indicating that a single and relatively homogenous aquifer may have existed over the entire MSS. Overall,  $\delta^{37}\text{Cl}$  and  $\delta^{81}\text{Br}$  profiles would then support the idea of a whole MSS dynamic towards equilibrium (dashed line in Fig. 3), that was interrupted by the cementation of the Middle unit. Subsequently, the Upper and Lower unit porewaters evolved independently toward equilibrium (shaded area in Fig. 2). This model suggests that before cementation, the palaeo-aquifer had a  $\delta^{37}\text{Cl}$  close to -0.4 ‰, therefore in agreement with the evaporative origin (Eggenkamp *et al.*, 2016) inferred from the low Cl/Br ratios (Panno *et al.*, 2013). Fluid inclusion microthermometry and *in situ*  $\delta^{18}\text{O}$  analyses of authigenic quartz (Fishman, 1997; Pollington *et al.*, 2011) both support a cementation temperature ranging between 100 and 130 °C in the presence of a brine with a salinity of ~20 % wt. equivalent NaCl (similar to present day salinity in Lower unit). This temperature range was reached at the maximum burial of the MSS, approximately 300 to 350 Myr ago (Fishman, 1997). According to this model, MSS porewaters were relatively static just before the significant cementation event. We speculate that the Lower unit, and to a certain extent the Upper unit (if we exclude the later dilution event), have been reasonably stagnant and isolated since then. These conclusions are consistent with the Cambrian age origin of these fluids (Labotka *et al.*, 2016) and add further support for the continued use of the MSS as  $\text{CO}_2$  sequestration reservoir.





**Figure 2** The gravitation-diffusion equilibrium slope dependence on temperature. When  $z$  is sufficiently small, Eq. 1 might be simplified to a first order approximation such that  $\Delta R \approx \frac{\Delta Mg}{RT} z \times 1000$  where the enrichment of the isotopic ratio is therefore linearly correlated to depth. This approximation attests that for a given isotopic system, the slope of the equilibrium will only depend on the temperature. We report  $Cl^-$  and  $Br^-$  concentrations (a,c), as well as  $\delta^{37}Cl$  and  $\delta^{81}Br$  (b,d) from the Lower unit aquifer, together with equilibrium enrichment profiles calculated for temperatures of 50 °C (actual temperature of the formation) and of 130 °C (cementation temperature; though highest temperature reached during burial was probably closer to 150 °C). Given the scale of the concentration plots (a,c) 50 °C and 130 °C equilibrium profiles are not distinguishable. Error is  $2\sigma$ .





**Figure 3** Concentrations and isotopic distributions for Cl (a,b) and for Br (c,d) reported with depth in the MSS. EC is the Eau-Claire Shale and PC is the Precambrian basement. We hypothesise the following scenario: 1) An all homogeneous (in concentrations and in isotope compositions) motionless fluid in the MSS (thin black line). 2) The cementation of the Middle unit occurred relatively rapidly, before equilibrium is reached throughout the entire MSS (dashed line). 3) Disconnected Upper and Lower aquifers then separately pursue their evolution toward equilibrium (blue shaded areas). The concentration decrease in the Upper unit (a,c) is then resulting from a dilution event (as proposed by Panno *et al.*, 2013) which must have occurred after stage (2).

Our study highlights the effect of gravitational settling on isotope distributions in a deep sedimentary formation, revising our fundamental understanding of the complex dynamics and residence time in continental groundwater systems. As a consequence, future studies on crustal aquifers should consider its potential fingerprint on isotope ratios for which the analytical precision is better than the minimum variation expected (*i.e.* calculated with Eq. 1) and employ a multi-level sampling approach where possible. Where fluid systems are isolated over sufficient periods of time, isotope gravitational settling could be observed. This opens the intriguing possibility that gravitational settling occurs within a wide variety of geological fluids, spanning a wide range of magnitudes.

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## Additional Information

**Supplementary Information** accompanies this letter at [www.geochemicalperspectivesletters.org/article1736](http://www.geochemicalperspectivesletters.org/article1736)

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